

Towards Large-Scale Fabrication of Plasmonic Nanomaterials by Fluid-Mediated Forces

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Abstract

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Nano-assembly promises powerful technological advances, yet there is a persistent need to make such assembly more economical before we see these benefits in daily life. Scalable and reliable nano-assembly of any kind has remained elusive to researchers worldwide. This thesis focuses on Capillary Force-assisted Assembly (CFA), particularly for plasmonic structures and materials. CFA assembles nanoparticles out of solution via liquid-mediated forces over a nano-template. It is significantly cheaper and faster than standard nano-fabrication routes.

CFA-assembled optical plasmonic materials have not been demonstrated over sizes larger than square-micrometers. An early goal of this work is to demonstrate centimetre-squared assembly. An unexpected hindrance emerged in the reliable manufacture of large-area nano-templates. Despite this, scaled-up assembly has been demonstrated, producing an optical two-tone metamaterial from plasmonic nanorod pixels.

Harnessing the CFA protocol is difficult. Experimenters rely heavily on the

current CFA model to guide their efforts. This model is widely accepted yet has received little critical analysis. In pushing the envelope of CFA, the conventional CFA model is inadvertently put to the test, and it is found wanting. A much-needed thorough review dismantles the conventional model from experimental and theoretical standpoints. An as-yet unmentioned type of capillary force is suggested to apply on nanoparticles in CFA, and its form is mathematically derived.

A new framework for CFA is proposed. In this framework, contact line pinning on template cavities, and the subsequent local enhancement of convective flows, are the primary assembly drivers. This model draws well from the limited existing nano-wetting theory, and conforms well to high-level experimental expectations.

However, for reliable and scalable CFA, core dynamics must be quantified and relevant experimental parameters ascertained. This is non-trivial, requiring knowledge of the time-resolved three-dimensional (3D) meniscus form during single CFA-assembly events. No techniques exist to non-invasively probe such dynamics.

Therefore, a novel experimental technique is developed to rapidly and non-invasively profile a meniscus shape in 3D on the micro-scale. Meniscus dynamics are observed over templated cavities with millisecond resolution, showing that the meniscus pins and closes down over cavities, acting to clamp particles in place. Moreover, evaporative dynamics can be modelled on the 3D micro-meniscus profiles, paving the way for crucial thermodynamic analysis.

Characterisation of the new model therefore begins by abundantly probing pinning dynamics on cavities. Surface tension is revealed to direct pinning dynamics down to the nano-scale; inertial / viscous forces become negligible. Interpolatable trends allow us to theoretically reconstruct meniscus forms under a range of experimental conditions at any moment during a single CFA assembly event.

From this versatile CFA-meniscus model, and armed with the ability for thermodynamic analysis, convective flows during assembly events are estimated and validated against extant literature. The subsequent kinematic behaviour of a nanoparticle in a cavity's vicinity during a CFA-assembly event is simulated under a variety of experimental conditions. This sheds valuable light on which experimental parameters are most crucial to optimise CFA dynamics, and why. This new and arguably successful model is called the pinned-convective model of nano-CFA.

(494 words)

Declaration of Authorship

This is to certify that:

1. This thesis comprises my own original work towards the degree of Doctor of Philosophy except where indicated in the preface
2. Due acknowledgement has been made in the text to all other material used
3. This thesis is fewer than the maximum limit of 100,000 words

A handwritten signature in black ink, appearing to read 'T. Mapperson', followed by a long horizontal flourish.

Timothy Mapperson

Preface

This thesis is my own work except for the following components. Unless stated otherwise, all persons are (former) members of the NanoScience Laboratory at the University of Melbourne. All acknowledgements are also made in the main text.

1. Section 2.2 details nano-template fabrication protocols. Templates were fabricated by Timothy James and Jasper Cadusch of the Optical Physics Group (University of Melbourne)
2. Section 2.4 details the conventional nano-assembly fluid cell apparatus designed and built by Tatiana Pinedo-Rivera.
3. Section 3.2.1 details nano-assembly on $30 \times 30 \mu\text{m}^2$ metamaterial arrays conducted collaboratively between Pinedo-Rivera and Mapperson
4. Gold nanorods were synthesised by Sarah Jaber (Section 2.3) and UV-Vis spectra in Section 2.3.2 were taken by Sarah Jaber
5. Atomic force microscopy in Sections 5.5.1 and 5.5.4 was conducted by Jianing Lu

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To my wife, Kanini—you have given me your steadfast support, continual patience and constant service to me and our family over these past years. You have allowed me to focus when needed, taking the burden of caring for our children while I am at conferences or working late. You have celebrated with me in the many small successes along the way and encouraged me through difficult times.

In the NanoScience Laboratory, Dr. Tatiana Pinedo-Rivera has been instrumental early in this work by developing the fluid cell apparatus, teaching me the ropes of nano-assembly by capillary forces, and walking with me through many early difficulties and perplexing results. Sarah Jaber has been a critical help particularly in synthesising nanorods. Jianing Lu has expertly done atomic force microscopy for me. I am deeply grateful for other help from Sean Collins teaching me spectroscopy, Xingzhan Wei helping me learn COMSOL, and Steven Barrow for early training in working with nanoparticles. These and other members of the NanoScience Laboratory have been a wonderful team of friends and colleagues. They have given their time, often patiently teaching me the basics of chemistry which I lacked coming into this project, and sharing their expertise with me as I explored novel ideas.

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Presentations

The following conference presentations were made in the course of this work:

Poster: ‘Template-Directed Assembly of Plasmonic Nanostructures’, Australian Institute of Physics (AIP) Congress, Sydney, 9-13 December 2012

Presentation: ‘Nanofabrication for Top-Down and Bottom-Up Plasmonic Metamaterials’, Australian National Fabrication Facility (ANFF) Annual Research Showcase 2013, Melbourne, 13-14 November 2013

Presentation: ‘Template-Directed Assembly of Plasmonic Nanostructures’, International Conference on Nanoscience and Nanotechnology (ICONN), Adelaide, 2-6 February 2014

Presentation: ‘Nanofabrication for Bottom-Up Plasmonic Materials’, ANFF Showcase, Canberra, 18-19 November 2014

Poster: ‘Template-Directed Assembly of Plasmonic Nanostructures’, Australian Colloid and Interface Society (ACIS) biennial conference, Hobart, 1-5 February 2015. The poster won second prize

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Introduction

1

Nano-assembly promises powerful technological advances, yet there is a persistent need to make such assembly more economical before we see these benefits in daily life. In this chapter we will introduce nano-assembly, focussing on Capillary Force-assisted Assembly (CFA), which is a strong candidate for scalable nano-fabrication. We examine existing theory relevant to this assembly approach, and discuss the current model of CFA in the literature.

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1.1 The Quest for Scalable, Economical Nano-Assembly

The nanoscale holds promise for immense technological scope and development. At the nanoscale, surface-area effects dominate over volumetric effects, close range forces dominate over long range ones, and electromagnetic waves become quasi-

static fields. Experimental and theoretical work has produced many breakthrough technologies, but they remain confined largely to research laboratories due to a lack of economical routes to fabricate the necessary nano-hardware.

This thesis addresses some outstanding challenges in nano-fabrication, be that fabrication of a single nanostructure, or an array of structures. The need in nano-fabrication is for an economical approach with reliability and precision in nanoparticle placement and/or orientation. Precise and reliable nano-fabrication is presently available through ‘top down’ methods like electron-beam lithography and focussed ion-beam milling, though these are very costly and time-consuming. A more economical approach is required.

‘Bottom up’ methods emerged to fill this gap, whereby nano-building blocks are synthesised in a wet chemistry environment and then assembled. Bottom-up fabrication tends to be very economical (and often faster), but suffers from poor precision and repeatability.

In reality, the optimal nano-fabrication solution is likely a combination of both approaches. Bottom-up methods often employ a template to guide nano-assembly. Templates rely on top-down methods for fabrication, but once a master template is made, copies can be made cheaply. To date, scaled-up template fabrication and nano-assembly have not been demonstrated together, and no ‘bottom up’ assembly technique has proved sufficiently reliable and scalable.

This thesis is centred on a widely used bottom-up technique known as capillary force assembly (CFA, or variations of that name). The nano-assembly dynamics underlying CFA are poorly understood and it is only now being scaled up for centimetre-squared optical materials. This thesis makes a key contribution in both of these areas, but primarily in elucidating CFA dynamics on the nanoscale. We will focus on CFA of metal nanoparticles for plasmonic applications.

It will be useful to define the terms ‘nano-CFA’ as CFA specifically in the nano-regime, and ‘micro-CFA’ as in the micro-regime. Comments about ‘CFA’ relate to CFA of any size regime in general.

In this chapter we briefly discuss the plasmonic and optical properties of metal nanoparticles and some of the applications that make them so relevant to nano-assembly efforts (Section 1.2). This is followed by an overview of the main requirements for nano-assembly in general, as well as the main techniques that have been

pursued to date (Section 1.3). In that we establish why CFA warrants our attention. The next two Sections (1.4 and 1.5) cover liquid dynamics on substrates and nanoparticles, respectively. These lead into the first thorough review of CFA literature to explain the currently accepted model of nano-CFA (Section 1.6). We close by outlining three thesis questions, and a summary of coming chapters.

1.2 Plasmonic and Optical Properties of Metal Nanoparticles

CFA has been widely employed to assemble biological cells [1], micro-vesicles [2], nanowires [3], lipid molecules [4] and DNA [5–7]. However, the assembly of aqueous metallic nanoparticles for plasmonic devices is by far the major application at present. Here we review the cause for such interest, with a particular focus on gold nanorods in aqueous media.

1.2.1 Localised Surface Plasmon Resonances

Metal nanoparticles exhibit the remarkable feature of localised plasmonics. A number of studies provide a good overview of nanoparticle plasmonic fundamentals [8–11]. The Drude model of electron behaviour in a bulk conductor treats the conduction electrons as a plasma—a cloud of freely moving negatively charged particles—amongst a fixed array of positively charged atomic nuclei. This plasma can sustain longitudinal oscillations that experience a restoring electric force from the displacement setup between the positive and negative charges. This model predicts a resonant frequency, called the plasma frequency ω_p , for the electron plasma of the bulk metal:

$$\omega_p^2 = \frac{ne^2}{\epsilon_0 m} \quad (1.1)$$

where n is the volumetric number density of free charge carriers, e is the charge carrier’s charge, ϵ_0 is the permittivity of free space and m is the mass of a charge carrier. When a wave of electron oscillations is setup on a metallic surface, it is called a surface plasmon resonance (SPR).

The plasma frequency is closely related to the relative permittivity of the metal

$\epsilon(\omega)$, describing its optical characteristics, given as

$$\epsilon(\omega) = 1 - \frac{\omega_p^2}{\omega^2 + i\gamma\omega} \quad (1.2)$$

In Equation 1.2, ω is the angular frequency of the incident wavelength and γ is the relaxation frequency of the metal (that is, the inverse of the mean time between scattering events of free charge carriers with the fixed atomic matrix). The term $i\gamma\omega$ describes collisional losses within the metal.

When $\omega < \omega_p$ the real part of $\epsilon(\omega)$ is negative and the metal is reflecting, and when $\omega > \omega_p$ the real part of $\epsilon(\omega)$ is positive and the metal is transparent. The plasma frequency (and interband electronic transitions) of most metals lies in the UV spectrum, which is why most metals appear a reflective grey colour. Gold and copper are two notable exceptions with interband transitions in the visible spectrum, giving them their respective colours.

The real part of Equation 1.2 is

$$\epsilon(\omega) = 1 - \frac{\omega_p^2}{\omega^2 + \gamma} \sim 1 - \frac{\omega_p^2}{\omega^2} \quad (1.3)$$

This is significant because it shows the very dispersive nature of the metal's dielectric function. This relation describes the reflectivity of metals for light below their plasma frequency ($\epsilon(\omega)$ is negative), and their transparency for light above the plasma frequency ($\epsilon(\omega)$ is positive).

When we reduce the bulk metal to a nanoparticle the electron plasma's resonance behaviour changes. It is clear conceptually that the electron plasma is now strongly confined by the physical boundaries of the particle, altering its resonance. In the bulk case we did not consider the permittivity of the environment, but a nanoparticle's electron plasma resonance is heavily influenced by the dielectric properties of its surroundings due to its much greater surface area to volume ratio. If the particle diameter is small compared to the wavelength of light, then the quasi-static approximation can be used treating the incident light field as an electrostatic field. In this case all these influences can be summarised by considering the electrical polarisability of the particle within its environment:

$$\alpha(\omega) = 4\pi R^3 \frac{\epsilon(\omega) - \epsilon_m}{\epsilon(\omega) + 2\epsilon_m} \quad (1.4)$$

Equation 1.4 is for a metal sphere (the simplest case), where R is the sphere radius and ϵ_m is the relative permittivity of the surrounding medium [8]. Higher order

polarisation modes exist, but for most metallic nanoparticles the dipole mode is by far the most significant and describes the overall optical response well.

This polarisability can be interpreted physically as an electric dipole being setup across the particle due to the incident electromagnetic field shifting the mean position of the electron plasma relative to the fixed positive nuclei. Such a resonance, when it is confined to a structure small enough for the quasi-static approximation to apply, is known as a localised surface plasmon resonance (LSPR). It is clear that the dipole is strongest when $\epsilon(\omega) = -2\epsilon_m$. It is at the frequency ω that satisfies this condition that forms the fundamental mode of the LSPR and for which the nanoparticle will strongly absorb and scatter light.

For non-spherical particles, such as rods and more complex shapes, the underlying principles are the same though the mathematical analysis is more involved. Depending on the asymmetry of the particle, different resonant modes may be setup, each requiring a unique wavelength and/or polarisation for excitation. A rod, for example, will have a longitudinal mode responsive to light polarised along its long axis, and similarly a separate orthogonally polarised mode, albeit at a shorter wavelength due to greater confinement, along its shorter orthogonal axis. Other shaped particles and particle geometries can possess interesting and useful resonances, and the reader can obtain relevant literature on this topic relatively easily.

It is enough to say that the above gives some explanation to the origin of LSPR in metal nanoparticles, and that such resonances are strongly dependent on the size, shape, composition and environment of the particle. Plasmonic resonant modes of particles can be unique in their excitable wavelength and polarisation (including circular polarisation).

1.2.2 Optical Extinction Cross-Sections of Metal Nanospheres

The two primary means of electromagnetic interaction are by absorption losses (due to collisional heating from the oscillating electrons) and scattering (due to accelerating electrons). It is useful to consider the cross-sections of these two loss mechanisms. We have already defined the polarisability, $\alpha(\omega)$, of the dipole mode for a sphere in Equation 1.4. The cross-sections are then given as

$$\sigma_{sca} = \frac{k^4}{6\pi\epsilon_0^2} |\alpha(\omega)|^2 \quad (1.5)$$

$$\sigma_{abs} = \frac{k}{\epsilon_0} \text{Im}[\alpha(\omega)] \quad (1.6)$$

where $k = 2\pi\sqrt{\epsilon_m/\lambda}$. These relations to the polarisability imply that scattering scales with R^6 while absorption scales with R^3 [12]. Thus for smaller particles absorption dominates and there is very little scattering, but for large particles scattering dominates. When we seek to use gold nanoparticles as nano-antennae, we rely on their scattering ability and the effect will be much more pronounced when we use particles larger than ~ 60 nm. For gold nanospheres, scattering starts to show up in spectra when $R > 20$ nm, and it becomes comparable with absorption when $R \approx 80$ nm [13]. The total extinction cross-section is the sum of the two loss mechanisms [12]:

$$\sigma_{ext} = \sigma_{sca} + \sigma_{abs} \quad (1.7)$$

1.2.3 Plasmonic Properties of Gold Nanorods and Applications

The asymmetry of a metal nanorod will enable two fundamental resonances of different wavelengths along the two primary axes. Since the axes are orthogonal to each other, the plasmon resonances are likewise only excitable by linearly polarised light of orthogonal polarisations. The longitudinal resonance denotes that of the length of the particle which resonates at a longer wavelength than the transverse resonance, which oscillates across the particle's width. The longitudinal resonance is also much stronger than the transverse, making it the dominant electromagnetic interaction.

The scattering intensity of nanoparticles depends heavily on their crystallinity and the surface smoothness [14]. This is demonstrated clearly with nanorods, whereby rods fabricated by electron beam lithography are polycrystalline and may be nano-rough. This leads to a high degree of collisional losses within the metal and the plasmon resonance is highly damped. After annealing the rods at 200°C for 120 minutes, their crystallinity and surface smoothness are greatly enhanced, and their scattering intensity increases by a factor of 3.

In contrast to lithographically made nanoparticles, chemically synthesised nanoparticles are inherently mono-crystalline. This lends them much better to plasmonic applications, as there is minimal ohmic damping of the plasmon resonance (see Figure 1.1).

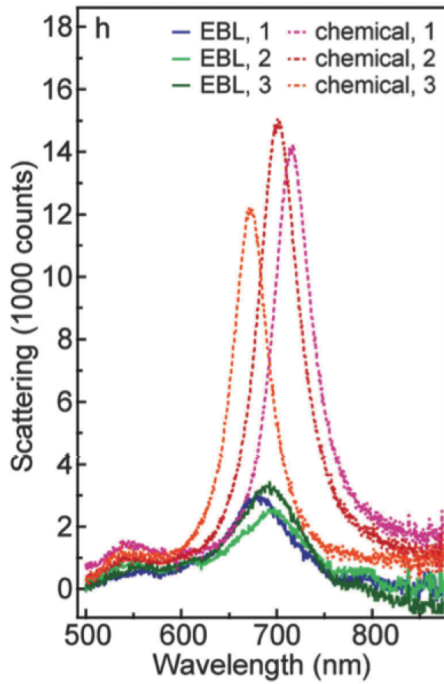


Figure 1.1: Single gold nanorod spectra obtained from lithographically prepared rods (EBL 1, 2 and 3) and chemically synthesised rods. The EBL rods were annealed to reduce their ohmic losses. The chemically prepared rods scattering much more strongly due to their mono-crystalline structure which minimises absorption losses. All rods are in the vicinity of $110 \text{ nm} \times 50 \text{ nm}$ in size. (From Ref [14])

As a result of the two dimensions of nanorods being excitable by different linear polarisations of incident light, and also scattering at different wavelengths, novel applications of nanorods are available. Individual nanorods can behave like colour changing polarisation-sensitive pixels. An array of such rods, suitably aligned on a rod-by-rod basis, can form a colour image [15, 16] or a high-density data storage device [15, 17] which is easily observable/readable with linearly polarised light. In other work, arranging three rods in a U-shaped structure can function as an all-optical signal modulator [18].

In summary, we have described how the electron clouds of metal nanoparticles can oscillate in sync with an impinging electromagnetic field, and we have described the nature of the fundamental resonance at which scattering and absorption will be strongest. We have considered this in more detail for gold nanorods and briefly presented some recent applications of nanorod formations. We now turn to the nature and requirements of nano-assembly in general, and then more specifically to how liquid mediated forces (capillary and convective forces) can be used for nano-assembly. After the coming section we will examine liquid forces relevant to nano-CFA and then the conventional model of nano-CFA itself.

1.3 Nano-Assembly Forces and Techniques

1.3.1 Requirements for Nano-Assembly

Nano-assembly techniques must control forces to reliably move, place and align nano-components. On the nano-scale, some forces diminish to be negligible (such as gravity) while others become dominant (such as van der Waals forces).

There are two threats to successful nano-assembly: (1) Brownian motion and (2) attractive van der Waals forces. Brownian motion is the random walk that very small objects experience due to collisions with the atoms and molecules of their thermal environment, especially in liquid. The nano-assembly force to override Brownian motion must have strength, but also fidelity to place particles with nanoscale precision.

Close-range van der Waals forces often simply refers to the electric adhesion (or repulsion) experienced by surfaces within atomic proximity. Van der Waals forces tend to pull surfaces together, which in nano-assembly can lead to unwanted aggregation. Van der Waals attraction must be prevented until the desired nanoparticle arrangement is achieved.

CFA (capillary force assembly) involves the capillary force (also called the meniscus force, Laplace force or surface tension force) and a convective flow force (also called the drag force). These two forces complement each other and can both be harnessed and controlled at the nanoscale.

Before we delve into the principles of capillary force assembly, let us briefly overview the other primary nano-assembly options that are presented in the literature, and why capillary force assembly is a particularly promising candidate.

1.3.2 Forces for Nanoparticle Assembly

A myriad of forces exist at the nanoscale, many of which have been employed in one fashion or another to move, align and/or collect nanoparticles in solution. (References are given for the interested reader to pursue; they will not be discussed further here.)

- Chemical-guided assembly: such as DNA mediated assembly [19] and preferential particle structures (e.g. chains) by chemical affinity and molecular recognition [20]
- Electric field-directed assembly: such as electrically patterned substrates to assemble patterns of charged particles [21–23]; electrophoretic and dielectrophoretic assembly and/or alignment of particles [24–29]
- Magnetic field-directed assembly: of magnetic field-sensitive particles [30–32]; using ferrofluid to position and/or align magnetically insensitive particles [33, 34]
- Optical manipulation: for nanorod positioning and/or alignment [35–39]; plasmonic trapping of particles [40, 41]; optical binding force to assemble ensembles of particles [42, 43]; optical trapping to position particles individually or in arrays [44, 45]
- Fluid-controlled assembly: such as convective and/or capillary force assembly [46–53]; assembly at fluid interfaces [54–57]; electric-field enhanced assembly at fluid interfaces [58–62]; droplet- or bubble-mediated manipulation of particles [63–65]; disjoining pressure-guided assembly [66]

The above is a small sampling of nano-assembly work for each force described, not to mention a number of published reviews [67–73]. Usually nano-assembly involves just one of the above forces, but occasionally two are combined.

Fluid-mediated capillary forces are a superior option in several respects, as they:

1. Have an inherent ability to apply on a large-scale (long range forces) yet also be tuneable on the nano-scale
2. Are readily implemented without costly or delicate experimental setups
3. Have versatility to apply to a range of particle types, shapes and sizes
4. Have an ability to yield a wide variety of well-defined particle structures.

All other techniques listed previously fail one of the four points above. For example, electric field-directed assembly works very well with single particles assembled in large-area arrays, but it becomes non-specific and unreliable once multi-particle structures are sought (i.e. it fails point 4). One key limitation of CFA is that it does

not easily create three-dimensional structures, but few techniques can to date (and those that do, like DNA-mediated assembly, have very poor yields to date).¹

1.4 Liquid Dynamics on a Substrate

In addressing liquid-mediated nano-assembly, it is vital to discuss liquid dynamics on a substrate and liquid forces on nanoparticles. This section addresses the first of these. The next section will explain liquid forces on nanoparticles. Then we will be in a position to explain nano-CFA.

Much literature has been written about static and dynamic wetting on smooth and rough substrates alike. The aspects most relevant for CFA will be reviewed here, which are dynamic contact angles, and pinning/depinning on substrate heterogeneities. A recent literature review discusses our first topic well [75].

1.4.1 Static and Dynamic Contact Angles

Static Contact Angles: When a small stationary liquid droplet wets a surface incompletely, it adopts an equilibrium spherical form that intersects the surface at a characteristic contact angle, known as the *static contact angle*. The shape and contact angle will minimise the surface energies (or *surface free energy*, or *surface tension*) of all three interfaces (see Figure 1.2a).

In 1805, Thomas Young derived a relationship between the ideal static contact angle and the surface energies. Known as the Young equation, the relationship is

$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cos(\theta_Y) \quad (1.8)$$

where θ_Y is Young's static contact angle and γ is the surface energy of the various interfaces (S - solid, L - liquid, V - vapour). In reality this equation is rarely accurate, simply because it assumes a perfectly smooth, homogeneous and inert surface. Most surfaces are not molecularly smooth. Theories of Cassie and Wenzel wetting were

¹Some literature claims 3D assembly by CFA (e.g. Ref [74]), but the '3D aspect' is quite crude, coming from piling many particles on top of many particles. A large 3D conglomerate is formed in a micro-cavity, but it is far larger than the nanoparticles that make it. It is not controlled assembly of individual nano-components, and thus it is not the 3D assembly we envision for true 3D nano-fabrication.

derived to account for such cases. Prior motion of the contact line also alters the accuracy of Young's equation, known as dynamic wetting.

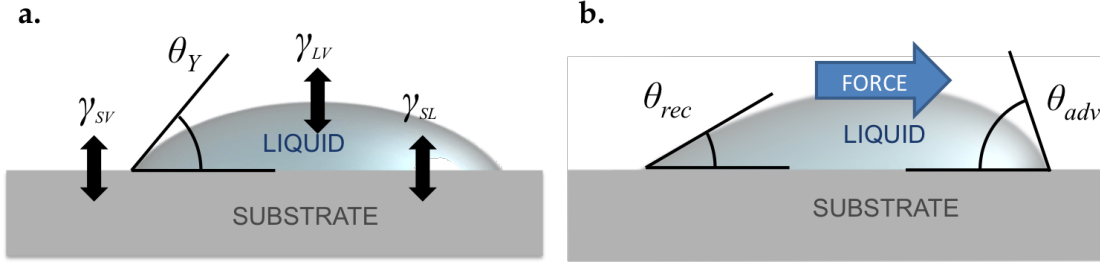


Figure 1.2: Depiction of the static contact angle (a) and the dynamic contact angles (b) of small sessile droplet. The static contact angle (θ_Y) depends heavily on the balance of surface energies (γ_{LV} , γ_{SL} and γ_{SV}), as well as any surface features that are present.

Dynamic Contact Angles: When a force is applied to move a droplet, the droplet absorbs the force by altering shape until it is energetically favourable to repeatedly desorb its contact line and move to a new position.

Thus the *advancing* contact angle of a droplet is larger than the static contact angle. Conversely, the *receding* contact angle is below its static equilibrium value. This is called contact angle hysteresis (see Figure 1.2b).

In a minimal sense, CFA involves a colloidal suspension of particles receding over a surface, whereby particles collect at the contact line and are there assembled onto the substrate. The contact angle of the meniscus is important in this regard, as it influences the balance of forces that enact assembly. In ensuring a suitable contact angle, we must therefore select a liquid-substrate system that has the appropriate balance of surface energies.

Of great significance also is the topography of the substrate. CFA substrates bear cavities in them (which are intended to capture particles as they are assembled), and these cavities are topographical unconformities, altering the local contact angle. Nano-CFA literature recognises the need to select a suitable contact angle, but the literature is almost silent when considering how the substrate's topography further influences the contact angle. This omission is somewhat puzzling, and it leaves an opportunity for a more thorough model of nano-CFA to be put forward, which this thesis aims to fulfil.

1.4.2 Meniscus Pinning and Depinning on Substrate Heterogeneities

Another liquid phenomenon of importance to CFA is the pinning of liquid menisci on substrate heterogeneities, be they of a morphological or chemical origin. Meniscus pinning has been studied repeatedly, but far from thoroughly, most especially on the nanoscale. The nano-pinning studies in this thesis are hence a wanted addition to the literature.

In the absence of gravitational effects, an advancing meniscus will pin on a heterogeneity in the template until the advancing contact angle condition is met on the surface just beyond the pinned site. Figure 1.3 represents this well. A receding meniscus will also pin until the receding contact angle condition is met on the unexposed surface.

The extent of pinning is highly dependent on substrate morphology [76], and particularly on changes in the substrate's surface angle [77, 78], which can be mathematically linked with the elastic force on the meniscus during pinning [79]. Other factors contribute to pinning to a lesser amount [78].

In 2010, Chang et al. [76] filled the absence of an analytical expression for meniscus pinning phenomena. They mathematically described the macroscopic pinning of water on geometric edges of a substrate, using a thermodynamic approach. They confirmed their theory with experimental data. Whilst their analytical expression is limited to an axisymmetric droplet and template (symmetry was needed to simplify the problem so an analytical solution could be obtained), their work shows that (in the absence of gravity) pinning and depinning is essentially an interfacial surface energy minimisation problem, just as was discussed with static and dynamic contact angles.

Micron-Scale: In the microscopic regime there are many pinning studies one can cite, likely because many real-world surfaces are micro-textured, and hence the motivation for study. A notable motivation for these works is to better understand super-/ultrahydrophobic surfaces [80–86]. Other studies focus on the dynamic wetting of micro-rough surfaces in general [77, 87, 88]. These works conclusively demonstrate that microscale pinning behaves in much the same way as macroscale pinning. This is relevant for micro-CFA, but does the effect continue on the nano-scale?

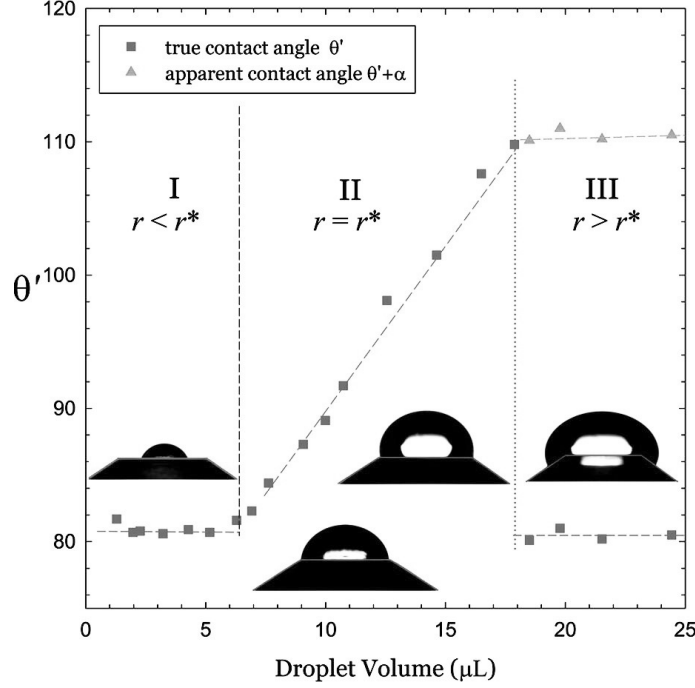


Figure 1.3: Macroscopic pinning and depinning of an advancing contact line on a geometrical heterogeneity, showing three regimes: Regime I shows advancement before the heterogeneity. Regime II shows pinning on the heterogeneity until the advancing contact angle condition is met on the region *after* the heterogeneity. Regime III shows subsequent advancement over the new surface. (from Ref [76])

Nano-Scale: Nano-topology has been known for some time to be of importance to the motion of contact lines. Much fewer papers are available owing to the difficulty of study at this size scale. In recent work, Ramiasan et al. [75] lament that “comprehensive theoretical and experimental studies of the role of these small scale heterogeneities in the wetting process are still lacking.” One of the first studies showed pinning on 3 to 10 nm high steps [89]. The researchers found that the defect size necessary to induce pinning scaled with the size of the liquid molecules, though the dynamic contact angle was independent of the molecular weight. This suggests that pinning is affected by molecular interactions, and is not necessarily (or entirely) an effect from micro-/macro-scale forces. Other useful studies on pinning and contact angle hysteresis in the nano-regime are referenced here for the interested reader [90–94].

Molecular-Scale: Moving to molecular scales we turn to simulations that leverage molecular kinetic theory. It appears that pinning results immediately at the contact line, within the space of a few liquid molecules [95], and translates to a macro-scale

effect through coupling with surface tension.

Summary: It is apparent, then, that pinning dynamics are significant on the nanoscale and ought to be considered in nano-CFA models. As mentioned previously, a CFA substrate is inherently heterogenous due to its cavities. To date, nano-CFA literature has not elucidated on the effect of pinning dynamics. The range of size scales over which pinning has been studied is exemplified in Figure 1.4.

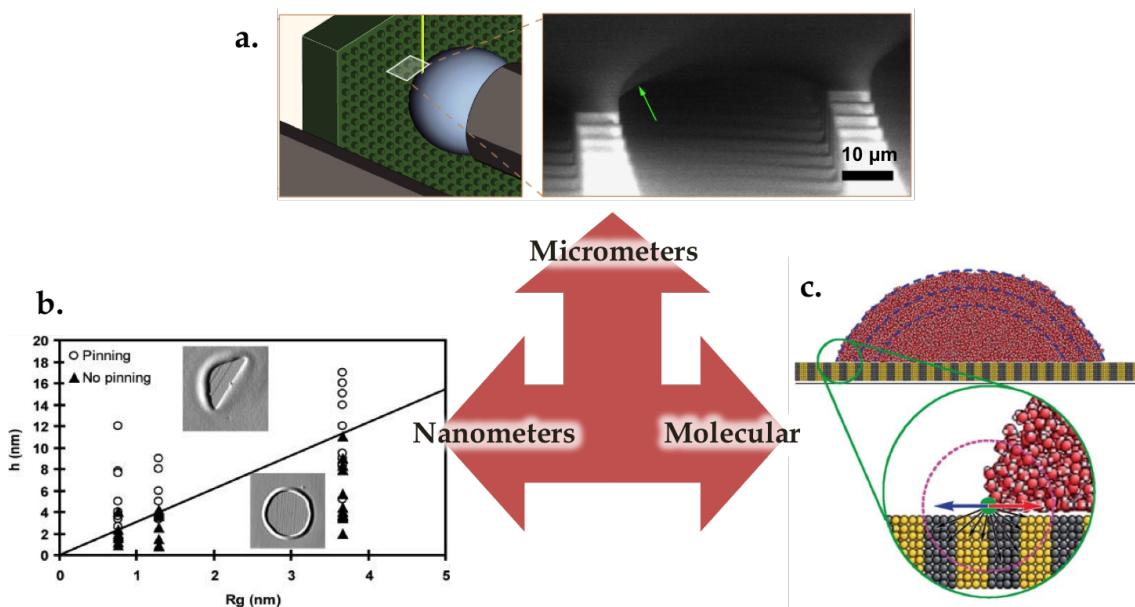


Figure 1.4: Pinning occurs on a wide range of scales, from micro-metric defects (*a*, from Ref [81]), to nano-metric defects (*b*, from Ref [89]), to defects just a few times the diameter of the liquid molecules (*c*, from Ref [95]). Pinning effects therefore ought to be considered in micro- and nano-CFA models.

1.5 Liquid Forces on Particles

Having briefly introduced how liquids interact with substrates, let us now turn to how liquids interact with nanoparticles. This is the final section of theory to be discussed before we can focus on nano-CFA.

In this major section we look into two primary liquid-mediated forces on nanoparticles: the capillary surface tension force and the convective drag force. Certain types of capillary forces are well covered in literature, while others are not. In this

section and the associated Appendix 1.A we argue against the current understanding about which types of capillary forces are most relevant for nano-CFA, providing new insights of capillary-particle interactions. Convective flows in evaporating liquid bodies are well covered in prior literature and only a brief review is given here.

1.5.1 Types of Capillary Forces and Their Scaling Behaviour

Capillary forces refer to particle-meniscus interactions arising due to a perturbed liquid interface, which bears a certain surface tension. They can be far reaching (relative to the size of particles) and can act on single particles and between multiple particles or any other physical object. The interaction of particles by capillary forces depends on the extent which a particle can ‘feel’ the meniscus perturbation caused by the particles around it. Meniscus deformation decays roughly exponentially from the particle surface, with the capillary length of the liquid film q^{-1} (in metres) being the decay length [96], where

$$q^{-1} = \sqrt{\frac{\gamma}{\Delta\rho g - \Pi'}} \quad (1.9)$$

$\Delta\rho$ is the difference in the mass densities of the liquid and gas phases, g is acceleration due to gravity and Π' is the derivative of the disjoining pressure of the liquid ($\Pi' = d\Pi/dh_{film}$, where h_{film} is the film thickness). Far from the particles in thick films ($h_{film} > 100\text{nm}$) the gravitational force keeps the film interface flat, whereas in thin films a positive disjoining pressure creates a repulsive force between the film surfaces keeping them parallel and reducing the capillary length according to Equation 1.9. For thick films the disjoining pressure derivative vanishes and the capillary length reduces to

$$q^{-1} = \sqrt{\frac{\gamma}{\Delta\rho g}} \quad (1.10)$$

The disjoining pressure is only significant if it varies strongly with varying film thickness, which is only the case in thin films. In thick films the liquid interfaces do not ‘feel’ each other and so changes in thickness have no bearing on the disjoining pressure present. The capillary length for thick films can be on the order of millimetres ($q^{-1} = 2.7\text{mm}$ for a water-air interface) and reduce to the order of nanometers in thinner films [97].

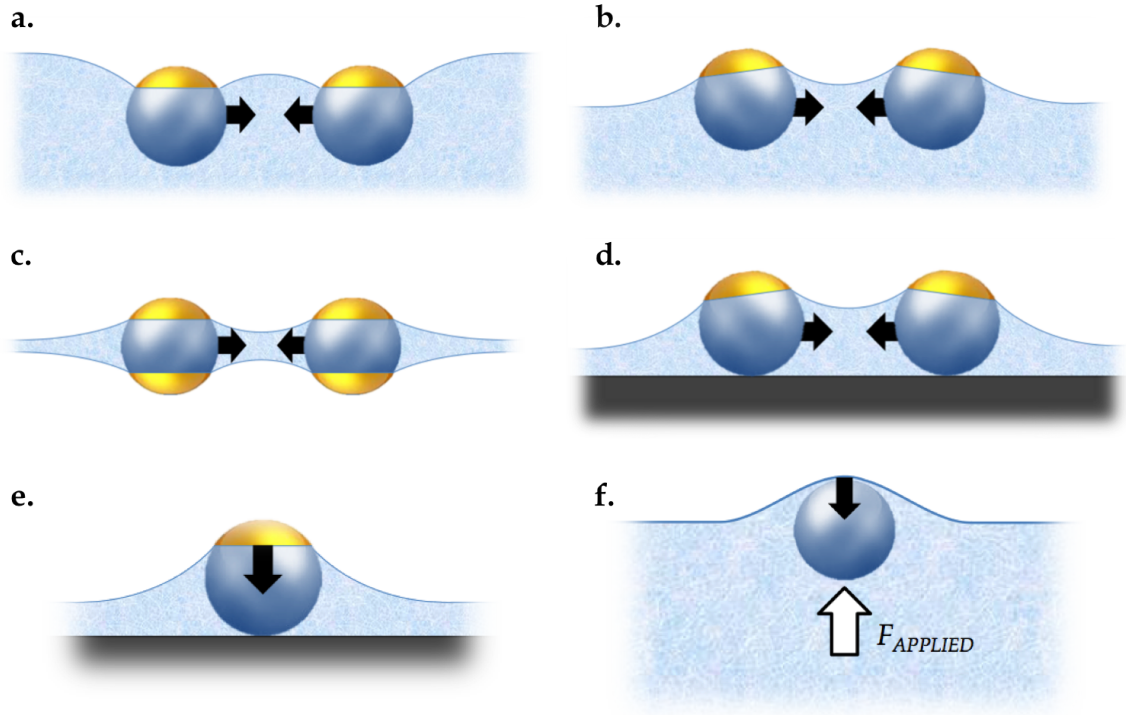


Figure 1.5: Examples of capillary forces on nanoparticles (meniscus deformation around particles is exaggerated for display purposes). The floatation regime for macroscopic particles is shown in (a) and (b), where the surface tension forces are driven by gravity. The immersion regime in a thin liquid film is shown in (c), and the same regime on a substrate is shown in (d). In cases (c) to (f) the forces are driven by the wetting properties of the particles, and thus the forces exist even on the scale of nanoparticles. Cases (d) and (e) are produced by a force applied to a particle to push it into the liquid-air interface, distorting the interface and inducing a countering capillary force.

Figures 1.5a and 1.5b depict buoyancy-induced capillary forces. For particles smaller than $10\text{ }\mu\text{m}$ their mass is insufficient to perturb the fluid interface and no floatation capillary forces exist [98].²

A regime that does allow particle size to fall to the nanometre range is that of immersion, which exists for radii down to 2 nm [98]. Figures 1.5c to 1.5f are cases of immersion capillary forces, where wetting properties cause attraction.

In Figures 1.5d to 1.5f, nanoparticles are supported by the substrate or an equivalent force. Hydrophilic particles create a downwards capillary force (e, f), which can be attractive between multiple particles (d). This is important for nano-assembly, and is discussed in more detail with supporting equations in Appendix 1.A. In the case of (f), the meniscus force is a short-lived restoring force, pushing the particle back into the bulk phase. This scenario has received little attention in literature. Most nano-CFA literature focuses on case (e). We will now present an alternative view.

1.5.2 Capillary Forces in Nano-CFA

The broken-meniscus capillary force (like in Figure 1.5e) is considered by many nano-CFA experimenters as the key assembly force. The literature assumes a particle will be exposed through the meniscus when the two are in contact. Moreover, the entire assembly process at the contact line is assumed to be from a broken meniscus acting on a particle protruding through it.

Nano-CFA literature does not consider a particle pressing against the meniscus but without breaking it (like in Figure 1.5f). This may stem from early ideas or assumptions about how nano-CFA operates. Authors of those nano-CFA works do not justify why a nanoparticle would break the meniscus.³

²Similar forces to Figures 1.5a and 1.5b can occur on nanoparticles if the particles are already thermodynamically adsorbed at the liquid-air interface (or more commonly, assembled at an immiscible liquid-liquid interface). They are not *floatation* capillary forces because gravity is not the means of distorting the interface. A nanoparticle at the interface will perturb it due to the two phases (liquid-gas or immiscible liquid-liquid) not wetting the particle surface equally. However, this is not directly applicable because in nano-CFA particles are not pre-assembled at the liquid-air interface.

³Microparticles would be much more likely to pierce the meniscus while they sit at the contact line, though whether they usually do is not conclusive. Wetting literature in general is also essentially silent on this topic.

It is unlikely that nanoparticles will pierce the meniscus until the very final moments of assembly due to their hydrophilicity and the energy required for a particle to break and displace the liquid-air interface.⁴ It is arguably more likely that a particle will press against the meniscus, deforming it like a ball against an elastic sheet, being quickly pushed back into the bulk liquid. The timeframe of this dynamic is very fast, insufficient to break the liquid-air interface.

Only at the very final moments of the assembly process are the conditions ripe for interfacial rupture—when a particle is lying against the substrate with a thin film of liquid rapidly evaporating down over it. Only in this scenario would a *broken* meniscus force reasonably apply. In nano-CFA, contrary to published assumptions, it is therefore the *intact* meniscus force (in conjunction with drag forces) that primarily operates. This is illustrated in Figure 1.6.

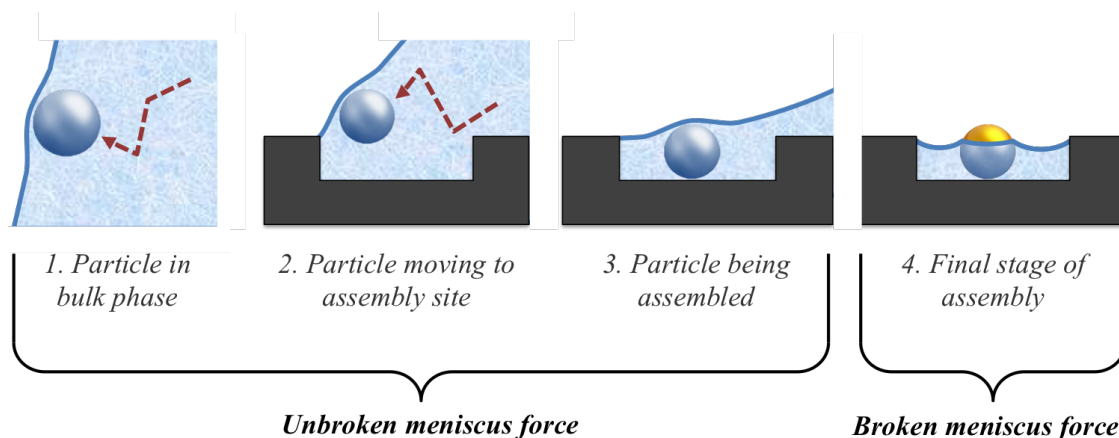


Figure 1.6: Diagram depicting the different stages of a particle’s lifetime, and whether the broken meniscus force or the intact meniscus force applies. The broken meniscus force only applies at the final moments of assembly, when a thin film evaporates down over the assembled particle. Extant nano-CFA literature has assumed a broken meniscus force applies from stage 2 onwards, though this would realistically only apply to microparticles and larger.

The distinction is made because, to the best of knowledge, no one has compared the capillary forces of the broken and intact menisci, or derived the force of an intact meniscus on nanoparticles. The work below is therefore novel to the field.

⁴This is why even amphiphilic nanoparticles do not spontaneously self-assemble at a liquid-air interface. Or from another viewpoint, the liquid interface will not easily rupture when impacted by a nanoparticle due to water’s high tensile strength, which can be well below -100 MPa [99, 100].

1.5.3 Work Done Compared to Brownian Energy

It is necessary to demonstrate that capillary forces are strong enough to supersede Brownian motion. Brownian motion is a statistical phenomenon and the energy involved can be expressed by kT , where k is Boltzmann's constant (1.3806×10^{-23} J/K) and T is the absolute temperature in Kelvin.⁵ To estimate the work done by immersion capillary forces, we integrate the force as it acts over a reasonable length scale on the particle, such as half the particle, which equates to the radius, R . This is akin to the meniscus pulling down from the top of the particle to its equator.

Derivations and discussions relating to the work done by capillary forces are largely novel to the field, but are in Appendix 1.A with only the main outcomes presented here.

The Correct Choice of Integration Variable: Other researchers have integrated the capillary force to estimate the work done on a nanoparticle, but there is doubt about the correctness of some choices of integration variable. For example, Cui et al. [48] choose a certain angle as their integration variable; the angle varies from 90° to 0° as the meniscus recedes over half the particle (their choice of angle to integrate over is similar to ψ in Figure 1.13).

Strictly speaking, the work done is only ever the *line integral* of the acting force. In our case that means integrating F_c with respect to the path that it traverses. Integrating according to an angle is an incorrect way to derive the work done, as an angle is not a distance (does not produce a line integral).⁶ Since we (like the rest of the literature in this regard) are considering a lone particle sitting on a flat substrate, the capillary force acts on the particle *vertically* at all times. We must include a parameter in our force equation that describes this vertical distance. The common expression of the immersion capillary force does not do this, so a more suitable derivation is given in the Appendix.

Incorrect analyses like Cui et al. still conclude that the work done is greater than Brownian energy, and in that they remain correct, but their mathematical analysis appears to be flawed.

⁵For example, at 25°C (298 K) the Brownian energy is 4.11×10^{-21} J.

⁶If one does dimensional analysis, then integrating with respect to an angle yields the units N·rad, which is clearly not a quantity of energy, which is N·m.

Work Done Compared to Brownian Energy: With the equations for the work done derived in the Appendix, here we convert them to be in units of Brownian energy. They are:

$$W_{Intact} = \frac{4\pi R^2 \gamma}{3kT} \quad (1.11)$$

$$W_{Broken} = \frac{4\pi R^2 \gamma}{3kT} \left(\cos(\theta_{REC}) - \frac{1}{2} \sin(\theta_{REC}) \right) \quad (1.12)$$

for the intact and broken menisci, respectively. In these equations R is the particle radius, γ is the liquid-gas surface tension, kT is the Brownian energy, and θ_{REC} is the receding contact angle of the liquid on the particle surface. The capillary force from an intact meniscus is identical to that of a broken meniscus with a receding contact angle of zero degrees.

The above energy equations are plotted in Figure 1.7 for various receding contact angles and various particle sizes. The surface tension is 0.072 J/m for a water-air interface, and the temperature is 45°C, which is common for nano-CFA experiments. It is seen that even for very high receding contact angles and for very small nanoparticles, the work done over half the particle is greater than the Brownian energy. This gives us confidence that meniscus forces, whether a three-phase contact line is formed or not, can greatly exceed Brownian diffusion effects.

It is also shown that particles will not leave the liquid and deposit onto the substrate by thermal effects alone, even at very high temperatures. A particle will mostly deposit on a substrate only if the capillary forces are suitably inclined (ignoring effects from aggregation, and also particle-substrate interactions which can be engineered into the system if desired). This means that we can potentially achieve great control over particle placement if we can adequately manipulate capillary forces.

In the following section we discuss convective and Marangoni drag forces.

1.5.4 Convective and Marangoni Drag Forces on Nanoparticles

The only other liquid-mediated force on nanoparticles paramount to nano-CFA is the drag force. This is the final aspect of theory to be covered before we explain the conventional model of nano-CFA.

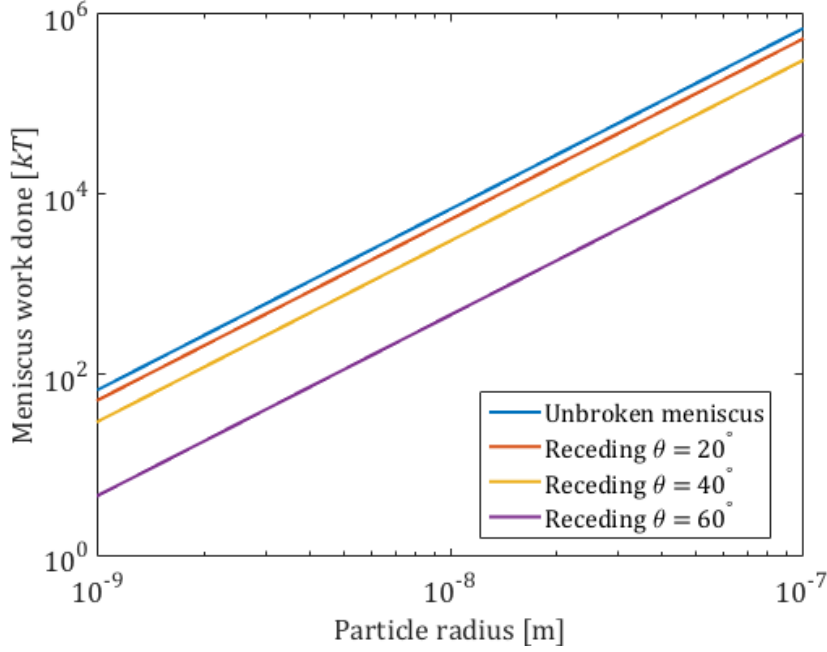


Figure 1.7: The net work done by the capillary force as the meniscus recedes from the top to the equator of a spherical particle. The work done is in Brownian units of kT , and is plotted for various receding contact angles and various particle radii. It is seen that even for large receding contact angles on very small nanoparticles, the net work done is still larger than the Brownian energy. It is also seen that the work done decreases as the receding contact angle increases. The maximum work is done when the meniscus remains intact, or when the broken meniscus wets the particle very strongly (very low receding contact angles).

Drag Force on a Nanosphere in Laminar Flow: The origin of the drag force is the differential velocity of the particle relative to the net motion of the surrounding liquid molecules. It is driven by friction between particle and liquid. Two primary types of liquid flows are present in evaporating liquid bodies: convective flows and Marangoni flows.

We consider only the case of laminar flow (as opposed to turbulent flow), which is given as a flow with Reynolds number, $Re < 10$ (for a sphere in a homogenous fluid). The Reynolds number is the ratio of inertial to viscous forces within the fluid. For a sphere in liquid, the Reynolds number is defined as

$$Re = \frac{\text{Inertial forces}}{\text{Viscous forces}} = \frac{\rho_f v d_c}{\mu_f} = \frac{v d}{\nu_f} \quad (1.13)$$

where ρ_f is the mass density of the fluid, v is the relative speed between the fluid and the sphere, d_c is the characteristic length scale of flow (which for our case, d

is the diameter of the sphere) and μ_f is the fluid’s dynamic viscosity. The kinematic viscosity (ν_f) of a fluid is ρ_f/μ_f , so we can write the equation in both forms above.

Stokes’ law governs the drag force in laminar flow, which for a sphere is

$$F_d = 3\pi \mu_f d v \quad (1.14)$$

where d is the diameter of the nanosphere.⁷

Given that Brownian motion is due to the *random* collisions of surrounding molecules with the nanoparticle, whereas the drag force is due to the *concerted* frictional forces from surrounding molecules under *uniform* motion, it is self evident that laminar drag forces will supersede Brownian diffusion and impart predictable motion to a nanoparticle in the direction of flow. We therefore now consider convective and Marangoni flows in relation to nano-assembly.

Convective Flows: Convective flow-driven movement of nanoparticles is clearly seen through characteristic deposition patterns after colloidal droplet evaporation, as many studies affirm theoretically and experimentally [102–111].

Most significantly, the evaporation rate dramatically increases close to the three-phase contact line, as in Figure 1.8a. The evaporation rate is limited only by the rate at which liquid vapour can diffuse away from the droplet surface into the ambient atmosphere [112, 113].

A strong convective flow is setup driving liquid and particles to the contact line. As the liquid evaporates, the particles held at the contact line will be deposited, producing the familiar ‘coffee-ring effect’ [115, 116]. Convective deposition at the contact line can be unlimited if there are no counteracting liquid flows, such as Marangoni flows.

Thermally-Induced Marangoni Flows: Marangoni flows refer to any liquid motion arising from variations in surface tension. Flow is directed to regions of higher

⁷Stokes’ law in water holds for particles larger than ~ 3 nm, or in other words when the Knudsen number is > 0.1 . The Knudsen number is the ratio of the mean free path length (of the molecules in the particle’s environment) to the particle size itself (to calculate the Knudsen number use an equivalent mean free path length in water ~ 0.2 nm). It indicates whether the environment will appear homogenous or particulate to the particle. For smaller particles, the Cunningham correction factor needs to be added to Stokes’ law to maintain accuracy [101].

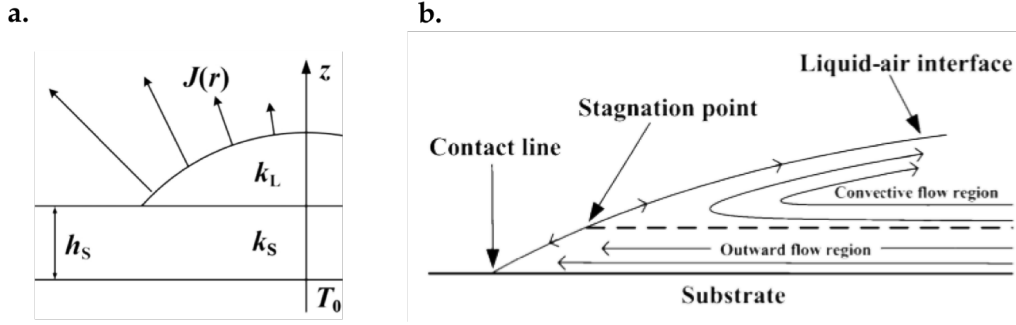


Figure 1.8: (a) A diagrammatic cross-section of a spherically-capped sessile droplet showing the increasing evaporation rate, $J(r)$, towards the contact line (from Ref [114]). The substrate thickness is h_s , the substrate temperature is T_0 , and the thermal conductivities of the substrate and liquid are k_s and k_l , respectively. (b) A diagrammatic cross-section of a sessile droplet showing the internal fluid flows (from Ref [110]). The stagnation point is due to the superposition of convective and Marangoni flows. Only particles in the ‘Outward flow region’ are collected at the contact line.

surface tension, and can be setup by a non-uniform concentration of surfactants or by variations in temperature [117] (higher temperatures lower the surface tension of water).

An evaporating droplet on a heated substrate will have the highest temperature (and lowest surface tension) near the contact line. The surface tension gradient draws liquid along the droplet interface away from the contact line [110, 118–120]. Such Marangoni flows will counteract evaporative convective flows and can limit ‘coffee-ring’ deposition or even prevent it entirely [121].

The real situation is often more complicated, however, due to evaporative cooling [122, 123]. Strong evaporation at the contact line cools that region, which means the minimum surface tension point is often not at the contact line, but slightly offset from it. Marangoni flows are directed away from this point, which is now a flow stagnation point, with flows emerging towards the contact line and towards to the droplet apex, as shown in Figure 1.8b. This scenario can even occur from the balance of convective and Marangoni flows without evaporative cooling. Internal droplet flows with surface Marangoni flows are also as shown in the diagram.

Whether Marangoni flows will actually exist, and how much they interact with convective flows is a complicated function of the substrate and ambient temperatures, the thermal conductivities of all phases, the substrate thickness, the ambient humidity, the contact line curvature and the contact angle of the liquid on the sub-

strate [104, 110, 114, 123–126]. All possible scenarios can be created, from one extreme where there is an ever-increasing deposition of particles at the contact line, to an intermediate case of a Marangoni-limited concentration of particles at the contact line, to the alternate extreme of a Marangoni-induced reversal of contact line deposition entirely.

The Challenge to Fluid-Mediated Nano-Assembly: This is highly relevant to liquid-mediated nano-assembly, as convective and Marangoni flows are the large scale driver of nanoparticles to the contact line for assembly. Marangoni flows in particular can be highly influential in nano-assembly [116, 121, 127–129].

These flows are well understood in spherically-capped sessile droplets (up to approximately 2 mm in diameter for water), but much less so in non-axisymmetric liquid bodies (like CFA). Understanding the flows in a particular nano-assembly system is non-trivial, and many experimenters appear to have taken it for granted that particles will simply collect in some fashion at the contact line. Yet flow strength must be mediated according to the required rate of deposition. Nano-CFA literature gives little discussion about how different assembly conditions (namely temperature, the receding contact angle and surfactant concentration gradients) affect the concentration of particles at the contact line, and it is also very difficult to meaningfully measure.

1.5.5 Comparison of Force Magnitudes

Having covered the forces relevant to fluid-mediated assembly, it is useful to compare their magnitudes. The forces are listed in Table 1.1. Where applicable, the separation (d) between particles is $2R$, where R is the particle radius. The particles have the density of gold ($\rho_{Au} = 19,300 \text{ kg/m}^3$), with a receding contact angle of $\theta_{rec} = 40^\circ$ for a Au/citrate-Water system [130]. The surface tension is $\gamma_{Water-Air} = 0.072 \text{ N/m}$. Capillary force equations assume a broken meniscus positioned at the particle equator to yield the largest contact line.

Figure 1.9 shows how the force magnitudes vary. Capillary forces are evidently the strongest over all nanoparticle radii, with the greatest competition coming from the Van der Waals and Brownian forces.

Force	Equation	Notes
Gravitational force	$F_{Grav} = m.g$	$g = 9.8 \text{ m/s}^2$
Van der Waals force	$F_{VdW} = AR/12d^2$	Adapted from Ref [131] for two identical spheres. $A_{Au-Water-Au} = 2.5 \times 10^{-19} \text{ J}$ [132]
Two particle lateral capillary force	(1) $F_{LatCap} = 2\pi\gamma Q_1 Q_2 q K_1(qd)$ (2) $Q_1 = Q_2 = R \cos(\theta_{rec})$	(1) Equation 1.38. (2) Based on Equation 1.39. $q^{-1} = 2.7 \text{ mm}$
Single particle immersion capillary force	$F_{ImmCap} = 2\pi R\gamma \cos(\theta_{rec})$	Based on Equation 1.17.
Drag force	$F_{Drag} = 6\pi\mu_f Rv$	Based on Equation 1.14. $v = 100 \text{ }\mu\text{m/s}$, $\mu_f = 8.9 \times 10^{-4} \text{ Pa.s}$
Brownian force	$F_B = kT/d$	This is an approximation to the Brownian force [133]. $k = 1.3806 \times 10^{-23} \text{ J/K}$, $T = 298 \text{ K}$

Table 1.1: Table of forces relevant to nano-CFA.

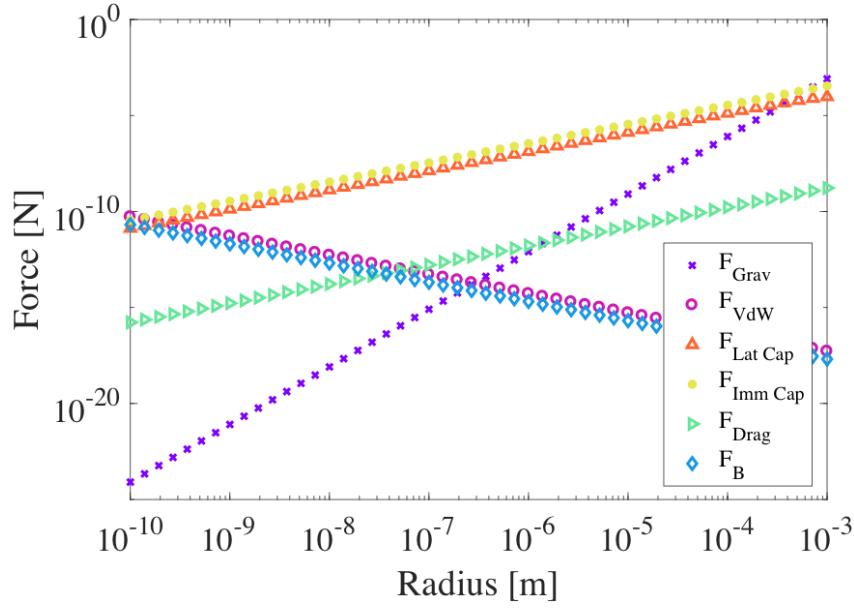


Figure 1.9: A comparison of forces relevant to fluid-mediated assembly, as given in Table 1.1.

1.6 The Conventional Model of Nano-CFA: A Review

1.6.1 Overview of the Conventional Model

Having covered the primary forces involved in CFA of metal nanoparticles, we are now in a position to explain CFA as it is presented in current literature. In the most basic sense, CFA operates by placing a colloidal suspension on a patterned substrate called the *template*, and allowing the liquid to evaporate. Cavities in the template are designed to hold particles in the desired arrangement. All CFA work presumes Wenzel wetting, not a Cassie-Baxter state (particles will not deposit in non-wetted cavities). As the liquid evaporates, the three-phase contact line sweeps over the template and particles are assembled into the cavities. Van der Waals forces are sufficient to hold the particles in place post-evaporation, securing the assembly.

A literature review of nano-CFA dynamics has not been published to date. Different papers suggest different dynamics and the discussion below is the first review of its kind. According to current literature, nano-CFA is reliant on:

1. A suitable receding contact angle [48, 53, 134–137]
2. A sufficiently high concentration of particles at the contact line [52, 53, 134, 136–138]
3. We can also add to the list a sufficiently low (or high) contact line speed to allow assembly [53, 135].

This conventional model is diagrammatically presented in Figure 1.10, and will be challenged later in this work.

Extant literature discussing nano-CFA dynamics focuses primarily on single cavities. The dynamics over a single cavity are essentially the same over an array, though probably scaled slightly different depending on array density. Understanding single-cavity dynamics is of foremost concern to understand scalable array-based nano-CFA.

Conventional Requirement #1. A suitable receding contact angle: As Figure 1.10 explains, the receding contact angle is thought to be critical in setting the direction of the capillary force. If the capillary force is too vertical, particles will deposit too easily; if it is too horizontal, particles will not deposit sufficiently.

Depending on the experimental setup, the receding contact angle may not be determined exclusively by wettability, and any additional forces on the liquid interface must be accounted for. The receding contact angle must be characterised for each degree of freedom in each experimental setup.

Conventional Requirement #2. A sufficiently high concentration of particles at the contact line: This aspect is strongly dependent on the liquid temperature, being convectively driven. Temperatures of approximately 50°C are often used. Thermally-induced Marangoni flows are often observed, and so the accumulation process tends to be self-limiting, with the extent of the accumulation zone being on the order of 10 μm or less away from the contact line [53]. If the temperature is raised high enough, then the evaporation rate and evaporative cooling can produce a mounting accumulation of particles at the contact line, eventually resulting in uncontrolled deposition and self-pinning.

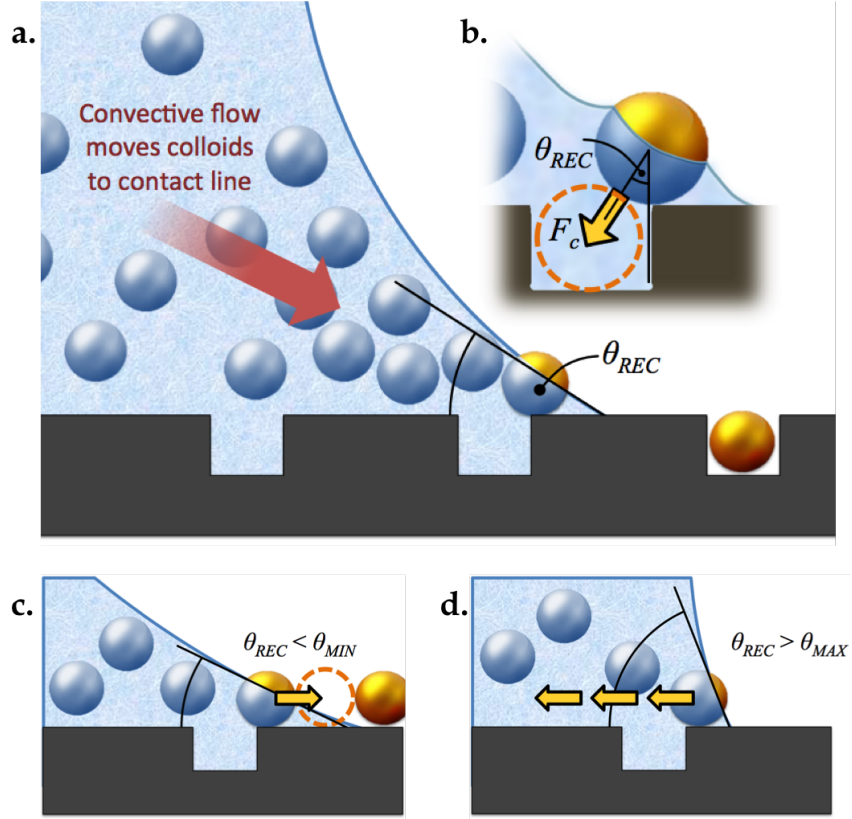


Figure 1.10: A diagram depicting the conventional model of nano-CFA, with its strong dependence on the receding contact angle. In image (a), the conventional model is portrayed as a convective flow of particles to the three-phase contact line. The second aspect of the conventional model entails particles at the contact line protruding through the meniscus and experiencing a capillary force, which drags particles along the template as the contact line recedes. In images (b), (c) and (d), the alleged role of the receding contact angle is shown. If the contact angle is suitable, it will direct particles into cavities (b), whereas if it is too low it will deposit particles even when no cavity is present (c), and if the angle is too high it will drag particles across cavities without assembling them (d).

Conventional Requirement #3. A suitable contact line speed: A suitable contact line speed for assembly is very rarely commented on. Studies will often state the speed of their contact line, but no one has yet systematically studied how it affects deposition patterns. Table 1.2 gives the typical speeds.

Published Experimental Implementations: This, then, is an overview of the conventional model of nano-CFA. Table 1.2 presents published parameters. Not all studies state the relevant experimental data. Only CFA of nanoparticles (not DNA, viruses, etc.) is used in the table to ensure comparability across all studies.

In the last two columns of the Table, the extent and density of assembly is shown. Ordered assembly of nanostructures, or even single nanoparticles, has not been demonstrated over areas larger than $100 \times 100 \mu\text{m}^2$, except for very recent work by Flauraud et al. [144] where they claim $5 \times 5 \text{ mm}^2$ nanorod assembly. However, Flauraud et al. do not demonstrate long-range order on close-packed arrays, nor do they show a macroscale optical effect, both of which are key goals of this work. Most prior works also assemble with comparatively large periodicities (μm 's), meaning the density is low and any far-field optical effect is likely to be weak or undetectable.

There are a variety of implementations of CFA, such as the sessile droplet evaporation method, or slowly withdrawing a template out of a colloidal bath, or manually dragging a colloidal suspension across a template, and other methods [46]. They all leverage the same principles described above and give different degrees of control over the CFA process.

1.6.2 The Two Flavours of the Conventional Model

Having presented the basics of the conventional model, let us now probe the model in more detail. Upon examining the nano-CFA literature, one finds that the conventional model actually comes in two flavours. No one has reviewed the literature to identify this prior to now. These two flavours are henceforth labelled as Scheme 1 and Scheme 2. To clarify, the two Schemes are not different methods of CFA, but are researchers' competing opinions about the as-yet undemonstrated nano-CFA dynamics.

The two Schemes are often not strongly evident in the actual *text* of papers,

Source	Contact Angle	Contact Line Speed	Maximum Array Area	Minimum Inter-Cavity Spacing
Cui et al. [48]	10° to 30°	Not stated	$100 \times 100 \mu\text{m}^2$	1 μm
Pinedo Rivera et al. [135]	24° to 37°	1.7 to 3.3 $\mu\text{m/s}$	Not stated	2 μm
Pinedo Rivera et al. [139]	30°	Not stated (but deduced to be ~ 1 to 3 $\mu\text{m/s}$)	Not stated	4 μm
Kuemin et al. [136]	56°	2 $\mu\text{m/s}$	$\sim 80 \times 80 \mu\text{m}^2$	1 μm
Fan et al. [137]	25°	0.6 $\mu\text{m/s}$	Not stated	2 μm
Rey et al. [140]	50°	0.1 $\mu\text{m/s}$	Not stated	Not stated
Kuemin et al. [138]	35°	0.5 to 1 $\mu\text{m/s}$	$50 \times 60 \mu\text{m}^2$	500 nm
Kraus et al. [134]	50° to 60°	0.3 $\mu\text{m/s}$	$\sim 80 \times 80 \mu\text{m}^2$	280 nm
Liddle, Cui and Alivisatos [141]	10° to 30°	0.17 $\mu\text{m/s}$	Not stated	1 μm
Gordan and Peyrade [52]	Not stated	0.1 to 2 $\mu\text{m/s}$	$100 \times 100 \mu\text{m}^2$	850 nm
Malaquin et al. [53]	30° to 60°	0.2 to 10 $\mu\text{m/s}$	Not stated	100 nm
Mehraeen et al. [142]	12°	1.7, 5 and 17 $\mu\text{m/s}$	N/A	N/A
Asbahi et al. [143]	12°	10 $\mu\text{m/s}$	$5.4 \times 4 \mu\text{m}^2$	27 nm
Flauraud et al. [144]	50°	1 to 2 $\mu\text{m/s}$	$5 \times 5 \text{ mm}^2$	> 500 nm

Table 1.2: Table of relevant published nano-CFA experimental parameters.

but one finds that they are clearly depicted in the *diagrams* that are given. This is because textual descriptions tend to be extremely generic, giving few details about the suspected assembly process, if any at all. Diagrams more evidently present what is in the mind of the researchers. The rarity of written statements is thought to reflect the lack of conclusive knowledge about the assembly process, whereas diagrams are more apt to communicate general ideas that lack clarity in the details.

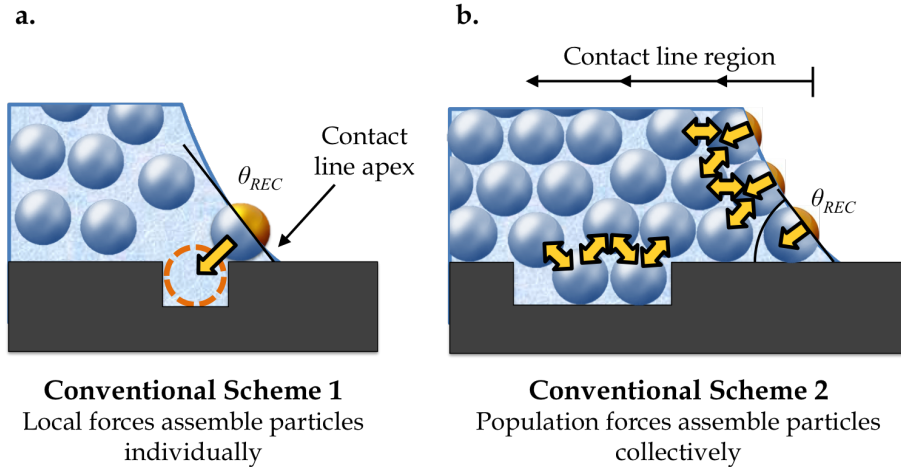


Figure 1.11: Diagrams depicting the two Schemes of the conventional nano-CFA model. Yellow arrows represent forces. In Scheme 1 (a) particles at the contact line apex experience a meniscus force, while particles nearby loosely constrain Brownian motion. Particles are assembled individually by the meniscus force. In Scheme 2 (b) the packing is semi-crystalline. There is a plane of particles against the liquid-air interface, which all experience a meniscus force, compressing the population against the template. Particles over a cavity are pressed into the cavity. Particles are assembled collectively before reaching the contact line apex.

Scheme 1—Assembly by Local Forces: Scheme 1 of nano-CFA is depicted in Figure 1.11a. Many early papers suggest this Scheme [48, 135–137, 139, 143, 145–147].⁸ Asbahi et al. [143] have used this Scheme to attempt simulation of sub-10 nm particle assembly.

In this Scheme, particles are loosely packed at the contact line. Particles in contact with the liquid-air interface experience a meniscus force, but due to the non-close contact between particles, this force is not reliably transmitted to other

⁸Interestingly, [135] depicts Scheme 1 in Figure 1 of their paper and Scheme 2 in their Figure 4, but they do not recognise these differing ideas in their text.

particles. Particles are assembled individually at the contact line apex by the meniscus force pressing a particle against the rear wall of a cavity wall (when a cavity is present there). The cavity traps the particle, preventing the meniscus force dragging it with the receding contact line. The loosely packed population of particles limits Brownian motion to prevent diffusion, and resupplies the contact line apex with new particles once others have been assembled.

This is as much detail as can be given according to published diagrams and descriptions. This mechanism would well apply to micro-CFA, owing to the low Brownian motion of microparticles, but for reasons detailed later it is unlikely to apply to most cases of nano-CFA.

Scheme 2—Assembly by Population Forces: Scheme 2 is illustrated in Figure 1.11b. Compared to Scheme 1, Scheme 2 is not as well described in its host papers [134, 135, 138, 140, 142, 148–150], except for in Mehraeen et al. [142] who describe this Scheme from the simulated assembly of sub-10 nm particles. They suggest it as a new model, but it is in reality just a more thorough description of an old model that has never been properly described (thus it appeared new to the researchers). Others clearly depict this Scheme in their published diagrams, and occasionally brief descriptions are given, but as usual, textual descriptions are typically vague, indicative of the lack of clear understanding about nano-CFA dynamics.

In Scheme 2, particles are semi-crystalline packed at the contact line all through the contact line region (from the apex to a distance of some μm away from the apex). There is a plane of particles in contact with the liquid-air interface which experiences a meniscus force that is transmitted to all other particles. The compressive force applied to the population by the meniscus pushes particles into cavities all at once. Particles are assembled collectively, not individually as in Scheme 1. The dense packing greatly limits Brownian motion and particles cannot diffuse anywhere. It also allows the meniscus force to compress the entire population against the substrate.

According to published diagrams and descriptions, this is as much detail as can be said about Scheme 2. For reasons given later, it is unlikely that this Scheme is actually describing true nano-CFA in most cases.

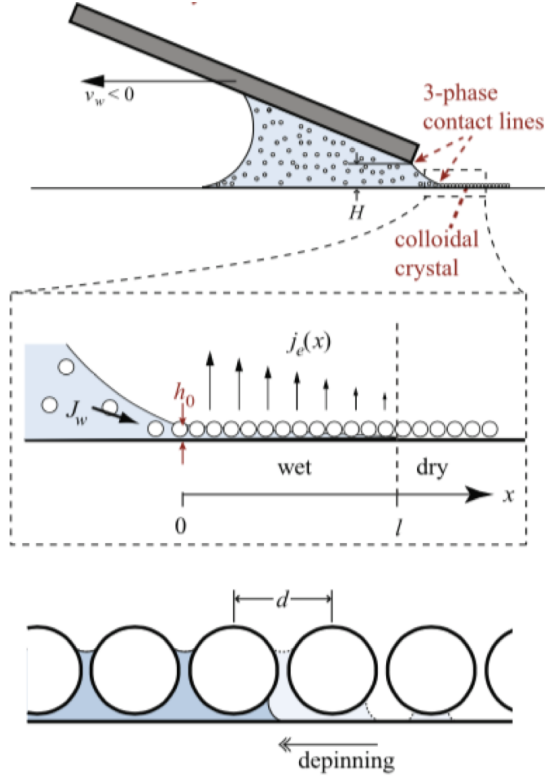


Figure 1.12: (Upper) A depiction of convective layer deposition from a slowly moving slider apparatus. (Middle) An illustration of colloidal activity at the contact line, forming a crystalline film. $j_e(x)$ is the evaporation rate and J_w is the convective flux of particles to the contact line. (Lower) The stages of depinning within the crystalline film, where capillary forces draw particles together and onto the substrate. (From Ref [47])

1.7 Convective Layer Deposition

In addition to CFA dynamics, it is worth briefly mentioning another form of assembly at low contact angles. Convective layer deposition (CLD) is when the convective flow drives particles to the contact line, as in CFA, but the contact angle is so low that particles are pressed onto the substrate by the receding meniscus, causing the contact line to pin momentarily. CLD is relevant because CFA transitions to CLD if the contact angle becomes too low or the contact line too slow. This concept will be addressed later, requiring a basic understanding of CLD.

Very low contact angles ($< 10^\circ$) cause particles to accumulate quickly enough such that a semi-crystalline layer(s) of particles grows out of the receding meniscus [46, 151]. Immersion capillary forces between particles (see Section 1.A) draw particles together into a dense arrangement [66]. Withdrawal speeds vary up to $100 \mu\text{m/s}$ at low humidities, but decrease with lower wettabilities [47]. This is depicted in Figure 1.12.

CLD can also be achieved at higher contact angles if the contact line moves sufficiently slow [152–154] ($\ll 1 \mu\text{m/s}$, and the deposition takes hours or days to complete). With such a slowly moving contact line, water evaporates away from

particles faster than the particles are dragged to a new position. Hence the particles remain deposited on the substrate.

The deposited layers typically have patches of crystalline packing [152, 155], and prior work has focussed on minimising the cracks between domains to produce crystalline layers [49, 156]. Crystalline layers are useful for purposes like lithography masks, nano-coatings, optical data storage and other applications [49, 151, 153].

1.8 Conclusions

The quest for nano-assembly has captured the attention of researchers worldwide who are seeking to build novel devices and materials. Liquid-mediated assembly of metallic nanoparticles is of particular interest to create plasmonic devices and materials. We have briefly reviewed the physics of plasmonics and some of its applications.

The two hurdles for nano-assembly are: (1) overcoming Brownian motion, and (2) doing so with enough fidelity that close-range attraction forces do not prematurely stick nanoparticles in unwanted positions. Nano-CFA has demonstrated the ability to overcome these hurdles, and a current challenge is to densely assemble particles over macro-scale areas.

The current model of nano-CFA has been presented, and a thorough review showed two different ideas about nano-CFA’s workings existing side-by-side in the literature. Whilst these ideas differ in their details, they both leverage the same basic principles of the ‘capillary force’ model. Detailed knowledge about nano-CFA dynamics is lacking in literature, and suggested assembly mechanisms appear as more conjecture than demonstrated fact.

It has been highlighted that the current model neglects to account for all liquid phenomenon relevant to nano-CFA, notably contact line pinning on cavities and the implications of this.

Scaled-up nano-assembly cannot be adequately pursued without a comprehensive model for nano-CFA. We must understand what the primary experimental factors are, and how to optimise them. This thesis aims to address this issue via the following three questions:

1. Is it feasible to scale-up nano-CFA to make centimetre-squared optical plasmonic nanomaterials?
2. The mechanism behind nano-CFA has not been well studied or elucidated to date. What are the key mechanisms behind nano-CFA?
3. Nano-CFA is a nano-scale process on very short timescales and so is not readily observable in detail. How can we probe the mechanisms of nano-CFA and quantify them for a comprehensive model?

In that light, Chapter 2 overviews conventional equipment and methods. Chapter 3 reports on scaling-up nano-CFA over centimetre-squared areas, and the difficulties encountered therein. Chapter 4 presents experimental and theoretical shortcomings of the current nano-CFA model, and Chapter 5 lays out an arguably more accurate model. The subsequent three chapters (6 to 8) demonstrate new experimental techniques and findings to probe the relevant liquid dynamics on the micro- and nanoscale, quantifying some key aspects of the new nano-CFA model. In the final chapter we tie together the key findings into a summary of nano-CFA, and explain opportunities for further work.

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Appendix

Appendix 1.A Capillary Forces on Particles: Derivations and Analyses

Capillary Force of a Broken Meniscus on a Single Particle

Various analyses of a particle piercing a thin film on a substrate can be found in-depth in literature on the wetting of particles at interfaces [1–9] and in less detail in various nano-CFA literature [10–13].

Consider a single sphere deforming a liquid-fluid interface, as depicted in Figure 1.13. In this scenario the substrate is applying the force required to push the particle through the liquid surface and create the interfacial perturbation leading to a capillary force, however in a theoretical sense a force equivalent to that of the substrate may be applied via an alternate means within the bulk liquid phase to create an identical interfacial perturbation. The only requirement is that the applied force be long-lived enough for the meniscus to break and form a three-phase contact line around the particle.

Surface Tension Analysis

The contact angle α of the system in Figure 1.13 obeys the Young equation (assuming the nanoparticle is molecularly smooth) [1, 14–16]

$$\frac{\gamma_{II} - \gamma_I}{\gamma} = \cos(\alpha) \quad (1.15)$$

where γ refers to the surface free energy densities of the particle-phase I interface (γ_I), particle-phase II interface (γ_{II}) and the phase I-phase II interface (γ).

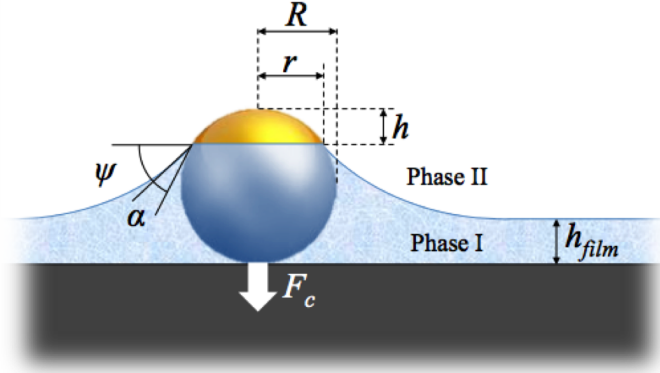


Figure 1.13: A single particle at a liquid-fluid interface (α is the contact angle, ψ is the meniscus slope angle, F_c is the net capillary force).

The magnitude of the vertical capillary force F_c can be found by integrating the interfacial tension along the path it acts on—the three-phase contact line [17]:

$$F_\gamma = \int \gamma dl = 2\pi r\gamma \quad (1.16)$$

where r is the three-phase contact line radius, given by geometry as [18]

$$r = R \sin(\alpha + \psi)$$

The capillary trapping force (F_c) is the component of F_γ normal to the mean liquid interface (in the case of Figure 1.13 this force is vertical) [11]

$$F_c = 2\pi r\gamma \sin(\psi) \quad (1.17)$$

This describes the magnitude of the capillary force pulling the particle onto the substrate. This is the most common expression of the capillary force in this scenario.

Laplace Pressure Analysis

Han, Li and Lin [19] refer to the capillary force as being the result of the pressure difference that develops across the liquid-air interface when the interface is distorted around a particle. Here we elaborate on their brief comments. The pressure across a liquid-gas or liquid-liquid interface is known as the Laplace pressure, and is given by the Young-Laplace equation

$$P_L = P_{liquid} - P_{vapour} = \gamma \left(\frac{1}{r_1} + \frac{1}{r_2} \right) \quad (1.18)$$

The size and sign of the interfacial curvature is directly related to the pressure difference. In equation 1.18, γ refers to the interfacial surface tension, and r_1 and r_2 refer to the principle radii of curvature (i.e. the radii of curvature of the two orthogonal axes of the interface). As seen by the equation, the pressure difference is maximum when the curvature is maximum (when the radii of curvature are minimum).

For a hydrophilic particle, like that shown in Figure 1.13, the interface bears a positive curvature on the air side of the interface. This translates to a lower pressure existing in the liquid phase around the particle. The air pressure surrounding the upper portion of the particle is greater than the liquid pressure surrounding the lower portion of the particle. Naturally the air pressure does not change, but the liquid pressure changes as a result of the curvature of the meniscus. The pressure differential results in a net force exerted at the interface, and directed towards the region of lower pressure, that is, downwards towards the substrate. Thus the capillary force can be interpreted as the force resulting from a pressure differential around the particle, as a result of the way the liquid wets the particle.

Liquid Displacement Analysis

In an alternative analysis, Keller (1998) shows that the vertical component of the interfacial tension force is equal to the weight of liquid displaced by the deformed meniscus, as depicted in Figure 1.14 (the green shaded region) [20]. An analytical expression for this scenario requires a mathematical description of the meniscus, which according to Kralchevsky *et al.* (2000) takes the form in cylindrical coordinates of [15]

$$\zeta(r_p) = r \sin(\psi) K_0(qr_p) \quad (1.19)$$

where r_p is a radial vector to an arbitrary point on the horizontal plane, and K_0 is the modified Bessel function of zeroth order.

One may also consider the hydrostatic pressure force F_p acting on the particle. For a particle at a liquid-gas interface Keller demonstrates that the vertical component of this force is equal to the negative of the net weight of fluid displaced by the

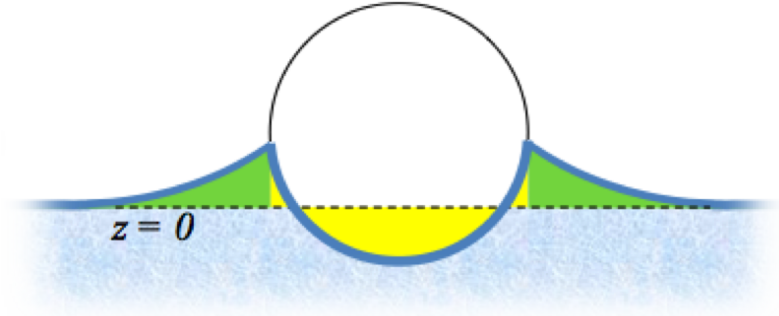


Figure 1.14: Calculation of interfacial tension force F_γ and hydrostatic pressure force F_p of a partially submerged particle, based on Keller (1998) [20]. The weight of water in the green region equals the vertical component of the interfacial tension force, and the weight of water in the yellow combines to equal the vertical component of the hydrostatic pressure force. Regions above the $z = 0$ line contribute negatively to the net force (downwards force); regions below the $z = 0$ line contribute positively to the net force (upwards force). The solid blue line marks the deformed liquid interface, whose height at all points relative to the $z = 0$ plane is denoted by $z(x, y)$

particle bounded by the meniscus above the horizontal fluid surface, also depicted in Figure 1.14 (the yellow shaded region) and conforming to [20]

$$F_p = -\rho g \int_{A_h} z(x, y) dx dy \quad (1.20)$$

where ρ is the liquid density, g acceleration due to gravity, and $z(x, y)$ the curve describing the height of the liquid interface across the horizontal x - y plane relative to the $z = 0$ plane. The integration boundary A_h is the circular area bounded by the projection of the three-phase contact line onto the x - y plane.

The buoyancy force (the gravitational force less the hydrostatic pressure force) is therefore closely related to the volume of the particle, which scales as R^3 . Indeed the buoyancy force of a particle fully absorbed into the bulk liquid phase is

$$F_b = \frac{4}{3}\pi R^3(\rho_{particle} - \rho_{liquid})g \quad (1.21)$$

This R^3 dependency causes the buoyancy force to quickly diminish relative to the vertical capillary force, which scales as R .

Capillary Force of an Intact Meniscus on a Single Particle

We now derive the force on a particle pressing against the meniscus but not rupturing it. This derivation is explained in more detail since it is not available in the literature.

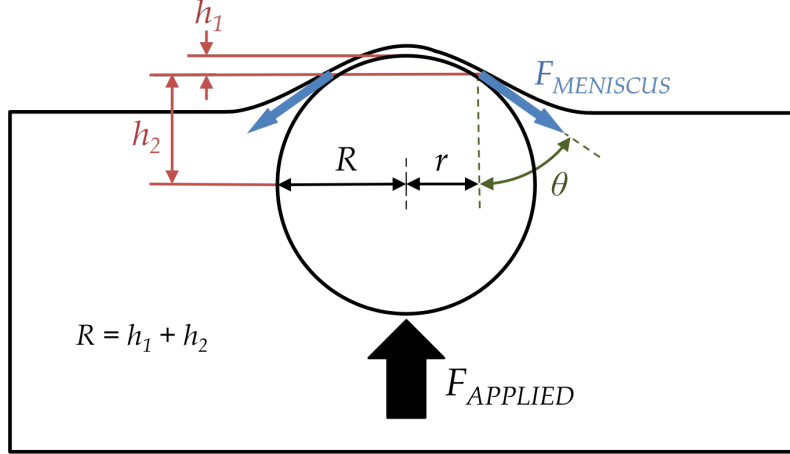


Figure 1.15: A diagram showing the key geometrical parameters for force analysis of a particle pressing against the meniscus yet without breaking the meniscus. R is the radius of the particle, while r is the radius of the inflection point in the meniscus, where the capillary force is applied. Distance h_1 is the height of the particle above the inflection point, and $h_2 = R - h_1$. Angle θ describes the direction of the meniscus force relative to the vertical axis. Note that the decay of the meniscus perturbation outside the particle has been greatly exaggerated. The true meniscus profile outside the particle would be much more gradual.

The relevant geometrical parameters are presented in Figure 1.15. Surface tension translates into a force when it is integrated over a length element, not an area. The capillary force is thus applied to the particle around the inflection point in the meniscus. This is similar to the force analysis applied to bubbles and immiscible droplets crossing a liquid interface (e.g. Ref [21]).

The inflection point stretches as a circle around the particle at a radius r from the vertical centreline of the particle. Parameters h_1 and h_2 represent the portion of the radius of the particle that are above and below the inflection point, respectively (and so $h_1 + h_2 = R$, the particle's radius). Parameter θ is the angle subtended by the meniscus (at the contact line) relative to a vertical axis. Note that the decay of the meniscus profile outside the inflection points has been greatly exaggerated in the diagram. In reality it would be much more gradual.

Following similar reasoning to that applied to a broken meniscus, the vertical component of the meniscus force in Figure 1.15 is

$$F_c = 2\pi r \gamma \cos(\theta) \quad (1.22)$$

It would be useful to represent Equation 1.22 in terms of parameters h_1 , h_2 and R . By trigonometry we can derive

$$\cos(\theta) = \frac{r}{R} \quad (1.23)$$

$$r = \sqrt{h_1(2R - h_1)} \quad (1.24)$$

$$= \sqrt{R^2 - h_2^2} \quad (1.25)$$

Substituting these into Equation 1.22 leads to the vertical meniscus force in terms of R and either h_1 or h_2 .

$$F_c = 2\pi \gamma h_1 \left(2 - \frac{h_1}{R} \right) \quad (1.26)$$

$$= 2\pi \gamma \left(\frac{R^2 - h_2^2}{R} \right) \quad (1.27)$$

These equations will be useful later on.

If we consider the relationship to the Laplace pressure, we first note that as per Equation 1.18, the pressure difference across the interface from a spherical distortion of curvature $1/R$ is

$$\Delta p = \frac{2\gamma}{R} \quad (1.28)$$

where R equates to the radius of the particle. From Equations 1.22 and 1.23 we can say that

$$F_c = \frac{2\gamma}{R} \cdot \pi r^2$$

which equates to

$$\begin{aligned} F_c &= \Delta p \cdot \pi r^2 \\ &= \Delta p \cdot A_p \end{aligned} \quad (1.29)$$

Therefore, the capillary force from an intact meniscus is equal to the interfacial pressure difference (Δp) applied to the surface of the particle that is pressing against the meniscus, scaled according to the projection of this surface onto the plane of the unperturbed meniscus ($A_p = \pi r^2$, i.e. projected in the direction of interest).

Note that in this analysis the liquid interface is assumed to be primarily distorted over the particle, with the distortion decaying only very gently away from

the particle. This is justified by the fact that we are here considering a particle distorting the meniscus in the bulk phase. The decay length of meniscus perturbations in the bulk phase is on the order of millimetres. This means that the meniscus curvature is high only over the cap of the particle (the portion that is pressing against the meniscus), and not in the surrounding meniscus as the perturbation decays into the flat liquid-air interface. The interfacial pressure differential is significant only where the particle is pressing against the meniscus. The negative interfacial pressure arising from the inverse curvature in the interface as the deformation decays away from the particle can thus be ignored, as it has been in the above equations.

Comparison of Broken and Intact Meniscus Forces

The broken meniscus force differs markedly from that of the intact meniscus and is worth discussing. In the case of an intact meniscus, the surface tension force is at all times essentially parallel to the tangent of the particle surface (see Figure 1.15). This means that the capillary force starts as a horizontal force at the very top of the particle and transitions to point vertically downwards when the inflection point is at the particle's equator.

With the case of the broken meniscus, however, the non-zero receding contact angle leads to the force not following the particle's surface tangent, as in Figure 1.16a. When the contact line is near the top of the particle, the capillary force can even point upwards slightly. This comprises a *disassembling* force, as it is pulling the particle off the substrate. This has remained unmentioned in wetting literature, and is certainly not considered in nano-CFA literature.

Figure 1.16b describes this further. Here the meniscus force is plotted at different heights on the particle (from the top down to the equator, or as $h_1/R : 0 \rightarrow 1$), and for different receding contact angles. The case of an intact meniscus is mathematically equivalent to a receding contact angle of zero. The surface tension is 0.072 J/m for a water-air interface.

In the Figure, a positive capillary force denotes a force directed down towards the substrate (i.e. an assembling force) whereas a negative force pulls the particle away from the substrate (i.e. a disassembling force). It is seen that near the top of the particle (where $h_1/R \rightarrow 0$), when the receding contact angle is non-zero, the force becomes negative and more so with higher receding contact angles. Consequently,

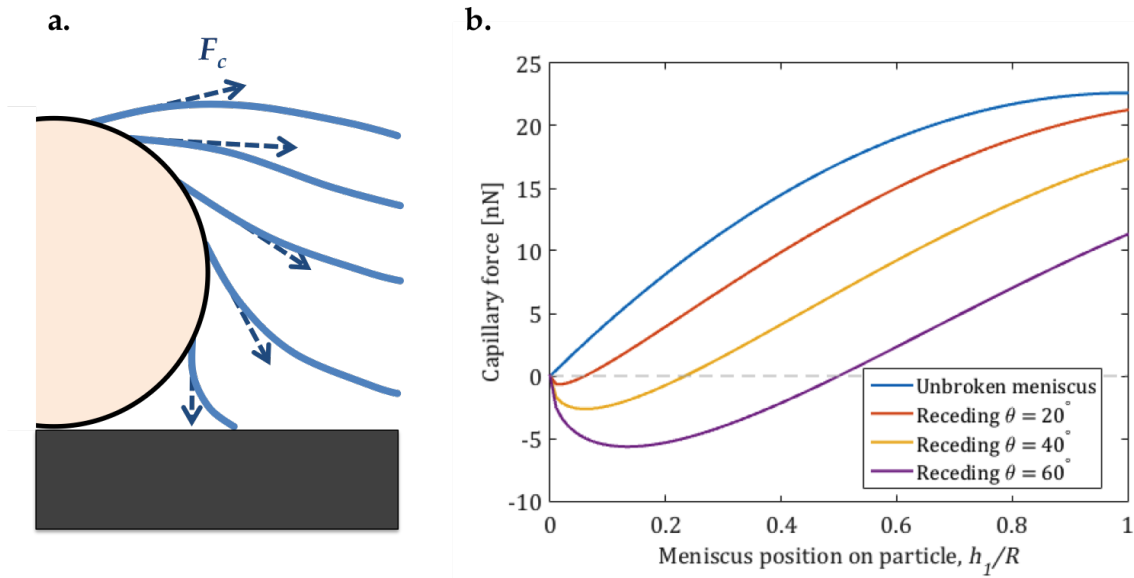


Figure 1.16: (a) A diagram describing the direction of the broken meniscus force as the contact line recedes down over the particle. The blue lines denote the meniscus profile at different positions. Note that when the meniscus is near the top of the particle the surface tension is pulling with a minor upwards component. (b) The instantaneous capillary force exerted on a particle as the contact line recedes down the from the top of a 50 nm particle ($h_1/R = 0$) to the equator ($h_1/R = 1$), plotted for various receding contact angles of the liquid over the particle surface. The receding contact angle significantly determines the duration and magnitude of a negative capillary force that pushes the particle away from the substrate.

it is most desirable to use particles that are very strongly wetted by the liquid, such that there is minimal negative capillary force, which would counteract assembly efforts, albeit only mildly.

An intact meniscus always acts to push the particle away from the interface. As such it constitutes a positive assembling force when it acts over a substrate.

Deriving the Work Done

It is necessary that we demonstrate that the capillary forces are strong enough to supersede Brownian motion and direct particle assembly. The mathematical analysis below are only partially found in existing literature, so we will derive them in sufficient detail for the reader to follow closely.

To estimate the work done by immersion capillary forces, we can integrate the

force as it acts over a reasonable length scale on the particle, such as half the particle, which equates to the radius, R . This is akin to the meniscus pulling down from the top of the particle to its equator.

It is best to have the capillary force equations in terms of either h_1 or h_2 (introduced earlier for the intact meniscus force, Figure 1.15). These parameters are distances in the direction that the capillary force acts over, which is perpendicular to the substrate. They both describe the vertical position of the capillary force on the particle, and thus make suitable integration variables to determine the work done.

Work Done by a Broken Meniscus

The common expression of the capillary force (see Equation 1.17) does not include a suitable integration variable to estimate the work done. Figure 1.17 presents the relevant geometrical parameters for a re-derivation in terms of h_1 and h_2 . This form of the force equation has not been found in the literature, but it is useful here for comparing the work done against that of the intact meniscus force, and that of Brownian motion.

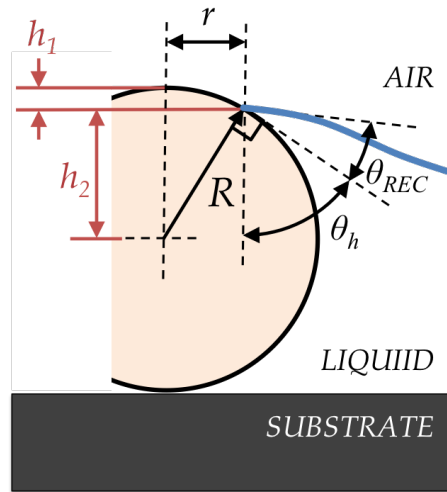


Figure 1.17: Diagram of the relevant geometrical parameters to describe the work done as a broken meniscus recedes down over a particle. The blue line denotes the meniscus profile coming off the particle.

In Figure 1.17, the blue line is the meniscus profile. The direction that the meniscus departs the particle surface is the direction of the meniscus force. The

meniscus makes an angle of $\theta_h + \theta_{REC}$ with the vertical axis, where θ_h is the tangential angle at the particle surface at the three-phase contact line, and θ_{REC} is the receding contact angle of the liquid on the particle surface.

We begin with the general surface tension force of Equation 1.16 and then take only its vertical component:

$$F_{meniscus} = 2\pi r \gamma$$

$$\therefore F_c = 2\pi r \gamma \cdot \cos(\theta_h + \theta_{REC})$$

Applying the cosine summation formula gives

$$F_c = 2\pi r \gamma (\cos(\theta_h) \cos(\theta_{REC}) - \sin(\theta_h) \sin(\theta_{REC})) \quad (1.30)$$

We put r in terms of h_2 using Equation 1.25, and likewise for $\cos(\theta_h)$ and $\sin(\theta_h)$ by

$$\cos(\theta_h) = \frac{r}{R} = \frac{\sqrt{R^2 - h_2^2}}{R} \quad (1.31)$$

$$\sin(\theta_h) = \frac{h_2}{R} \quad (1.32)$$

We use h_2 instead of h_1 on this occasion for mathematical simplicity. Combining these back into Equation 1.30 and rearranging yields

$$F_c = \frac{2\pi\gamma}{R} \left((R^2 - h_2^2) \cdot \cos(\theta_{REC}) - h_2 \sqrt{R^2 - h_2^2} \cdot \sin(\theta_{REC}) \right)$$

We integrate this with respect to h_2 for the limits of $h_2 : 0 \rightarrow R$ to emulate the contact line receding down over the top half of the particle:

$$W_{Broken} = \int_0^R F_c dh_2 = \left[2\pi\gamma R \cos(\theta_{REC}) \cdot h_2 - \frac{2\pi\gamma}{3R} \cos(\theta_{REC}) \cdot h_2^3 + \frac{2\pi\gamma}{3R} \sin(\theta_{REC}) ((R - h_2)(R + h_2))^{3/2} \right]_0^R$$

Applying the integration limits yields the net work done over half the particle.

$$\therefore W_{Broken} = \left[2\pi\gamma \cdot \cos(\theta_{REC}) \left(R^2 - \frac{R^2}{3} \right) \right]_{h_2=R} - \left[\frac{2\pi\gamma}{3} \sin(\theta_{REC}) \cdot R^2 \right]_{h_2=0}$$

$$= \frac{4}{3} \pi R^2 \gamma \left(\cos(\theta_{REC}) - \frac{1}{2} \sin(\theta_{REC}) \right) \quad (1.33)$$

Work Done by an Intact Meniscus

The work done by an intact meniscus is relatively straightforward to derive. The force (Equation 1.26) is integrated with respect to h_1 as $h_1 : 0 \rightarrow R$ to emulate the particle pressing further and further into the interface. This yields the net work done, W_{Intact} , over half the particle:

$$\begin{aligned}
 W_{Intact} &= \int_0^R 2\pi\gamma h_1 \left(2 - \frac{h_1}{R}\right) dh_1 \\
 &= 2\pi\gamma \left[h_1^2 - \frac{h_1^3}{3R} \right]_0^R \\
 &= 2\pi\gamma \left(R^2 - \frac{1}{3}R^2 \right) \\
 &= \frac{4}{3}\pi R^2\gamma
 \end{aligned} \tag{1.34}$$

We obtain the same result if we use the force equation that is written with respect to h_2 (Equation 1.27) and integrate by that variable instead. This is entirely as expected and affirms our choice of integration variables.

We can write the net work done in terms of the Laplace pressure to help visualise in a different manner what is happening. Consider Equation 1.34, which is reproduced and then modified below.

$$\begin{aligned}
 W_{Intact} &= \frac{4}{3}\pi R^2\gamma = \frac{1}{2} \cdot \frac{4}{3}\pi R^3 \cdot \frac{2\gamma}{R} \\
 &= \frac{1}{2}V_{particle}\Delta p
 \end{aligned} \tag{1.35}$$

The net work done is therefore interpreted as the interfacial pressure difference integrated over the volume of the particle that the work is done over ($\frac{1}{2}V_{particle}$ in our case here).

This is entirely consistent with the prior derivation of the capillary force in terms of the Laplace pressure (Equation 1.29). To compute the instantaneous force we found that we could simply apply the Laplace pressure over the projected area of the thin-film-wetted particle surface. If we integrate that over the height of the particle, as if the inflection point is lowering over the particle surface (i.e. the particle is pressing into the meniscus more and more), then the projected area of the force equation simply becomes the volume that we see in the energy equation above (Equation 1.35).

Thus we can compute both the force and the work done on a particle pressed into an intact meniscus purely in terms of the particle size and the Laplace pressure. This has been derived from the beginning for spherical particles only. More rigorous mathematical analysis is required to determine whether this principle extends unchanged to non-spherical particles.

Work Done Compared to Brownian Energy

Comparing Equations 1.33 and 1.34, the net work done by the broken meniscus is equal to that of the intact meniscus, scaled by a trigonometric function of the receding contact angle, $f(\theta_{REC}) = [\cos(\theta_{REC}) - \frac{1}{2} \sin(\theta_{REC})]$. This function accounts for the fact that when a contact line is present, the meniscus is not tangential to the particle.

If the receding contact angle is close to zero (i.e. the liquid wets the particle very well), then the meniscus is closely tangential to the particle, like with an intact meniscus. Mathematically speaking, $f(\theta_{REC}) \approx 1$ and Equation 1.33 collapses to Equation 1.34, affirming the similarity between a near-zero receding contact angle and an intact meniscus.

Finally, we wish to show that the work done is greater than the Brownian energy. A straightforward way of doing this is to divide each capillary energy equation by the Brownian energy, kT , putting them in units of Brownian energy:

$$W_{Intact} = \frac{4\pi R^2 \gamma}{3kT} \quad (1.36)$$

$$W_{Broken} = \frac{4\pi R^2 \gamma}{3kT} \left(\cos(\theta_{REC}) - \frac{1}{2} \sin(\theta_{REC}) \right) \quad (1.37)$$

Note the these two equations are calculated for the work done as the meniscus recedes only from the top of a spherical particle to the equator. The broken meniscus equation also assumes the meniscus is broken from the top of the particle and does not have a period of being intact before rupturing.

The above energy equations are plotted in Figure 1.18 for various receding contact angles and various particle sizes. The surface tension is 0.072 J/m for a water-air interface, and the temperature is 45°C, which is common for nano-CFA experiments. It is seen that even for very high receding contact angles and for very small nanoparticles, the work done over half the particle is greater than the Brownian

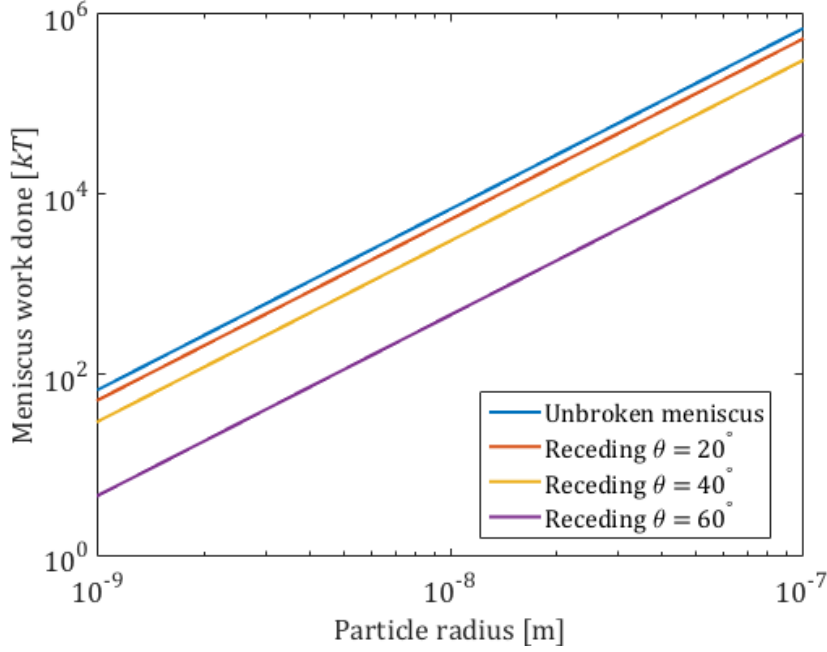


Figure 1.18: The net work done by the capillary force as the meniscus recedes from the top to the equator of a spherical particle. The work done is in Brownian units of kT , and is plotted for various receding contact angles and various particle radii. It is seen that even for large receding contact angles on very small nanoparticles, the net work done is still larger than the Brownian energy. It is also seen that the work done decreases as the receding contact angle increases. The maximum work is done when the meniscus remains intact, or when the broken meniscus wets the particle very strongly (very low receding contact angles).

energy. This gives us confidence that meniscus forces, whether a three-phase contact line is formed or not, can greatly exceed Brownian diffusion effects.

A further beneficial consequence can be raised which is yet unmentioned: particles will not leave the liquid and deposit onto the substrate by thermal effects alone, even at very high temperatures. A particle will mostly deposit on a substrate only if the capillary forces are suitably inclined (ignoring effects from aggregation, and also particle-substrate interactions which can be engineered into the system if desired). This means that we can potentially achieve great control over particle placement if we can adequately manipulate capillary forces.

The Real Situation is a Hybrid of Both Forces

As the liquid evaporates down over a particle in the final stage of assembly, the meniscus does not rupture immediately when the particle and meniscus meet, rather it would actually remain intact for a period, stretching like an elastic skin over the particle surface (the intact meniscus analysis applies here). At some point in time, however, the meniscus would thin out beyond its limit and rupture, leaving the top of the particle exposed and creating a three-phase contact line that continues to recede down the particle surface. Thus we transition from the intact meniscus to the broken meniscus.

The time at which the meniscus ruptures is not well understood, but meniscus rupture in general appears to be dependent in part on the liquid's tensile strength [21–23], which is fundamentally an issue of molecular dynamics. The place of rupture is around the inflection point, which is where the liquid is the thinnest [21] and where negative liquid pressure builds.

Recalling that the presence of a receding contact angle alters the work done compared to an intact meniscus, it is evident that the duration before meniscus rupture would alter the net work done. The duration before rupture also influences whether the broken meniscus is a *disassembling* force at any point in time.

In this thesis we focus only on the two exclusive cases of a meniscus that is always intact or one that is ruptured from the very beginning. We do not calculate the hybrid case, since the work done by a mixture of the two forces would lie between the two aforementioned bounding cases.

This concludes our discussion of capillary forces on single particles. We have shown that such forces are amply sufficient to overcome Brownian motion if they can be well controlled and directed. The final aspect of capillary force discussion is the force exerted between particles immersed in a thin liquid film.

Capillary Interaction between Particles

Capillary interactions can exist *between* particles, altering their separation distance. This has been shown to assist in long-range assembly of nanoparticle crystal lattices and other ordered structures [12, 24–27]. Attractive or repulsive forces can be setup between particles purely as a result of superimposed meniscus perturbations. The

interaction of particles by capillary forces depends on the extent which a particle can ‘feel’ the meniscus perturbation caused by the particles around it.

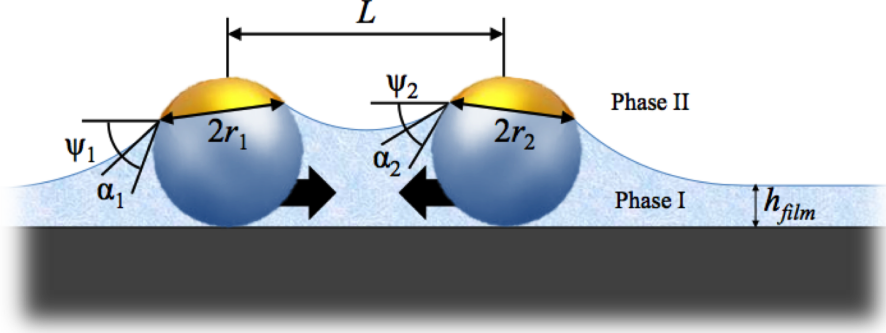


Figure 1.19: Two particles deforming the meniscus of a thin film on a substrate. Particles experience an attractive lateral force due to capillary forces.

Consider Figure 1.19. When the meniscus deformation of one particle interferes with another, the liquid pressure and interfacial tensions forces on either particle lose symmetry and lateral forces are exerted on both particles. This can be seen qualitatively in Figure 1.19 where the menisci encircling the top of either particle are slightly angled to the horizontal, as opposed to the horizontal meniscus for the single particle case in Figure 1.13. The lateral capillary forces on partially submerged particles draws them together, provided their wetting properties are not opposite (hydrophilic/hydrophobic).

Kralchevsky *et al.* (1994) gives the following Equation for the lateral force between two particles [1]

$$F_c = 2\pi\gamma Q_1 Q_2 q K_1(qL) \quad (1.38)$$

where K_1 is the modified Bessel function of the second kind, first order, and L is the separation between the two particle centres. The terms Q_1 and Q_2 are the so-called “capillary charge”, named so because they constitute the capillary equivalent to the behaviour of Coulombic charge in electrostatic interactions. They are given by

$$Q_i = r_i \sin(\psi_i), \quad (i = 1, 2) \quad (1.39)$$

where r_i is the meniscus radius of particles 1 and 2, and ψ_i are the meniscus slope angles. Equation 1.38 holds on the assumption that $r_i \ll q^{-1}$ and $r_i \ll L$ [28], and when the meniscus slope is small (i.e. $\sin^2(\psi_i) \ll 1$) [18]. When $L \sim q^{-1}$ discrepancies develop between Equation 1.38 and experimental results [18], however

for large separations Equation 1.38 can be simplified to [1, 17, 27, 29]

$$F_c \approx 2\pi\gamma \frac{Q_1 Q_2}{L} \quad (1.40)$$

This shows that the capillary interaction between particles adsorbed onto a liquid surface can be far reaching, decaying as $1/L$, and can be useful for self-assembly purposes.

The energy of lateral capillary interaction $\Delta W_{lateral}$ can be determined by integrating the lateral capillary force from L to infinity (the energy required to move one of the particles to a point where there is no capillary interaction).

$$\Delta W(L) = \int_L^\infty F(L') dL' \quad (1.41)$$

Noting that in the case of $R_1 = R_2 = R$ and $r_i \ll L \ll q^{-1}$ one has [9, 15]

$$F_c \propto \gamma R^2 K_1(qL) \quad (1.42)$$

Derivations therefore show that the capillary interaction between particles adsorbed onto a liquid surface can be far reaching, decaying as $1/L$, and can be useful for self-assembly purposes [1, 17, 27, 29]. The energy of a lateral capillary interaction ΔW is plotted relative to kT in Figure 1.20, where it is seen to be dominant over Brownian motion for even small nanoparticles.

Also worthy to examine is how the lateral capillary interaction energy varies with particle separation for a given particle radius. Figure 1.20b plots the interaction energy in kT units for a fixed radius of 15 nm and varying particle spacing from $L = 2R$ to $200R$. The interaction energy is consistently above Brownian energy, and rises more steeply as the separation approaches the limit of $L = 2R$. This justifies the use of lateral capillary forces for nanoparticle assemble in thin liquid films.

Despite the fact that lateral capillary interactions can be far reaching, many-particle interactions are limited by the ‘field of view’ from one particle to those around it. This is referred to as the screening effect. Referring to Figure 1.21, the angle between the tangents of particle i from the centre of particle O is β . This angle is reduced to an effective ‘field of view’ angle of θ by the obstruction of particle j . Nishikawa *et al.* suggest that an appropriate modification to the lateral capillary force on O from i is [27]

$$F_{c(O)} = F_{c(O,i)} \times \frac{\theta}{\beta} \quad (1.43)$$

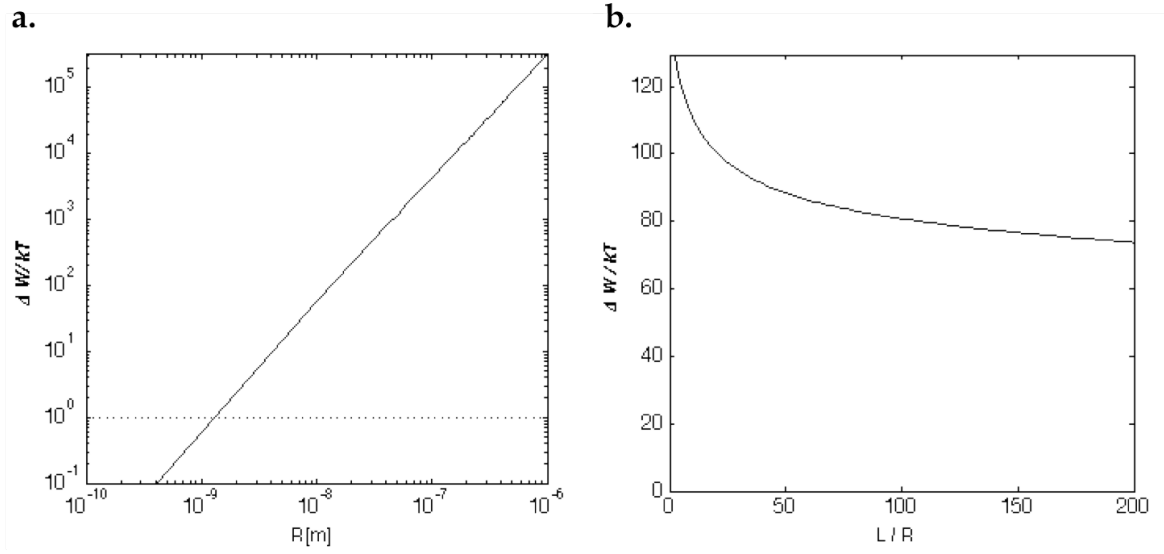


Figure 1.20: Capillary interaction energy ΔW in units of kT . Parameters used are $\gamma = 0.072$ N/m (water-air interface), $\Delta\rho = 1000$ kg/m³. In both plots Brownian energy intersects the vertical axis at 1. In (a), capillary interaction energy is plotted against particle radius for a fixed separation of $L = 4R$, and in (b) it's plotted against the ratio of particle separation to radius (L/R); particle radius is fixed at $R = 15$ nm.

where $F_{c(i)}$ is the lateral capillary force on O resulting from i in the absence of particle j . This suggests that the effective lateral capillary interaction of a many particle system is short range in nature, due to the obstruction or overcrowding of particles. This can slow the large-scale ordered self-assembly of colloids in the absence of other guiding forces and prevent large 2D crystal arrays forming.

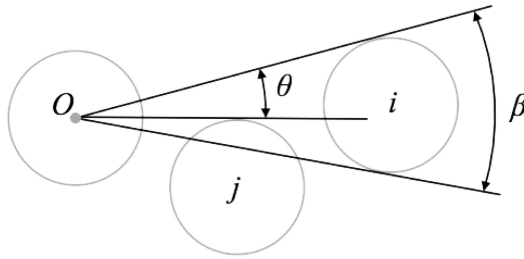


Figure 1.21: Schematic illustrating screening effect of lateral capillary forces from particle i to particle O .

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Experimental Methods and Instrumentation

2

This chapter details the conventional experimental methods and instrumentation used in this thesis.

<i>Introduction ...</i>	<i>2.1</i>
<i>Template Fabrication and Treatment ...</i>	<i>2.2</i>
<i>Nanoparticles ...</i>	<i>2.3</i>
<i>Conventional CFA Fluid Cell ...</i>	<i>2.4</i>
<i>Slider-CFA Apparatus ...</i>	<i>2.5</i>
<i>Contact Angle Measurement ...</i>	<i>2.6</i>
<i>Optical Characterisation ...</i>	<i>2.7</i>
<i>Software ...</i>	<i>2.8</i>

2.1 Introduction

Conventional instrumentation and protocols used in the course of this work are detailed below, while novel experimental methods will be reported on in later chapters.

2.2 Template Fabrication and Treatment

Template fabrication was done by by Timothy James and Jasper Cadusch of the Optical Physics Group (University of Melbourne) using electron beam lithography (EBL) and nano-imprint lithography (NIL) at the Melbourne Centre for Nanofabrication (Clayton, Victoria). EBL has a resolution of 20 nm and good repeatability. NIL is less repeatable but is much faster and cheaper than EBL.

Templates were designed using KLayout. All templates were poly(methyl methacrylate) (PMMA) or SU8 spun onto 4 inch silicon (Si) wafers. Early templates were made by EBL, and later ones by NIL. NIL master templates were made by EBL of hydrogen silsesquioxane (HSQ) on Si. The master template was sometimes etched to leave a Si template without a HSQ layer. EBL and NIL methods and some templates are shown in Figure 2.1.

Electron Beam Lithography (EBL): The EBL tool used is a Vistec EBPG 5000+ ES. The process for a HSQ master template is as follows:

HSQ: 6%, spun onto a Si wafer at 4000rpm, baked at 150 °C for 3 minutes

Exposure: 750-1500 $\mu\text{C}/\text{cm}^2$

Develop: 1 minute in AZ 726 MIF

Etch: See below

Anti-Stiction Layer: 7100 lubrication fluid, spun on at 3000rpm

Reactive Ion Etching (RIE): The RIE tool used is an Oxford Instruments PLASMALAB100 ICP380. The process is as follows:

Etch with 30 sccm Ar (sccm = standard cubic centimetre per minute) and 5 sccm Cl_2

ICP power: 1200 W

RIE power (RF bias power): 150 W

Pressure: 5 mTorr

Temperature: 12 °

Etch rate ~ 200 nm/minute

Etch time: 45 seconds

Nano-Imprint Lithography ('Hot Embossing', NIL): The NIL tool used is an EVG 520 IS. The process is as follows:

SU8 2005: spun onto a Si wafer at 3000rpm, baked at 95 °C for 5 minutes

NIL: 10 minutes at 18 kN of pressure across a 4 inch wafer

Release: Scalpel ran around the edge of the two wafers

Post NIL: Flood with UV light, 3 minutes, post-baked at 95 °C for 5 minutes

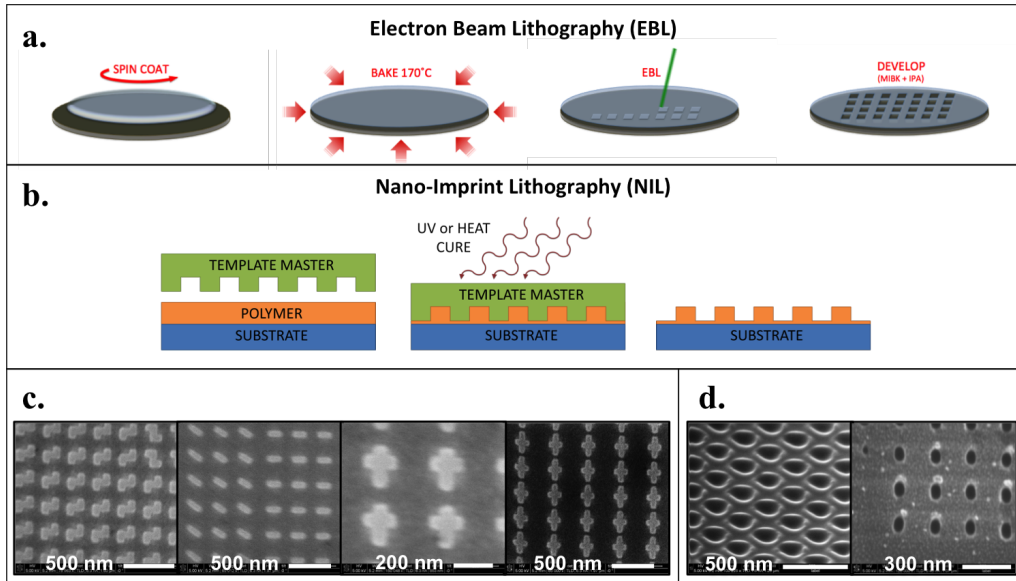


Figure 2.1: Illustrations of the EBL (a) and NIL (b) methods of template fabrication, and some examples of EBL templates (c) and NIL templates (d). The NIL templates are evidently less refined than the EBL templates.

Preparation for Scanning Electron Microscopy (SEM): To prepare a template (pre- or post-assembly) for scanning electron microscopy, it is first washed with ethanol, isopropanol and dried with nitrogen. Then it is sputter coated with approximately 2 nm of chromium (Sputterer: Emitech K575, 15 seconds at 50 mA) and then 50 nm of gold (3 minutes at 50 mA). Gold is added as it leaves a cleaner surface for SEM compared to chromium.

2.3 Nanoparticles

2.3.1 Nanoparticle Synthesis

Nanoparticles were either purchased from BBI Solutions or synthesised in-house. Particles from BBI Solutions were spherical gold of 20 nm, 50 nm, 100 nm and 150 nm.

In-house synthesised particles used in this work are gold nanorods, 107×45 nm, with good monodispersity (see Figure 2.2). The rods are stabilised by cetyl trimethylammonium bromide (CTAB). Rods were synthesised by Sarah Jaber, based on the protocol by Ye et al. [1]. Details are given in their Supplementary Information, Table S3, for the nanorods in Figure 3f of the paper.

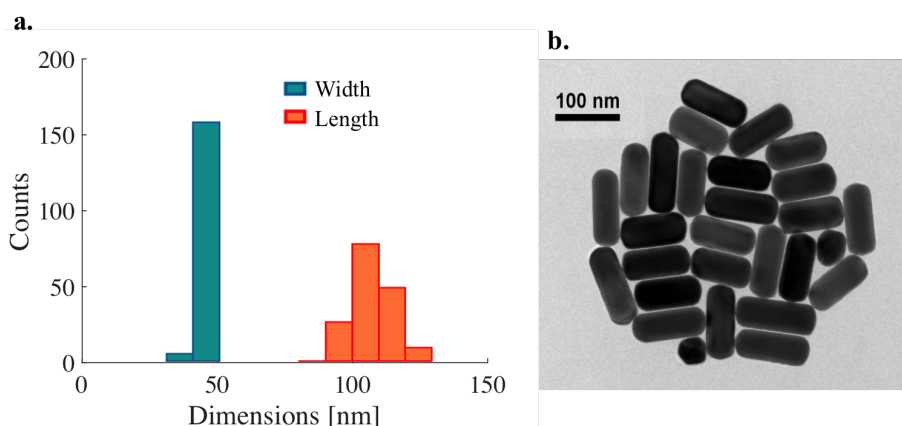


Figure 2.2: (a) A histogram of the dimensions of the nanorods used in scale-up trials, showing good monodispersity. (b) A TEM image of the nanorods.

Briefly, the protocol is as follows: The seed solution is prepared by mixing 5 mL of 0.5 mM HAuCl_4 with 5 mL of 0.2 M CTAB solution in a 20 mL vial. Dilute 0.6 mL of fresh 0.01 M NaBH_4 with water to 1 mL, and inject into the Au(III)-CTAB solution while stirring vigorously (1200 rpm). The solution colour changes from yellow to brownish yellow, and after 2 minutes the stirring should be stopped. The seed solution is then aged at room temperature for 30 minutes prior to use.

To prepare the growth solution, dissolve 9.0 g CTAB and 1.234 g NaOL in 250 mL of warm water ($\sim 50^\circ\text{C}$) in a 1L Erlenmeyer flask. Allow the solution to cool down to 30°C and add 24 mL of 4 mM AgNO_3 solution. Keep mixture undisturbed at 30°C for 15 minutes, after which add 250 mL of 1 mM HAuCl_4 solution. The

solution becomes colourless after 90 minutes of stirring (700 rpm). 1.5 mL of HCl (37 wt. % in water, 12.1 M) is then introduced to adjust the pH. After another 15 minutes of slow stirring at 400 rpm, add 1.25 mL of 0.064 M ascorbic acid (AA) and stir the solution vigorously for 30 seconds. Finally, inject 0.1 mL of seed solution into the growth solution. Stir the resultant mixture for 30 seconds and leave undisturbed at 30°C for 12 hours for nanorod growth. The final products should be isolated by centrifugation at 7,000 rpm for 30 minutes, followed by removal of the supernatant. No size and/or shape-selective fractionation is needed.

2.3.2 Na-PSS Ligand Exchange

This ligand exchange protocol is used to remove CTAB from the synthesised nanorod solution, and replace it with a non-surface active alternative [2]. 50 ml nanorods (previously centrifuged once and redispersed in water) was centrifuged at 6500 g for 1 hr at 25 °C. The supernatant was removed. 50 ml of 0.15 wt % sodium polystyrene sulfonate (PSS, 70 kDa mol weight) was added to the residue and swirled gently. The rods resuspended easily. The solution was then centrifuged at 7500 g for 30 min. After centrifugation, slight aggregation could be seen on the side of the Falcon tube. The supernatant was removed and the same process repeated as above. With gentle sonication all the rods redispersed. A UV-Vis spectrum of this solution shows no peak broadening or shifting. Another 7500 g centrifugation for 30 min was done, then the supernatant was removed and the residue was redispersed in 10 ml Na-PSS. The solution can be washed multiple times to bring the surface tension to near that of DI water, as shown in Figure 2.3a. Figure 2.3b shows UV-Vis spectra of the nanorod solution before and after washes. The peaks have not shifted in location, indicating that the rods have not reshaped at all (the loss in peak intensity is due to the concentration of rods reducing slightly with each wash).

2.4 Conventional CFA Fluid Cell

The conventional CFA fluid cell was designed and built by Tatiana Pinedo Rivera.

Design: Figure 2.4 diagrams the basic setup and operation. A PDMS fluid cell with a $5 \times 5 \text{ mm}^2$ void footprint is prepared and sandwiched between a glass slide

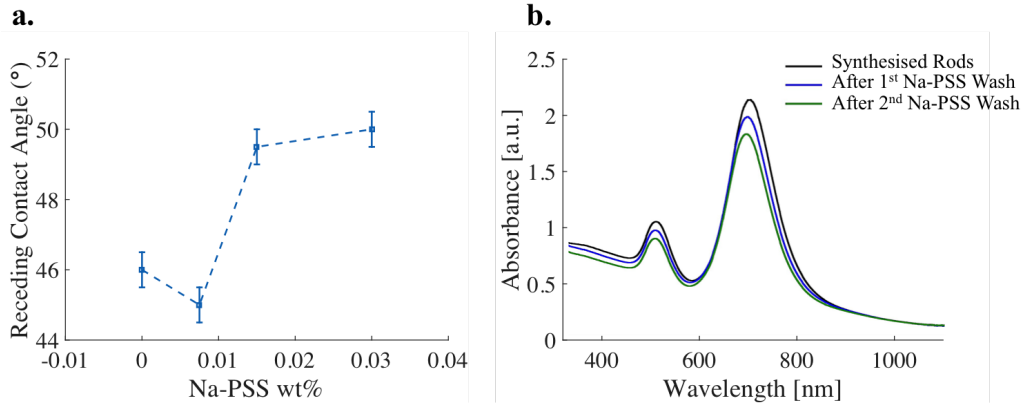


Figure 2.3: (a) Receding contact angle data of aqueous Na-PSS at varying concentrations on SU8. Low concentrations ably approach the wettability of pure water. (b) UV-Vis spectra of the gold nanorods before during and after ligand coating with Na-PSS, with CTAB twice washed out of the solution. (Spectra courtesy of Sarah Jaber.)

above and a heated base plate below. The glass slide is useful for viewing the assembly process. The glass slide should be much less wettable than the template to ensure colloids accumulate at the template's contact line and not at that on the glass slide. This necessitates a hydrophobic pre-treatment (the commercial product, Rain-X, was used). The substrate is held in place under the PDMS cell walls for a watertight seal. An air suction needle is inserted through a hole moulded in the PDMS cell, for a relatively airtight seal to control the humidity in the cell.

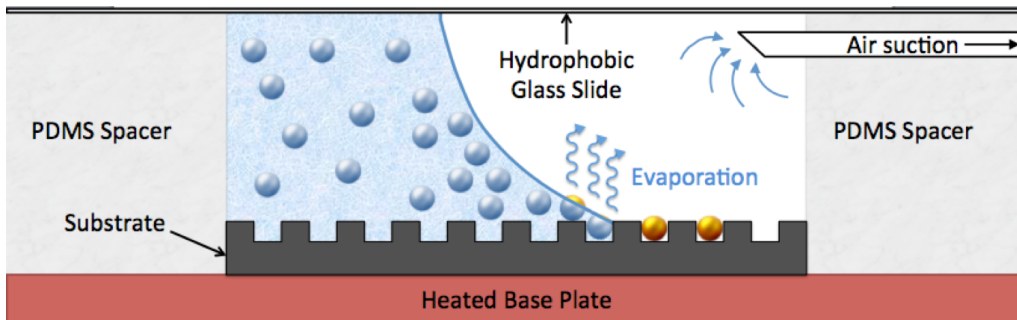


Figure 2.4: A diagram of the conventional fluid cell setup and operation. The temperature and air suction rate are the two controllable variables to set the evaporation rate, contact line speed and receding contact angle.

Implementation: Figure 2.5 shows the fluid cell installed on a Nikon Eclipse LV100D-U microscope fitted for bright-/dark-field microscopy in reflection mode,

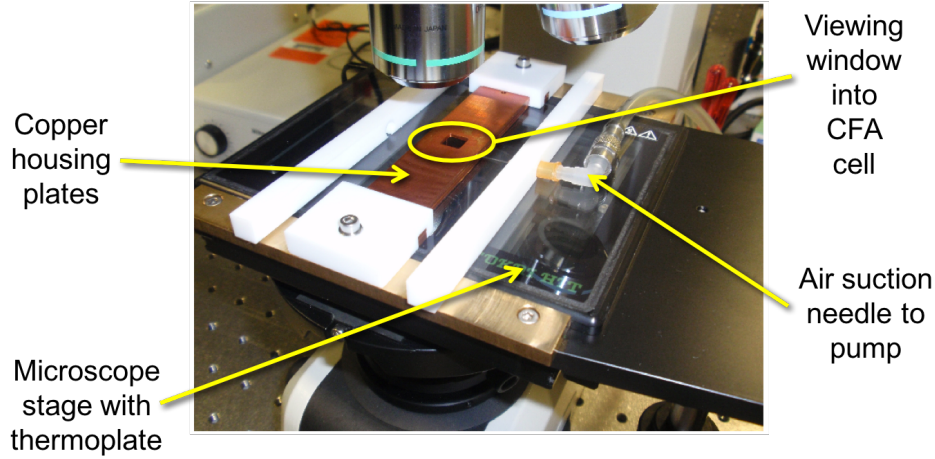


Figure 2.5: A photo of the small fluid cell installed on the microscope stage.

with a 50 W halogen light source (Nikon LV-LH50PC). The microscope stage is fitted with a Tokai Hit thermoplate for temperature control, and a Cole-Parmer Masterflex L/S peristaltic pump provides the necessary variable air suction (pump tubing size used is L/S 16).

The fluid cell is contained within a copper housing structure. Copper is used for good heat conduction. These are held in place by teflon brackets, screwed into the microscope stage. The viewing window is situated beneath the microscope objective. Two long brackets are also installed to hold the needles for liquid injection and air suction. The PDMS cell and copper housing are prefabricated with channels for needle insertion into the top of the cell.

Protocol: After installing the cell and peripheral components, the colloidal solution can be injected. To ensure even coverage across one end of the cell, and a near-straight contact line, injection must be done from the left and then the right sides. After sufficient liquid is injected, the air suction needle is inserted into a liquid-free part of the cell. The temperature and air flow rate are then set as desired. Typical values are 30-50°C and 50-120 mL/min. A high temperature and air flow rate may be used at first, to concentrate particles at the contact line and allow the contact line to begin receding.

It is necessary to have the contact line begin at least 500 μm away from the cavities to be assembled. This gives time for the particle concentration at the contact line to build up and stabilise, and for the contact line motion to also stabilise. The cavities should be in the centre of the cell, as the particle concentration dramatically

increases in the latter stages of the process as the liquid evaporates. An ideal assembly situation has a smooth and uniformly receding contact line, with a bright yellow nanoparticle haze when viewed under dark-field microscopy.

2.5 Slider-CFA Apparatus

Another common implementation of nano-CFA is with a slider apparatus. This is detailed below.

Design: Figure 2.6 depicts the slider-CFA design. Slider-CFA operates by forced motion of a liquid body relative to the template. It is an open-air setup, and is thus readily scalable. A slider (typically a hydrophobised glass slide) is held flat above the template, and liquid is injected between the two forming a liquid bridge. The substrate is heated to convectively concentrate particles at the contact line. In the present case, to monitor the assembly zone, the upper slide is fixed to the microscope stage and the template is moved beneath it, as shown. Unlike the fluid cell, the speed is controlled independent to the evaporation rate, which is a great benefit.

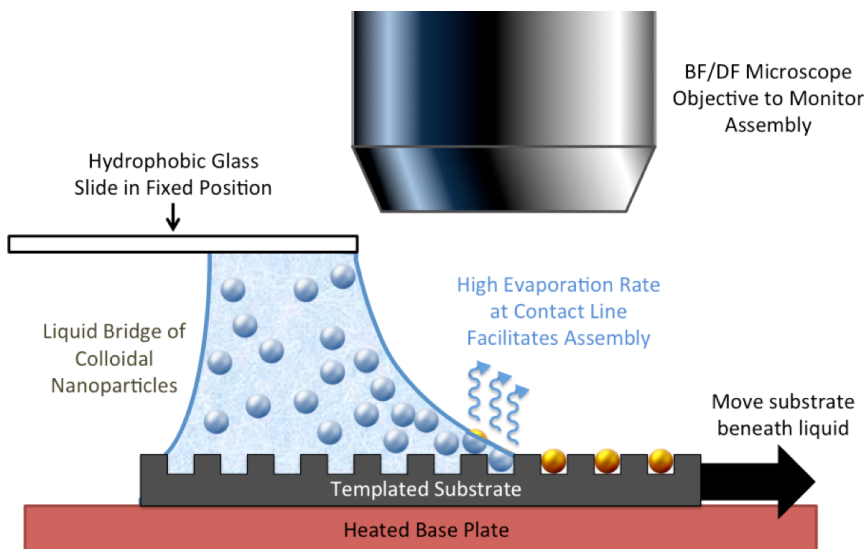


Figure 2.6: A diagram of slider-CFA operation on a microscope stage.

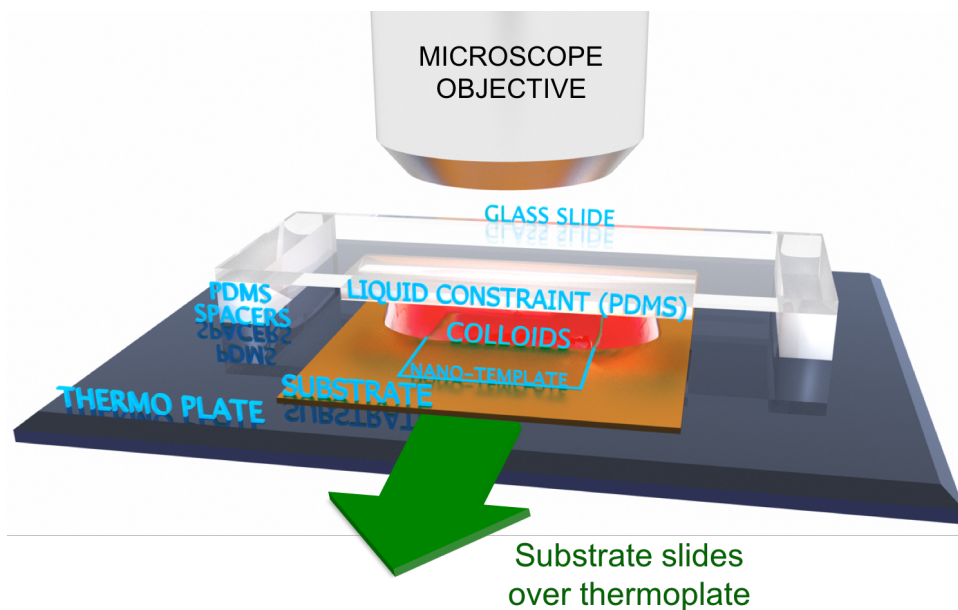


Figure 2.7: A diagram of the slider-CFA setup on a microscope stage.

Implementation: The slider-CFA apparatus is installed on a Nikon Eclipse LV100D-U microscope fitted for bright-/dark-field microscopy in reflection mode, with a 50 W halogen light source (Nikon LV-LH50PC). The microscope stage is fitted with a Tokai Hit thermoplate for temperature control. The template is placed directly on the thermoplate. Figure 2.7 diagrams the actual setup, whereby PDMS spacers hold the glass slide 600 μm above the template surface. A PDMS block is glued to the glass slide to act as the hydrophobic liquid restraint. A modified Nima Technology dip coater is used to push the template across the microscope stage. It has a minimum speed of 17 $\mu\text{m/s}$.

Protocol: Once all components are in place on the microscope stage, the dip coater arm is retracted away from the template. When fully retracted, the template is slid into its starting position beneath the glass slide, and the colloidal solution is injected beneath the PDMS liquid constraint. As with the fluid cell device, the contact line needs to be straight over the assembly region. The curved edges on the left and right sides of the liquid body should be at least 5 mm away from the cavities, as the particle concentration is higher in those regions due to their curvature. This can produce inconsistent assembly. The cavities should be traversed only by the straight portion of the contact line. After the liquid is setup and the substrate temperature set, the dip coater arm is manually moved to sit against the template, ready to push the template beneath the stationary slider as the dip coater progresses through its

programmed cycle.

2.6 Contact Angle Measurement

2.6.1 Sessile Droplets

Setup: Contact angle measurements of sessile droplets were done to test the wettability of various liquid-substrate combinations. Measurements were conducted in the ambient room-temperature environment. Humidity, air temperature and dew point were measured with an Extech Instruments RH300 digital psychrometer.

The substrate was placed on a thermoplate and set to the desired temperature (always relative to dew point to ensure consistent evaporation between studies). A 10 μL drop was placed on the substrate using a micropipette. To ensure the drop was placed in the desired location quickly and without lateral movement (which may distort the drop placement and affect the measurement), the pipette was held in a retort stand so the nozzle could swivel down to the hover just above the substrate. The operator then need only swivel the pipette down and quickly dispense the liquid when required.

Substrates were prepared by gently wiping with a kimwipe and ethanol, then rinsing with ethanol, isopropanol and blow drying with nitrogen. If necessary, an Eppendorf of the liquid to be dispensed was placed on the heated base plate at the correct temperature for at least 10 mins to dissolve any crystallised surfactant. Experiments showed that pre-heating the liquid before dispensing did not affect the results compared to dispensing at room temperature.

A diffuse white planar LED backlight was used to create a silhouette of the droplet, viewed with a USB microscope positioned with a retort stand. The microscope must be positioned so it is just above lateral to the substrate, to view the base of the droplet and the droplet height without viewing angle distortion. (The LED backlight was too bright, so it was shone onto a piece of white paper, which served as a suitable background to create a silhouette of the droplet.)

Measurement: An ImageJ plugin was written by Mapperson to capture an image of the droplet every 5 seconds. The software automatically detects when the droplet

is deposited so that capturing begins at the moment of deposition. This is to avoid slight timing discrepancies between studies with rapid droplet dynamics.

A second plugin was written by Mapperson to then analyse the results. The sequence of photographs from droplet evaporation are loaded into ImageJ and the droplet baseline, droplet dimensions and contact angle are automatically detected. Contact angle is inferred from a circular fit to the droplet profile, which is standard procedure for droplets smaller than the capillary length of water. The data is output to a CSV file which can be loaded into Matlab for analysis.

Analysis: To analyse the receding contact angle, traditionally the contact angle is plotted against time. A typical plot is shown in Figure 2.8. The receding contact angle is the flattened region. It correlates to when the contact line depins and the droplet footprint begins shrinking. Mapperson found that for highly wetting liquids a plateau region in the plot is not evident. A more robust means of detecting the receding contact angle was found by plotting the contact angle as it varies with the droplet diameter. The receding contact angle is the point of inflection.

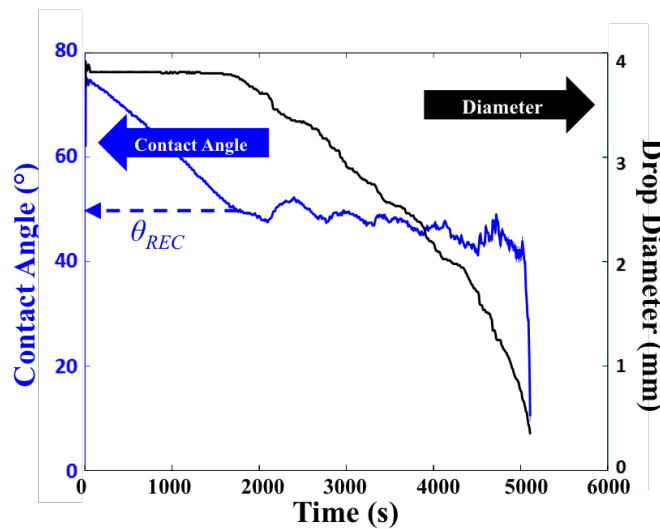


Figure 2.8: Example sessile droplet contact angle and diameter data showing the receding contact angle. This data is from water on biaxially oriented polypropylene. The receding contact angle is when the droplet diameter starts reducing.

2.6.2 Slider-CFA

To measure the contact angle in slider-CFA, a simplified slider-CFA apparatus was setup on the microscope stage, and a USB microscope was held in a retort stand on the side to look along the contact line. A diffuse white planar LED backlight was used to create a silhouette of the liquid body. The substrate was smooth and unpatterned for characterising liquid behaviour under the slider apparatus (patterned substrates were used later for assembly work). Photographs were manually taken from the USB microscope (e.g. Figure 2.9) and analysed manually in ImageJ for the contact angle. The contact angle can be reliably read in this way because the liquid interface in a slider CFA apparatus is very planar.

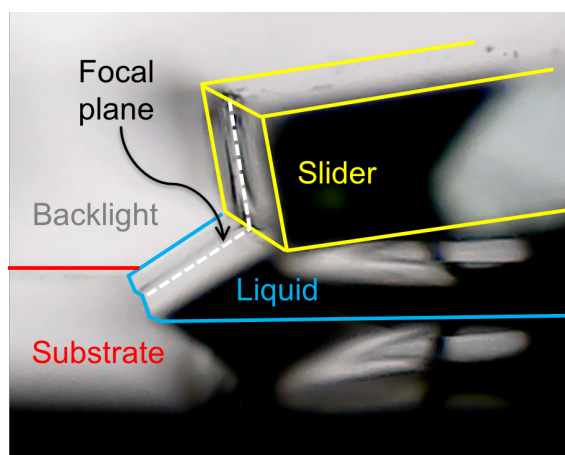


Figure 2.9: Example CFA silhouette for receding contact angle measurement, showing all major components. The contact angle and slider height can be measured at the focal plane.

2.7 Optical Characterisation

Equipment: Assembled nano-arrays were optically characterised on a Nikon Eclipse LV100D-U microscope fitted for bright-/dark-field microscopy in reflection mode. A 50 W halogen light source was used, and an Acton MicroSpec 2150i spectrometer fitted with a Pixie 1024BR detector for spectroscopy. The microscopy setup is shown in Figure 2.10. By aligning the polariser at 45° to assembled rods, and the analyser at 0° or 90° , background scattering in bright-field mode can be reduced and nanorod resonances are more apparent.

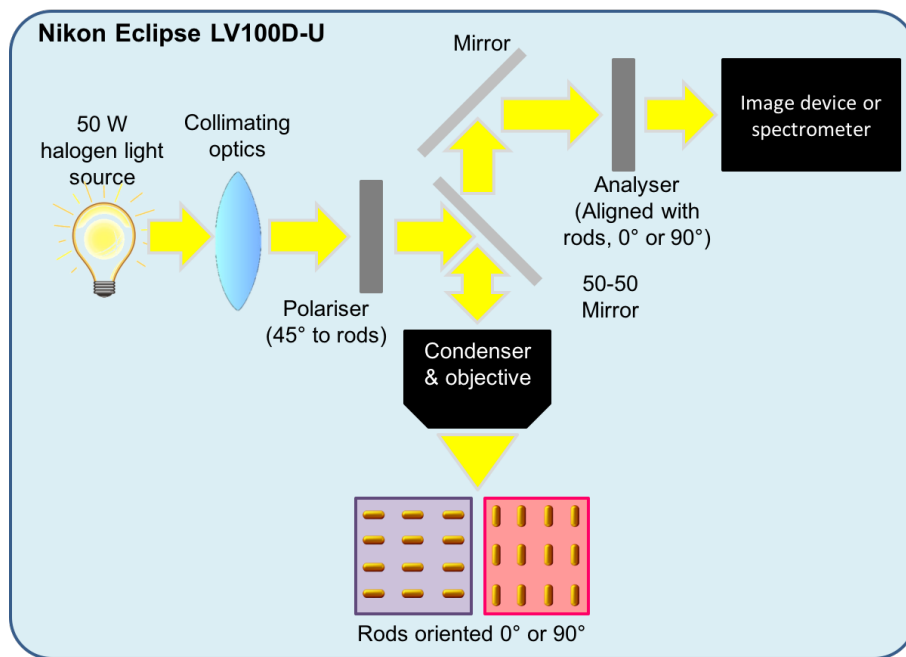


Figure 2.10: Diagram of the optic microscopy setup to characterise plasmonic nano-assemblies.

Visualisation of Plasmonic Nano-Structures: It is not unusual in nano-CFA for aggregated deposition to accompany nano-assembly on an array, as shown by the bright yellow portions on the arrays in Figure 2.11b. The arrays are identical, shown under transverse and longitudinal bright-field polarisation (red and green colouration), and then with unwanted scattering extinguished to highlight the assembled nanorods.

It is possible to selectively reduce scattering from both the background and from aggregated structures by aligning the polariser at $+45^\circ$ to assembled rods, and the analyser at -45° (Figure 2.11a). When this is done, light scattered from the background and non-plasmonic structures is extinguished by the cross-polarised polariser-analyser pair. There is, however, a $1/\sqrt{2}$ component of the incident light that aligns with the nanorods' axes, equally for transverse and longitudinal resonances alike. Thus plasmonic structures are excited and scatter polarised light at $\pm 45^\circ$ to the analyser, causing them to be visible. This shown on the righthand image of Figure 2.11b. This technique allows one to visually assess the quality of assembly against the possibility of aggregated non-plasmonic deposition.

Assessing Assembly Quality: The quality of an assembly is initially assessed visually. This process is rapid, not costly, and clearly isolates the most promising

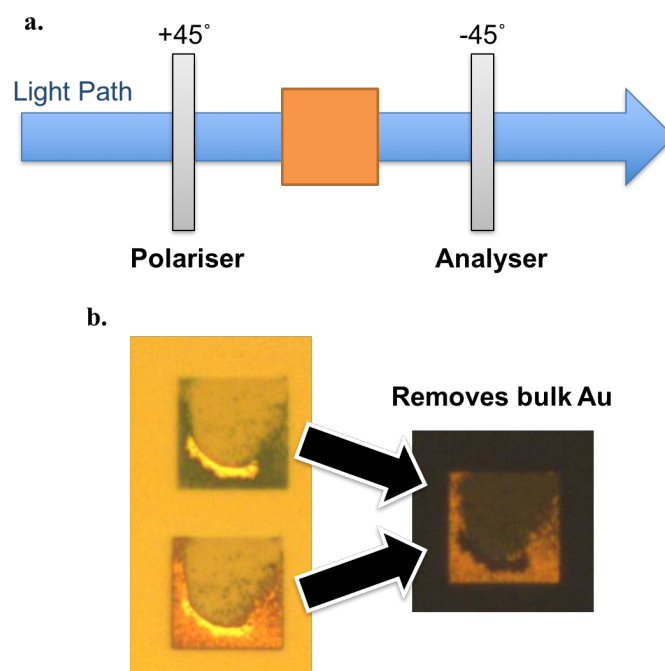


Figure 2.11: Illustration of the technique used to visualise plasmonic nano-structures isolated from aggregated deposition. The arrays in (b) are all the same array, shown under orthogonal polarisation (lefthand images) and with non-plasmonic scattering extinguished (righthand image).

results. All templates are designed to hold a polarisation-sensitive optical signature based on the plasmonic resonances. Using the method detailed in Figures 2.10 and 2.11, a high-quality assembly is evidenced by an optical signature that is:

- Polarisation sensitive showing the anticipated hues
- Strong (a bright colour variation evidences relatively uniform nanoparticle arrangements that are optically isolated from each other)
- Uniform (colour variation is consistent across the assembled area)
- Widespread (covers a high proportion of the array(s))
- Area-selective (only areas with cavities yield a plasmonic signature)
- Conforms to the expected polarisation angles (assemblies have the expected alignment)

The only means of producing such an optical signature is an assembly that has low aggregation, uniform filling, and is template-directed.

More demanding/costly characterisation methods (SEM and statistical analysis) are then be employed to validate and quantify the assemblages where necessary.

2.8 Software

In addition to the software packages given above, other software was used as follows:

- Chapter 5: Figure 5.1 shows 3D rendered artistic impressions of nanorods being assembled into a template. The images were built using SketchUp and rendered using Kerkythea. A ‘Kerkythea Exporter’ plugin can be installed in SketchUp for easy transition between the software packages. The curved and perturbed meniscus shape was built using a SketchUp plugin called Soap Skin Bubble. Renderings of the CFA apparatus were also made with these software packages.
- Chapter 6: Meniscus profilometry software was written in Matlab.
- Chapter 7: Contact line pinning measurements were done with Tracker (open-sourcephysics.org) or Kinovea, and analysis was done in Matlab. Curve fitting to data was done either with the Matlab Curve Fitting toolbox, or when that failed to generate a suitable fit, alternative software called CurveExpert was used.
- Chapter 8: Evaporative and convective nano-CFA simulations were done with COMSOL Multiphysics and custom Matlab scripts.

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- [2] Jonathan G Mehtala, Dmitry Y Zemlyanov, Joann P Max, Naveen Kadasala, Shou Zhao, and Alexander Wei. Citrate-Stabilized Gold Nanorods. *Langmuir*, 30(46):13727–13730, November 2014.

Scaling Nano-CFA: From Micro to Macro

3

Scalable and reliable nano-assembly of any kind has remained elusive to researchers worldwide. In this chapter we demonstrate macro-scale nano-CFA to produce an optical two-tone metamaterial from plasmonic nanorod pixels. This chapter highlights the various hurdles facing scalable nano-CFA, and some pertinent lessons learned. Throughout this journey the conventional model of nano-CFA is found to be deficient, thus setting the scene for the remainder of this thesis whereby we pursue an accurate description of CFA. The work presented here is a significant and promising step forward in the quest for scalable nano-assembly.

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3.1 Introduction

Nano-assembly over macro-scale areas promises to deliver novel and powerful technologies, but it has proved exceedingly difficult to achieve. Nano-CFA is a promising candidate solution, and the first question this thesis seeks to answer is whether nano-CFA can indeed assemble plasmonic optical nanomaterials over macroscale areas. This chapter is given to that goal.

Let us consider the nature of the desired material. The material is plasmonic—its building blocks will be metal nanostructures with precise placement and orientation. The material is optical—it should give rise an optical effect strong enough to be visible, putting an upper limit on particle sparsity. A strong response preferences the fundamental plasmonic mode. Particle proximity and the template material should not significantly dampen or red-shift the plasmonic response. To that end, this chapter culminates in macro-scale assembly of aligned gold nanorod ‘pixels’ with 300 nm periodicity in SU8 showing a visible polarisation-dependent colour change.

The chapter begins with experimental demonstrations of nano-CFA over micro-scale areas (Section 3.2). We then turn to discuss a scalable CFA apparatus (Section 3.3) and issues surrounding scalable template fabrication (Section 3.4). The following two sections (3.5 and 3.6) give the experimental details, results and discussion of macro-scale nano-CFA trials. The final section (Section 3.7) discusses valuable lessons learned. Work in Section 3.2.1 was done collaboratively between Pinedo-Rivera and Mapperson. All other work is by Mapperson.

3.2 Fluid Cell Nano-CFA for Micro-scale Materials

Before we seek scaled-up nano-CFA it is necessary to demonstrate micro-scale assembly. A well established method is the fluid cell apparatus (see Section 2.4), pioneered by Tatiana Pinedo-Rivera and co-workers [1] and well-used since then [2–5].

3.2.1 Overview of Setup and Results

Templates: EBL was used first for template fabrication because of its reliability and high resolution. The first series of templates consist of arrays of cavities written into PMMA, and later SU8, on silicon wafers (Si). Arrays have side lengths of 30 μm and later 100 μm . Each template has a mixture of cavity shapes and sizes: some for single particles, others for dimers, trimers and occasionally more complicated arrangements. The arrays are metamaterial arrays, meaning their periodicity is equal to, or smaller than, half a wavelength of light (periodicities are between 225 nm and 350 nm). Cavities are written through the PMMA or SU8 layer to expose the Si substrate. Cavities are typically 50 nm deep.

Assembly Protocol: A typical assembly protocol involves placing the arrays in the centre of the $5 \times 5 \text{ mm}^2$ fluid cell, and injecting liquid to cover the template from one end of the cell to beyond the arrays by approximately 2 mm. The contact line is slightly convex at this stage. Then the air flow rate and substrate temperature are set to their desired values, typically 100 mL/min and 40°C, respectively. The contact line will begin receding after some time, acquiring a speed of 0.5 $\mu\text{m/s}$ to 1.5 $\mu\text{m/s}$. The condition of the contact line should be monitored, adjusting the air flow rate as necessary to reduce or increase particle concentration and/or the contact line speed. If the contact line is too slow it may pin and deposit a line of colloids. If it is too fast it may reach the arrays before becoming concentrated enough to assemble them. Adjusting the temperature can take a few minutes to take effect, so it is typically not adjusted during an experiment. Other aspects of the assembly protocol are described in Chapter 2, Section 2.4.

Spherical particles were purchased from BBI Solutions (bearing a proprietary surface chemistry) and used at their stock concentrations of (particles/mL) 4.50×10^{10} (50 nm), 5.60×10^9 (100 nm) and 1.66×10^9 (150 nm). Particles were stored in the fridge until used, being hand-shaken immediately prior to use. Proprietary particles were used initially because the fluid cell had been demonstrated at length with them. Later in this work in-house synthesised particles were used.

Sample Results: Some sample assemblies are shown in Figure 3.1, from joint work by Pinedo-Rivera and Mapperson. They are on $30 \times 30 \mu\text{m}^2$ metamaterial arrays. The largest assembled area is slightly less than one full array.

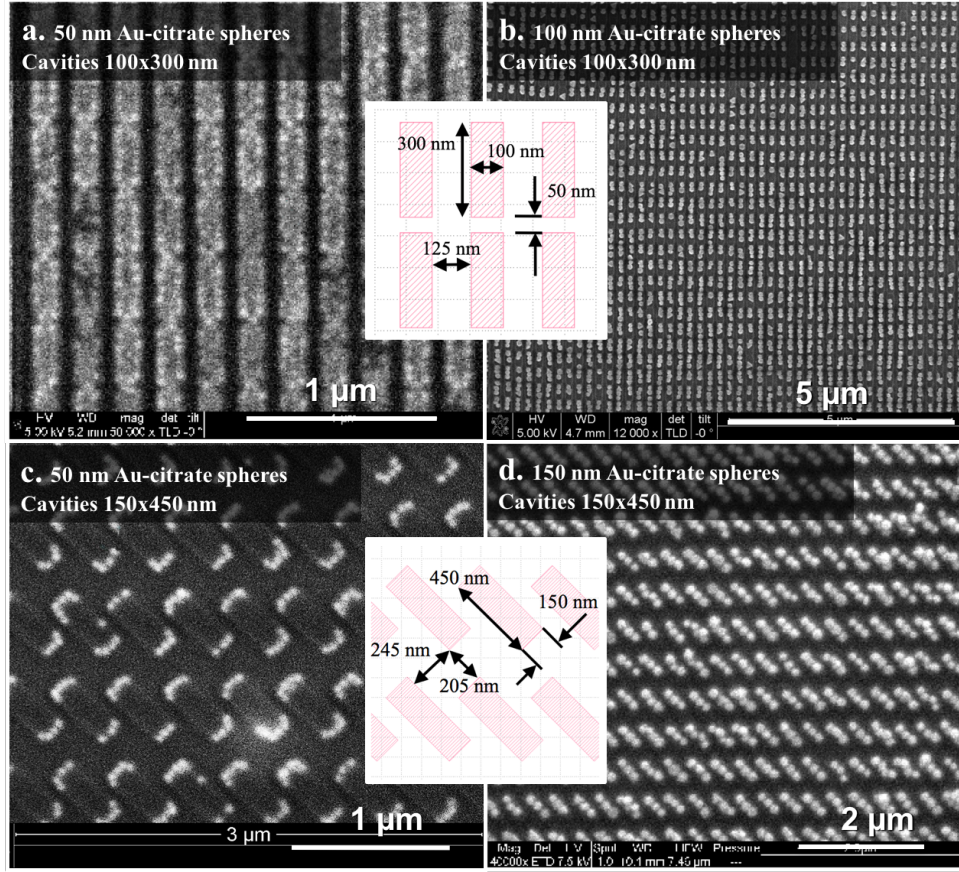


Figure 3.1: Assemblies of spherical gold particles of various sizes. The cavities in (a) and (b) are the same, as are the cavities in (c) and (d) (see inset diagrams of cavities). These results illustrate the versatility of assembling with different particle sizes and different colloid concentrations. Structures in (a), (b) and (d) show mild visible polarisation responses under dark-field illumination.

The dense assemblies (Figures (a), (b) and (d)) show a mild visible polarisation response, particularly when viewed under dark-field illumination. The dense assembly in Figure (a) is because particles much smaller than the cavity size are used. When particles comparable to the cavity size are used, more defined structures emerge (Figure (b)), specifically linear dimers and trimers in this case.

Comparing Figures (c) and (d) shows that relatively small particles at low concentration has an alternative effect to filling the cavities. Post-CFA capillary forces between the assembled particles and the cavity walls draws particles to the cavity extremities upon drying. This effect is discussed more in Chapters 4 and Chapter 5. Whilst these structures were not tested for their optical properties, they are similar to split-ring resonators, which have exotic uses like in negative-refractive index materials [6–8].

Working Towards Larger Arrays: After assembling the $30\ \mu\text{m}$ side-length arrays above, assembly was sought on arrays of $100\ \mu\text{m}$ and then $150\ \mu\text{m}$ side lengths, with much less success. Larger arrays slow the contact line significantly and the particle concentration dramatically increases, causing heavy over-deposition. Smaller arrays tend to yield higher quality assemblies by being less disruptive to the overall contact line shape.

3.2.2 Intermediate Scale-Up Results

Initial attempts at major scale-up involved NIL fabrication of $30 \times 30\ \mu\text{m}^2$ metamaterial arrays with $20\ \mu\text{m}$ separation, repeated over the entire $5 \times 5\ \text{mm}^2$ fluid cell area. Arrays are composed of $220\ \text{nm} \times 110\ \text{nm}$ cavities, with $300\ \text{nm}$ periodicity in both directions.

Assembly was done with $50\ \text{nm}$ gold nanospheres (BBI Solutions) with results shown in Figure 3.2, along with bright-field microscopy of pre- and post-assembled arrays.

Figure (a) shows that the NIL process left cavities that are poorly defined, more like undulating depressions. This produced poor assembly consistency. Figure (b) shows a large portion of an array where dimers dominate, whereas (c) shows part of another array having larger particle clusters. Post-assembly capillary forces pulled particles together, rendering clusters with well-defined inter-particle spacings (not more than a few nm) from the ligand shell.

Figures 3.2e and 3.2f show the visible polarisation-sensitive assemblies. The scattering response of a dimer will be a transverse scattering of similar wavelength to that from a single sphere ($\sim 530\ \text{nm}$) and a longitudinal scattering wavelength that is red-shifted to approximately $700\ \text{nm}$ [9]. Peak extinction at these wavelengths explains the exhibited green-to-red colour change. It is not readily clear what caused the large worm-like gold deposits. It may be that the colloidal solution developed some aggregates, or small defects or debris on the template perturbed the particle-rich contact line, resulting in a heavy deposition point which grew into a large deposit

The size of the net area assembled in this example is hundreds of micrometers in size, which is substantially larger than published works of a similar structure density. Each array has 100×100 cavities, meaning an order of 10^6 nanostructures were

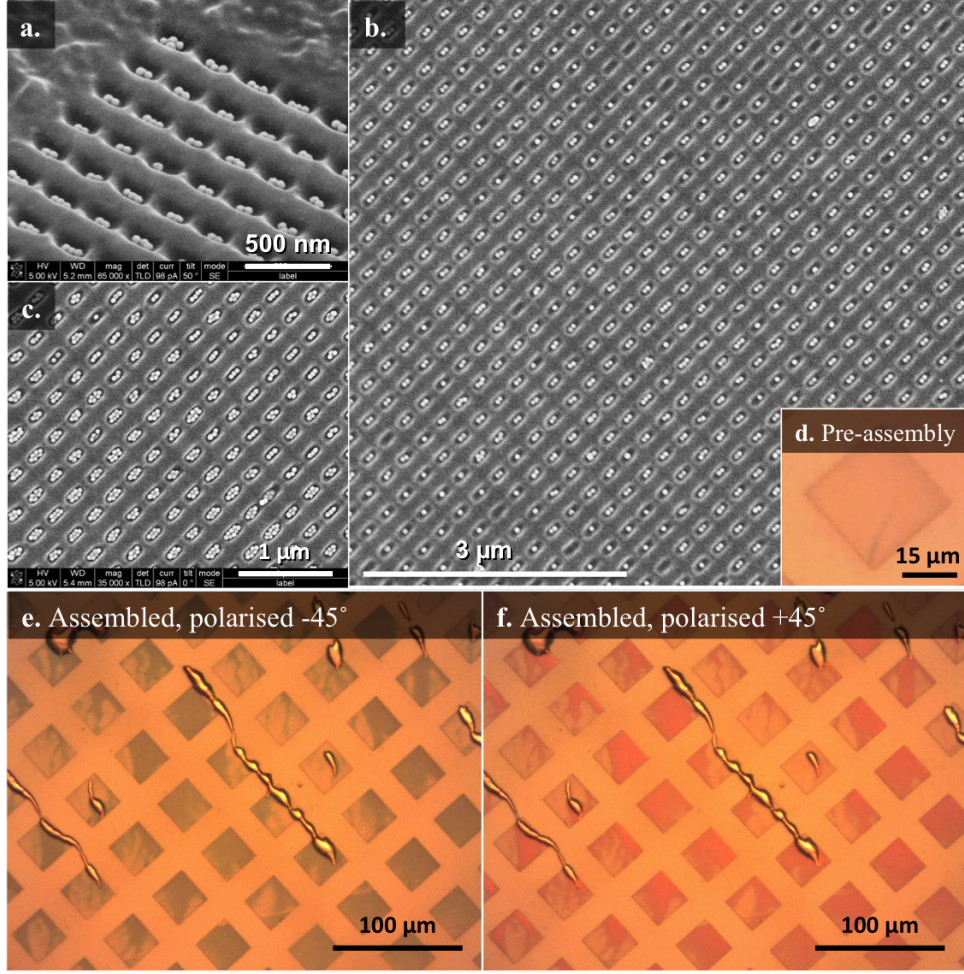


Figure 3.2: (a) to (c): SEM images of 50 nm gold spheres assembled into $900 \mu\text{m}^2$ arrays. In (a) it's seen that the cavities are not well defined, yet (b) demonstrates some consistent assembly of dimers. There are also arrays with many-particle clusters instead of dimers or trimers (c). (d) to (f): bright-field microscopy images of pre- and post- assembled arrays. The pre-assembled array shows no colour change at any polarisation, whereas the assembled arrays clearly do.

assembled. The assembly, however, is not clean, nor is it consistent. Optimisation was sought by adjusting the bulk colloid concentration, substrate temperature and air flow rate. It was found that conditions to prevent aggregated deposition also prevent assembly. This highlights the plausibility of scaling-up nano-CFA, but also the non-triviality of scale-up using a fluid cell.

3.2.3 Flaws with the Conventional CFA Model

Over the course of experimentation it was found that the conventional nano-CFA model was a poor guide to achieve good assembly. The conventional model stipulates three criteria: (1) a suitable receding contact angle, (2) a densely packed contact line, and (3) a suitable speed of recession. Even when these criteria were varied over the range of published values, consistent assembly could not be achieved. The reasons for occasional successful assembly in light of many unsuccessful attempts were equally elusive. The conventional model seemed, for the most part, to be disconnected from the reality experienced in the laboratory. This sets the scene for the next chapter wherein the conventional model is critically analysed, and found wanting. From there the remainder of the thesis is centred on elucidating a more accurate model.

3.3 A Scalable CFA Apparatus

Given that scalable assembly is the goal, what follows is discussion on the scalability of the nano-CFA apparatus and of NIL template fabrication.

3.3.1 Difficulties Inherent in Fluid Cell CFA

The CFA apparatus must be reliable and simple to scale, but experiments reveal four areas of difficulty inherent to the fluid cell approach. The cons of the fluid cell apparatus have not been reviewed in the literature, so they are explained below.

Inconsistent Contact Line Shape and Recession: The contact line may begin with a straight or convex profile, but morphs to concave as it recedes due to friction on the cell walls. This unfavourably alters particle density along the contact line during the experiment, since particles are convectively driven to the most extended contact line regions.

The cell walls are hydrophobic PDMS, but mild contamination, roughness or colloidal deposition can cause contact line pinning. Strong pinning can halt the entire contact line, which may then jump over a large portion of the template upon

depinning. Pinning on the cell wall is more prevalent as the fluid cell ages implying deposition as a causal factor.

When contact line recession is slowed by wall friction it can over-concentrate particles at the contact line. This is because the upper contact line (against the glass slide) recedes well despite the lower contact line slowing, and this drags the contact angle on the substrate lower, enhancing convective flows there. Overall, the presence of an enclosed fluid cell is disruptive to uniform contact line motion and consistent particle concentration.

Tuning Colloid Concentration During Assembly: Particle concentration during assembly is affected by (1) inconsistent contact line shape and recession (see above), and by (2) an ever-increasing particle-to-liquid volume ratio throughout an experiment. In the latter part of an experiment, particle concentration is high enough to spontaneously deposit large particle aggregates. To account for this, the templated area must be a small fraction of the cell area (severely limiting the maximum assembly extent). It's also necessary that the contact line traverses the arrays at a similar time into each experiment, otherwise the particle concentration over the arrays may vary considerably between experiments (this is an unnecessary complication).

Strongly Coupled Experimental Parameters: A significant issue with any fluid cell device is the inseparable interplay between experimental controls. For example, the contact line speed is a function of the evaporation rate (based on the dialled-up temperature and air flow rate), and is thus coupled strongly to the particle concentration at the contact line and to the receding contact angle. The settings for the optimal concentration may not coincide with the settings for optimal speed and contact angle, and vice versa.

A Fluid Cell is Not Scalable: In addition to the above difficulties, the fluid cell approach is not easily scalable. An enlarged fluid cell was designed to hold a $5 \times 5 \text{ cm}^2$ substrate. The cell is 2.5 mm high, meaning the liquid front from wall to wall is long and narrow. This is problematic as the surface tension is too weak to maintain a straight contact line over that distance. Perturbations quickly develop and grow from a range of causes. Perturbations in one part of the contact line are

not felt strongly in another part, and the contact line does not recede smoothly and evenly.

A slider-CFA apparatus is seen to be much more suitable for CFA and scaleable. The next section discusses the slider-CFA apparatus, with which macro-scale nano-CFA is demonstrated.

3.3.2 Key Benefits of Slider-CFA

Recognising the shortcomings of fluid cell CFA, a slider-CFA apparatus is preferred. Slider-CFA is well used elsewhere [10–18]. Other implementations include 'drop casting and evaporation' [19–21], 'immersion and extraction' [22], and 'immersion and evaporation' [23–25]. The 'immersion and extraction' method most closely resembles slider-CFA, with the others being less controllable but invoking similar dynamics.

Slider-CFA avoids the issue of multiple assembly conditions being dependent on just a few experimental parameters. Contact line stability is more readily available than with a fluid cell, and the recession speed is directly controllable by the slider speed independent to evaporation. Evaporation can be exclusively set for the desired convective flow rate without affecting other variables. The contact angle can be controlled by the choice of liquid-substrate wettability, and during the experiment by the height of the slider and the slider speed. Slider-CFA is also found to be easily scalable, making it the apparatus of choice for the rest of this project.

3.3.3 Understanding the Forces in Slider-CFA

This section describes the balance of forces in slider-CFA, which is important for characterising the apparatus. It is assumed the reader is familiar with the basic setup (see Chapter 2, Section 2.5).

The liquid in slider-CFA bridges the substrate and slider, which are in relative motion to each other, so the liquid is under constant tension between the substrate and slider. The balance between these two competing forces governs the:

1. Receding contact angle (θ_{REC}): when the substrate and slider begin moving relative to each other, the contact line remains pinned on both until the energy of adsorption on the substrate is overcome by the elastic energy (tension)

building up across the meniscus. The effect of this is that θ_{REC} is pulled lower and lower until recession begins on the substrate. (Note: if the surface tension is not high enough to quickly overcome contact line adsorption, θ_{REC} will reduce so low that convective deposition or thin film formation occurs, negating CFA.)

2. Contact line stability: a stable contact line is resistant to large-scale perturbations, thus preventing uneven assembly, self-pinning and spontaneous deposition. This requires high tension across the interface.

The following sections characterise these two aspects of slider-CFA, improving our understanding of slider-CFA.

3.3.4 Characterising the Receding Contact Angle

As stated above, the receding contact angle is a function of wettability and the balance between tension and adsorption forces. Figure 3.3 shows the receding contact angle as it varies with slider height and speed, for four different surfactant-temperature combinations. Higher surfactant or temperature create a liquid with lower inherent interfacial tension. Higher speeds apply a greater tension to the interface, and conversely for higher slider heights. Each plot is from 39 independent measurements on average.

Contact Angle Relation to Speed: Each plot shows a minimal line, or a contact angle valley, indicated by the white dashed line, most clearly seen in Figure 3.3a. Recall that there is a time lag between the apparatus moving and the contact line moving on the substrate. Thus θ_{REC} reduces until the contact line begins receding, at which point θ_{REC} stabilises. When the substrate moves faster, it also moves further before the contact line desorbs. This explains the trend to the left of the minimal line: θ_{REC} reduces as speed increases.

We also note that greater speeds put the liquid interface under greater tension. As the speed increases beyond the minimal line, the ever greater interfacial elastic energy becomes large enough to depin the contact line sooner (leading to a higher θ_{REC}). Thus a minimal line exists and θ_{REC} rises with speed beyond that point.

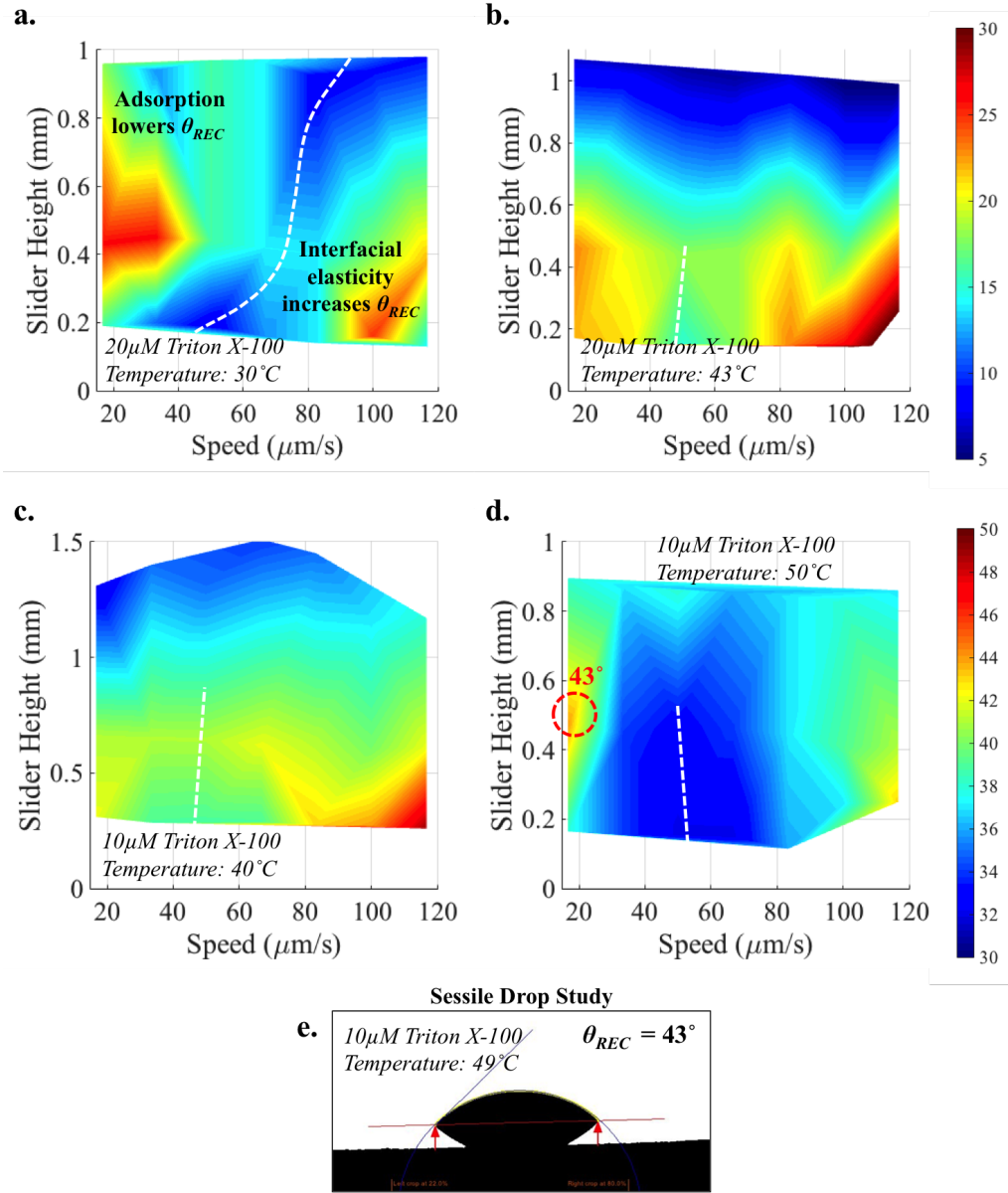


Figure 3.3: Receding contact angles of a slider-CFA apparatus at Triton X-100 concentration and substrate temperature combinations of (a) 20 μM , 27°C, (b) 20 μM , 37°C, (c) 10 μM , 24°C, and (d) 10 μM , 35°C. The solvent is water and the substrate is PMMA. Colour bars apply to both plots on the same row. Figure (e) shows the sessile droplet receding contact angle akin to scenario (d). The sessile droplet angle is the maximum angle found in (d), indicating that adding a slider only ever lowers the receding contact angle. The white dashed lines indicate contact angle minima.

Contact Angle Relation to Slider Height: In plots (b) and (c) it is clearly seen that increasing the slider height above a certain threshold removes the θ_{REC} dependance on speed; θ_{REC} is uniform across all speeds. θ_{REC} is also seen to decrease

as slider height increases beyond this threshold. This is understood by noting that a higher slider equates to a larger liquid interface, reducing the elastic energy per unit area of interface. For each unit area of the liquid interface along the contact line, the adsorption energy therefore increasingly dominates with greater slider heights, thus consistently lowering θ_{REC} and removing its speed-dependence.

Correlation with Sessile Droplet Analysis: In addition to tuning θ_{REC} by slider height and speed, wettability plays a key role. Wettability is most readily studied by sessile droplet analysis. We therefore wish to correlate the above measurements with sessile droplet studies. This is done via a comparison of Figures (d) and (e). The liquid and temperature used in (d) was duplicated in a sessile droplet study and θ_{REC} found to be 43° as shown in (e). Correlating this with the slider apparatus data in (d) reveals that the sessile droplet θ_{REC} reflects the maximum slider θ_{REC} . The slider apparatus can lower θ_{REC} by up to 15° , depending on the speed and slider height settings.

3.3.5 Slider Contact Line Stability

Having characterised how the contact angle varies in the slider apparatus, we now characterise the contact line stability. Stability of the contact line refers to its straightness and its ability to recover from perturbations. A straight contact line is necessary for an even distribution of particles, necessary for consistent assembly. Perturbations may develop in the contact line when there is small spontaneous deposition (causing resistance to contact line motion, or even pinning), or more often when there are slight variations in template wettability. An unstable contact line will see these perturbations persist or grow. Perturbations locally increase the particle concentration, which may strengthen pinning and grow the perturbation in a detrimental feedback loop.

Contact line stability can be qualitatively measured, being assigned a certain *stability factor*, defined as:

- 0: The contact line doesn't desorb on its own, forming a growing thin-film as the slider moves; wholly unsuitable for nano-CFA
- 1: The contact line recedes but with no control of form, large perturbations develop and grow endlessly, entirely unstable; unsuitable for nano-CFA

- 2: The contact line has perturbations larger than desired, but moderate stability prevents them growing endlessly; not suitable for nano-CFA, would yield very patchy assembly at best
- 3: A mostly straight and reasonably stable contact line, only small perturbations; suitable for nano-CFA but may not produce completely uniform assembly
- 4: A completely straight and highly stable contact line, perturbations are small and quickly self-correct; excellent for nano-CFA uniformity

Figure 3.4 presents contact line stability data, under the same experimental conditions in Figure 3.3. Figure 3.4d shows the best overall stability.

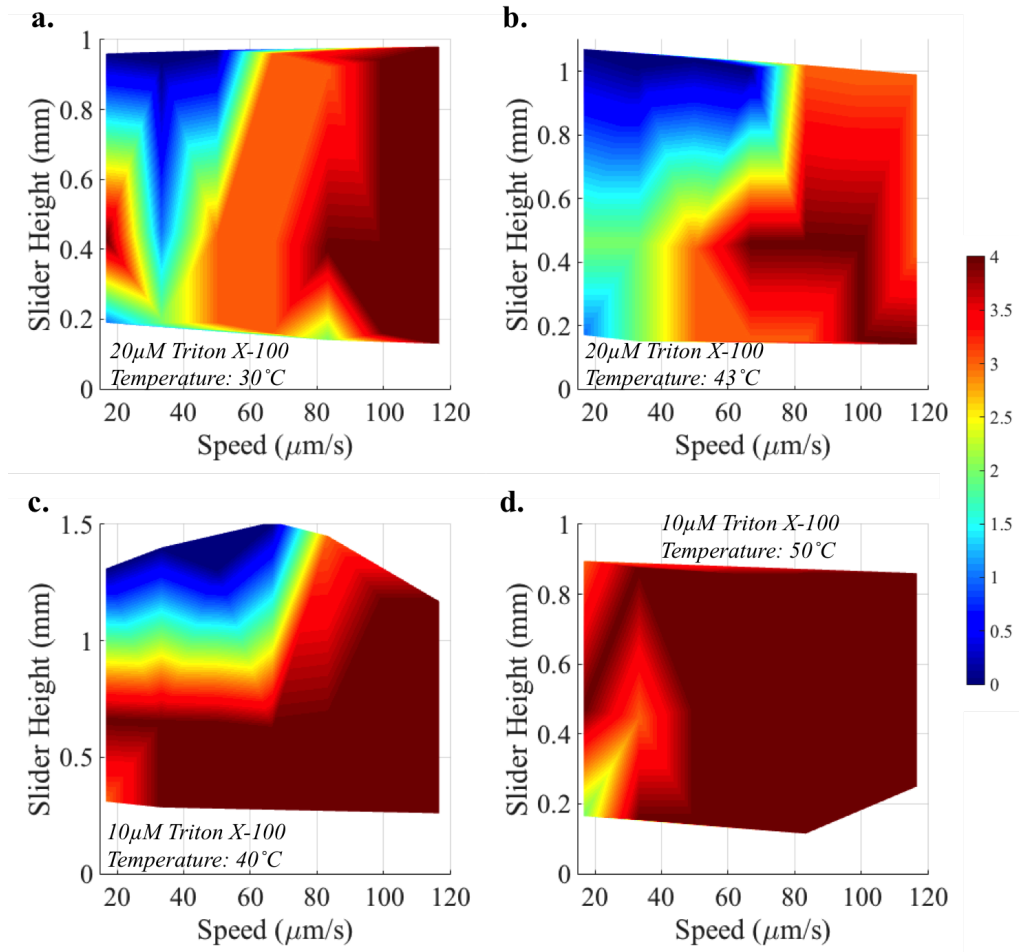


Figure 3.4: Contact line stability factor of a slider-CFA apparatus at Triton X-100 concentration and substrate temperature combinations of (a) 20 μM , 27 $^{\circ}\text{C}$, (b) 20 μM , 37 $^{\circ}\text{C}$, (c) 10 μM , 24 $^{\circ}\text{C}$, and (d) 10 μM , 35 $^{\circ}\text{C}$. The solvent is water and the substrate is PMMA.

Contact line stability is directly related to the elastic energy per unit area, and

as such it is optimal when speed is high, the slider is close to the substrate and the liquid has an inherently high surface tension. This is well reflected in the data.

Less apparent is the link between contact line stability and θ_{REC} . Correlating Figures 3.3 and 3.4 reveals that contact line stability is also lower when the receding contact angle is low. This is understood by noting that a lower θ_{REC} often means the liquid interface is stretched large. Thus the elastic energy per unit energy is reduced compared to a smaller interface at a higher θ_{REC} .

3.3.6 Selecting Slider-CFA Parameters

Based on the above results we can choose suitable setup parameters for nano-CFA. In the ideal case the contact line will be highly stable, the temperature will be high, the receding contact angle moderate (approximately 40°), and the slider speed slow. These conditions can be found in scenario (d), at a slider height in the vicinity of $500\text{ }\mu\text{m}$ to $600\text{ }\mu\text{m}$ and at the slowest speed the slider can achieve, which is $16.7\text{ }\mu\text{m/s}$. This, then, is what was used for the scale-up trials.

3.4 Scalable Template Fabrication

With a scalable CFA apparatus, we now turn to consider scalable template fabrication. EBL produces high quality templates but centimetre-squared templates take hours of write-time. A scalable method is NIL. NIL involves imprinting a master template into an uncured resist, such as SU8 or HSQ. High pressure and temperature are required.

In the initial stages of this work, the template fabrication team was unaware of the fragility and vulnerability of NIL. In the present section, such challenges in NIL, and their impact on nano-CFA, are explained. It is concluded that reliable template production is itself a pertinent issue for scaling-up nano-CFA.

Inadequate Imprint: Defects can arise from a faulty imprint, from insufficient or uneven pressure, or inadequate heat distribution during imprint. Cavities emerged as dimples and barely reflect the intended cavity footprint shape. Dimples may also have a lip around them, where the imprinted material was squeezed out of the ‘cavity’ but not flattened. Figure 3.5 demonstrates this on an SU8 template.

Such poorly defined cavities do not present a significant topographical feature to attract assembly. According to the conventional model the absence of steep cavity walls should mean no assembly, yet some assembly was achieved on this inferior template. This cannot be readily explained by the conventional model.

Roughness: For unknown reasons, roughness is often observed. Well-defined cavities indicate good reproduction of the master, and so a faulty master template is concluded (see Figure 3.6).

Liquid dynamics of nano-CFA are simply responsive to template topology. When the scale of roughness is comparable to the cavity size or particle size, it therefore interferes with the CFA process. Roughened areas assemble more readily than smooth areas, producing highly variable assemblies where roughness is not consistent. Roughened areas also yield less-consistent assembly on their own (Figures 3.6a and b).

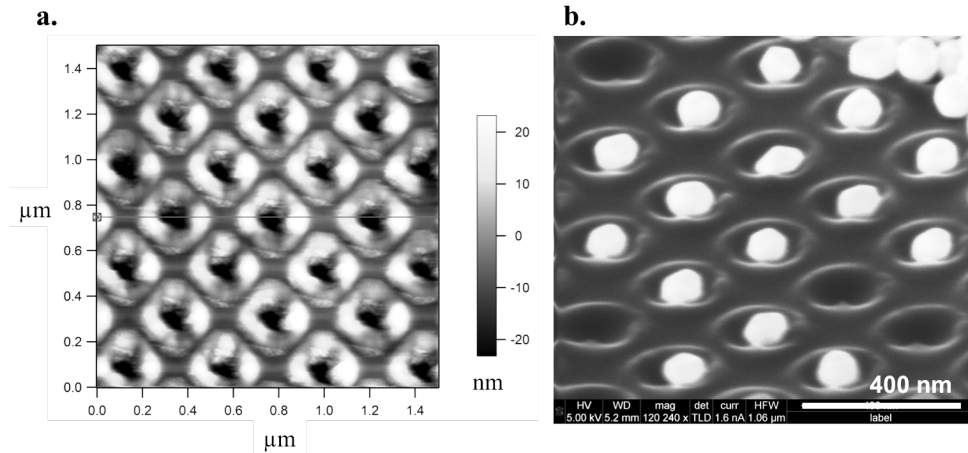


Figure 3.5: (a) AFM and (b) SEM images of template defects from an incomplete NIL imprint. The cavities are instead dimples with lips 20 to 30 nm high protruding around their perimeter. 100 nm gold particles are shown assembled in some dimples.

Reactive Ion Etching: A robust master template can be made by reactive ion etching (RIE) after EBL, leaving a Si mould of the lithographically produced resist pattern. The etching must be done carefully—insufficient etching will not replicate the cavities, and prolonged etching will exaggerate cavities. The latter is shown in Figure 3.7, where an entire array of cavities was indented by 200 nm by etching.

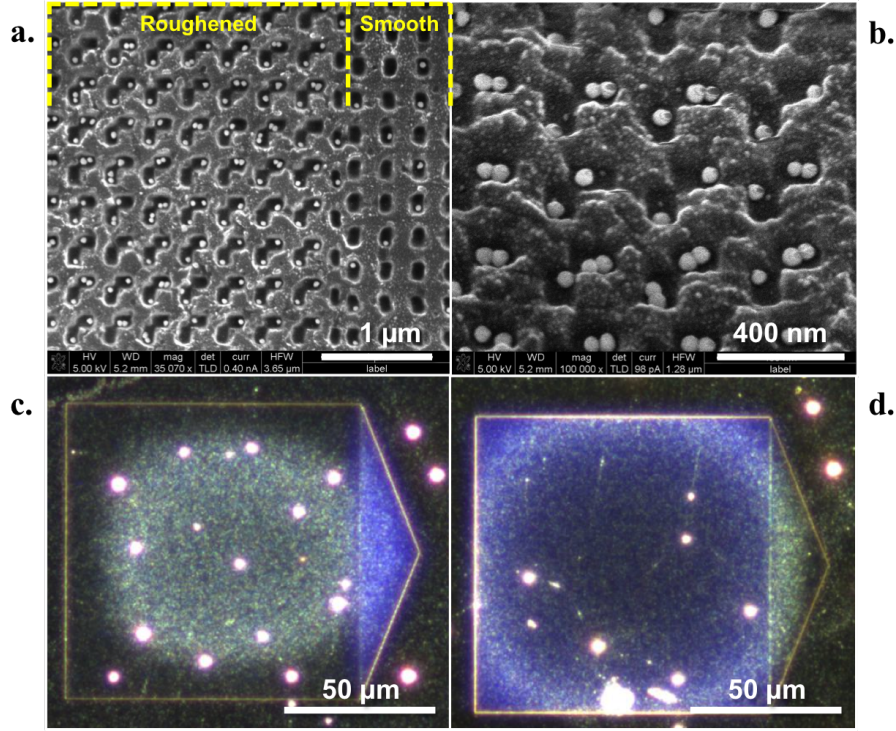


Figure 3.6: Figures (a) and (b) show SEM images of template roughness and assembly on the same. Figures (c) and (d) show dark-field microscopy images of two cavity arrays. The rough areas scatter more light and comprise the bright disk (c) and ring (d). Arrays with both rough and smooth areas cannot be consistently assembled.

All unintended nano-features are disruptive to nano-CFA. The exampled nano-wall pins the contact line around the array, preventing its recession. The liquid eventually depins, jumping a large portion of the array and often leaving aggregated deposition around the formerly pinned edge (Figure 3.7b).

NIL Chemistry: On other occasions templates may have large conglomerates of resist, or areas where resist peeled away (see Figure 3.8). This may be due to old resist, or to a poor anti-stick layer preventing clean separation of the master from the secondary template. Such sizeable defects are evidently detrimental to nano-CFA.

Concluding Remarks: Whilst NIL is economical, it is vulnerable to defects not found in EBL. The above problems are inherent in the NIL process, irrespective of the size of the arrays being fabricated. In this present work, all NIL templates were defective in one or more ways given above. This proved a persistent barrier to

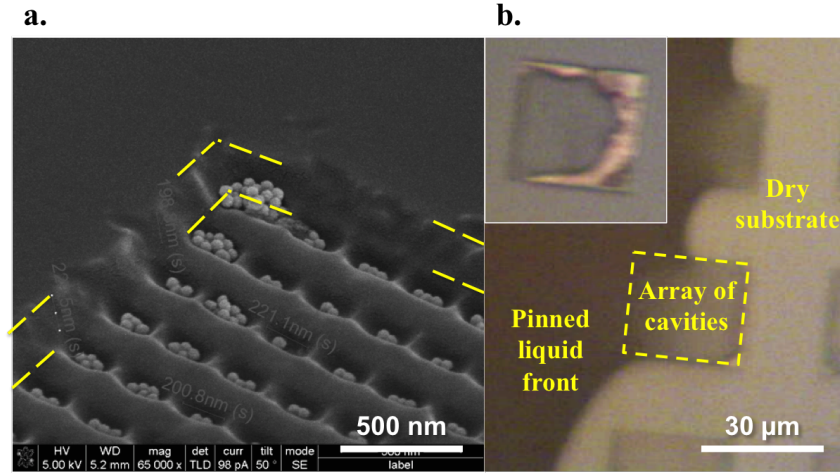


Figure 3.7: (a) An SEM image showing an etched Si template. The cavity array indented by a wall approximately 200 nm high. In (b) a bright-field microscopy image shows how the contact line pins on these array walls, often leaving a large lump of particles around that edge (inset).

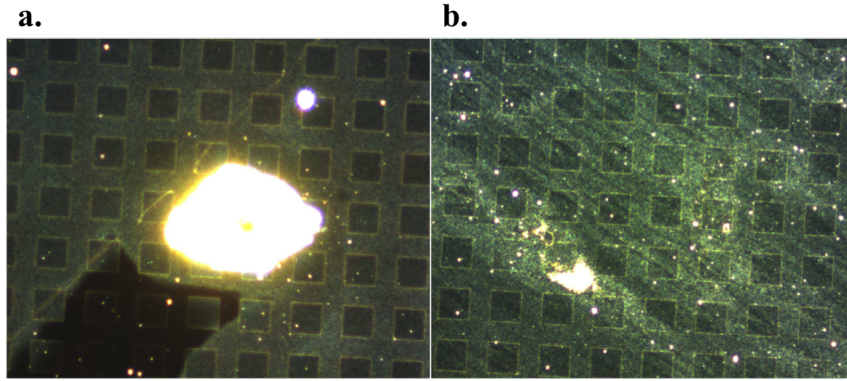


Figure 3.8: Dark-field microscopy images showing templates after the NIL process. The squares are 30 μm arrays of nano-cavities. All the bright spots are template defects, often conglomerates of resist. The inter-array regions should be black, and their speckled colour indicates nano-roughness.

achieving consistent scaled-up assembly. Time expired for the fabrication team to attempt more NIL templates, and scale-up trials were conducted on templates with patchy roughness and entire arrays indented by 100 nm walls.

On a more optimistic point, the variety of template defects presented unique topographies to study CFA dynamics. Whilst they are clearly a limiting factor in macro-scale assembly, they temporarily served a useful purpose.

3.5 Macro-Scale Nano-CFA: Experimental Section

This section details the particles, template and experimental parameters used in macroscale assembly of a two-tone plasmonic image.

3.5.1 The Particles

To produce a strong optical signature and more reliable assembly, nanorods were assembled instead of nanosphere dimers (recall Section 3.2.2). Gold nanorods were synthesised in-house by Sarah Jaber with cetrimonium bromide (CTAB) ligands (Section 2.3). They measure $45\text{ nm} \times 107\text{ nm}$ and have good monodispersity. CTAB is a strong surfactant, lowering the surface tension, and excess CTAB is required in solution to retain rod stability. Therefore the rods were washed three times to stabilise them with Na-PSS (Section 2.3.2). They were then washed twice in pure water to remove excess salts, and then washed once more and redispersed in $10\text{ }\mu\text{M}$ Triton X-100 to bring the sessile droplet receding contact angle nearer to 40° . The stock concentration is estimated to be 3×10^{10} particles/mL.

3.5.2 The Template

The template has been designed for maximum filling over a large area ($1.5 \times 1.2\text{ cm}^2$). This constitutes CFA assembly of a metamaterial about two orders of magnitude larger than that reported in current literature. The design features the University of Melbourne logo composed of $220\text{ nm} \times 110\text{ nm}$ cavities.

A master template was made by EBL into HSQ on Si, then dry etching to leave a Si master, then NIL of the master into SU8 on Si. The University of Melbourne logo was converted to black and white (no greys), setting white pixels as horizontally-aligned cavity arrays, and black pixels as vertically-aligned arrays (see Figure 3.9). Arrays have $30\text{ }\mu\text{m}$ side length, separated by $20\text{ }\mu\text{m}$. Arrays larger than this distort the contact line too severely, causing aggregated deposition or uneven assembly.

The nanorod plasmon peaks lie at 520 nm (transverse) and 706 nm (longitudinal), which are expected to produce an inverted red-green colour scheme upon rotating polarisation over an array of aligned rods.

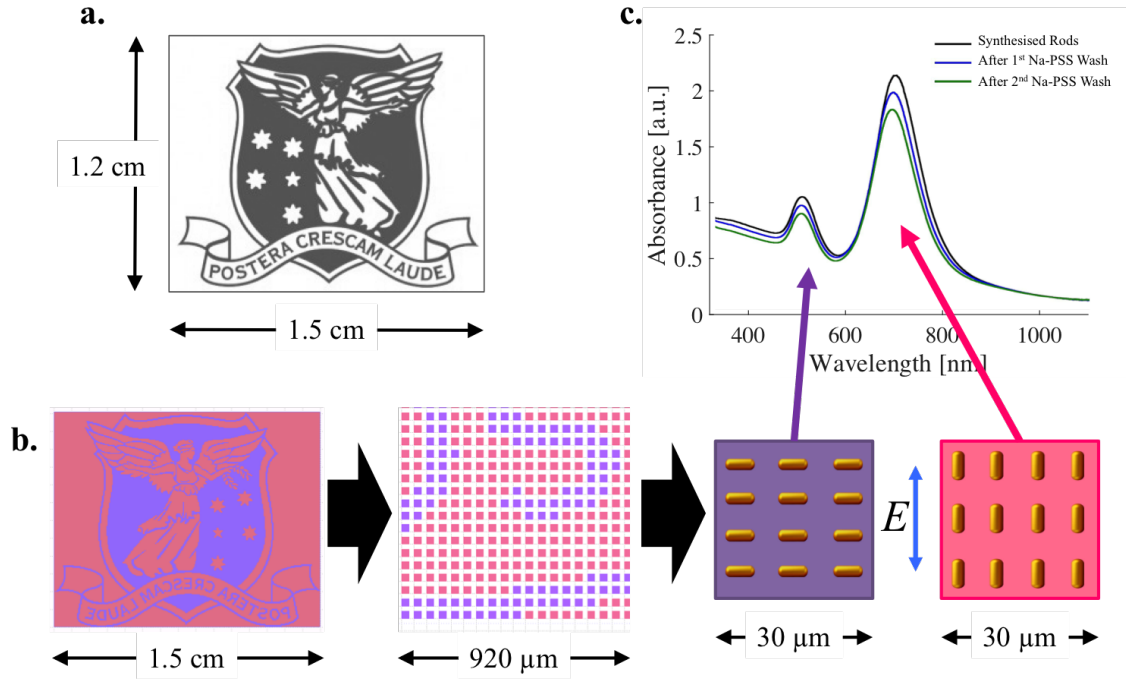


Figure 3.9: (a) The University of Melbourne logo, as a two-tone image. (b) The GDS file showing details at different size scales. (c) The transverse and longitudinal plasmon peaks of the rods, which are excited by a vertically aligned electric field (E) incident on rods orientated as shown in the arrays of (b). The rods shown in (b) are to illustrate alignment only and are not to scale.

As mentioned in Section 3.4, the arrays are surrounded by a 100 nm wall, and patches of roughness cover large portions (compare Figures 3.10(a) and (b)). Figure (c) is a photograph of slider-CFA in action. The blue-green boxes are individual EBL write regions, scattering light due to their surface structure. Variability in scattering colour and intensity indicates structural non-uniformity, which is expected to produce unwanted variation in assembly.

3.5.3 Assembly Conditions

For assembly the slider height is set at 630 μm, with a speed of 16.7 μm/s (the minimum speed the apparatus could accomplish at the time). The substrate temperature was held at 50°C, which is 39°C above dew point and the maximum of the thermoplate.¹ Note that in Figure 3.10c the contact line is very straight over the full array width, as expected based on the chosen setup parameters. In Appendix

¹Dew point: 11°C, humidity: 44 %, room temperature 23.8 °C.

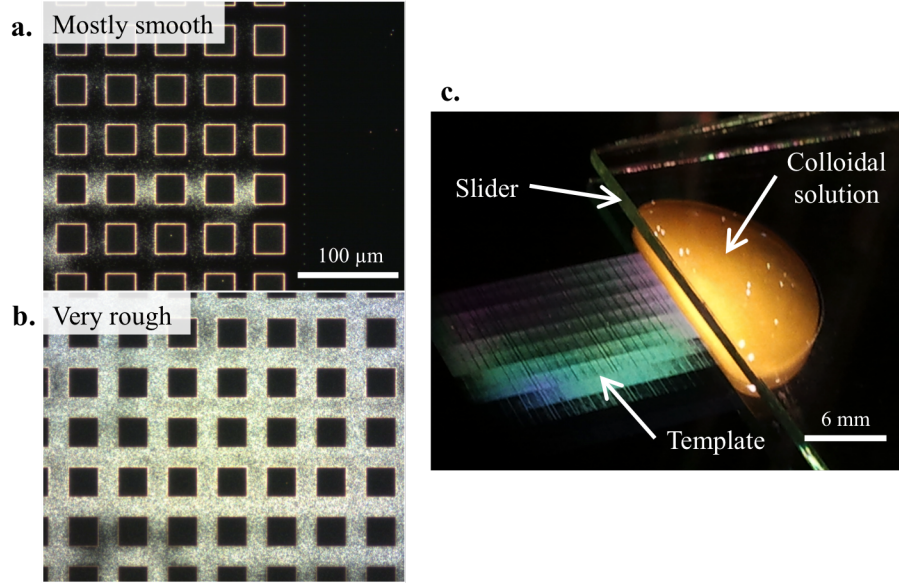


Figure 3.10: A mostly smooth portion of the template (a) can be compared with a very rough portion (b). Both (a) and (b) are dark-field microscopy images from the same template. In (c) is a photograph of the template in an experiment. The light scatters off the template in varying colours and intensity, indicative of unintended variability in template topography.

3.A is a brief discussion about the suitable size of liquid body to assemble from, for uniform assembly density.

3.6 Macro-Scale Nano-CFA: Results and Discussion

This section discusses results of assembling a macroscale two-tone plasmonic image.

3.6.1 Assembly Extent and Quality

A macro-scale optical image of the assembled template under polarised bright-field illumination is shown in Figure 3.11. Clear assembly was observed over large areas, but not the whole template. Template non-uniformity likely played a key role in inconsistent assembly, which was denser in roughened regions, as expected from Section 3.4. The anticipated red-green two-tone image is evident, though washed out by the

yellow tinge of the template itself.² The black spots are aggregated deposits.

The quality of assembly is exemplified in Figure 3.13. Histogram data shows a definite clustering of rods around the vertical direction with the vast majority of cavities having only one rod. This is ideal for a polarisation-sensitive two-tone image. The mean rod deviation from vertical is 9.5° , and the 2σ confidence interval is 29° . More sharply defined cavities would reduce these figures, but they are nonetheless entirely sufficient for the desired optical effect.

3.6.2 Optical Characterisation

To characterise the material, normal reflectance spectra from individual arrays was taken (see Figure 3.12). The spectra have been corrected for the source and detector bias, and the background spectra from an empty array subtracted. The spectra are normalised to the background reflected spectra of an empty array. There are extinction peaks at 511 nm and 661 nm. These are slightly blue-shifted from the UV-Vis spectra because the effective dielectric constant surrounding the assembled particles (majority air, with some SU8) is slightly lower than that of water.

Figure 3.12b.i shows the computed patch colours of the polarised rod spectra. The colours are slightly washed out compared to the bright-field photographs. The colour change from pink to blue is what would be seen if the rods were viewed in transmission through a clear substrate. In reflection, however, the template colour alters the result to that shown in Figure 3.12b.ii. Appendix 3.B demonstrates that when we superimpose the reflected template hue onto the patch colours in Figure 3.12b.i, the hue of the patches matches those of the bright-field photographs. This verifies that the supplied spectra are those of the nanorods. In Figures 3.12c and 3.12d the difference in extinction is shown as it varies by wavelength and by polarisation angle.

3.6.3 Optical Modelling

In this section the optical response from a nanorod array is modelled and compared with experimental dark-field spectra.

²With a $20\text{ }\mu\text{m}$ spacing between each $30\text{ }\mu$ array, each array unit cell has only 36 % of its area assembled, leaving more blank template than assembled even with every cavity filled.

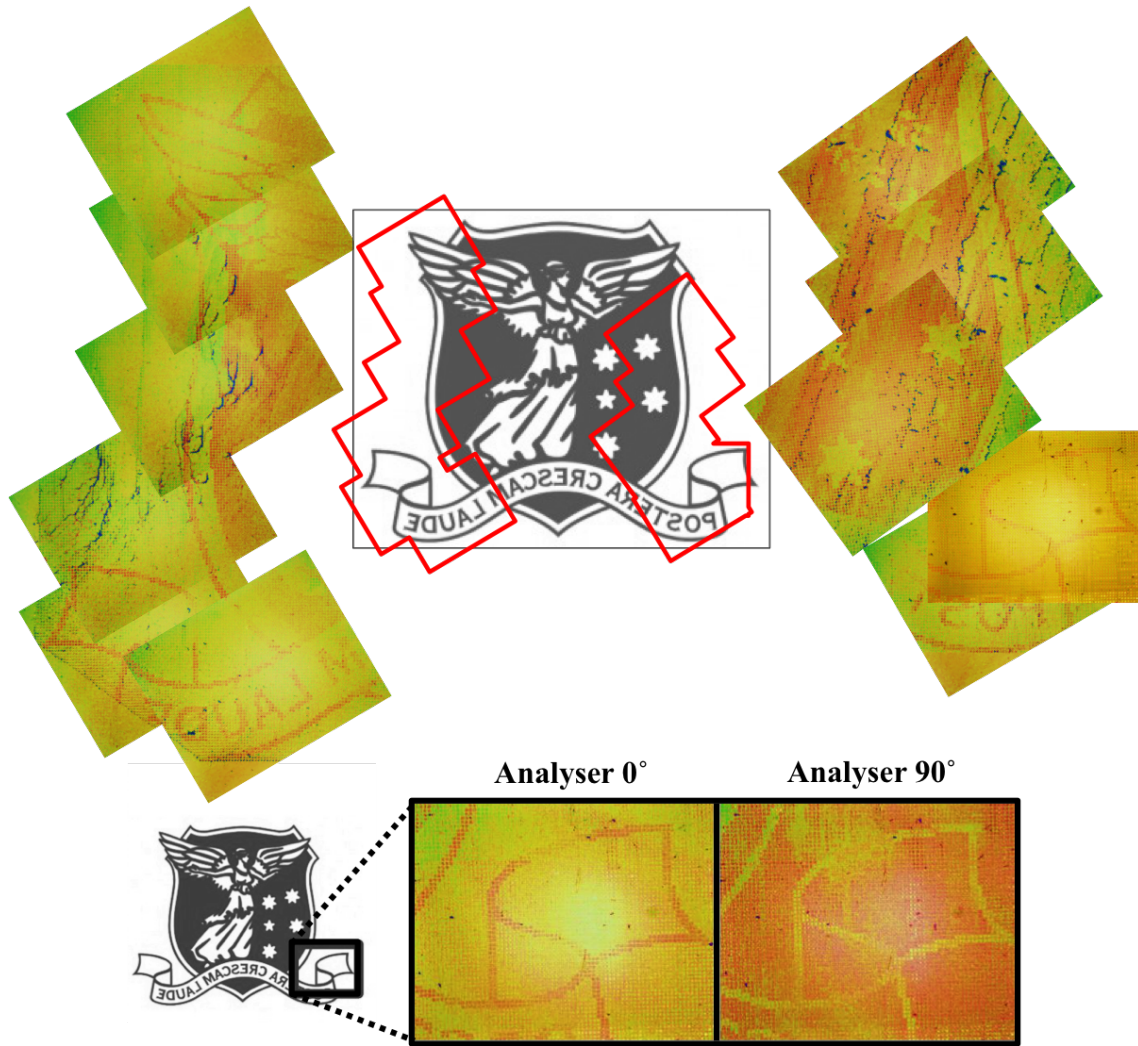


Figure 3.11: A macro-scale optical image of the assembled template under polarised bright-field illumination. The full logo is $15 \times 12 \text{ mm}^2$. The contrast has been enhanced for clearer viewing because reflection from the bare template between arrays reduces the assembled signature. For unaltered photographs of individual assembled arrays see Figure 3.12b.ii.

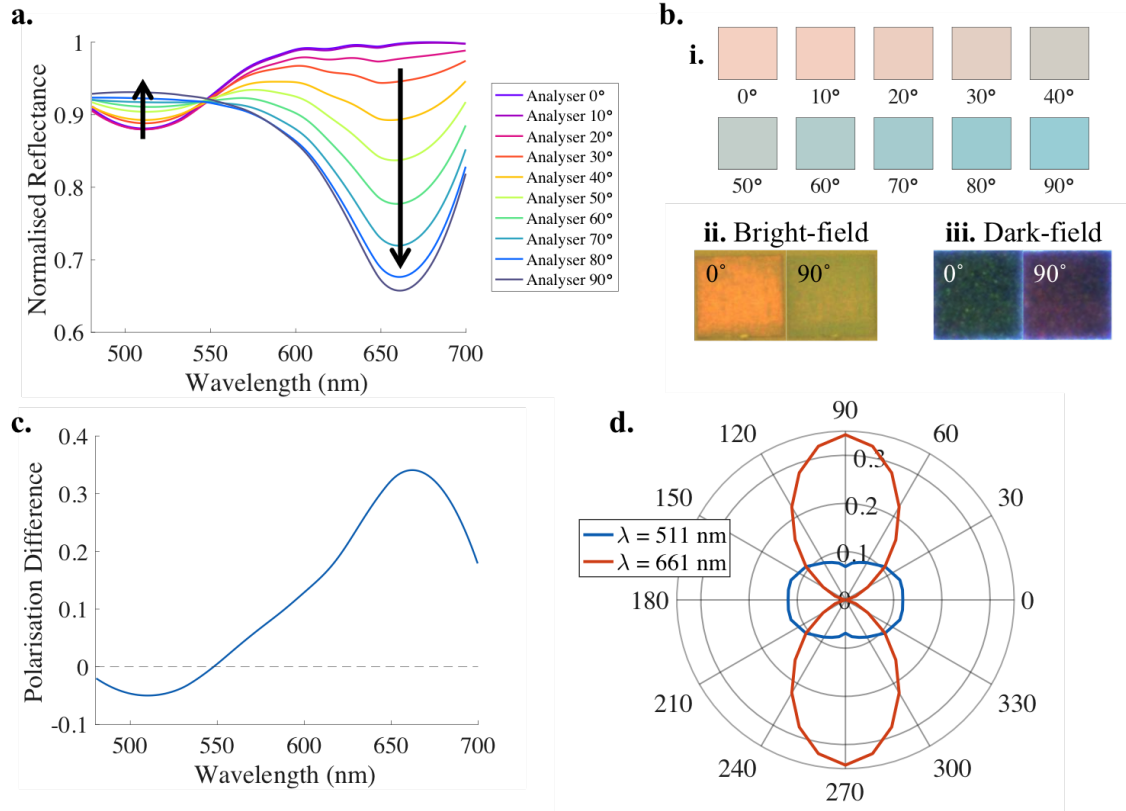


Figure 3.12: (a) The polarisation-dependent reflectance spectra of a complete nanorod array. In (b.i.) is shown the colour each polarised spectrum in (a) represents after converting into RGB values, together with unaltered bright-field (b.ii.) and dark-field (b.iii.) photos of arrays. (c) The difference in normalised extinction between 0° and 90° polarisations. (d) The normalised extinction magnitude at the two peak wavelengths as they vary with polarisation. In (d) the illumination is from above and the azimuthal scale is the polarisation angle.

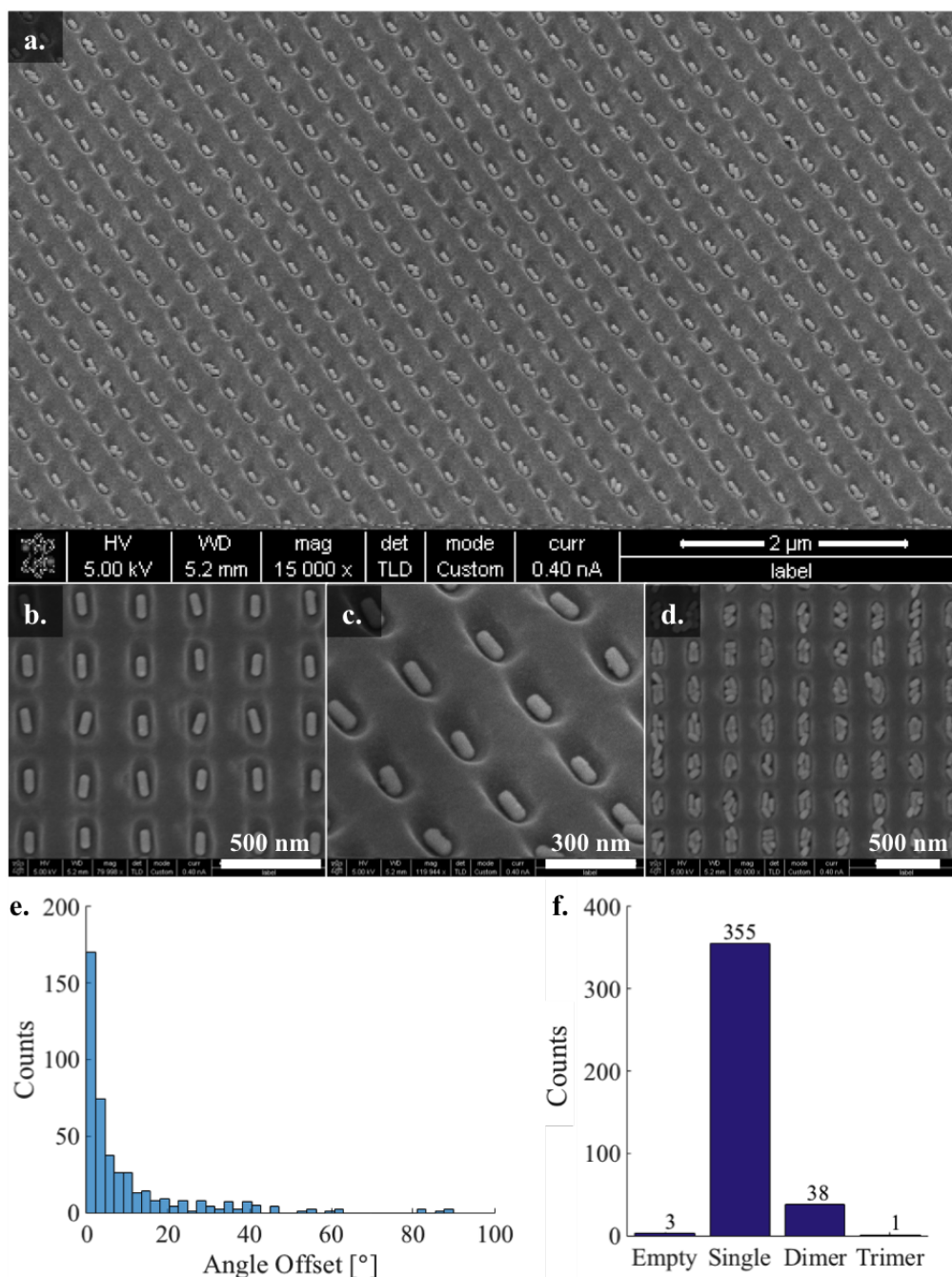


Figure 3.13: (a) to (c): SEM images of assembled rods showing good allotment per cavity and good alignment. In (d) is an example of some arrays that have heavier deposition. Whilst unwanted on this occasion, it shows the ability to tightly pack particles into cavities. (e) A histogram of the rod alignment in an average cleanly-assembled array. Angles are the offset from vertical. (f) A histogram of the number of rods per cavity, showing the strong predominance of single rods as desired.

Determining the Effective-Medium Dielectric Constant: To model the optical response of the assembled material we must estimate the effective-medium dielectric constant of the air-SU8 environment. The nanorods are mostly surrounded by air ($n = 1$), with SU8 ($n = 2.56$)³ near the sides and touching the base. UV-Vis spectra are taken in water ($n = 1.77$).

Jun et al. [26] show that the longitudinal extinction peak of gold nanorods has a linear dependence on the surrounding dielectric constant, blue shifting by 87.6 nm with every unit decrement in dielectric constant. The difference between the longitudinal extinction peak of the assembled rods versus rods in water is a 45 nm blue shift, equating to an effective-medium dielectric constant of 1.26.

The effective proportion of a rod's environment that is SU8 can be found by the Maxwell Garnett theory of effective medium approximation. The effective-medium dielectric constant (ϵ_{eff}) is given by

$$\epsilon_{eff} = \epsilon_m \frac{2\delta_i(\epsilon_i - \epsilon_m) + \epsilon_i + 2\epsilon_m}{2\epsilon_m + \epsilon_i + \delta(\epsilon_m - \epsilon_i)} \quad (3.1)$$

where ϵ_m and ϵ_i are the dielectric constants of the primary (air) and secondary (SU8) surrounding media, respectively, and δ_i is the proportion of the secondary medium to the primary one. The equivalent proportion of SU8 (δ_i) is found to be 23 %, which is a very reasonable result.

Model Setup: Modelling the optical properties of the assembled material was done in COMSOL Multiphysics. A single unit cell of an array of rods is modelled, which is a nanorod centred on a $0.3 \times 0.3 \mu\text{m}^2$ area. The height of the model is at least three times the array constant above and below the rod (thus set at $2 \mu\text{m}$ in total). Illumination is from above, as is the port for measuring the light reflected normal to the plane of the array. Periodic boundary conditions are used on the vertical sides of the unit cell to emulate an infinite array. The material is best modelled in dark-field (only light scattered from the rod is measured), achieved by placing the nanorod in a single effective medium matching the air-SU8 mix.

Modelling Results: Figure 3.14 shows the experimental and modelled polarised dark-field spectra. Spectra are normalised to the incident light in both cases. They

³<http://memscyclopedia.org/su8.html>

agree well in form and peak scattering wavelengths. The scattering intensity difference is likely because the experimental array occupies a small percentage of the microscope field of view, whereas the modelled array is infinite.

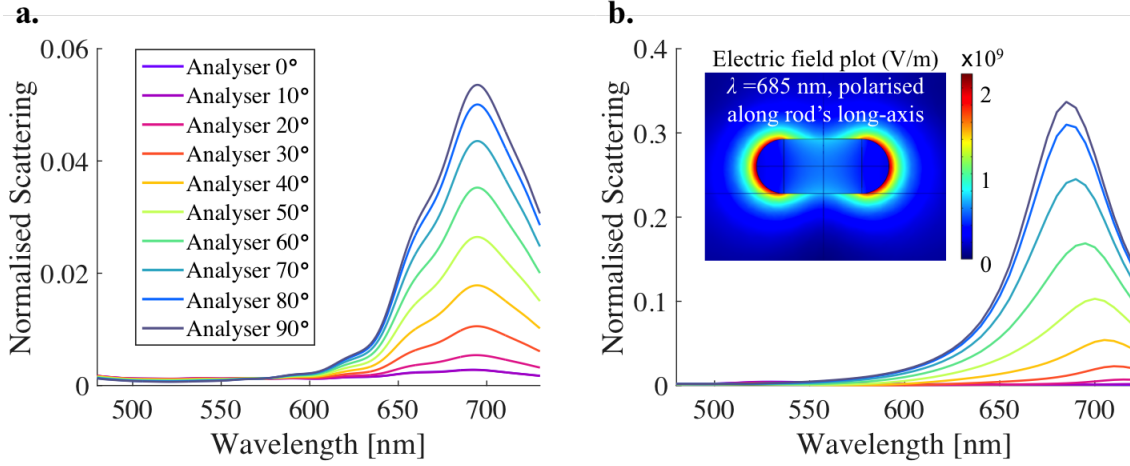


Figure 3.14: Experimental (a) and modelled (b) dark-field spectra of a nanorod array, showing good agreement. The inset in (b) is an output from the modelling showing the electric field magnitude around a single nanorod when illuminated normally with 685 nm light polarised along its long axis.

The transverse peak is absent in both experiment and simulation since only scattered light is recorded. Various studies show that the nanorod absorption cross-section is multiples larger than the scattering cross-section [27–29]. Scattering scales as R^6 whereas absorption scales with R^3 (R is the particle radius, and see Section 1.2.2). Scattering is significantly less than absorption, leaving primarily absorptive losses in the transverse band which do not show up here, but do show in reflectance spectra (Figure 3.12a) where full extinction is measured. This also explains why the longitudinal scattering efficiency here is relatively low compared to the reflectance measurements (Figure 3.12a).

3.7 Insights About Nano-CFA

Throughout this work various insights were gleaned about nano-CFA, useful for future experimental work. They are as follows:

Array Size, Shape and Orientation: Arrays of cavities will slow the contact line locally, causing it to extend compared to the bulk contact line (e.g. Figure 3.15). This concentrates particles in the extended region, which can lead to aggregated deposition if the perturbation is too strong. Thus the maximum array size ought to be limited. Larger assemblies should use smaller arrays separated by unpatterned spaces, or cavities should be spread more sparsely. In the present case, arrays sized $30\text{ }\mu\text{m}$ were highly acceptable but $100\text{ }\mu\text{m}$ arrays were not.

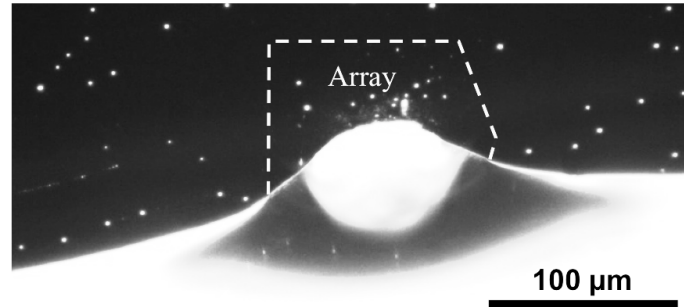


Figure 3.15: An example of a large contact line perturbation over a large nano-cavity array.

The edge of an array will also pin a contact line more strongly than the interior of the array. If the contact line meets the array along a long flat edge, the pinning can be severely prolonged (as if the array is itself one large cavity), causing aggregated deposition along the pinned edge. A workaround is to reshape/reorient the array so the contact line approaches over a non-straight edge, such as diagonally over a corner. This more gradually introduces the array to the contact line.

Uniformity of Nano-Features: All nano-features on a template will interact with the contact line. Care must be taken to ensure that cavities cause the strongest interaction. Slight nano-roughness can be tolerated, but it must be uniform. Non-uniformity in unintended nano-features forces non-uniformity in the contact line, disrupting consistent assembly.

Cavity Definition: Cavities are intended to interact with the contact line, being a topological discontinuity. If cavities do not present a strong surface discontinuity, assembly dramatically diminishes. This potential defect is unlikely from EBL (where well-defined cavities are easily achieved), but it is a pertinent concern with NIL.

Particle Concentration: Particles must be packed at the contact line before assembly will begin. Figure 3.16 examples a minimum observation to aim for. There is a bright glow of yellow colour, and an orange haze just beyond the glow as particles diffuse around.

The experimenter can detect when the particle concentration is approaching the upper limit, as the contact line begins to slow and grow in brightness. Unless the temperature is quickly reduced, particles may begin depositing spontaneously in small aggregates or as a long ribbon along the contact line.

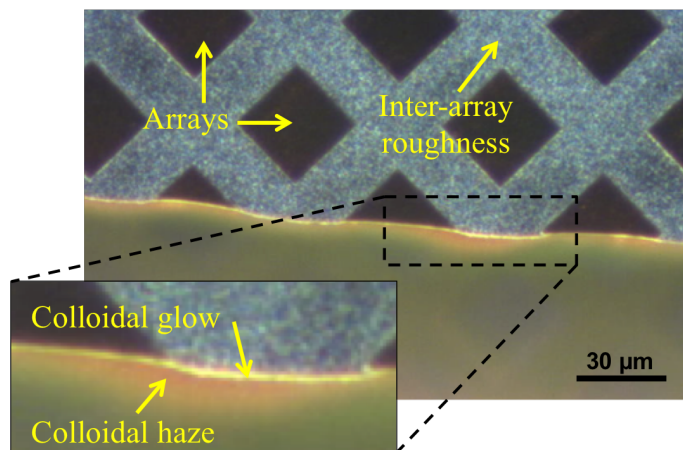


Figure 3.16: A dark-field photograph (50 $\times$ magnification) showing the characteristic glow and haze from particles concentrated at the contact line. This depicts the minimum particle packing to aim for.

Surfactant Concentration If surfactant is used, then it ought to be well below the CMC to prevent it depositing along with particles. Surfactant deposits can blanket particles, severely dampening their optical signature. If surfactant is required to stabilise particles, particles must be washed prior to assembly, or restabilised with a non-surface active ligand.

3.8 Conclusions

We began this chapter with a standard fluid cell for micro-scale nano-CFA. Micro-scale assemblies of gold dimers showed a clear polarisation response. Template and fluid cell problems prevented consistent assembly. Template issues could not be remedied, but slider-CFA was used instead of a fluid cell, with great success.

The slider-CFA was characterised beyond provisions of published literature, and used for centimetre-squared assembly of rods for a two-tone plasmonic image. Accounting for template defects, dense and uniform assembly was demonstrated. The resulting material was characterised optically, and compared with modelling, all showing a well-assembled material with the anticipated optical signature.

The goal of macro-scale nano-assembly of dense two-dimensional plasmonic materials has eluded researchers for a long time. This chapter demonstrates that nano-CFA can be successfully scaled-up to meet this need. Further work is particularly needed in economical large-area template fabrication.

The failure of the conventional model of nano-CFA has also been highlighted, and this sets the scene for the next chapter, wherein the experimental and theoretical concerns with the conventional model are laid out in detail. Consequentially, the door opens for a new and more robust description of nano-CFA. Fulfilment of that goal forms the remainder of this thesis, and enables us to pursue scaled-up CFA more knowledgeably. This makes an arguably significant contribution to the field of nano-assembly by liquid forces.

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Appendices

Determining a Suitably Sized Liquid Body for Assembly ... Appendix 3.A

Further Discussion on Bright-Field Polarised Spectra ... Appendix 3.B

Appendix 3.A Determining a Suitably Sized Liquid Body for Assembly

It is observed that there is sometimes an increase in deposition density in the later portion of a template. This is most likely due to a continual loss of solvent increasing the bulk particle concentration.⁴ We will briefly discuss the size of liquid body necessary to alleviate this issue which produces non-uniform assembly and aggregated deposition.

The size of a liquid body large enough to sweep over the full template can be approximately $20 \times 6 \times 0.63 \text{ mm}^3$ in size, equating to $76 \text{ }\mu\text{L}$ of liquid. The net evaporation rate over the liquid surface exposed to air is on the order of 10 nL/s to 30 nL/s (the variation accounts for differing substrate temperatures)⁵. The amount of liquid lost over 15 minutes is approximately $10 \text{ }\mu\text{L}$ to $30 \text{ }\mu\text{L}$, which is 13 % to 39 % of the liquid volume. Ignoring the fraction of particles deposited during assembly (which is very small), this is the equivalent rise in bulk particle

⁴It is unlikely that the density of particles at the contact line had not stabilised over the experiment run time, which is 15 minutes.

⁵These figures are based on the size of the exposed surface and published works such as Wang et al. [1]

concentration. Changes in bulk particle concentration by evaporation are therefore significant.

To minimise the increase in rod concentration, an initial liquid body size some four times larger is recommended (upwards of 300 μL), bringing the net liquid lost to a quarter of the above percentages. Experiments by Mapperson affirm that more uniform assembly results when larger liquid bodies are used.

From another point of view, a benefit of having a steady and appreciable increase in bulk particle concentration over a template is the ability to assess what concentration might be ideal for assembly. The limited number of templates available prevented such optimisation for the present work.

Appendix 3.B Further Discussion on Bright-Field Polarised Spectra

The colour patches in Figure 3.12b.i are based on the detected spectra of nanorod assemblies only (the spectrum of an empty array was subtracted). They are noticeably different from the bright-field photographs of assembled arrays in Figure 3.12b.ii. In this appendix we demonstrate that adding the template's reflected light to the computed spectra colours yields a colour very similar to the bright-field photographs.

Figure 3.17 demonstrates the process, whereby a section of bare template is chosen and overlaid unaltered onto the computed spectra colour patches. The template is overlaid at 50 % transparency, converting the pink patch to orange and the blue patch to green. The colour of the 'spectra + template' matches the hue of the bright-field photographs very closely, as expected. The intensity of the colour is lower than the photographs, and this is a scaling issue. This simple demonstration verifies that the supplied spectra do match those of the assembled nanorods alone.

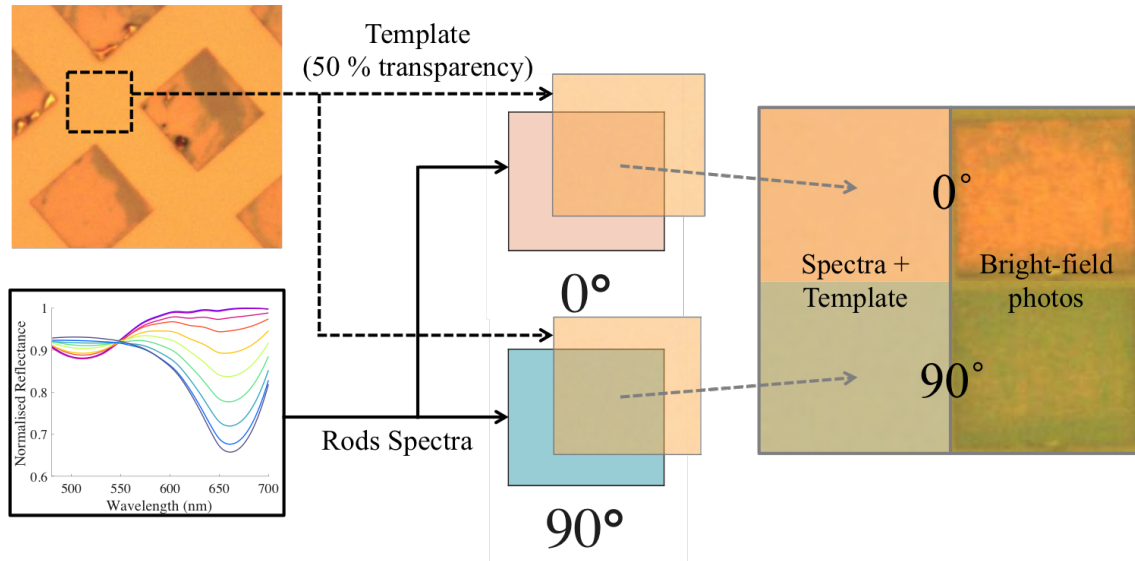


Figure 3.17: A demonstration that the hues computed from the nanorod array spectra are brought very close to the photographed bright-field arrays when they are overlaid with the template's reflected hue.

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A Critical Analysis of the Conventional Model of Nano-CFA

4

The conventional model of nano-CFA is widely accepted, yet it has received little critical analysis in scientific literature. Indeed there exist sound reasons to question the validity of the model. In this chapter we present the first review of the conventional model in light of the range of relevant experimental and theoretical knowledge. The model is found to fall short. This opens the door for a more accurate model to be established in its stead.

Introduction ...	4.1
Experimental Considerations ...	4.2
Theoretical Consideration #1: Nanoparticle Thermodynamics ...	4.3
Theoretical Consideration #2: Meniscus Pinning ...	4.4
Allusions to a More Accurate Model ...	4.5
Conclusions ...	4.6
Appendix	

4.1 Introduction

The conventional model of nano-CFA (explained in Section 1.6) is only loosely presented in CFA literature. Generalised diagrams are often used, and textual descrip-

tions are brief and without clear justification. There appears to be a general lack of understanding about CFA dynamics.

Three notable efforts to explain nano-CFA dynamics are Malaquin et al. (2007) [1] and a pair of 2015 papers that attempt to simulate the conventional model [2, 3]. All papers reference the conventional model without modification. Simulation results affirm the conclusion of Malaquin et al., that “the mechanism leading to particle deposition is not yet fully understood.” The conventional model, whilst ubiquitous in CFA literature, seems to be insufficient to fully explain particle trapping.

CFA dynamics appear to have been deduced from high-level observations without the benefit of dedicated studies from first principles. Dedicated studies from first-principles are essentially absent,¹ though this type of study is necessary if CFA is to be harnessed for all its potential.

From a first-principles approach, one indeed finds sound arguments that dismantle the conventional model. This chapter presents these arguments, first from an experimental standpoint, and then from a theoretical standpoint. No literature to date has thoroughly critiqued the conventional model from first principles. This chapter presents the need for a more accurate model.

The next chapter presents a new model of nano-CFA, built from first-principles. The remainder of this thesis further analyses and quantifies the proposed model, giving it a solid footing in both experiment and theory. This present chapter therefore acts like a bridge, transitioning us away from the failings of the conventional model and preparing us to receive a more sound theory of nano-CFA dynamics, equipping us to push the boundaries of nano-assembly.

4.2 Experimental Considerations

There are a variety of experimental outcomes that call into question the conventional model of nano-CFA. These are described below.

¹With Reference [2] being an exception.

4.2.1 Inaccurate Predictions from Scheme 1 of Nano-CFA

Scheme 1 of the conventional model (see Chapter 1, Section 1.6.2) claims that particles are loosely packed at the contact line apex and that particles are assembled individually by a capillary force. This predicts certain outcomes that are not supported by experiments.

Assembling Large Cavities: The most problematic result for Scheme 1 is that particles can assemble in large cavities far from any cavity wall. Scheme 1 relies on the capillary force to push a particle into a cavity. A particle would only be assembled when a particle is pressed up against a templated structure, as Figure 4.1 illustrates. It is self-contradictory for Scheme 1 to claim that particles will not assemble on the flat unpatterned substrate, and yet will assemble in the middle of a large cavity void. Figure 4.2 shows experimental results contradicting Scheme 1 predictions.

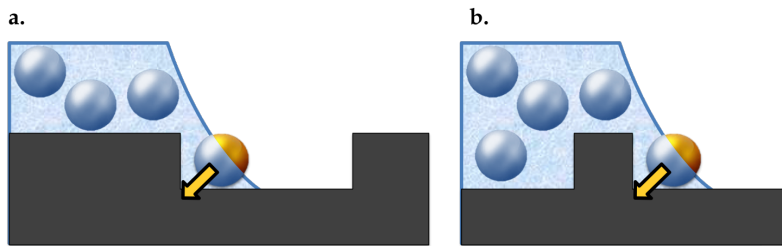


Figure 4.1: Diagrams depicting the predicted assembly behaviour of Scheme 1. Particles are anticipated to be dragged along by the receding meniscus until a suitable barrier is reached to hold the particle in place. This barrier may be the end wall of a cavity (a), or a protrusion rising out of the substrate (b). This means that dense assembly in large cavities (as in Figure 4.2), where most assembled particles are not in contact with a cavity wall, is generally not predicted by Scheme 1.

Cavity Filling Density: A further failure can be seen in the density of filling. A densely filled cavity implies a high rate of assembly. In Scheme 1, particles are loosely packed at the contact line, and they are only assembled individually. This would produce a low assembly rate and sparse filling, not prolonged dense filling, as Figure 4.2 shows.

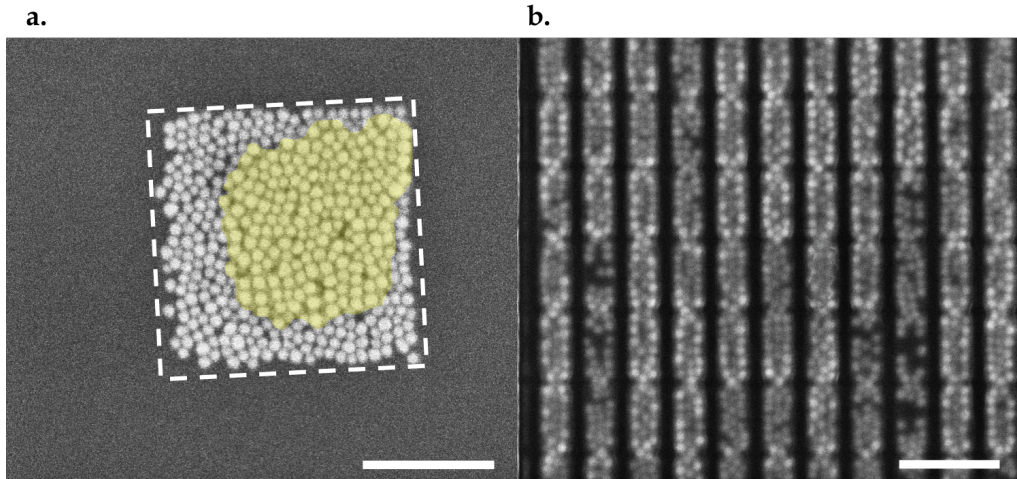


Figure 4.2: SEM images of particles that have been densely assembled into large cavities, implying a high rate of controlled deposition. Such a high rate of deposition is not a hallmark of Scheme 1 of the conventional model. Image (a) shows a $1 \times 1 \mu\text{m}^2$ cavity filled with 50 nm gold particles. The dashed line marks the cavity boundary, and the yellow shaded area marks where two layers of particles have been deposited. Image (b) shows cavities that are slightly larger than $100 \times 300 \text{ nm}^2$, and are cojoined, due to over-exposure during the EBL step of fabrication. Their cojoining means they are effectively long corrugated channels. They too are densely filled with 50 nm gold particles stacked two or three layers deep. Scale bars are 500 nm.

Simulations: Asbahi et al. [3] simulated Scheme 1 using a template of cavities that would house a single particle each. Any particle that is pushed into a cavity would therefore immediately come into contact with the walls of the cavity and be assembled. This is extremely favourable to Scheme 1, yet the simulated assembly yield was well below experimental outcomes under similar conditions. This suggests that Scheme 1 is either incomplete or wrong.

4.2.2 Inaccurate Predictions from Scheme 2 of Nano-CFA

We have seen that Scheme 1 fails experimental validation, and so does Scheme 2 (see Chapter 1, Section 1.6.2). Scheme 2 claims that particles are semi-crystalline packed at the contact line and are compressed collectively into a cavity. This ought to leave all cavities very densely filled, yet experiments often show cavities under-filled or empty. Figure 4.3 shows example results. Under-filled cavities are also more often reported in the literature than densely filled cavities [4–10].

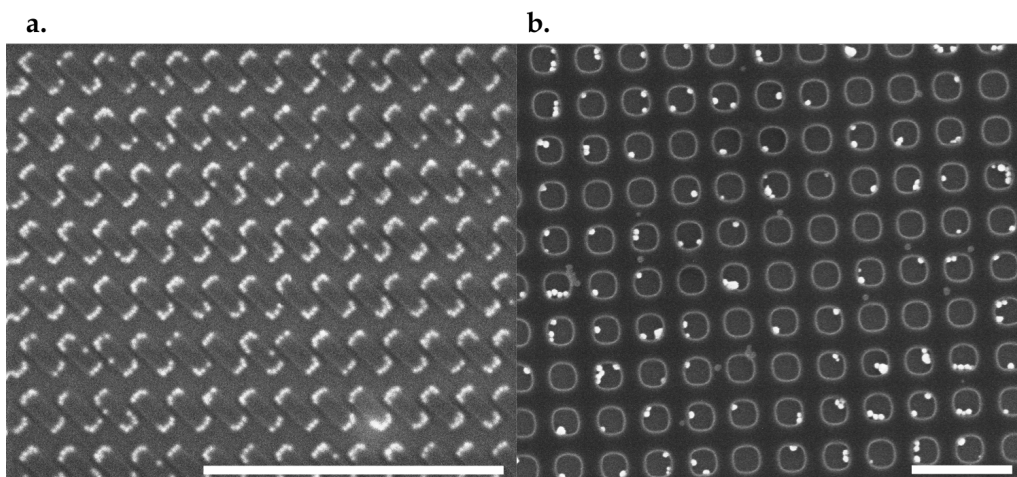


Figure 4.3: Cavities that are greatly under-filled by particles suggests that dense packing of particles at the contact line is either not reality, or it is not directing the assembly process. This calls into question Scheme 2 of the conventional model. Image (a) presents $150 \times 450 \text{ nm}^2$ cavities with 50 nm gold particles that are well ordered on a larger scale. Image (b) presents more randomly deposited 30 nm gold particles in $120 \times 120 \text{ nm}^2$ cavities. Scale bars are $3 \mu\text{m}$ and 500 nm, respectively.

These results indicate that particles are either not densely packed at the contact line, or else their dense packing is not controlling the assembly dynamics. Both of these stand fundamentally against Scheme 2.

4.2.3 A Complicated Combination of Assembly Dynamics

We have shown that dense and sparse assemblies invalidate the conventional model in both its forms (Schemes 1 and 2). Intriguingly, experiments sometimes show on the one template that large cavities fill densely while small cavities remain empty, or the opposite occurs—nano-cavities fill densely while the micron-sized cavities do not (see Figure 4.4). Where does this cavity selectivity come from, and why does it sometimes exclusively favour large cavities or small cavities? Evidently a process quite different to both Scheme 1 and Scheme 2 is in operation.

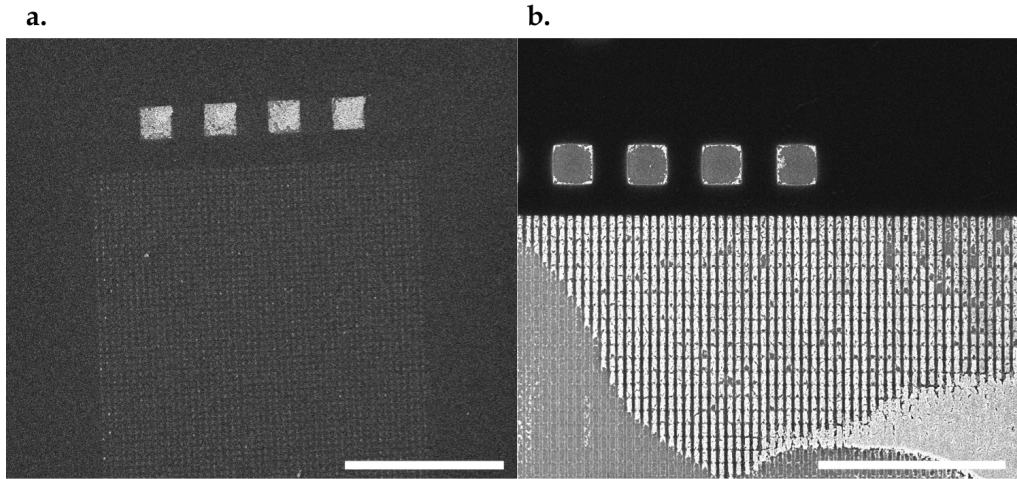


Figure 4.4: Two similar templates showing the opposite assembly preferences in terms of cavity size. Assembled particles are bright in the SEMs. In image (a) it is seen that the large $1 \times 1 \mu\text{m}^2$ cavities filled densely with multilayers of 50 nm gold particles, while the nano-cavities are essentially unfilled. The faint array below the four large squares is the array of nano-cavities. The scale bar is 5 μm . In image (b), the contrary is the case, where the $1 \times 1 \mu\text{m}^2$ cavities are nearly empty, while the nano-cavities below them were mostly filled densely, and some even over filled and caused self-pinning of the contact line and clumped deposition (lower right of image). The scale bar is 5 μm .

4.2.4 Disagreement Amongst Recommended Experimental Parameters

In Table 1.2 (see Section 1.6), published experimental parameters of nano-CFA work are given, and it is easily noticeable that different authors propose vastly different parameter values for successful nano-CFA.

For example, some studies found a contact angle of 10° to 30° as the workable range, while others found that only angles around 50° are successful. Indeed, Cui et al. [5] and Liddle, Cui and Alivisatos [4] cite that they cannot achieve any assembly *above* 30° , whereas Malaquin et al. [1] cite that they cannot get assembly *below* 30° . Again, the former studies [4, 5] claim controlled assembly at contact angles down to 10° , while the latter study [1] states that below 15° they observe complete deposition producing a monolayer of particles. Mapperson and Pinedo-Rivera even found assembly at $\sim 0^\circ$, as Figure 4.5 shows. Of course there were other differences between these studies besides the contact angles, but what is evident is that we are

not yet understanding the full picture of nano-CFA.

The alleged dependence on the receding contact angle is also brought into question here. In the conventional model, the reason why the receding contact angle is important is quite straightforward—we must control the direction of the capillary force. The vast incongruence in published successful experimental parameters suggest that even this simple aspect is misunderstood. It seems more likely that the receding contact angle has an *indirect* influence on the assembly outcome, in conjunction with other parameters that all together determine what range of contact angles are suitable for assembly. What are these other factors and what is the interplay between them? How does the receding contact angle influence assembly?

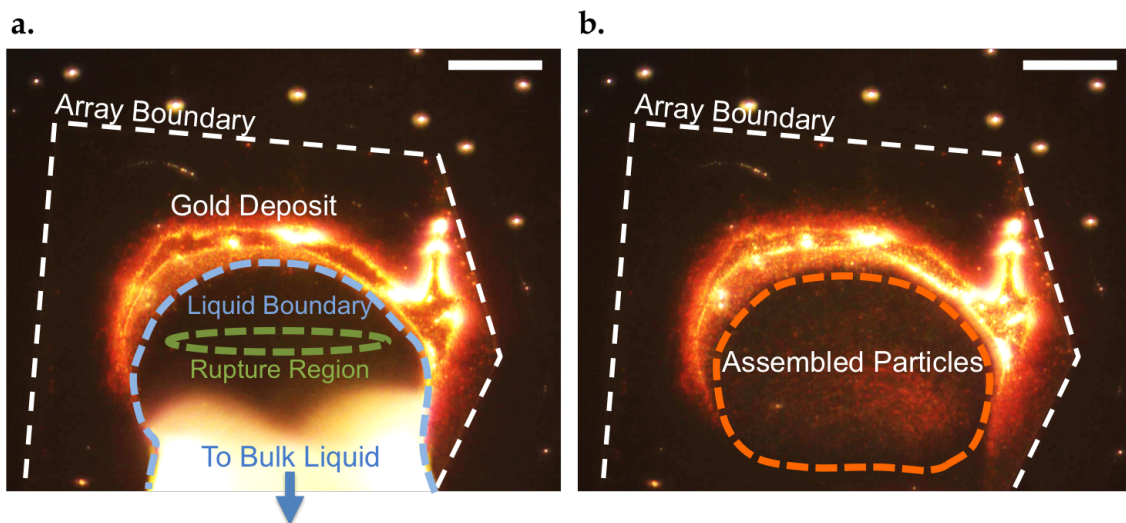


Figure 4.5: Dark-field microscopy video frames before and after dewetting over an array, showing assembly in a region of very low contact angle. In image (a), a heavy deposit of particles has pinned the contact line over the array, and the liquid is stretched to form a thin film over the lower half of the array (the dark region within the shaped marked ‘Liquid Boundary’). There is no assembly outside the heavy deposit or the liquid film in (a), as the array is black like the surrounding substrate. The thin film subsequently ruptures, beginning in the green region shown in (a), and moments later leaves (b): a dry array with particles assembled without clumping or over-deposition. The liquid film became so thin that it ruptured on its own, and yet particles were assembled over that entire area, and not elsewhere. The thin film and its rupture means the macroscopic contact angle is close to 0° . Scale bars are $25\ \mu\text{m}$.

4.2.5 Liquid Remaining in Cavities

A number of studies cite the fact that liquid remains in a cavity after the contact line has passed, and that this can rearrange the particles by immersion capillary forces as the liquid evaporates [4–8]. Typically this leads to a separation of the particles to the cavity extremities, as Figure 4.6 shows. Gordon & Peyrade [6] focus on this effect alone. Yet no CFA literature ventures to say *why* liquid remains in the cavities *after* the contact line has passed. The conventional model does not predict it.

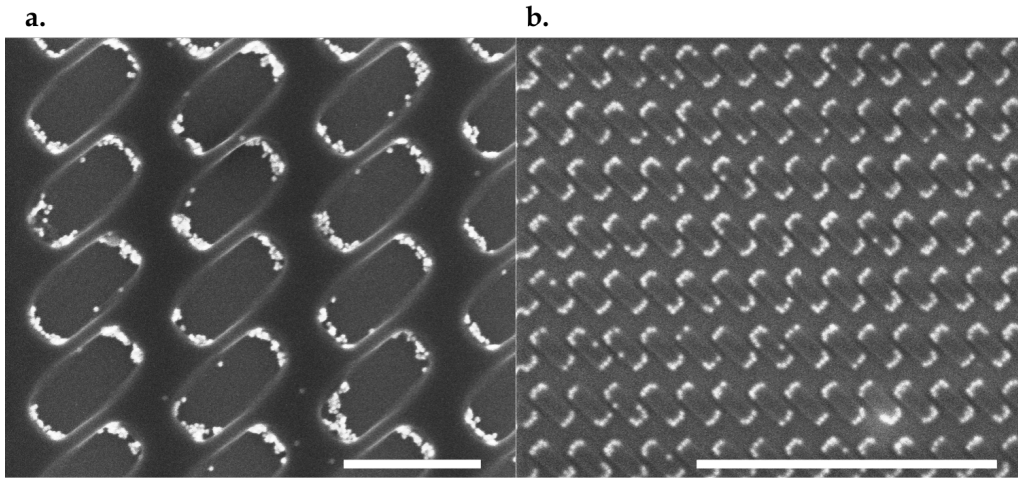


Figure 4.6: SEM images of particles that were assembled and then separated to the extremities of cavities, presumably by post-assembly immersion capillary forces. Notice that the particles are very evenly distributed to either end of the cavities; they don’t show a preference of direction. Results like these question the conventional model because they evidence liquid covering the floor of cavities after the contact line has passed. Cavities in both images are $150 \times 450 \text{ nm}^2$. In image (a) the gold particles are 20 nm in size; the scale bar is 500 nm. In image (b) the gold particles are 50 nm in size; the scale bar is $3 \mu\text{m}$.

Particle arrangements suggest that liquid uniformly covers the cavity floor after the contact line has receded—even very under-filled cavities show particles separated uniformly to cavity extremities. There is no preferential direction of separation, and this shows that the effect truly is after the receding meniscus force has passed. Moreover, if liquid is being pinched off from the bulk phase to remain in the cavity post-assembly, then it is also possible that the dynamics to produce this would impact on the assembly process itself. No one has discussed this with any clarity.

A variety of experimental results therefore invalidate the conventional model. In addition to this, there are two pertinent theoretical considerations, as the following sections explain.

4.3 Theoretical Consideration #1: Nanoparticle Thermodynamics

4.3.1 Brownian Diffusion

The conventional model imagines a nanoparticle residing semi-permanently at the contact line, protruding slightly through the meniscus, and thus subject to a semi-continuous meniscus force in a direction fixed by the receding contact angle. For a particle to experience a quasi-static meniscus force, it must be quasi-statically pressed into the meniscus. This may be the case for micron-sized particles, but it is not realistic for nanoparticles because of Brownian diffusion.

Many studies mention that Brownian motion is a competing force that must be overcome, but Kuemin et al. [9] stand alone in highlighting that the meniscus force is truly transient and momentary on nanoparticles because of their thermal motion (especially for Scheme 1, where particle packing is not dense). This point is in need of further justification.

Aqueous nanoparticles will experience a random walk due to thermal collisions with the surrounding liquid molecules. Thermal diffusion of the particles is governed by the Brownian diffusion coefficient (also called the Stokes-Einstein diffusion coefficient) [11, 12]:

$$D_B = \frac{k_b T}{k_{drag}} = \frac{k_b T}{6\pi\mu_f R} \quad (4.1)$$

where k_b is Boltzmann's constant, T is the absolute temperature, k_{drag} is the drag coefficient of a spherical particle in liquid, μ_f is the dynamic viscosity of the liquid and R is the particle radius.

We are most interested in the situation during assembly, so let us consider the case of a nanoparticle near the contact line, and a square cavity beneath it that will fit only one particle, and a receding contact line speed of $v = 10\mu\text{m/s}$. The time taken for the contact line to drag past the cavity is then $\delta t = 2R/v$, and the

mean particle displacement over this time is given by (where $\vec{r}$ is the displacement vector):

$$\sqrt{\langle |\vec{r}|^2 \rangle} = \sqrt{6D_B \delta t} \quad (4.2)$$

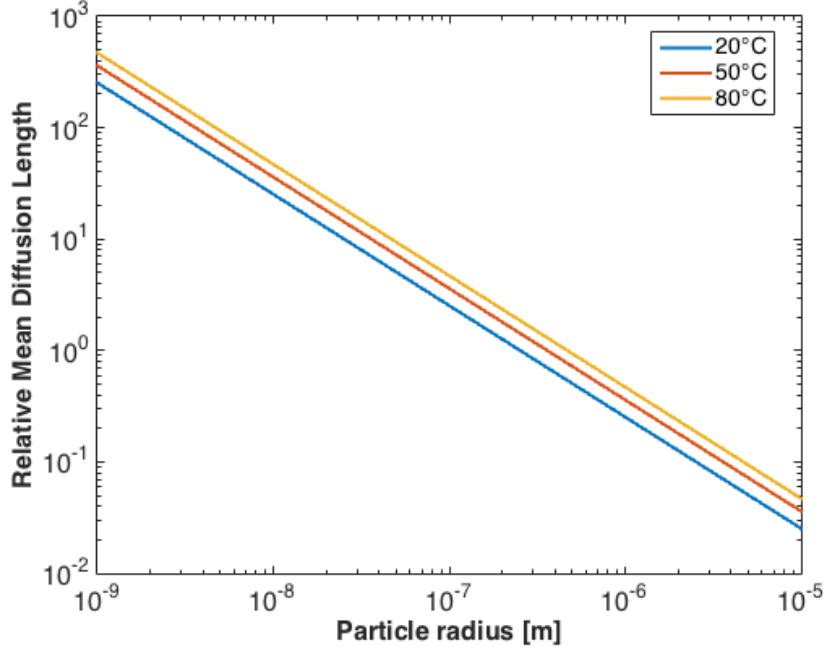


Figure 4.7: The ratio of the mean Brownian diffusion length of particles to the particle size, $\sqrt{\langle |\vec{r}|^2 \rangle}/2R$, in water at three different temperatures.

Mapperson suggests that a more helpful parameter to examine is the *relative* mean particle displacement, which can be defined as the ratio of the mean displacement to the particle size, $\sqrt{\langle |\vec{r}|^2 \rangle}/2R$. In Figure 4.7 this quantity is plotted for various particle sizes at 20°C, 50°C and 80°C.

What is evident is that microparticles have a relative mean diffusion distance much less than one, which represents the size of the particle itself (and our hypothetical cavity size). This means their thermal motion is negligible compared to the lateral motion of the particle from the receding meniscus. It is reasonable that such particles could be assembled in a manner similar to the conventional model. Whatever the means of assembly of microparticles, studies like Xia et al. [13] show that very strong patterning and precise arrangement of microparticles can be achieved by CFA.

Nanoparticles, on the other hand, will diffuse away with distances ranging from several to hundreds times their own size. Nanoparticles will therefore ordinarily

diffuse away from the cavity faster than they can be assembled into the cavity by the receding meniscus.

4.3.2 Packing at the Contact Line—An Aid or Hindrance?

Dense Packing as an Aid: To rescue the conventional model in this regard, investigators typically reference dense contact line packing as the Brownian motion inhibitor. But what is the density of packing? Our best attempt is a qualitative approach, which several studies provide insight for:

- Simulations suggest hexagonal packing for 8 nm spherical particles in Scheme 1, though not all the way to the apex [3] and in Scheme 2 [2]. In Scheme 1, this leaves particles at the apex with non-negligible Brownian motion, while those slightly further away are much more immobilised.
- Polarised scattered spectra from the contact line *in situ* indicate crystalline arrangements for nanorods under strong convective flows [14].
- Bulk deposition of nanorods in a CFA environment demonstrates ordered crystalline domains of forming along the contact line [15].
- Iridescence at the contact line while assembling with 500 nm polystyrene spheres indicates *in situ* polycrystalline arrangements [1]. It is expected that such large particles will densely pack into the contact line more easily than nanoparticles.

It seems reasonable, therefore, to assume that the packing can be quite dense, implying that good restriction of Brownian motion is possible. This appears to invalidate Scheme 1 that suggests particles be only loosely packed, and therefore still subject to Brownian motion. Computational modelling of phase transitions in populations of hard nanorods reveals a strong tendency for particles to self-pack into a semi-crystalline arrangement [16]. If particles are packed densely prior to assembly, why then do cavities easily remain unassembled? Simulations by Asbahi et al. [3] may hold the answer.

Dense Packing as a Hindrance: Asbahi et al. simulated assembly of 10 nm particles. They found that the assembly rate dramatically *decreased* when particles were hexagonally packed. Whilst their studies do not accurately reflect assembly dy-

namics in full, they do reflect the interaction between Brownian motion and packing density, and their results are not what was expected.

When two or more layers of particles accumulated at the contact line, the particles quickly arranged into crystalline packing. What was unexpected is that this overly immobilised particles and they were unable to move into cavities. A significantly lower assembly yield resulted.

This finding is significant, though the implications for nano-CFA are not discussed at length in the paper. Aside from affirming that dense packing restrains Brownian motion, it shows that dense packing restricts *all* motion, including motion into a cavity for assembly. The population of particles becomes like a rigid structure made of nanoparticle ‘bricks’, which does not flex or dismantle easily. Particles will not assemble unless an additional force is present to *extract* particles out of their crystalline arrangement and move them into a cavity. What is this unknown force that initiates the assembly process? The conventional model does not account for it, but any new nano-CFA model must address this pertinent question.

4.3.3 Nano-CFA Simulations

Recent work by Mehraeen et al. [2] and Asbahi et al. [3] were able to simulate and experimentally conduct assembly of 8 nm particles from hexane into templates. Asbahi et al. simulated according to Scheme 1, whereas Mehraeen et al. simulated according to Scheme 2. These simulations were excellent attempts to elucidate nano-CFA from the fundamental physics. However, for reasons given in Appendix 4.A, neither of these simulations alleviate concerns about the conventional model.

4.4 Theoretical Consideration #2: Meniscus Pinning

A final and very significant objection to the conventional model emerges from meniscus behaviour as it passes over a cavity. In the conventional model, the meniscus sweeps over a cavity at the receding contact angle (imparting a capillary force). This is the major reason why the receding contact angle has received much attention in nano-CFA literature (with a few exceptions). To date, there is no CFA literature

that focuses on meniscus behaviour over a cavity.

The goal of any CFA model is to explain how particles are assembled into cavities, yet ironically, the conventional model cannot apply when a cavity exists at the contact line. The phenomenon of importance is the pinning of liquid menisci on substrate heterogeneities. Every cavity in a template is a discontinuity that will stimulate pinning.

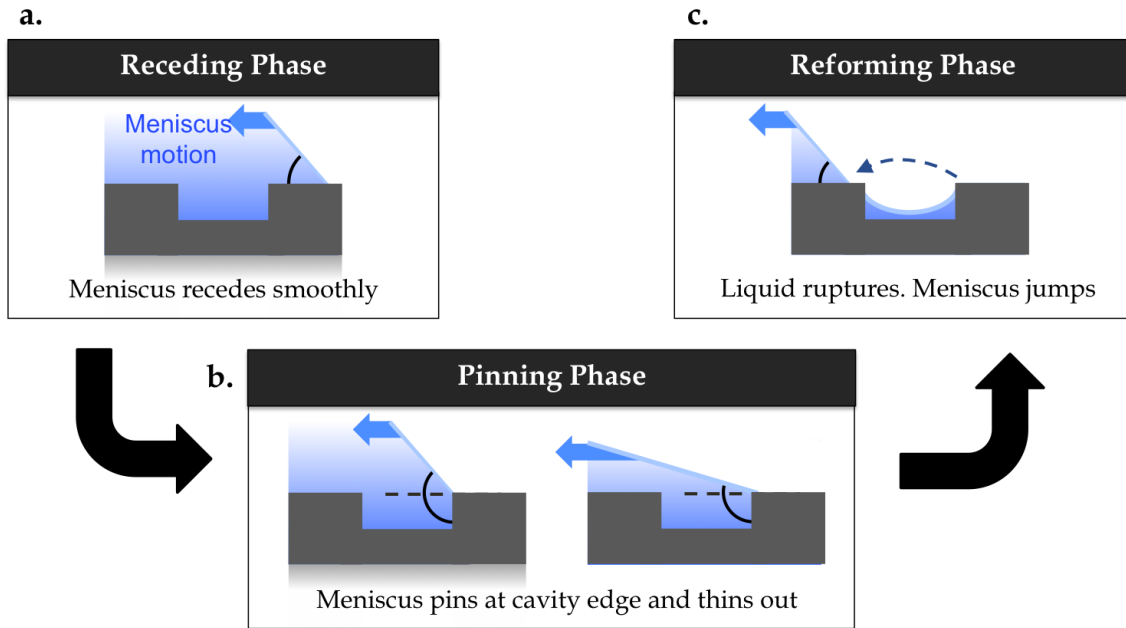


Figure 4.8: Depiction of the true meniscus behaviour at a cavity as the bulk liquid recedes past the cavity. The meniscus pins on the leading edge of the cavity due to the sudden increase in contact angle with the cavity wall. Pinning continues until the liquid thins so much that it ruptures and the contact line reforms past the cavity.

Consider the case of a liquid body receding over a flat surface, as depicted in the left panel of Figure 4.8. The liquid front recedes smoothly at the receding contact angle (assuming a chemically homogeneous surface, which is a reasonable assumption for controlled CFA experiments). When the cavity's leading edge meets the contact line, the effective contact angle instantly increases by a large angle (such as by 90° , see middle panel). The contact line halts under what dynamic wetting literature refers to as Gibbs inequality condition [17].

The liquid front only recede further when the receding contact angle condition is met at some point around the pinned cavity perimeter, or when some other effect causes the pinned liquid body to rupture. The latter tends to be case with micro- and nano-cavities, as will be shown later. Upon rupturing (right panel of the Figure), the

liquid front jumps and snaps over the cavity towards the bulk phase, reforming the contact line at some point beyond the cavity. If the liquid ruptures over the cavity itself, then some liquid will remain in the cavity, which will enable capillary forces to act on whatever has been deposited in the cavity prior to rupturing (discussed further in Chapter 5, Section 5.4).

There is much more to consider from pinning, but what is clear for now is that the liquid front ceases to recede when a cavity is present, and then it jumps over the cavity. Since the meniscus *stops* moving at a cavity, there can be no continuous lateral capillary force to push particles into cavities. A continuous meniscus force directed by the receding contact angle only applies on the smooth unpatterned regions of the template, and serves to sweep the unpatterned substrate clean. This basic consideration calls into question a fundamental premise of the conventional model, most especially of Scheme 1.

4.5 Allusions to a More Accurate Model

We have established that a new model is needed for nano-CFA (and possibly micro-CFA). After having developed just such a model (which the following chapter describes) an in-depth review of the literature was conducted to ascertain whether other researchers had hinted towards the same. What was found were brief comments showing either discontent with the conventional model, or suggestions alluding to the new model presented in this thesis. The new model has been called the *pinned-convective model*. As the name suggests, the model relies heavily on meniscus pinning dynamics on cavities.

The following papers show knowledge of cavity-level pinning during nano-CFA, and occasionally express a discontent at not being able to relate it to the assembly mechanism. However, none of these papers go on to clearly explain an assembly mechanism different to the conventional model.

- Liddle, Cui and Alivisatos [4] state that cavity-level pinning might be important to drive particles into cavities, in addition to the conventional capillary immersion force. Based on the observation that sessile droplets pin and deposit a ‘coffee-ring’ of particles, they suppose that a cavity on a template may also pin a moving contact line. They infer that this would lead to a rapidly diverging evaporation rate over the feature, which would drive particles to the

feature site. They conceptualise that particle concentration may increase near template features due to pinning. They do not discuss the concept beyond these brief suggestions. The bulk of their paper relies on the conventional model. This work was published in 2004, but surprisingly, despite the logic of their reasoning about pinning and convective flows, their comments appear to have gone unnoticed in all later nano-CFA literature.

- Malaquin et al. [1] repeatedly mention that the meniscus pins on templated features. Most of their studies are on raised features (not cavities) or on extremely large cavities ($4 \times 4 \mu\text{m}^2$). Both of these are atypical for nano-CFA, so applicability to nano-CFA is very limited. They mention that the rupture of the meniscus after pinning appears to be relevant to assembly, but they are not sure how. They also note the importance of cavity geometry for pinning, stating that, “The magnitude and the direction of the capillary forces induced by the contact-line pinning depend strongly on the geometry of patterns.” They note that, “Changing the orientation of the structure with respect to the motion of the contact-line direction influences the pinning of the meniscus,” and that, “This effect can be used to tune the number and the position of particles,”. Again, they do not venture to discuss how pinning might affect deposition, though they recognise its potential importance.
- Kraus et al. [18] cite the work of Malaquin et al. in the preceding point when they mention that the local contact angle changes during pinning. They write that, “the local contact angle during assembly also depends on the pinning caused by the structures on the template’s surface.” They also mention that, “arrays that capture single particles pin the meniscus only very slightly [compared to micro-cavities], and the assembly takes place very close to the contact line.” Moreover, in discussing micro-cavities the authors recognise that micro-scale flows are setup, and particles flow into the feature. However, regarding the assembly mechanism on nano-cavities they presume the conventional model operates, and only at the instant of depinning. The authors therefore recognise pinning but interpret its role as simply dictating the *timing* of assembly, making no mention of its impact on the assembly *mechanism*.
- Kuemin et al. [9] state that, “Capillary forces act only transiently, as the contact line is pinned at the assembly site. Thus, for a particle to be assembled, it has to reside in the assembly site at the moment of capillary breakup.” They

are in effect making a conclusion about the timing of assembly at the end of a pinning event, as Kraus et al. do above. Nothing else is said regarding the full assembly process. There is no mention of convective flows from pinning events.

- Gordan and Peyrade [6] simply recognise depinning from cavities, for they mention “the contact line of the bulk solution pinches off from the hole”. There are no other comments regarding pinning; they do not relate it to an assembly mechanism.
- Diguët et al. [19] also mention pinning as relevant to assembly, stating that the contact line, “was pinned on the edges of the microstructures due to the steep increase of the contact angle, which resulted in the trapping of phospholipid solution in the substrate holes.” There is no discussion of forces or dynamics that enact assembly.
- Lecarme et al. [8], clearly draw the meniscus as pinned on a cavity (see illustrated Figure 1a of their paper), but they do not comment on pinning in the text.
- Much more recently (and near the completion of this thesis), Flauraud et al. [15] state some of the basic conclusions given earlier, namely that pinning (1) invalidates the conventional model, (2) reduces the local contact angle and (3) enhances local evaporation rates. They provide very little discussion on the assembly mechanism beyond these statements, focussing instead on how assembly could be disrupted, and on optimising their own assemblies.

Various authors recognise that cavity-level pinning is real, and that it might affect the timing of when assembly can occur. How pinning might affect/alter assembly processes has not gone unrecognised, but it is limited to very brief and inconclusive comments. There is amongst some researchers a discontent about the lack of knowledge of the assembly process, but no solution has yet been provided.

4.6 Conclusions

To summarise then, the conventional model has been considered in light of the variety of experimental outcomes seen in nano-CFA, and it has been found wanting. The conventional model cannot predict the wide range of experimental results known

from this technique.

The two different Schemes of the conventional model predict exclusively sparse or dense assemblies, yet sometimes both types of assemblies are observed from the same assembly run on the same template. Evidently neither Scheme is a complete explanation.

It was also found that Brownian diffusion is not sufficiently harnessed in Scheme 1, and a suitable assembly director force is therefore lacking. Whilst a suitable assembly force may be present in Scheme 2 where Brownian motion is duly restricted, that Scheme is not supported by many experimental outcomes.

No review of nano-CFA data like this, and no assessment of the current nano-CFA model has been conducted to date. The review presented in this thesis is the first of its kind and it shows the current model to be wanting.

The absence of an effective explanation of nano-CFA has left an opportunity and a challenge for a more complete nano-CFA model to be put forward. It is proposed that the necessary model can be found if we derive the correct assembly dynamics from first principles. In the next chapter an arguably more accurate description of nano-CFA is presented.

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Appendix

Appendix 4.A Notes Regarding Nano-CFA Simulations

Comments on Why Recent Nano-CFA Simulations do not Alleviate Concerns About the Conventional Model

Recent simulations by Asbahi et al. [1] and Mehraeen et al. [2] show excellent attempts to elucidate nano-CFA using fundamental physics. Interestingly, they saw both Scheme 1 and Scheme 2 in operation from their simulations, in papers [1] and [2], respectively. The authors of these studies conclude that the conventional model explains nano-CFA. Contrary to this conclusion, these simulations are not sufficient to alleviate concerns about the conventional model, for the following reasons:

- The hexane solvent had a very low contact angle (12°) that is not representative of the vast majority of nano-CFA works (aqueous solvent, 30° to 60° contact angle). This shallow contact angle would have been unusually restrictive of particle diffusion, a characteristic not shared by most CFA experiments. The simulations cannot be taken as representative of usual nano-CFA dynamics.
- The simulations did not fully reproduce the experimental results. The assembly yield predicted from the simulations was substantially lower than from the experiments, indicating the simulations do not accurately reflect reality.
- None of the simulations included evaporative liquid flows, which may have been substantial in some (but not all) of their experimental work.
- The work by Asbahi et al. required a liquid film only 15 nm to get close

to the experimental assembly rate. This prevented semi-crystalline particle arrangements that would have overly restricted particle motion. A liquid film just 15 nm is not realistic in nano-CFA.

- The simulations did not include liquid pinning effects on cavity edges, which will interrupt the liquid dynamics predicted by the conventional model (see Section 4.4). This likely contributed to the lower assembly yield from simulations compared to experiments. Personal discussions with Mehraeen were centred on this question specifically, concluding that these pinning effects may resolve the discrepancy between experiment and simulation.
- Curiously, these two works use exactly the same physical model,² differing only in the cavity layouts (template designs), and yet they appear to exclusively support both Schemes of the conventional model. How can the same physical model arrive at two incompatible explanations? The template configurations have a lot to do with how the liquid, and therefore the particles, behave at the contact line.

There are four special cases given in Chapter 5 (Appendix 5.A) where the assembly dynamics are expected to be similar to the conventional model. The template used by Asbahi et al. matches Special Case 1, and the template used by Mehraeen et al. matches Special Case 4. These two works cannot vouch for the conventional model beyond these special cases in which a semi-conventional model is expected to apply anyway. The two papers propose different mechanisms for assembly, and only in this thesis is there reconciliation of this apparent paradox.

The works of Mehraeen et al. and Asbahi et al. present a unique regime of nano-CFA where the conventional model does work better than in most other nano-CFA conditions, yet even there the conventional model is not sufficient to fully replicate experimental data.

APPENDIX REFERENCES

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²They use the same liquid, substrate material, receding contact angle, ambient temperature, particle composition, ligands and particle size, similar speeds and the same fundamental physics.

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A Pinned-Convective Model for Nano-CFA

5

The failure of the conventional model of CFA has opened the way for a new explanation. In this chapter a pinned-convective model is proposed to fill the gap. This chapter overviews the development and dynamics of this model, high-level experimental data supporting this model, and sheds light on controversial experimental results in light of the new model.

<i>Introduction ...</i>	<i>5.1</i>
<i>The Challenge of Developing an Accurate Nano-CFA Model ...</i>	<i>5.2</i>
<i>Overview of the Pinned-Convective Model ...</i>	<i>5.3</i>
<i>Post-Assembly Forces and Particle Arrangements ...</i>	<i>5.4</i>
<i>Case Studies Supporting the Pinned-Convective Model ...</i>	<i>5.5</i>
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<i>Appendix</i>	

5.1 Introduction

In Chapter 3 we saw that scaling-up nano-CFA has been pursued based on the conventional model, owing to its ubiquitous acceptance in the literature. This proves troublesome, as the conventional model often fails to explain experimental results. Consequently, a number of theoretical and experimental concerns with the conventional model were explained in Chapter 4.

The failure of the conventional model has opened space for an alternate model. In this chapter a new model is proposed, called the pinned-convective model to highlight the two primary contributing dynamics—meniscus pinning and local convective flows.

The purpose of this chapter is to give the reader a conceptual overview of the new model, with brief high-level experimental support. To quantify the model, dedicated experiments must be designed, and these are covered in subsequent chapters. Nonetheless, the model detail, theoretical deductions and experimental support presented in this chapter are a valuable contribution to the field.

We will begin by considering *how* an accurate model for nano-CFA might be developed, and what the hurdles in this process will be.

5.2 The Challenge of Developing an Accurate Nano-CFA Model

5.2.1 The Three Barriers to Decomposing Nano-CFA

There are three persistent barriers to decomposing nano-CFA. These have likely been the reason for minimal study in this area to date. The hurdles are (1) a distinct lack of nano-wetting literature, (2) an inability to directly observe the relevant dynamics, and (3) an overly complex parameter space to quantify. These are explained as follows.

1. The Role and Limitations of Theory The assembly dynamics of interest are on a size scale smaller than the diffraction limit of light. We are limited to high-level observations and then making *inferences* about the nanoscale dynamics. It is hence important that we have a good grasp of relevant nano-wetting theory.

Unfortunately, nano-wetting literature in general is scarce, and is basically non-existent for *dynamic* nano-wetting (of which CFA is a part). Moreover, the parameter space is large and convoluted. Existing theory is inadequate on its own to inform us of the key nano-assembly dynamics.

2. The Role and Limitations of Observation Observational data can only be of indirect use. We proceed, however, and Mapperson captured many hours of video of controlled and uncontrolled CFA phenomenon on the assumption that studying them can provide clues regarding the unseen nano-dynamics.

One emerging pattern is that deposition density appears to be controlled in part by the duration and severity of contact line deformation. This suggests a more thoughtful consideration of meniscus pinning is needed, and of how convective flows are modified by pinning events. As explained below, a model including these two effects will be substantially different to the conventional model.

3. The Limitations of Quantification It is of course desirable to quantify meaningful observations so trends can be demonstrated and studied. Here we are faced with another hurdle, as the observations mentioned above are varied and often unrepeatable. To attempt quantification loses so much specificity so as to almost become meaningless.

Moreover, we are faced with a plethora of parameters that may be relevant, many of which we cannot quantify anyway (such as local surfactant gradients and concentrations, particle packing density, micro-convective flow rates, particle-substrate interaction strength, and so on). The convoluted interplay between many parameters makes it very difficult to know exactly what should be quantified.

5.2.2 A Three-Point Approach

Given the hurdles above, it is apparent why researchers have struggled to identify and demonstrate the core mechanisms of nano-CFA. Dissatisfied with the status quo, here we propose a three-step approach:

1. Use known liquid dynamics on the micro-scale to deduce the basic liquid dynamics that ought to apply in a nano-CFA scenario. This presumes similar wetting behaviour in micro- and nano-regimes, which is not unreasonable. This step comprises Sections 5.3 and 5.4 below. The model at this point will be purely conceptual and propositional, but a valuable place to start.
2. Having developed a basic framework, we look for high-level experimental results that might affirm or deny the framework and add further guidance. The purpose is to provide quick initial validation before we invest much time to

resolve the model in detail. This step is Section 5.5 below, and concludes this present chapter, giving the new model a relatively confident footing.

3. With a reasonably solid framework now in place, we seek to resolve and quantify the model in detail. This involves designing specialised experiments (Chapters 6 and 7), and where this cannot be done, specialised modelling is used (Chapter 8). That will close off this thesis, barring a concluding chapter (Chapter 9).

In this way we answer the two remaining questions undergirding this thesis—(1) what are the key mechanisms behind nano-CFA, and (2) how can we quantify them for a more comprehensive model?

We will now overview the pinned-convective model of nano-CFA.

5.3 Overview of the Pinned-Convective Model

The pinned-convective model emerges in part from what is known of contact line pinning on micro- and nano-cavities, and from the ensuing impact pinning has on evaporation, convective flows and capillary forces. We can break the model down into three sequential phases that describe the entire nano-CFA process. These phases are illustrated in Figure 5.1, which the text below makes implicit reference to. Preparation for assembly occurs in Phase I when no cavities are present. Phase II is where assembly is activated by a cavity, and Phase III describes the period of transition back to Phase I after the cavity has passed.

5.3.1 Phase I: Convective Concentration of Particles at the Contact Line

During the first phase, the meniscus recedes smoothly across the unpatterned template, sweeping particles across the substrate. Particles are convectively packed at the contact line. The receding contact angle describes the direction of the meniscus force on particles. This is very similar to the conventional model.

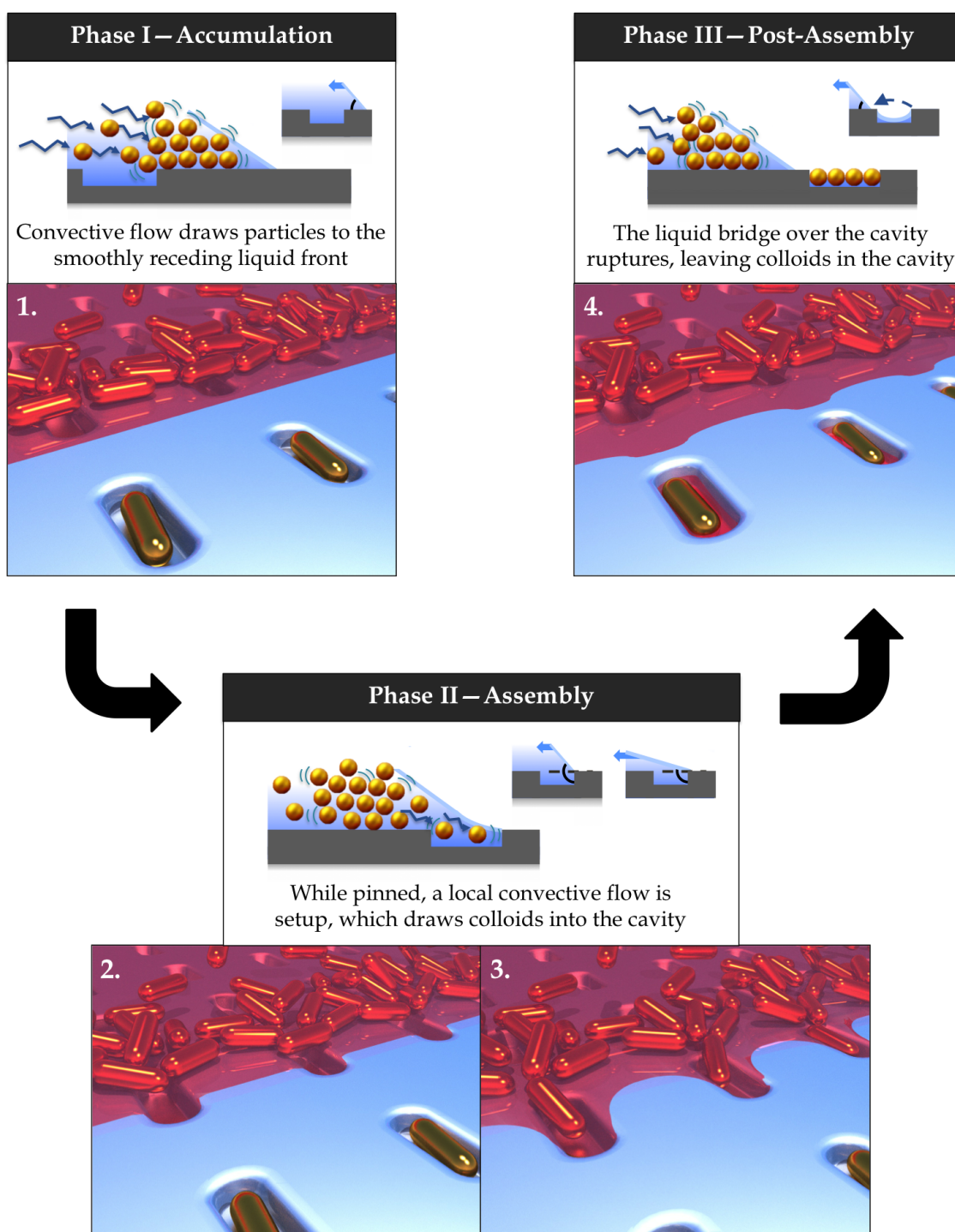


Figure 5.1: Depiction of suggested nanoparticle behaviour at the contact line as a result of meniscus dynamics. The three phases are discussed in the text. These three phases combine to create the pinned-convective model. The three-dimensional renderings are a loose artistic conception of the assembly process. Note that the artistic rendition does not reflect the semi-crystalline packing that is thought to occur at the contact line.

5.3.2 Phase II: Pinning and Assembly Dynamics

Phase II begins when a cavity meets the contact line. The contact line pins on the leading edge of a cavity, while the bulk liquid body either side of the cavity continues to recede. This causes a thinning of the liquid body immediately above the cavity, a lowering of the local contact angle there, and an increasing net evaporation rate over the cavity. Part of this is captured in the photograph shown in Figure 5.2.

The semi-crystalline population of particles at the contact line behaves like a semi-rigid bar spanning the contact line. It does not easily follow the pinned deformation but continues to recede with the bulk contact line. This leaves a growing void over the cavity itself, which is still covered by the pinned meniscus. At this point three new dynamics come into play that are thought to cause assembly:

1. A localised convective flow
2. A clamping meniscus force
3. Regional convective flows over arrays of cavities

These are illustrated in Figure 5.3a, b and c, respectively, and are discussed below.

Assembly Dynamic 1: Local Convective Flows: The increasing evaporation rate over the cavity as the meniscus thins out leads to a small burst of convective flow into the cavity itself. It is thought that this convective flow is one of two key forces missing from the conventional model. Just as particles are driven from the bulk phase to the contact line by bulk convective flows in Phase I, here particles are driven out their semi-crystalline arrangement at the contact line and into a cavity by *local* convective flows. This is illustrated in Figure 5.3a.

Local convective flows only exist over a cavity and slightly beyond it. They are short-lived as per the duration of pinning, and grow in intensity as pinning progresses, abruptly ceasing when the meniscus ruptures or depins. A dense population of particles must be present along the contact line before pinning begins.

Assembly Dynamic 2: Meniscus Clamping Force: The second dynamic pertinent to assembly is the meniscus lowering over the cavity, like a lid clamping down over the cavity mouth, until it ruptures or depins. This is illustrated in Figure

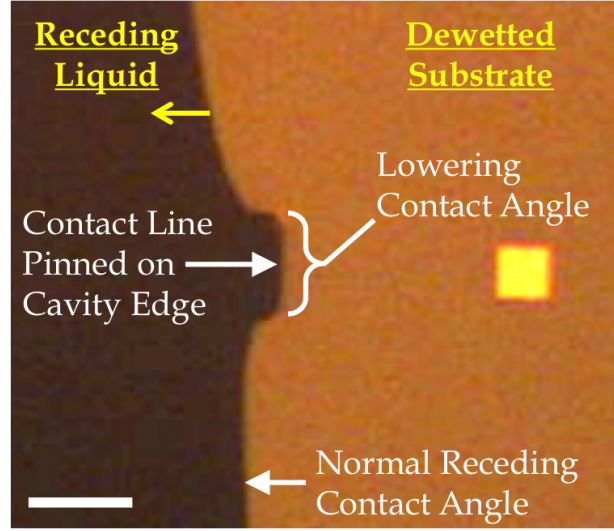


Figure 5.2: This microscope photograph of liquid receding over a cavity shows the contact line pinned on a $100 \times 100 \mu\text{m}^2$ cavity's leading edge. The pinning is evidenced by a distortion in the liquid front (dark portion of the photo). At the top and bottom of the photo, the liquid front is receding at normal speed, and the receding contact angle is largely unaffected. Over the pinned region the contact angle is rapidly lowering and the evaporation rate increasing. (The yellow square to the right is a $50 \times 50 \mu\text{m}^2$ cavity that has already dewetted.) The liquid is deionised water without particles. The scale bar is $100 \mu\text{m}$.

5.3b. Particles jostling over the cavity are closed into the cavity by transient capillary forces. The direction of the meniscus force over a cavity is not according to the receding contact angle, but it starts at that angle and becomes increasingly vertical.

This impacts on the lifetime of an assembly event as well. The conventional model posits that the lifetime of an assembly event is dependent on the contact line recession speed. The pinned-convective model suggests the lifetime to be the lifetime of pinning, which can be much longer than in the conventional model (see Section 7.3).

Assembly Dynamic 3: Regional Convective Flows: The third dynamic relates to an array of cavities. Local convective flows will operate over each cavity, but if the cavities are close enough together they will gently distort the contact line over the entire array. An increased evaporation rate results, and a greater convective concentration of particles follows. This can be advantageous to assembly, and is

pictured in Figure 5.3c. This dynamic causes aggregated deposition if the array is too dense and too large.

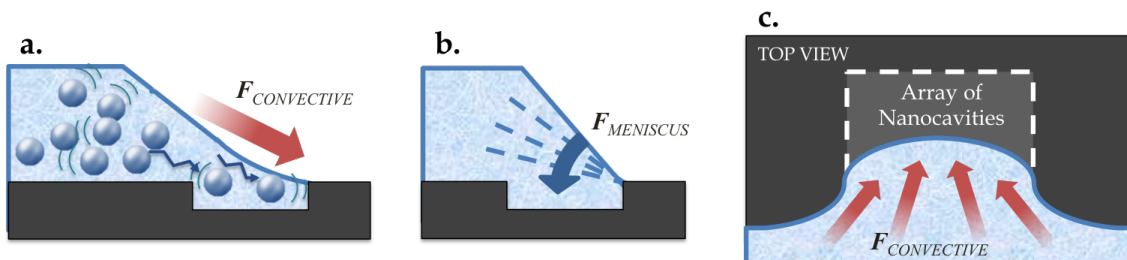


Figure 5.3: The three means by which meniscus pinning on cavities aids and enacts nano-CFA: (a) local convective flows into cavities draw particles from the bulk contact line into the cavity itself; (b) the pinned meniscus lowers down over the cavity as the bulk phase continues to recede past the cavity, clamping particles into the cavity as it does so; (c) if cavities are close enough together, their combined pinning effect distorts the contact line over the array of cavities to enhance the particle concentration there, aiding assembly.

These, then, are the three assembly dynamics of the pinned-convective model, and they all occur as a result of cavity-level pinning.

5.3.3 Phase III: Depinning and Post-Assembly Dynamics

The final phase of the assembly process is when the thinning liquid film ruptures over the cavity. The contact line jumps over the cavity and equilibrates with the bulk contact line. Some liquid remains in the cavity after rupture, evaporating almost instantaneously. Post-rupture liquid in cavities creates immersion capillary forces that predictably arrange particles, as experiments show.

Figure 5.4 shows this dewetting behaviour with water (no particles) on a micro-cavity. In the latter stages of pinning the liquid above the cavity thins out, evidenced by the interference fringes (a 543 ± 22 nm optical filter narrows the band of illuminating wavelengths). The moment of rupture lies between frames (d) and (e), and it is seen to leave liquid in the cavity. The hydrophilic cavity causes the liquid to retreat into a corner as it evaporates. After depinning, the ruptured meniscus snaps back into equilibrium with the bulk contact line and continues receding (as seen in frame (e)). Thus we have gone full circle and are now back at Phase I, where the meniscus sweeps over the unpatterned substrate.

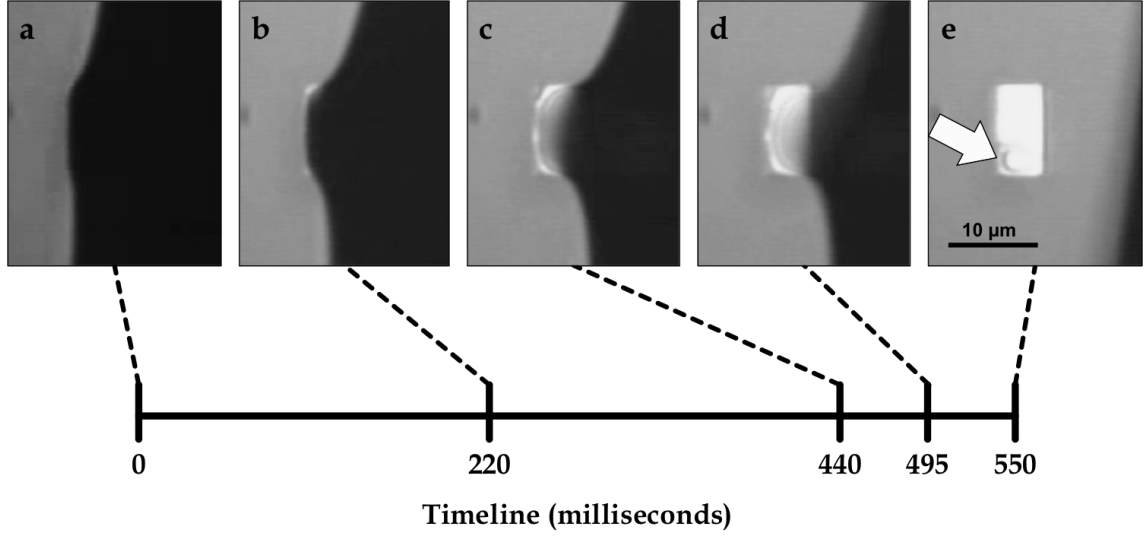


Figure 5.4: Microscopy video frames of a meniscus depinning from a $10 \times 5 \mu\text{m}^2$ cavity (200nm deep, PMMA on Si). The liquid (dark regions in photos) is water at room temperature and is manually dragged across the substrate. Interference fringes in (c) and (d) are evidence of a thinning liquid body just prior to rupture. Frame (e) is post-rupture and shows liquid remaining in the cavity (yellow arrow). The liquid in the cavity evaporates within 200 ms of the rupture.

Scaling Results: Note that the observations above for Phase III were obtained with micro-cavities, since nano-cavities cannot be seen optically. Surface tension is thought to be the primary directive, and this force scales linearly with distance. The effects that we observe on the microscale in these dewetting experiments ought to translate sensibly to nano-cavities. Surface tension forces will only cease to scale linearly with distance when we approach the scale of water molecules (which are $\sim 3 \text{ \AA}$).

5.3.4 Cavity Filling Rates

Having broadly explained the pinned-convective model, let us examine the rates at which cavities might be filled under a pinned-convective regime. It is well-known that cavities can emerge empty, under-filled, well-filled or over-filled. To describe this, we will assign three types of loading rate: (i) the under-balanced case which leads to under-filled cavities, (ii) the balanced case leading to well-filled cavities, or (iii) the over-balanced case leading to over-filled cavities. These are depicted in Figure 5.5.

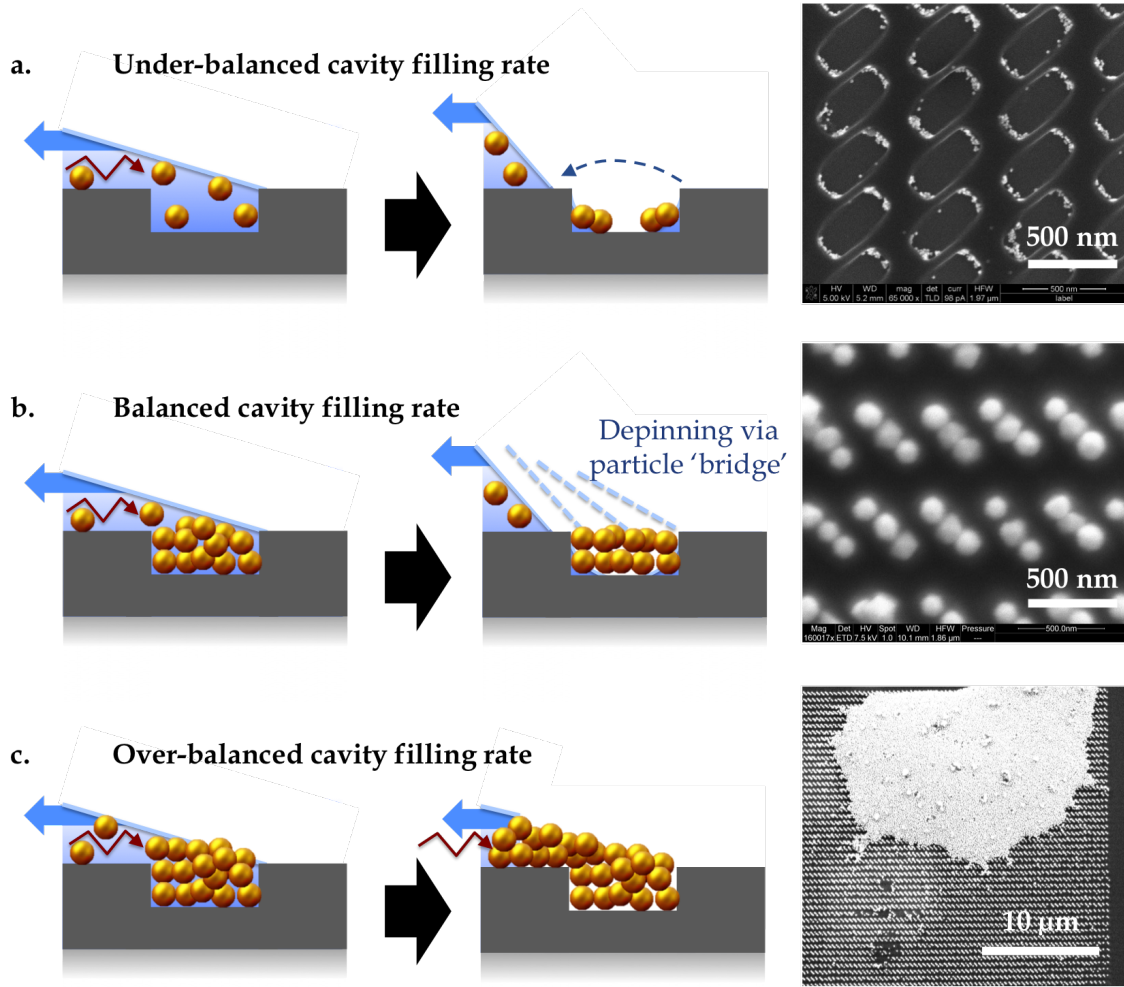


Figure 5.5: Three different cavity filling rates, leading to (a) under-filling, (b) dense-filling or (c) over-filling of cavities. Each is discussed in the main text.

Under-Balanced Loading Rates: In the under-balanced case (Figure 5.5a), the meniscus depins before the cavity fills. This is the most common outcome from nano-CFA trials. Room is left in the cavity for post-assembly capillary forces to characteristically arrange particles, allowing a limited range of deterministic structures to be created.

Balanced Loading Rates: This often-desired scenario leaves cavities densely filled but without spilling over (Figure 5.5b). Post-assembly forces can only make minor alterations to particle positions in the crowded cavity. The cavity shape is most effective here to dictate the assembled structure, as also seen in References [1–8]. In this scenario the pinned meniscus may not rupture and jump the cavity, as the

dense filling effectively transforms a cavity void into a nano-rough patch that the contact line can recede over in nano-steps.

Over-Balanced Loading Rates: This scenario sees more particles deposited than what the cavity can accommodate (Figure 5.5c). The aggregated deposit pins the contact line more strongly than the cavity, and more particles are deposited, creating a positive feedback loop. This is always detrimental to assembly.

The contact line will slowly drag across the growing structure. When particle transport to the structure eventually diminishes, the contact line is halted and the pinned liquid body thins out, eventually halting particle transport entirely, and the liquid soon ruptures. This is illustrated and exemplified in Figure 5.6. Once this type of deposition begins the experimentalist can only let it run its course, sacrificing that portion of the template.

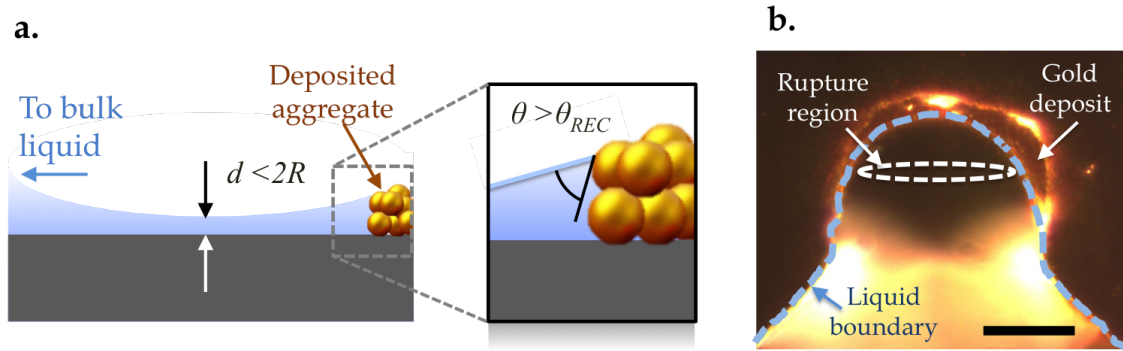


Figure 5.6: Image (a) presents a diagram of the meniscus pinned on a large over-deposit of particles. The film is thinning out too much to allow more particles to flow to the pinning structure. The close-up of the pinning structure shows how the meniscus cannot achieve the receding contact angle, and so it remains pinned on the colloids. Eventually the liquid film becomes thin enough to self-rupture, thus ending the process. In image (b) a dark-field image shows an example of this. A crescent-shaped deposit has developed, and the liquid is thinned out (dark region of liquid body) and is about to rupture from the area marked. The large deposit was initiated and grew from an over-deposit on an array of nano-cavities. The scale bar is 25 μm .

5.3.5 Factors that Influence the Cavity Filling Rate

Given the variety of cavity filling rates, we wish to consider what factors might influence the outcome. Conventionally the assembly efficiency has been thought to depend on (1) packing density along the contact line and (2) the receding contact angle to direct the capillary force. The pinned-convective model presents a different picture, whereby the filling rate ought to logically be a function of:

1. **The lifetime of meniscus pinning over a cavity.** The pinning duration is logically dependent on cavity features such as its size, three-dimensional shape and orientation. These are reliant on the template fabrication method and can be outside the experimentalist's control, particularly with NIL. Pinning duration also depends on liquid features such as surface tension, the contact line speed and the wettability of the liquid-substrate system.
2. **The strength of the local convective flow.** This is evaporatively driven, and so depends on the temperature and liquid-substrate wettability. The intensity of local flows increases with pinning duration, and is thus dependent on all factors under the previous point as well.
3. **The hydrodynamic drag force that particles will experience in local convective flows.** Aside from the flow intensity, this depends on the hydrodynamic radius of particles and the liquid viscosity.
4. **The density of particle packing at the contact line.** This point is not new, and simply relies on the temperature and the liquid-substrate wettability.

Pinning and convective dynamics will be revisited in detail in Chapters 7 and 8. It is enough for now to conclude that assembly efficiency can vary greatly for many reasons, some of which are beyond the experimentalist's immediate knowledge or control.

5.3.6 Concluding Remarks on the Introduction to the Pinned-Convective Model

With this brief overview, let us review where the pinned-convective model stands out against the conventional model. The new model is a first-principles attempt to explain nano-CFA. At first glance it appears to comfortably address three problems

plaguing the conventional understanding:

1. **Post-Assembly Capillary Forces:** Experiments consistently show that particles are subject to capillary forces after being assembled, yet the conventional model cannot account for liquid remaining in cavities post-assembly. As shown above, the pinned-convective model explains this in the depinning phase.
2. **A Force to Extract Particles Out of Their Semi-Crystalline Packing:** It was previously found that particles self-arrange in a semi-crystalline fashion along the contact line, and this prevents them easily being assembled. The pinned-convective model provides the necessary extraction force via local convective flows.
3. **A Wide Variation in Assembly Density:** Although particles are packed densely at the contact line, assembly density can vary from none to excessive. This variability has remained unexplained under the conventional model. It is answerable by considering the wide range of factors that influence local convective flows, and thereby influence the assembly efficiency.

This preliminary pinned-convective model is both more comprehensive and more versatile than the conventional model, suggesting answers to some long-standing questions. Now that we have a model that can explain post-assembly dynamics, we will explore these dynamics a little deeper in the coming Section. In the subsequent Section this model's predictions will be compared with a range of experimental observations, which will supply necessary high-level experimental support. From this position of confidence, we embark on explaining and quantifying pinned-convective dynamics in detail, for a more comprehensive description of nano-CFA.

5.4 Post-Assembly Forces and Particle Arrangements

The pinned-convective model benefits us by explaining post-assembly dynamics. Here we consider in a little more detail what these dynamics are and how they can influence assembly outcomes. Discussion in published literature on this matter is fairly narrow. Liddle, Cui and Alivisatos [2] observe and briefly discuss post-assembly particle ordering. Others more briefly note this phenomenon. The most dedicated work in this area is by Gordan and Peyrade [9], who harness post-assembly dynamics to achieve controlled microparticle arrangements. Post-assembly rearrangement

of nanoparticles has not been visited to the extent given below.

Post-assembly capillary forces appear in one of two forms and subsequently lean towards one of two respective outcomes—capillary forces will be (1) an inter-particle force (F_{PP}) that draws particles together, or (2) a particle-to-wall force (F_{PW}) that draws particles to the cavity’s most corner-like features. These two forces are illustrated in Figure 5.7.

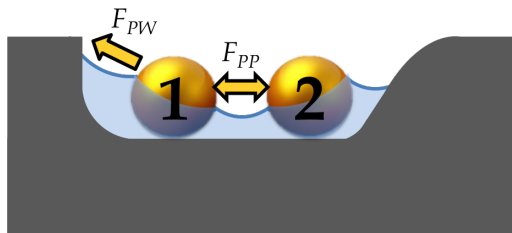


Figure 5.7: Diagram illustrating the two competing post-assembly capillary forces: inter-particle (F_{PP}) vs particle-wall (F_{PW}). Their relative strength and duration dictates whether particles cluster together, or move to the cavity perimeter, or a mixture of both. The wall next to particle 2 is angled and F_{PW} there is weak, exemplifying the significance of cavity topography.

Depending on the application for which the assembly is to be used, it would at times be desirable to have particles separated to the cavity corners, or maybe to line up along the walls, or to form a dense cluster or monolayer in the cavity centre. Published literature rarely considers these options and how they are created.

5.4.1 Particles Drawn to the Cavity Extremities

It is most common for particles to be drawn to the cavity extremities. Hydrophilic cavities and particles will see the liquid adhere most to regions of greatest surface area. Cavity corners thus tend to be the final resting place of particles. The situation is similar to that depicted in Figure 5.8a, which is a common diagram in CFA literature. The outcome is like that shown in Figure 5.8b. Figure 5.8c shows an alternative outcome by having cavities populated with a single large particle each.

Other arrangements arise when altering cavity shape or size. For example, elongated corner-less cavities see particles drawn to the most corner-like feature, creating the counter-facing U-shaped structures in Figure 5.9a. Without corners or

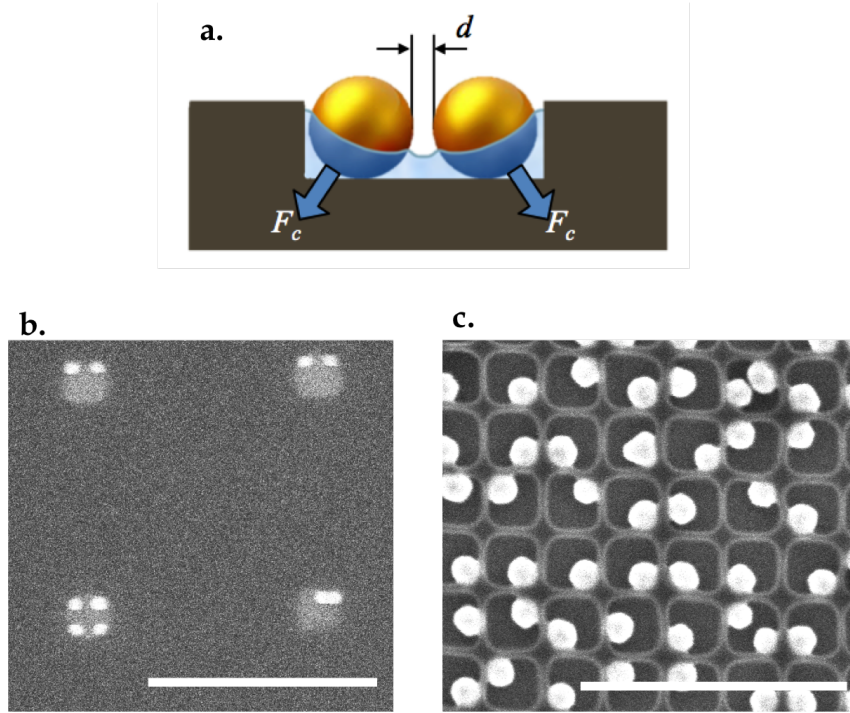


Figure 5.8: (a) Hydrophilic particles in a cavity experience the immersion capillary force, F_c , as the liquid in the cavity evaporates. This often draws particles to the cavity extremities, such as the corners, as shown in (b) and (c). In (b) are 50 nm gold particles deposited into $150 \times 150 \text{ nm}^2$ cavities. The particles are mostly evenly separated. In (c) are 100 nm gold particles in $200 \times 200 \text{ nm}^2$ cavities. The particles are mostly drawn to cavity corners. The lack of directional preference demonstrates that their final arrangement was established *after* the contact line had receded. Scale bars are $1 \mu\text{m}$. (Substrate: PMMA on Si).

an elongated axis, particles are drawn randomly to the walls (Figure 5.9b). Inter-particle capillary forces draw particles into chains or clusters against the walls. This randomises the assembly when many particles are present without strong corner features (Figure 5.9c).

If particle-to-wall are required to be strong, the cavity should be well-defined—sharp corners and steep edges. It also helps if the cavity is not larger than a few particles. Cavities larger than this should not be densely populated, so that inter-particle forces are rare.

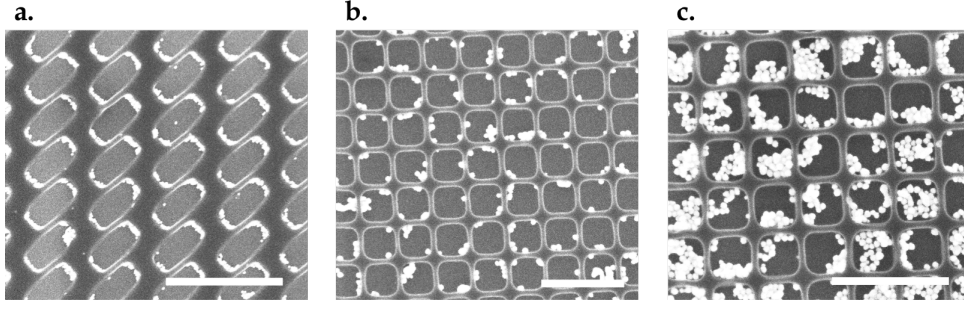


Figure 5.9: Particles are drawn to the most corner-like features. The assembly is more randomised when corner-like features are less pronounced and the assembled particle density increases, as in (a) to (c). All particles are gold and are 20 nm in (a) and 30 nm in (b) and (c). Scale bars are 1 μm , 500 nm and 500 nm, respectively.

5.4.2 Particles Collected in the Cavity Centre

When inter-particle forces dominate over particle-to-wall forces, particles cluster together in the centre of the cavity (Figure 5.10a). Factors that cause this include (1) cavity topography, (2) cavity filling density and (3) cavity size relative to particle size. Each are exemplified below.

Cavity Topography: Figure 5.10b) shows clustering because the cavities are cup-like, with poorly defined walls, so F_{PW} is inherently weak and particles cluster together.

Filling Density: Figure 5.10c) shows particles clustered because the many particles per cavity leads the probability of F_{PP} to be higher than F_{PW} for any given particle. Thus clustering dominates statistically, even though F_{PW} is also present.

Cavity Size Relative to Particle Size: If the cavity cannot hold many particles, then particle-to-wall forces dominate. For example, when the cavities in Figure 5.10c are filled with just two 1 μm particles, they don't cluster but easily separate to the corners (see results in Ref [10]).

The density of filling is mostly significant if the cavity can hold many particles, as then the likelihood of inter-particle forces can dramatically increase. For example, Figure 5.10d shows identical cavities assembled to different densities. The densely

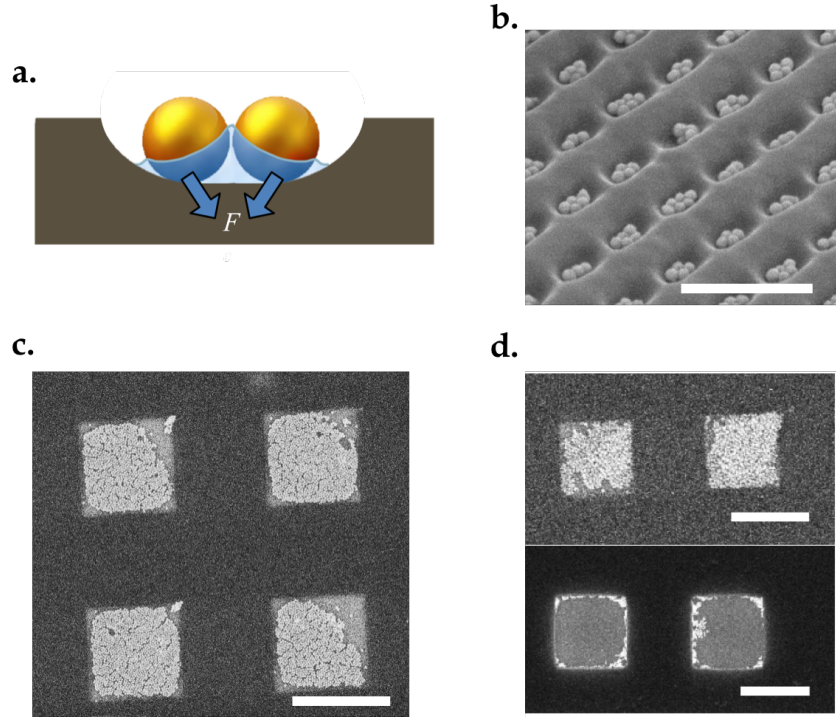


Figure 5.10: When the inter-particle capillary force is stronger than that from the cavity walls, particles cluster together where they are. This may be because of a poorly defined cavity, as in (a) and (b), or because the cavity is densely populated, so the probability of an inter-particle force being felt is much higher. All particles are 50 nm gold spheres. Cavities in (b) are approximately $100 \times 200 \text{ nm}^2$, in (c) are $2 \times 2 \text{ }\mu\text{m}^2$, and in (d) are $1 \times 1 \text{ }\mu\text{m}^2$. Scale bars are 500 nm, 2 μm , 1 μm and 1 μm , respectively.

assembled cavities are well clustered, whereas sparse assembly allows particle-to-wall forces to dominate. Additionally, evaporation begins in the cavity centre, so capillary forces will first be felt there to stimulate clustering if enough particles are present.

This brief treatment of post-assembly dynamics has revealed two competing post-assembly capillary forces, and also the conditions that lead one to dominate over the other. This knowledge is highly relevant to creating deterministic structures by nano-CFA. In the next and final section of this chapter, we will seek experimental affirmation of the preliminary pinned-convective model over the conventional model.

5.5 Case Studies Supporting the Pinned-Convective Model

At this point the pinned-convective model is still only conceptual and propositional. Experimental validation is desired before investing in specialist experimental work to probe and quantify the model in detail.

In this section we will consider four case studies designed to differentiate between pinned-convective dynamics and the conventional model's dynamics. Each case study predicts markedly different assembly outcomes based on the two competing dynamics, allowing for clear affirmation of the more accurate model.

5.5.1 Nano-CFA Template for Case Studies 1 and 2

The first two case studies use a template that consists of dimples (shallow craters) each surrounded by a raised lip (see Figure 5.11). Relative to the flat unpatterned surface, the dimples are 20 nm deep and lips 20 to 30 nm high.¹ This template is from an imperfect NIL attempt in SU8 on Si. Whilst it is inadequate for metamaterial assembly, it serves a useful purpose in these case studies. CTAB-stabilised gold particles with high polydispersity are used to allow for more versatile characterisation of the assembly dynamics. Assemblies were conducted in a fluid cell apparatus.

5.5.2 Case Study #1

The first case study looks at how particles are assembled in the flat regions between consecutive craters (see Figure 5.12). The conventional model drags particles along by the receding meniscus until a stopper structure is met, such as the outer edge of a cavity's lip. The pinned-convective model has the liquid pinning on lips, and particles subsequently diffusing into the pinned region and clamped in place by the lowering meniscus. The conventional model would thus have particles assembled pressed against lips, according to the direction of contact line recession, while the new model would have particles assembled more centrally between adjacent cavities and away from protruding lips.

¹Atomic force microscopy conducted by Jianing Lu.

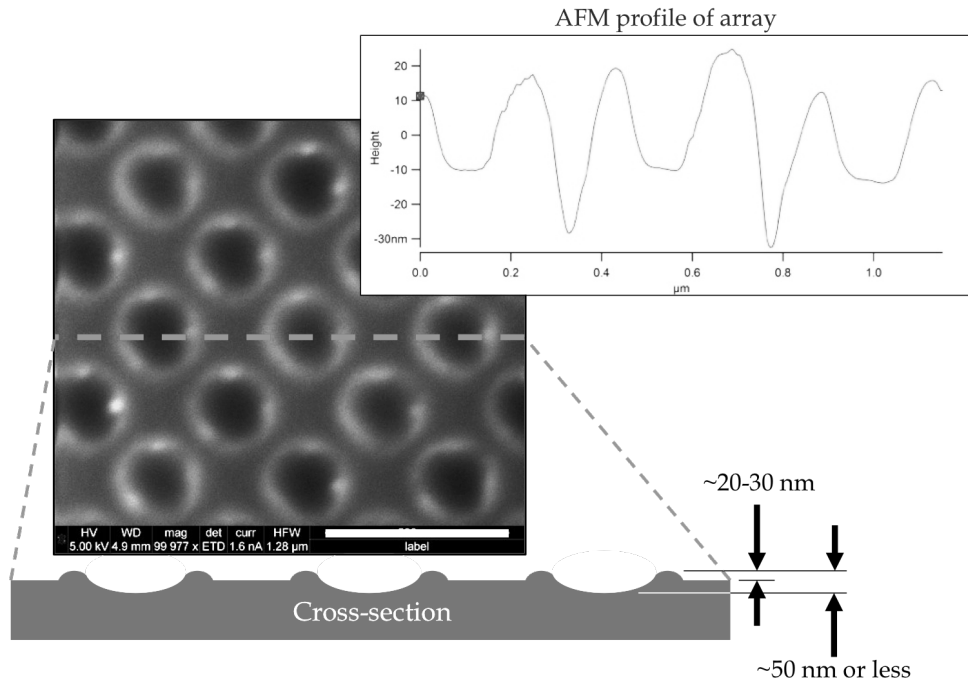


Figure 5.11: An SEM of the unassembled template used in case studies 1 and 2 (scale bar 500 nm). An atomic force microscopy cross-section shows the measured height profile along part of the dashed line in the SEM. An idealised diagram demonstrates the cross-section.

Figure 5.13 shows that large and small particles alike are assembled centrally in the inter-cavity spaces, away from protrusions, giving exclusive support for the pinned-convective model. Indeed no deposition shows signs of being pushed across the template by a receding contact line. The Figure shows that this effect is consistent over a large area.

5.5.3 Case Study #2

This template holds further evidence of the pinned-convective model. Consider the narrow corridors between cavities that are very closely adjacent to each other (as marked in Figure 5.14a). The conventional model would see particles dragged over these narrow corridors with little reason to expect assembly. The pinned-convective model would see the liquid pinned as shown in Figure 5.14b, selectively allowing only small particles to convectively diffuse into the corridors and be clamped in position by the lowering meniscus, but disallowing larger particles (Figure 5.14c).

The assembled template (Figure 5.15) reveals the smallest particles are indeed

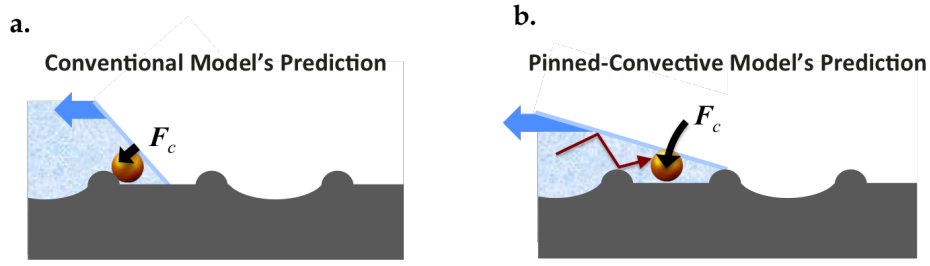


Figure 5.12: The differing predicted inter-cavity assembly arrangements based on the conventional model (a) and the pinned-convective model (b).

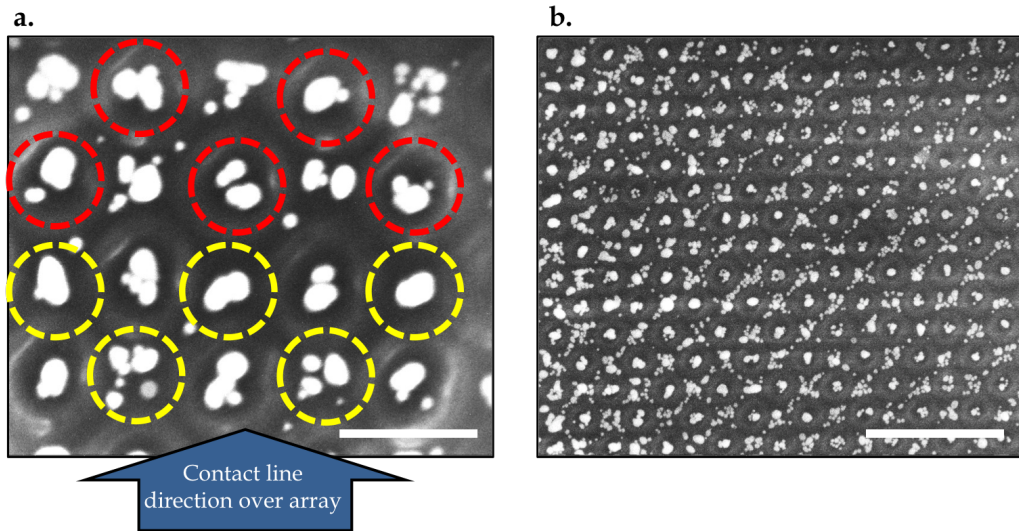


Figure 5.13: SEM images showing assembly results. The contact line moved in the direction of the blue arrow. The red circles highlight cavities; the yellow circles highlight the flat inter-cavity regions. Large and small particles are assembled in inter-cavity regions. The image in (b) shows that this effect is large scale. Scale bars are 300 nm and 1 μm , respectively.

assembled centrally in inter-cavity corridors and large particles are excluded. The particles are not large enough to be jammed in place, and they are not pressed against lips. This matches excellently with the pinned-convective prediction and is very difficult to explain under the conventional model. Again, the Figure shows the effect is widespread.

5.5.4 Case Study #3

The third case study again affirms diffusive and meniscus clamping dynamics. The template comprises rectangular cavities to hold three 150 nm spheres. The template

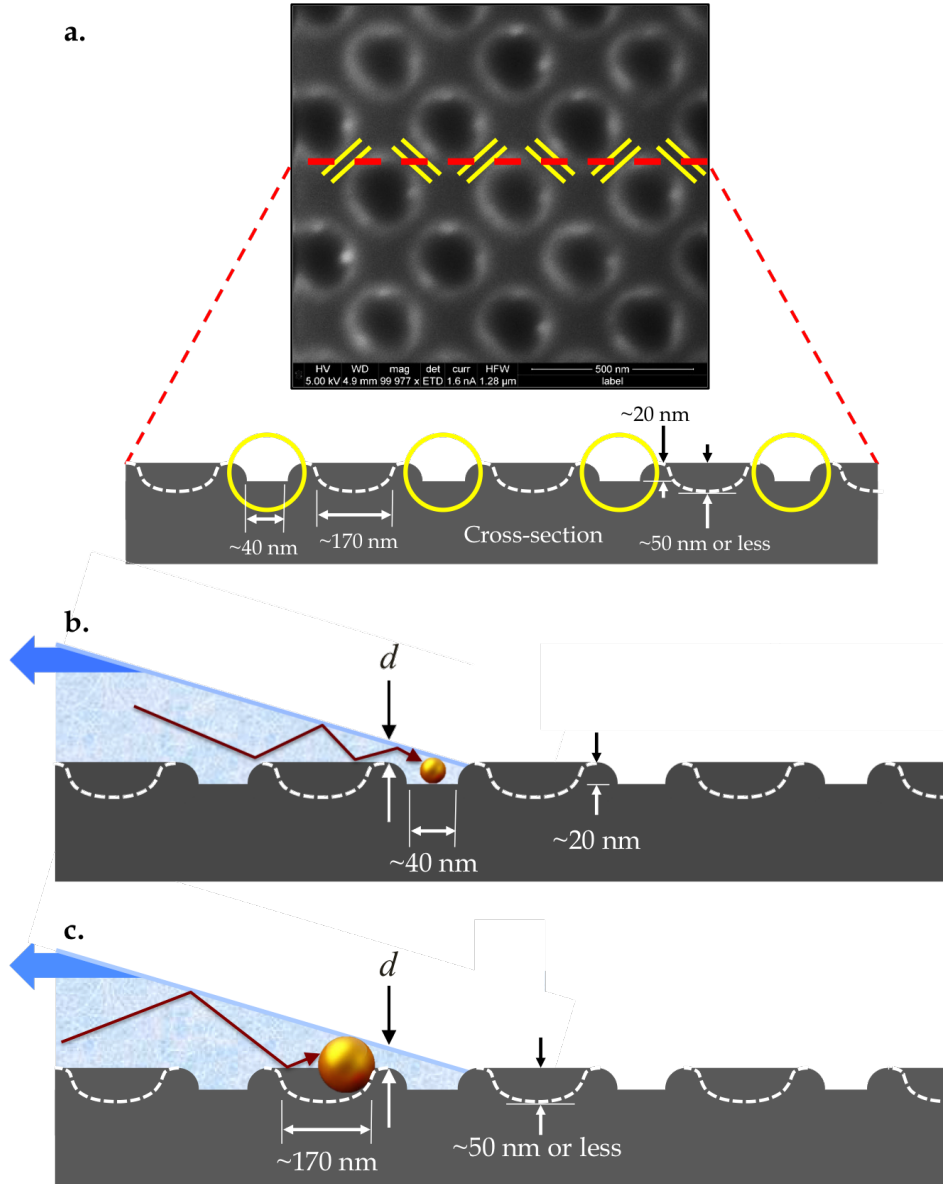


Figure 5.14: The cross-section (a) is taken through the edges of cavities, with the yellow markings highlighting the very narrow corridors that separate closely adjacent cavities (cross-section illustration is not to scale). If the pinned-convective model is operating, then we would expect small particles to diffuse into the narrow corridors while the meniscus is pinned (b), but not large particles (c).

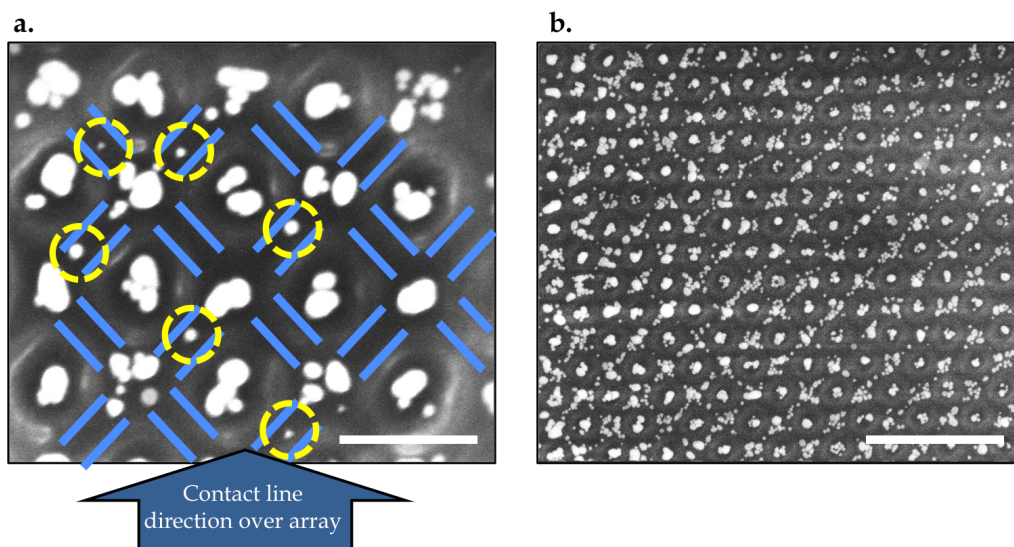


Figure 5.15: Narrow inter-cavity corridors are marked by pairs of blue lines. Yellow circles highlight assembly of the smallest particles centrally in some corridors. Image (b) shows this to be a large scale phenomenon. Scale bars are 300 nm and 1 μm , respectively.

was made by EBL of 100 nm PMMA on Si. An atomic force microscopy (AFM) image is in Figure 5.16a. Large scale assembly and a zoomed portion are shown in images (b) and (c) after an acetone bath has removed the PMMA layer. A solid ligand shell is seen encasing the dried out particles in (c).

The assembly is mostly as predicted according to the cavity shape, but what is of interest is the two-tier structures, like that in image (c). In both SEMs the meniscus receded vertically up the image. The second tier particles sit well above the 100 nm-thick template (prior to the acetone bath). Second-tier particles are nearly consistently deposited at the *back* of their underlying structures. In one $15 \times 15 \mu\text{m}^2$ area there are 936 assembled nano-trimers; 22 are the two-tier type and 21 of those have their second tier placed at the *back*. How were they trapped so far above the template, and why only at the rear? The conventional model cannot readily offer an explanation.

As image (d) illustrates, this result is conceivable from pinned-convective dynamics where particles diffuse on top of the lower tier to build a second tier. The clamping meniscus locks them into place. Because the meniscus rises to the rear of the structure, the second tier is nearly consistently trapped at the rear. The timing for all this to occur must be just right, hence only $\sim 2\%$ of cavities produced these

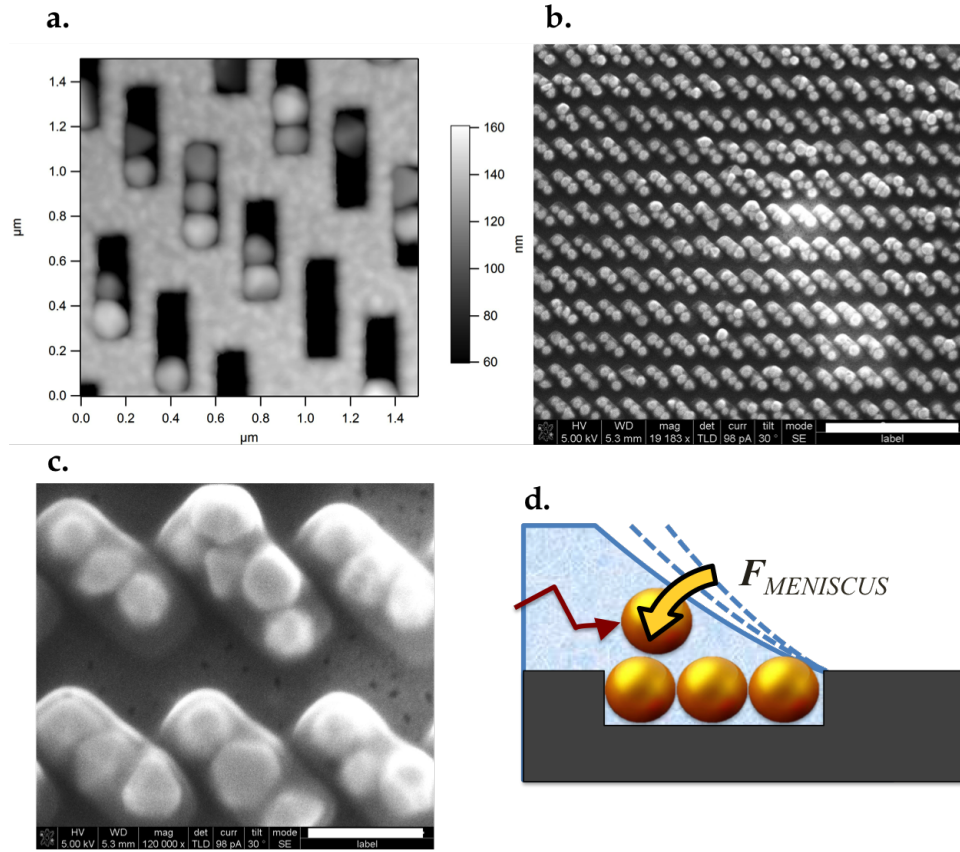


Figure 5.16: (a) An AFM scan of a partially assembled template showing cavity shape and size. Images (b) and (c) show SEM scans of the assembly of 150 nm gold spheres. In (c) is a close up of a two-tier structure, with the highest second-tier particle assembled at the back of the underlying structure. In (b) and (c) the meniscus receded vertically up the image. Scale bars are 2 μm and 300 nm, respectively. Image (d) is a diagram explaining how the pinned-convective model accounts for two-tier structures.

two-tier structures.

5.5.5 Case Study #4

The final case study refers to two published works. Kuemin et al. [11] used nano-CFA to successfully assemble 25 nm-wide nanorods into individual 37 nm-deep cavities. Other researchers, Rey et al. [12], replicated this work with the same particles, but instead of isolated nanorods they used long channels to hold chains of nanorods end-to-end. Note that these long chains were *perpendicular* to the contact line, so the contact line had to recede a substantial distance before the chain was complete. Where Kuemin et al. assembled into 37 nm-deep singular cavities, Rey et al.

required 60 nm-deep channels for their nanorod chains to assemble.

Rey et al. mused over the discrepancy in cavity depth, rightly concluding that the assembly mechanism must be different between the two template designs, though without further comment. Why were deeper cavities required for long chains compared to single-particle cavities?

The answer emerges from a pinned-convective model of assembly. In this model particles are driven into cavities by local convective flows which are setup by strong meniscus distortions from a pinned contact line. Without a pinned contact line, there are no local convective flows and no clamping capillary force. Only the less intense bulk convective flow remains to drive particles.

With Kuemin et al.'s single-particle cavities, assembly of each cavity could be completed within the duration of pinning. The full suite of pinned-convective dynamics was therefore available for each and every particle to be assembled. With Rey et al.'s very long cavities, the meniscus depins just after a nanorod-chain begins forming. Pinned-convective dynamics cease at that instant and only the weaker bulk convective flow remains to assemble particles for the majority of the chain length. For this less efficient mechanism to be effective, the cavity had to be much more pronounced and exaggerated to attract some kind of assembly. Only when we recognise the presence of pinning dynamics can we explain the differing results of these two templates.

5.6 Conclusions

The goal of this chapter was to explain and demonstrate a pinned-convective framework for nano-CFA. This has been done, purportedly answering the second question of this thesis: What are the key mechanisms behind nano-CFA?

We began with a brief evaluation of the difficulties facing us in decomposing nano-CFA into its basic dynamics. Then, clues from high-level observations guided a first-principles consideration of cavity-level pinning. Three key dynamics emerged that could reasonably enact assembly, given a dense population of particles already at the contact line. These three dynamics are:

1. Cavity-level convective flows
2. A meniscus clamping force during pinning

3. Regional convective flows over arrays of cavities

We then considered how this model can give rise to varied rates of assembly, thus explaining the seemingly unpredictable world of nano-CFA where some cavities might remain empty whilst others might over-fill. We then summarised the explanatory power of this new model to solve some pertinent unanswered problems in the conventional model. Special focus was also given to explore how post-assembly capillary forces can bring about varied configurations of particles.

To give some direct experimental affirmation of the new model, four nano-CFA case studies were presented that find a clear explanation in the pinned-convective model. These case studies not only further dismantle the conventional model, but they provide a confident footing for us moving forwards.

On that basis, the remainder of this thesis extensively details and quantifies a pinning-convective understanding of nano-CFA. The coming chapter (Chapter 6) presents a new experimental technique to create time-resolved three-dimensional reconstructions of meniscus forms on the micro-scale. This powerful technique is leveraged in Chapter 7 for in-depth study of cavity-level pinning dynamics. Pinning dynamics are further built on in Chapter 8 with evaporative modelling and an analysis of convective flows during pinning. Thus the remaining chapters answer this thesis' third and final question: How can we probe the mechanisms of nano-CFA and quantify them for a comprehensive model?

In this chapter's Appendix, four more special cases are presented showing that under unique conditions the pinned-convective model can actually collapse to an approximation of the conventional model. This accounts for small portions of published work that claim experimental support for the conventional model. More than that, through these four special cases it becomes evident why extant literature has settled on two seemingly exclusive Schemes for the conventional model: when the pinned-convective model collapses to the conventional model, the design of the template will lead to either traditional Scheme 1 or 2 emerging. This resolves an important disagreement in the literature, and sets the pinned-convective model as the dominant and overarching explanation for nano-CFA.

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Appendix

Appendix 5.A Special Cases that Revert to the Conventional Model

Published literature occasionally asserts experimental or simulated validation of the conventional model of nano-CFA. In this Appendix, four such special cases are reviewed. It is seen that in each case, after applying pinned-convective dynamics, a version of the conventional model (or similar) emerges. This gives credence to the published findings, but also demonstrates that the conventional model is only applicable in these four specific cases. What uniquely describes these special cases is their template design. The ability to describe these special cases from one ‘parent’ model speaks to the authority of the pinned-convective model.

Templates with Cavities for Single Particles

The key to this special case is that on a template where cavities house single particles only, assembly can take place just before the meniscus pins on a cavity’s leading edge.

Recall that in Phase I of the pinned-convective model the meniscus is receding and applying transient capillary forces to nearby particles. The momentary capillary force is directed according to the receding contact angle. This is essentially Scheme 1 of the conventional model. During this phase of operation, if conditions and timing are just right, then a single-particle cavity present at the contact line might well receive and trap a particle just moments before pinning begins. This is illustrated diagrammatically in Figure 5.17, where it is also shown (in image (b)) that a lower

contact angle may provide a greater chance of this type of assembly.

This special case only reasonably applies to single-particle cavities because for a particle to be trapped in the moments preceding pinning, the rear wall of the cavity must be within reach to hold the particle in place.

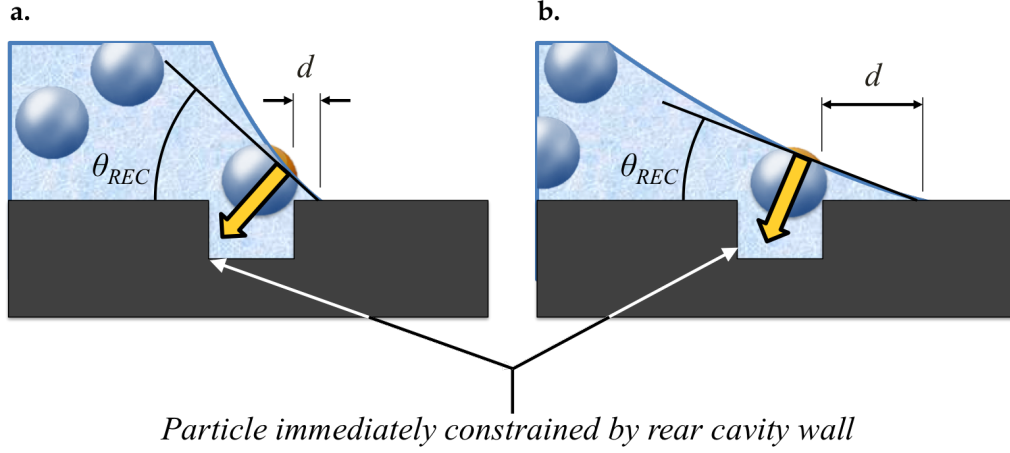


Figure 5.17: (a) A particle experiencing a transient capillary force moments before the contact line pins on a single-particle cavity. There is a momentary opportunity for assembly to occur. This opportunity will be increased if the contact angle is very low, as in (b), where there is a longer timeframe between the particle meeting the cavity and the meniscus pinning on the cavity (signified by the larger distance d in (b)).

This template design matches that studied by Asbahi et al. [1] in both experiment and simulation. This is likely why their conventional model simulations could achieve some assembly. However, less than 50 % of their experimental assembly yield could be reproduced in simulation, suggesting that this special case may have played a role in the experiment, but standard pinned-convective dynamics remained the dominant assembly driver.²

Templates with Raised Structures

Raised templated structures, like that shown in Figure 5.18, can also assemble particles based on the conventional model. This is demonstrated only occasionally in

²Mapperson presented part of the pinned-convective model to Mehraeen, the primary author of the simulations, and Mehraeen concluded that pinning dynamics are an important factor that had not been considered, and in his view likely accounts for the discrepancy between simulation and experiment.

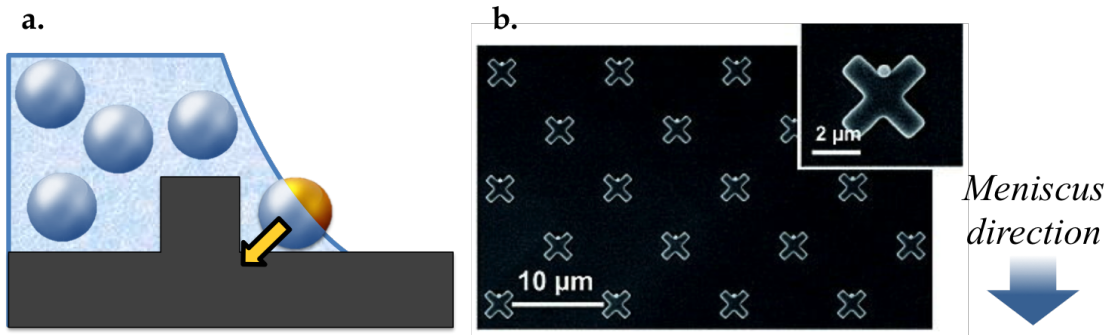


Figure 5.18: A particle residing near the contact line just before a raised template structure is met. In this special case, the conventional nano-CFA model could reasonably assemble the particle. Image (a) is reproduced from Figure 4.1b. Image (b) shows this type of assembly with 500 nm polystyrene particles, reproduced from Ref [2].

CFA [2] as most CFA work uses cavities, not raised structures (cavities are more versatile in the type of nano-structures they can create). The leading wall of a raised structure can trap particles much like the trailing edge of a cavity can.

Templates with Cavities that Depin Prematurely

The key to this special case is that at times the contact line depins from a cavity but it does not jump past the cavity. This may be because (1) the cavity shape causes premature depinning, or (2) the cavity is very long. In this case, after depinning the meniscus recedes along the cavity floor like in Phase I of the pinned-convective model. Particles can thus be dragged along the base of the cavity until they are trapped against the rear wall of the cavity. This is therefore similar to trapping a particle against a raised structure, as in the previous special case. It is similar to Scheme 1 of the conventional model.

An example of this is shown in Figure 5.19 where there exists a through-channel between each cavity. This prevents the meniscus pinning and particles are dragged until being lodged in the narrower through-channel.

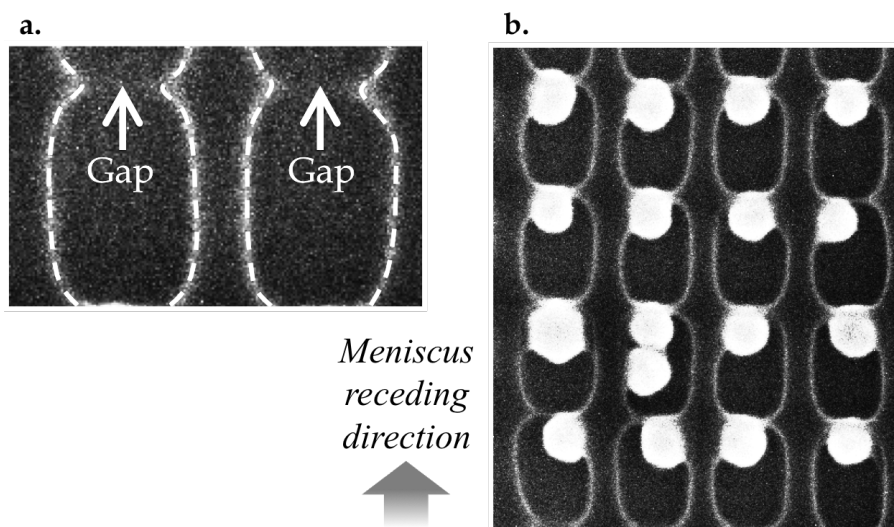


Figure 5.19: (a) The cavities in this template have through-channels that prevent the meniscus pinning. This means that particles are dragged along with the meniscus until they are lodged in the narrower through-channel, as shown in the SEM (b) with 100 nm gold particles.

Templates with Long Channels Perpendicular to the Contact Line

The final special case is that of a template with long channels perpendicular to the contact line. The assembly process begins with pinned-convective dynamics as the contact line pins at the start of the channel. Particles assemble into the front-most segment of the channel. When the meniscus depins, it jumps part-way down the channel and continues receding (similar to the previous special case).

Experiments show that filling the head of the channel can be very dense and complete. It is also often seen that after depinning, the contact line does not jump beyond the filled region, but recedes over the top of the filled region. At this point the assembly process reverts to standard convective deposition (see Section 1.7, and Figure 5.20a below).

While the meniscus recedes down the channel, normal convective flows drive particles into the channel, continuing to build on the assembly that began in the channel head. This is similar to Scheme 2 of the conventional model. Very dense assembly may even see particles assemble out the rear end of the channel, as shown in images (b) and (c).

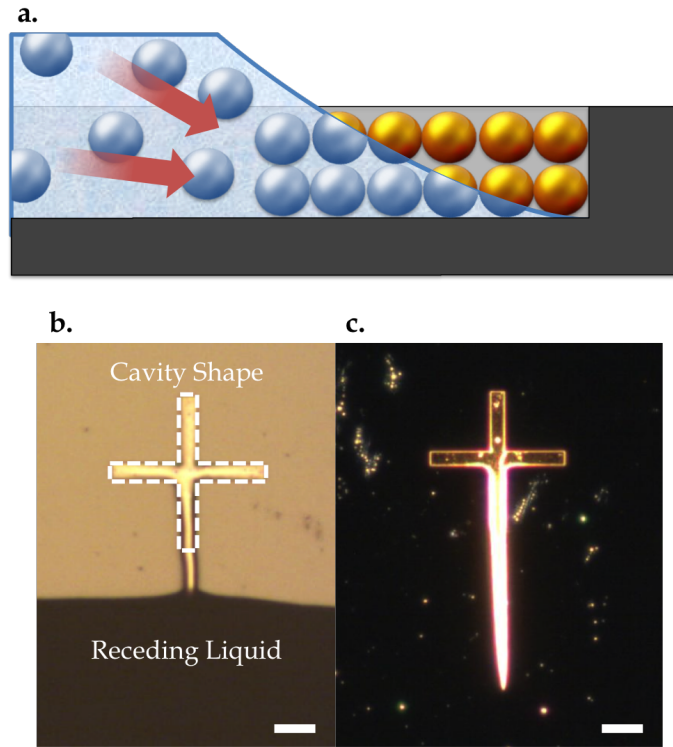


Figure 5.20: In this illustration (a) the cavity is a long channel perpendicular to the contact line. The cavity’s great length means that prolonged convective flows are setup like in standard convective assembly, which fully assembles the channel. In (b) and (c) an example is shown, where the templated structure is a ‘+’ design, $50\ \mu\text{m} \times 50\ \mu\text{m}$ (arm widths $5\ \mu\text{m}$), as outlined in (b). The meniscus is receding down in the image. Assembly of $50\ \text{nm}$ gold particles was dense enough to continue out the end of the southern arm, extending $60\ \mu\text{m}$ beyond the end of the ‘+’ structure. The dark-field image (c) shows the final assembly. Scale bars $15\ \mu\text{m}$.

This special case matches experiment and simulation by Mehraeen et al. [3] (see Figure 7 in their paper for an image of what they simulated). Their model is the conventional Scheme 2, which is similar to the convective deposition model. They found that their simulations qualitatively matched their experimental results. This further supports the claim that a template with long channels is a special case reverting to the conventional model.

Summary

The simulations published by Asbahi et al. and Mehraeen et al. (referred to in the first and final Special Cases, respectively) find two different Schemes of assembly

operating. It is important to note that both simulations are from the same research group, and both simulations are based on the same physical model in all respects except for the templates used. Despite this, Schemes 1 and 2 emerge from each, respectively. The papers make no mention or discussion of this apparent paradox. Based on the new and more comprehensive pinned-convective model, a clear explanation has been offered above as to why two different assembly schemes emerge. Outside of the four special cases presented here, it is difficult to conceive of the conventional model applying instead of the pinned-convective model.

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A Method for Micro-4D Meniscus Profilometry and Thermodynamic Analysis

6

To probe the dynamics of the pinned-convective model in detail it is necessary that we understand the time-resolved 3D form of the meniscus. To that end, this chapter explains a new experimental method to scan and reconstruct a meniscus in 4D, with micro-scale resolution. This method forms the basis for in-depth thermodynamic studies of meniscus and liquid dynamics. In later chapters this is applied to study dynamics of the pinned-convective CFA model.

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Requirements for Meniscus Profilometry ...	6.2
A Novel Micro-4D Scanning Method for Use With CFA ...	6.3
Implementation of the Micro-4D Scanning Method ...	6.4
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Thermodynamic Information from Meniscus Reconstructions During CFA ...	6.6
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6.1 Introduction

In the previous chapter we saw how a pinned-convective model presents an arguably accurate explanation of nano-CFA dynamics. In this chapter we focus on a new experimental technique that will enable us to quantify and characterise these assembly dynamics in greater depth.

The pinned-convective model suggests two key dynamics at the single cavity level: (1) a locally enhanced convective flow into a cavity, and (2) a clamping meniscus force. These depend heavily on the three-dimensional (3D) meniscus profile throughout a pinning event. We require time-resolved micro-3D meniscus profilometry.

Several meniscus profilometry methods already exist (see Appendix 6.A for a brief review). The motivation for this chapter is that no existing methods can profile the unique CFA meniscus shape. A new method is here given as a novel and powerful meniscus interrogation tool. Scaling laws will allow us to knowledgeably interpolate trends over nano-CFA.

This chapter covers three broad components. First we present a functional and theoretical overview of the profilometry method (Sections 6.2, 6.3 and Appendix 6.B). The second component demonstrates implementation of the method, involving a case study with accuracy and error analysis (Sections 6.4 and 6.5). In the third and final component we example the suite of thermodynamic data that we can infer or calculate from a 3D meniscus profile (Section 6.6). Thermodynamic analysis demonstrates the power of this profilometry method to deliver insights that have been previously inaccessible for non-trivial meniscus forms. In the following two chapters we apply these methods to a CFA context, deducing potential assembly dynamics.

6.2 Requirements for Meniscus Profilometry

The chosen meniscus profilometry method must meet the following requirements:

1. Be able to capture the three-dimensional meniscus form.
2. Be able to resolve meniscus details in the lower end of the micron scale.

3. Be able to capture with a temporal resolution that is small compared to the duration of a pinning event (i.e. millisecond resolution).
4. Be operable with a CFA apparatus. This precludes setups that would interfere with the normal liquid motion during CFA.
5. Not require a transparent substrate/liquid, as the nature of the CFA setup on the microscope makes full transparency without strong distortion difficult.
6. Accommodate the wide range of meniscus angles and meniscus heights that are present in a CFA liquid body.

The range of existing profilometry techniques can be categorised as either electrical conductance/capacitance, optical absorption/fluorescence, interferometric, or external/internal reflection based. As Appendix 6.A explains, none of these approaches are suitable. The theoretical basis of a new meniscus profilometry method is hence explained in the next section.

6.3 A Novel Micro-4D Scanning Method for Use With CFA

This major section begins with an overview of the new meniscus scanning method (Section 6.3.1). Following that is a brief explanation of how an optical pattern suitable for micro-3D scanning is generated (Section 6.3.2, with detailed coverage in Appendices 6.B and 6.C). Then we discuss how the method interfaces with the existing CFA microscopy platform (Section 6.3.3), as well as the inverse-mapping equations for 3D surface reconstruction (Section 6.3.4). The next major section (Section 6.4) presents the implementation and a case study to assess accuracy and sources of error.

6.3.1 Overview of the Method

The 4D meniscus reconstruction method is a novel variation of 3D scanning technology known as the ‘structured light’ method. Generally speaking, 3D scanning technologies are designed to scan solid opaque macro-scale objects, and often static objects as well. In that respect, the developments presented here are a significant

step forward in that we will produce a *time-resolved* scan of a *liquid* surface on the *microscale*.

The method involves projecting a pattern of bright and dark optical fringes onto the specimen. A suitable choice of liquid solution will scatter the projected pattern off its surface, as if it were a solid opaque object. Distortions in the scattered light pattern can be inverse-mapped to deduce the specimen's 3D shape. Scans are single photographs, allowing time-resolved scans at the camera's frame rate.

Inferring the 3D topography necessitates having a reference image of the optical pattern on a known topography. We use a flat surface to obtain the reference pattern. The optical pattern is focussed onto the microscope stage covering the objective's field of view. This method is applicable to a liquid surface of almost arbitrary shape, making it a noteworthy addition to the interrogation tools available for the study of micro-scale liquid phenomena.

6.3.2 Generating the Light Pattern

The theory, simulation, measurement and optimisation of the optical pattern generator are described in detail in Appendix 6.B, with mathematical derivations in Appendix 6.C. What follows here is a brief description highlighting the most relevant points.

An interferometer unique to this work generates the structured light pattern. The interferometer is to the side of the microscope stage (see Figure 6.1). Beams of several orders are generated, the first two of which are directed onto the microscope stage where they interfere, creating a pattern of bright and dark parallel fringes (only the zeroth order beam is shown in the Figure).

To create a high-contrast visible interference pattern, a 532 nm continuous wave laser is used as the light source (500 mW, diode-pumped solid state laser, Shanghai Dream Lasers, Model: SDL-532-DL-150T). The laser is passed through a beam expander (not shown in the Figure) to create a full beam waist of 2.5 cm (to cover the microscope's field of view) before entering the interferometer.

Figure 6.2a shows a photograph of the interference pattern on the microscope stage, and Figure 6.2b shows its cross-sectional intensity profile, showing excellent agreement with the theoretical pattern.

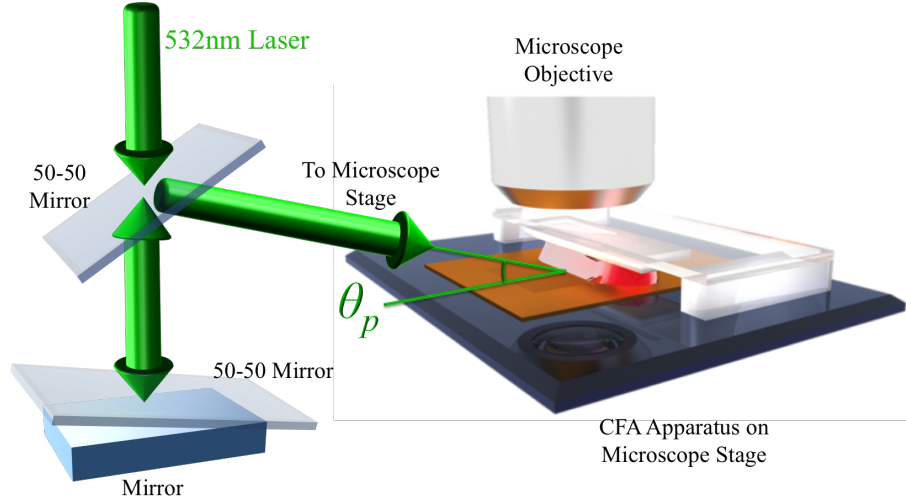


Figure 6.1: A diagram of the interferometer positioned next to the microscope stage, where the structured light pattern is created. Shown on the microscope stage is a red colloidal solution positioned within the slider-CFA apparatus, beneath the microscope objective.

The beams are projected onto the stage at an angle of $\theta_p = 30^\circ$. The spacing between fringes reflects the minimum feature size that can be scanned. The fringe spacing is continuously variable by adjusting the angle of the lower 50-50 mirror in Figure 6.1. Modelling indicates a minimum fringe spacing of $7 \mu\text{m}$ with this interferometer. The pattern intensity, however, reduces with the fringe spacing, giving a practical limit of approximately $20 \mu\text{m}$ (in agreement with theoretical estimates, see *Practical Optimisation* in Appendix 6.B).

6.3.3 Interfacing with the Microscopy Platform

Projecting the optical pattern onto the microscope stage at a relatively shallow angle means that the light does not enter the microscope objective unless it is scattered by the surface being scanned, similar to dark-field microscopy.¹ Applying and reading the optical pattern does not interfere with the microscope's normal operation, so bright-/dark-field microscopy can be performed simultaneously to meniscus profilometry. The only microscopy requirement is that the working distance (WD) of the microscope objective must be large enough for unobstructed projection of the optical pattern onto the objective's entire field of view. This may restrict which

¹That is, barring the possibility of small regions of specular reflection of the laser beams.

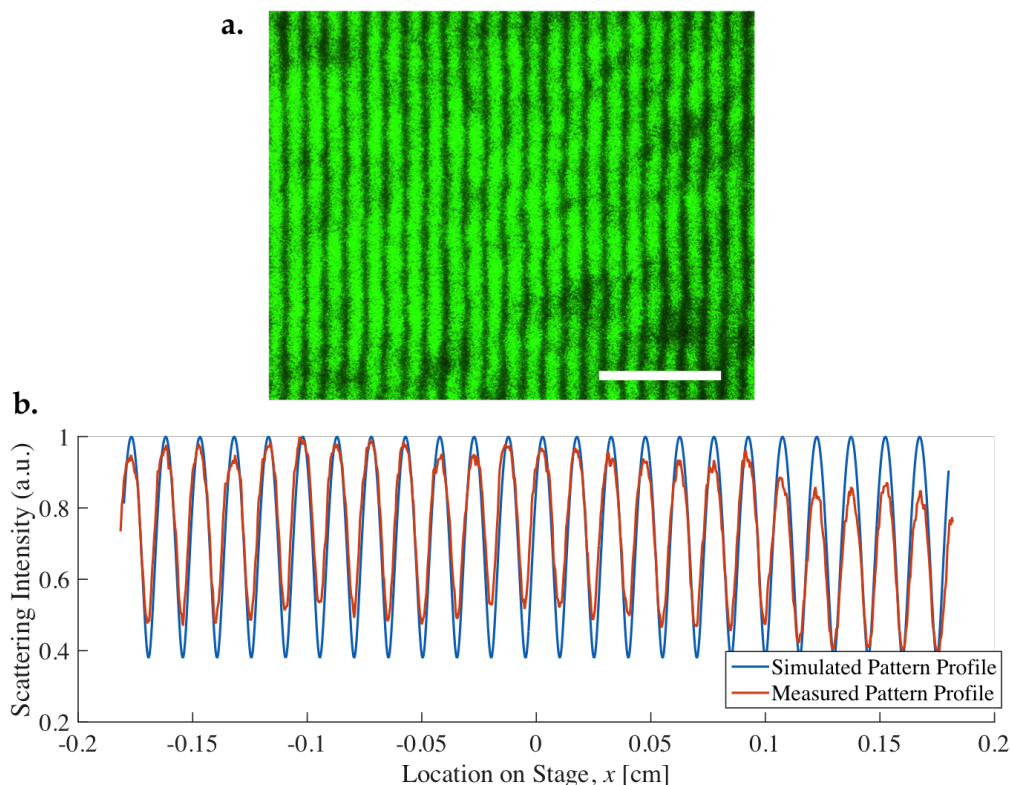


Figure 6.2: Photograph (a) and profile (b) of the structured light pattern on the microscope stage. The photograph shows a fringe spacing of $150\ \mu\text{m}$ (scale bar $900\ \mu\text{m}$). Wobbles in the fringes are due to slight undulations in the substrate. The profile plot shows both the simulated and measured profiles of the pattern in (a). The simulated profile is fully derived in Appendices 6.B and 6.C.

objectives can be used.² We will now consider how the optical pattern can be used for profilometry.

6.3.4 Inverse-Mapping Equations to Obtain 3D Topography

The pattern scattering off the specimen, when observed from above, will be distorted according to variations in the specimen's surface height. Two 3D profile reconstruction methods have been derived, and both are implemented for greater accuracy.

²Regarding the work presented here microscope objectives with the greatest WD available were the 2x (WD 7.5 mm) and the 50x (WD 9.8 mm). Objectives giving 20x and 100x magnification had working distances that were too small for a clear projection path, at 4.5 mm and 1 mm, respectively. This presented a practical limit to the magnification of the scan.

6.3.4.1 The Fringe-Spacing Method (FSM)

The fringe-spacing method leverages the fact that the gradient of the sample's surface in the direction perpendicular to the fringes will determine the observed fringe spacing in that region. This applies to positive and negative surface gradients, and is illustrated for a positive gradient in Figure 6.3. According to geometry, the change in height between two adjacent fringes is correlated with the fringe spacing by

$$\delta h = (d_0 - d) \tan(\theta_p) \quad (6.1)$$

where δh is the change in height from one fringe to the next and d is the observed spacing between the fringes. The projection angle is θ_p , and d_0 is the reference fringe spacing as seen on a flat surface.

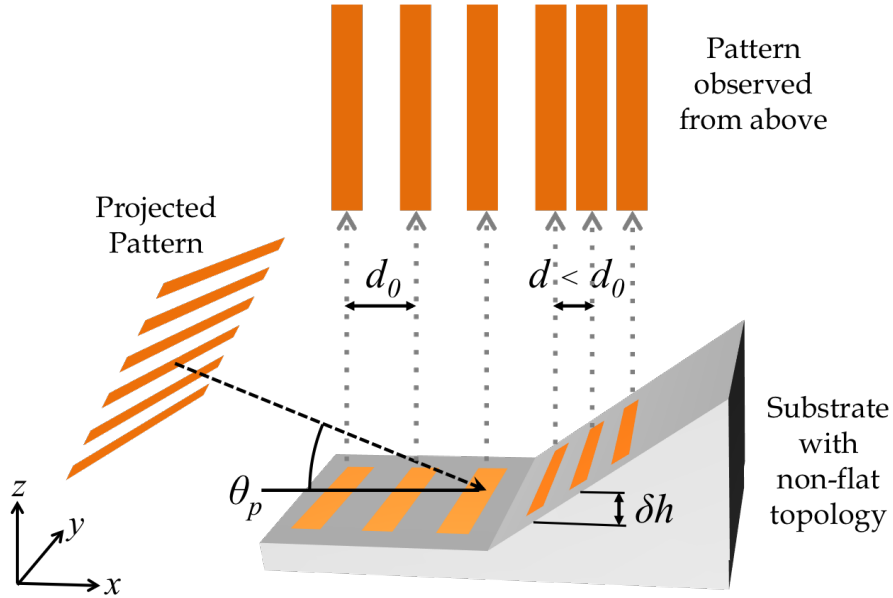


Figure 6.3: Illustration of how the fringe-spacing method can determine the relative change in height of a surface based on the change in observed fringe spacing. In the diagram, d_0 is the reference fringe spacing and d is the spacing modified by a non-zero surface gradient.

Equation 6.1 reveals that

$$\Delta d = d_0 - d = \frac{\delta h}{\tan(\theta_p)} \quad (6.2)$$

This shows that the greatest change in fringe spacing for any given variation in surface height is achieved with low projection angles when viewed from directly

above. In general terms, optimal height sensitivity is when the projection angle approaches 90° relative to the viewing angle.

The quantity $\delta h/d$ is the average x -axis surface gradient between adjacent fringes. We can hence say that the average surface gradient between any two fringes of separation d on the surface S is

$$\left\langle \frac{\partial S}{\partial x} \right\rangle = \frac{\delta h}{d} = \left(\frac{d_0}{d} - 1 \right) \tan(\theta_p) \quad (6.3)$$

Rearranging to give the fringe spacing relative to the reference fringe spacing, in terms of the surface gradient yields

$$\frac{d}{d_0} = \frac{1}{1 + \left\langle \frac{\partial S}{\partial x} \right\rangle \cot(\theta_p)} \quad (6.4)$$

In general, the fringe spacing will decrease ($d/d_0 < 1$) with positive surface gradients (surfaces increasing in height towards the positive x -axis) and will increase ($d/d_0 > 1$) on negative surface gradients.

This method only detects average surface gradient between two points perpendicular to the unperturbed fringe structure (i.e. in the x -axis). For this reason, the fringe alignment ought to be set perpendicular to the direction of maximum meniscus gradient in the region of interest.

Figure 6.4 plots how the fringe spacing varies with the surface gradient in the x -axis. Fringe spacing is increasingly sensitive to surface gradient as the gradient decreases.

A wide range of positive surface gradients can be accommodated, and negative surface gradients much less so. For any projection angle there exists a minimum negative surface gradient whereby the surface becomes parallel to the direction of light projection. At this gradient the fringe spacing is infinite, and beyond this gradient the surface is in the shadow of the projected pattern and cannot be scanned. The minimum surface gradient that can be measured is

$$\frac{\partial S}{\partial x_{min}} = -\tan(\theta_p) \quad (6.5)$$

Lower projection angles have a smaller range of negative surface gradients that can be scanned. There is hence a trade-off in projection angle: lower angles give a greater sensitivity to changes in surface gradient, but they are more restricted to mostly positive gradients. If the surface being scanned does not have negative surface gradients (as in CFA) then this is of course not an issue.

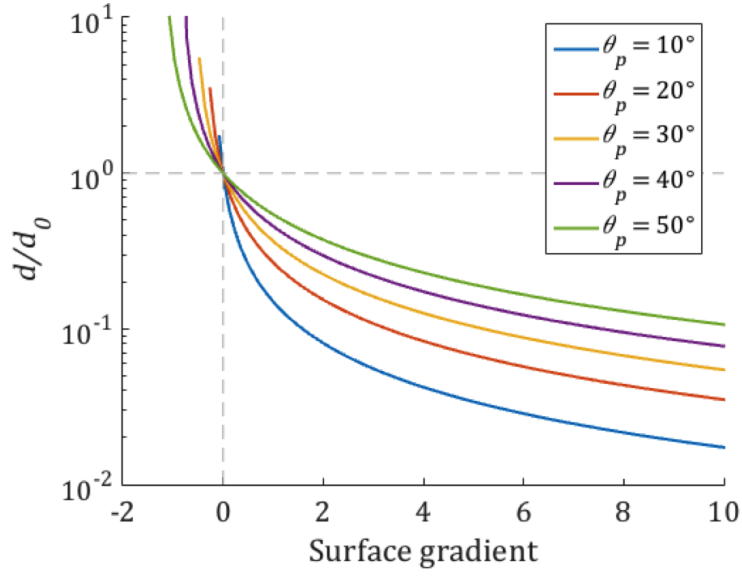


Figure 6.4: A plot of how the fringe spacing varies with surface gradient in the x -axis. The fringe spacing varies most with the gradient either side of zero (a flat surface). Highly negative surface gradients are in the shadow of the projected pattern; they show no fringes and so cannot be scanned.

6.3.4.2 The Fringe-Deviation Method (FDM)

The second method of topography reconstruction leverages the fact that the path of any single fringe predictably deviates according to changes in height along the fringe's length. The previous method detects changes in height perpendicular to the fringes, whereas this method detects changes along a fringe, as shown in Figure 6.5.

By geometry, the relationship between fringe deviation and relative surface height is

$$\delta h = \delta d \tan(\theta_p) \quad (6.6)$$

The deviation δd is measured over a certain length of the fringe, denoted by the points O and P in the Figure. The y offset between these points is δy and the straight line distance between the points is

$$\overline{OP} = \sqrt{\delta d^2 + \delta y^2} \quad (6.7)$$

The average surface gradient over the vector $\overrightarrow{OP}$ is then

$$\langle \nabla S \cdot \overrightarrow{OP} \rangle = \delta h / \overline{OP} = \frac{\delta d \tan(\theta_p)}{\sqrt{\delta d^2 + \delta y^2}} \quad (6.8)$$

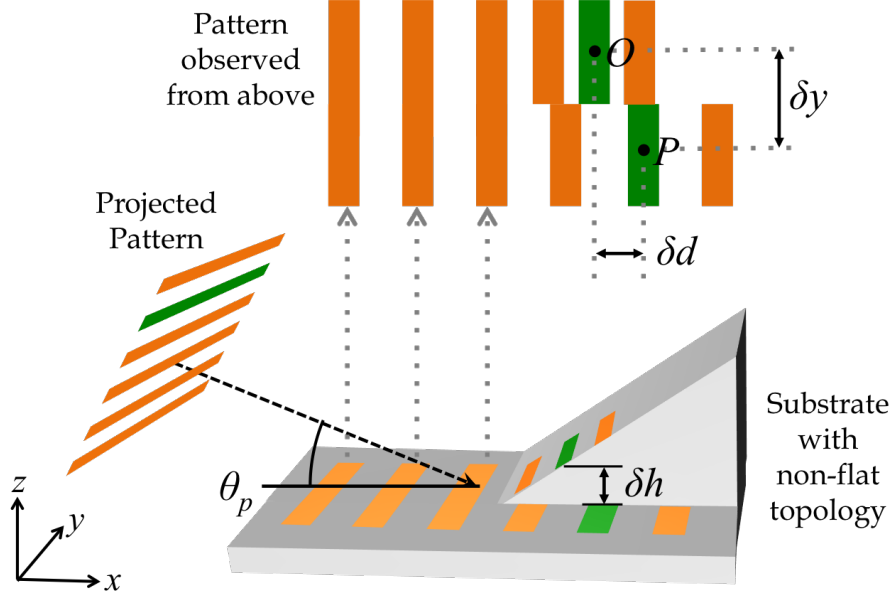


Figure 6.5: Illustration of how the fringe-deviation method can determine the relative change in height of a surface based on the change in the lateral position of points along a single fringe (the fringe in green is used as the example). In the diagram, δd is the size of the fringe deviation at some point along the fringe's path.

where S is the surface. The angle that $\overrightarrow{OP}$ makes with the negative x -axis is $\theta_{OP} = \tan^{-1}(\delta y / \delta d)$. Using this, we write the average surface gradients in the x and y axes as

$$\left\langle \frac{\partial S}{\partial x} \right\rangle = \langle \nabla S \cdot \overrightarrow{OP} \rangle \cdot \cos(\theta_{OP}) \quad (6.9)$$

$$\left\langle \frac{\partial S}{\partial y} \right\rangle = \langle \nabla S \cdot \overrightarrow{OP} \rangle \cdot \sin(\theta_{OP}) \quad (6.10)$$

Using the relationships,

$$\cos(\theta_{OP}) = \cos \left(\tan^{-1} \left(\frac{\delta y}{\delta d} \right) \right) = \frac{1}{\sqrt{1 + \left(\frac{\delta y}{\delta d} \right)^2}} \quad (6.11)$$

$$\sin(\theta_{OP}) = \sin \left(\tan^{-1} \left(\frac{\delta y}{\delta d} \right) \right) = \frac{\frac{\delta y}{\delta d}}{\sqrt{1 + \left(\frac{\delta y}{\delta d} \right)^2}} \quad (6.12)$$

we can simplify the average axes gradients to

$$\left\langle \frac{\partial S}{\partial x} \right\rangle = \frac{\tan(\theta_p)}{1 + \left(\frac{\delta y}{\delta d} \right)^2} \quad (6.13)$$

$$\left\langle \frac{\partial S}{\partial y} \right\rangle = \frac{\frac{\delta y}{\delta d} \tan(\theta_p)}{1 + \left(\frac{\delta y}{\delta d} \right)^2} \quad (6.14)$$

Naturally, the closer together our points O and P are, the greater will be the resolution of our scan.

This concludes the first component of this chapter: the micro-4D scanning method in theory. In the coming sections we explore the second component: how the profilometry method can be implemented, and what the limits of accuracy are. We will reconstruct part of a sessile droplet's surface as a case study.

6.4 Implementation of the Micro-4D Scanning Method

In this Section we begin with what is required of a liquid solution to make it suitable for 3D scanning (Section 6.4.1). Following this we present a description of the 3D reconstruction algorithm, and demonstrate its use on a sessile droplet (Section 6.4.2).

6.4.1 Liquid Solutions Suitable for 3D Scanning

There are three aspects of the liquid solution that we will consider: (1) the general optical properties, (2) the scatterer density and (3) the scatterer size.

6.4.1.1 Liquid Optical Properties

As can be expected, the optical scattering properties of the specimen greatly affects the scan quality. Here we discuss the options of liquid that were tried and why a colloidal nanoparticle solution is suggested.

Emulsions and suspensions scatter light strongly. Various liquids were tested, three of which are exemplified in Figure 6.6, as sessile droplets showing a wide range

of outcomes. An identical banded light pattern (532 nm wavelength) was projected onto all droplets. The brown-orange area around each droplet is the flat substrate under low light illumination from the microscope, to clearly show the droplet boundary.

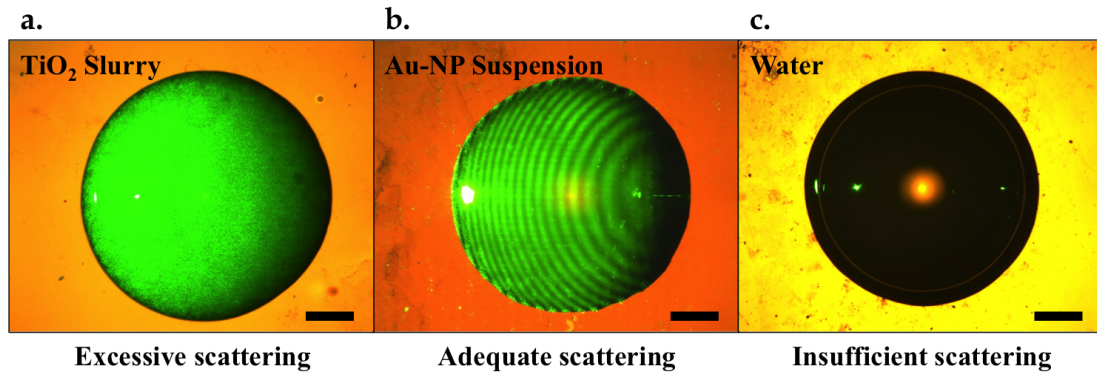


Figure 6.6: Three liquids showing different quantities of optical scattering. Sessile droplet (a) is a TiO_2 slurry (variously sized microparticles), (b) is a suspension of 63 nm gold spheres, $\sim 10^{10}$ particles/mL, and (c) is pure water. Only the gold nanoparticle solution renders the incident pattern well through surface scattering. Scale bars, 450 μm .

In the Figure it is seen that (a) a slurry of titanium dioxide (TiO_2) particles ranging in size up to hundreds of micrometers scatters too strongly and the pattern is washed-out. At the other extreme is water (c) which does not scatter. A suitable liquid is a colloidal suspension of 63 nm gold nanospheres (b) at a concentration of $\sim 10^{10}$ particles/mL, which very clearly reproduces the pattern with a curved distortion characteristic of the droplet's spherical surface.

Other liquids that were tested include water-oil emulsions and a colloidal suspension of gold nanorods. The emulsions gave similar results to the TiO_2 suspension since their vesicles are on the scale of micrometers and scatter strongly. Gold nanorods are an inferior but acceptable alternative to nanospheres.

To understand why a colloidal nanoparticle solution is ideal we will now discuss the roles of scatterer density and size.

6.4.1.2 Scatterer Density

Theory: The optical scattering coefficient (cm^{-1}) of a medium is essentially the scattering cross-sectional area per unit volume.

$$\begin{aligned}\mu_s &= \rho_s \sigma_{sca} \\ &= \left(\frac{n_s}{V} \right) \sigma_{sca}\end{aligned}$$

where ρ_s is the density of optical scattering entities and σ_{sca} is the scattering cross-section per entity. Scatterer density is the number of scatterers (n_s) per unit volume (V , in cm^3 or mL), therefore also conveniently the same as the particle concentration in particles/mL. (The scattering cross-section of metal nanoparticles is defined by Equation 1.5, Section 1.2.2). The gold nanoparticles that were used have a fundamental plasmonic resonance very close to the laser wavelength of 532 nm, and so scatter this wavelength well.

Observations: To understand the role of the scatterer density, ρ_s , a sessile droplet of highly concentrated gold nanoparticles was allowed to evaporate completely, during which time the particles slowly deposited out of solution, varying the scatterer density from its initial value of $\sim 10^{11}$ particles/mL to an extremely dilute solution. Snapshots throughout the evaporation process are shown in Figure 6.7. It is immediately obvious that scatterer density plays an important role the clarity of the scattered pattern.

Interpretation: When the light strikes the liquid surface it is elastically absorbed by a particle near the surface and re-radiated as from a dipole antenna (at 532 nm we are exciting the fundamental dipole plasmon mode). Some of this light exits towards the microscope objective and is imaged. Some of the light is scattered into the droplet where it moves through a chain of absorption and re-radiation events with other particles. (Huang & El-Sayed [1] indicate that for 63 nm gold spheres, $>2/3$ of the incident light energy is lost to heat absorption within particles.)

A very low particle density will evidently not reproduce the optical pattern. When the scatterer density is too high, the optical energy is too readily transported around the droplet by repetitive absorption/scattering events. The entire liquid surface appears washed-out. A similar effect occurs when the scattering cross-section is too large, as with microparticles/vesicles.

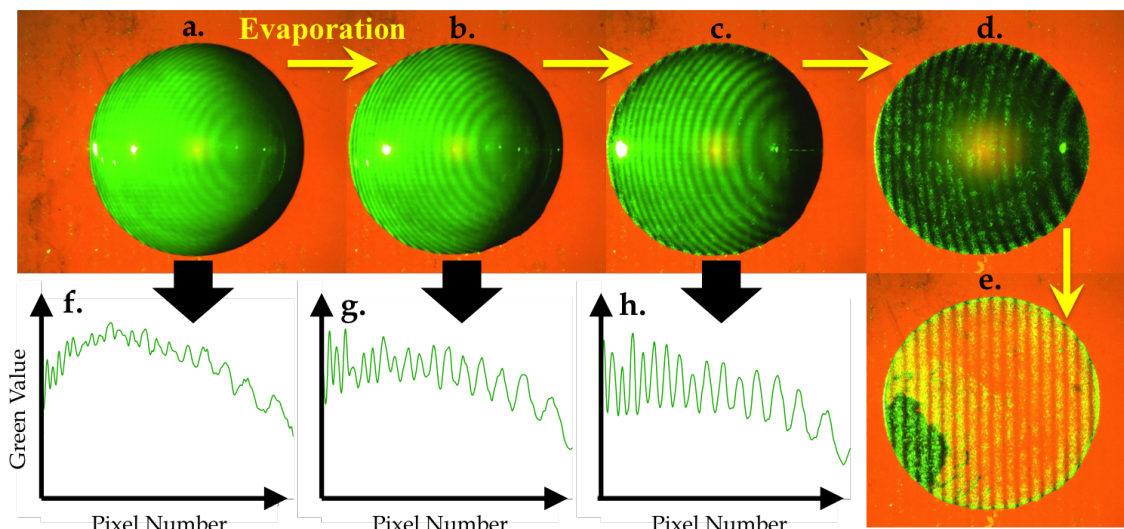


Figure 6.7: (a, b, c and d) Time-sequence photographs of an evaporating capillary-size sessile droplet of 63 nm gold spheres in water, with an initial concentration of $\sim 10^{11}$ particles/mL. Photo (e) shows the deposited particles after all liquid has evaporated. Plots (f, g and h) show the green colour channel of a line cross-section through each droplet photo above them. The banded pattern is most clearly reproduced in photo (c).

The optimal particle concentration is a function of scattering/absorption cross-sections and the incident light intensity. Gold nanospheres scatter stronger than nanorods, and so require a lower concentration (nanospheres: $\sim 10^{11}$ particles/mL (Figure 6.6), nanorods: $\sim 10^{11}$ particles/mL (Section 6.4.2)).

6.4.1.3 Particle Size

Microparticles are individually resolvable by the microscope, appearing as bright scattering points. This can be seen in the washed-out TiO_2 droplet of Figure 6.6a where there appears to be ‘noise’ or speckle in the droplet surface. Reducing the scatterer density to avoid washing-out the optical pattern leaves the pattern too speckled to resolve, as Figure 6.8 demonstrates with a low concentration TiO_2 slurry.

Nanoparticles cannot be individually resolved as easily, effectively giving a greater scattering resolution and a smoother, less speckled surface (e.g. compare the speckled TiO_2 droplet (Figure 6.6a) with the non-speckled nanoparticle droplet in Figure 6.7a). A gold nanoparticle solution is ideal, which is also convenient for CFA which typically assembles these particles.

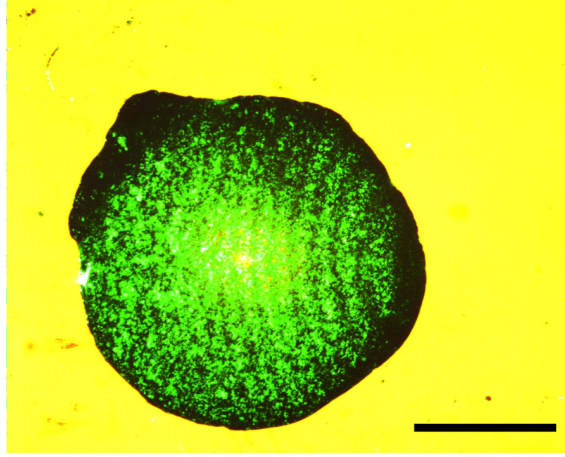


Figure 6.8: Image of a sessile droplet of TiO_2 slurry, diluted to reduce the scattering density so the pattern is not washed out. It is seen that the scatterers are too bright and sparse to render the pattern smoothly. The excessive speckling makes analysis for 3D scanning problematic. Scale bar is $900\ \mu\text{m}$.

6.4.2 The Surface Reconstruction Algorithm Applied to a Sessile Droplet

We now describe the process of reconstructing a sessile droplet. A sessile droplet is chosen as we can assess the reconstruction accuracy against a theoretical model.

Image Processing Prior to Reconstruction: Figure 6.9a presents the original scan image of a sessile droplet of 63 nm gold citrate-capped nanospheres on a SU8/Si substrate. Before the image can be analysed, artefacts must be manually removed. These include specular reflection (black arrow in the Figure) and highly scattering clusters that may confuse the fringe detection algorithm (encircled in pink).³

Detecting the Contact Line and Isolating the Liquid: The substrate does not scatter the projected light pattern, being either transparent (e.g. SU8, PMMA, PDMS, ITO) or reflective (e.g. Si). Thus in the image there is a scattering region (the meniscus) and a non-scattering region (the dry substrate), bordered by the contact line. The liquid is essentially black except for the green scattering pattern,

³Artefacts can be easily removed by touching up the image with an image ‘clone’ tool, being careful to not disturb the contours of the fringes. High-end graphics software like Adobe Photoshop have these tools in their standard tool palette, though Gimp (an open-source alternative to Photoshop) was used in this work.

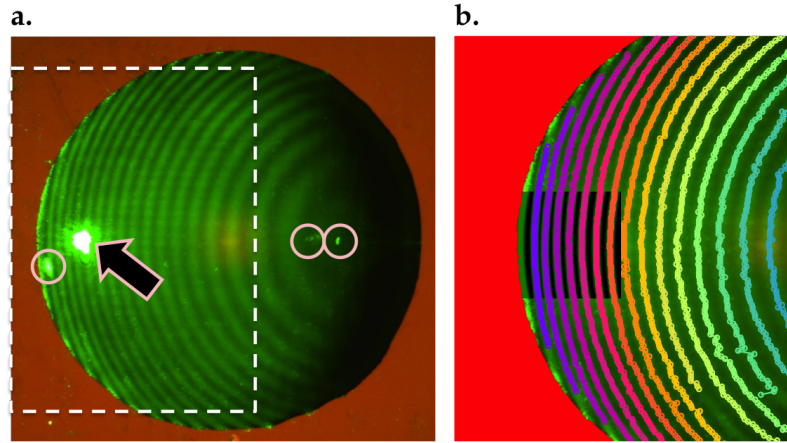


Figure 6.9: (a) An original scan image of a gold nanoparticle sessile droplet. Artefacts need to be manually removed: specular reflection (black arrow) and highly scattering clusters (pink circles). The droplet is 2.85 ± 0.02 mm in diameter. The white dashed line marks the region of interest (ROI) that will be reconstructed. (b) The ROI is shown after artefacts are removed and the image has been analysed to detect fringes (colour lines). Substrate colour has been red-enhanced to aid auto-detection of the contact line.

while the substrate has a strong red component. Analysing colour channels allows us to clearly isolate the contact line.

We begin by taking cross-sectional slices of the image perpendicular to the undistorted fringes (i.e. horizontal slices for the sample in Figure 6.9). Each slice (row of pixels) is separated into its red, green and blue colour components. Example slice colour profiles are shown in Figure 6.10a. The contact line correlates with the sharp change in red value.

Detecting Fringes: The fringe pattern is evident in the green profile (Figure 6.10b). A moving average filter removes noise, and the non-wetted region is masked by forcing it to zero. Fringe detection programmatically searches for local peaks and troughs in the signal,⁴ as shown in Figure 6.10b.

As a general rule, the peak closest to the contact line must be ignored, as it is not always clear whether that peak represents part of a fringe or a fringe centreline. Fringe centrelines are required for accurate 3D reconstruction. The resulting fringe map is shown in Figure 6.9b.

⁴A minimum peak-to-trough amplitude must be specified to avoid small false peaks.

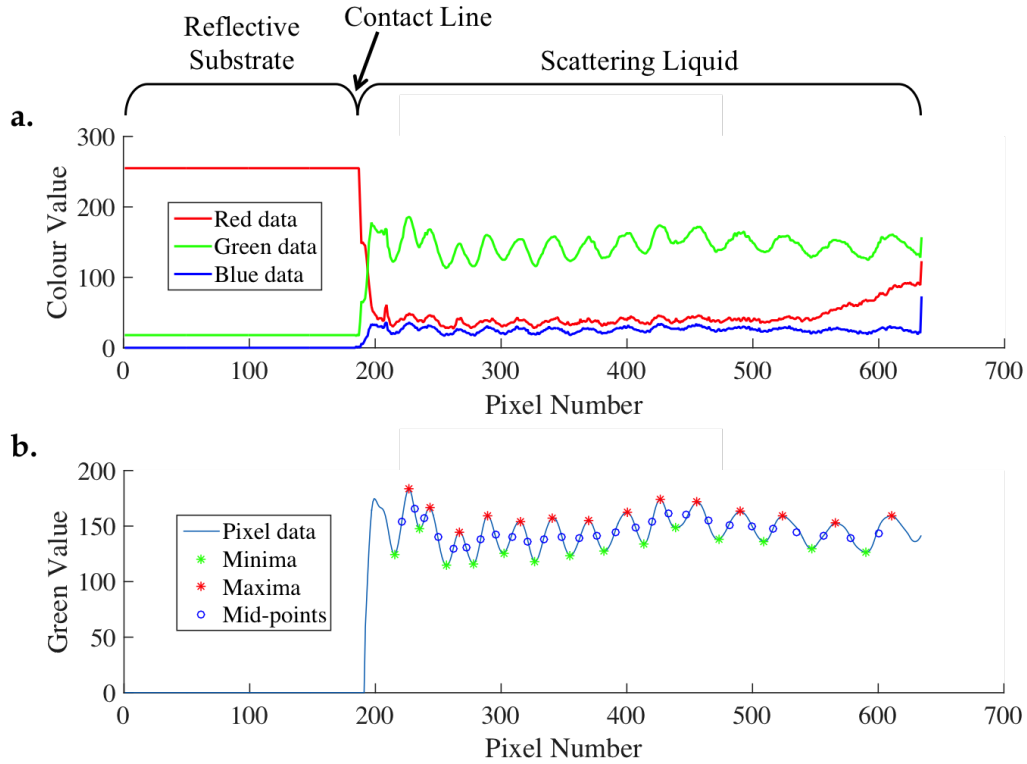


Figure 6.10: (a) The red-green-blue colour profiles from a slice of the scan image in the previous Figure. The sudden change in the red colour value denotes the position of the contact line. (b) The green profile data after smoothing (to remove noise) and masking (setting all non-liquid regions to zero). The fringe pattern is clearly seen in the oscillating profile, which has been analysed for the peaks and troughs as shown.

Combining FSM- and FDM-Analyses to Construct a 3D Surface: Constructing the meniscus is a four-step process, with outputs shown in Figure 6.11:

1. The fringe-deviation method is applied to determine the change in surface height along each fringe independently. The relative height between adjacent fringes is unknown at this point. The surface height data is shown in Figure 6.11a (called the FDM surface).
2. The fringe-spacing method is applied on one slice through the image that cuts across all fringes. This estimates the change in height from one fringe to the next, allowing each fringe to be positioned correctly in vertical space. The resulting surface is shown in Figure 6.11b (called the FDM_{HC} surface).
3. The fringe-spacing method is performed again, this time on all sampled points independent of the existing FDM_{HC}-surface (producing the FSM surface). Thus we have two independent surface maps, arrived at by independent recon-

struction methods. The two surfaces are correlated and averaged to produce the more complete surface in Figure 6.11c (called the $\text{FDM}_{\text{HC}} + \text{FSM}$ surface).

4. At this stage the bulk of the meniscus surface is complete, except for portions adjacent to the contact line. Since fringe centrelines cannot be reliably detected next to the contact line, there is an absence of sample points in that vicinity. The meniscus must be fitted to the contact line and interpolated over the missing points, producing the surface shown in Figure 6.11d, the final reconstruction.

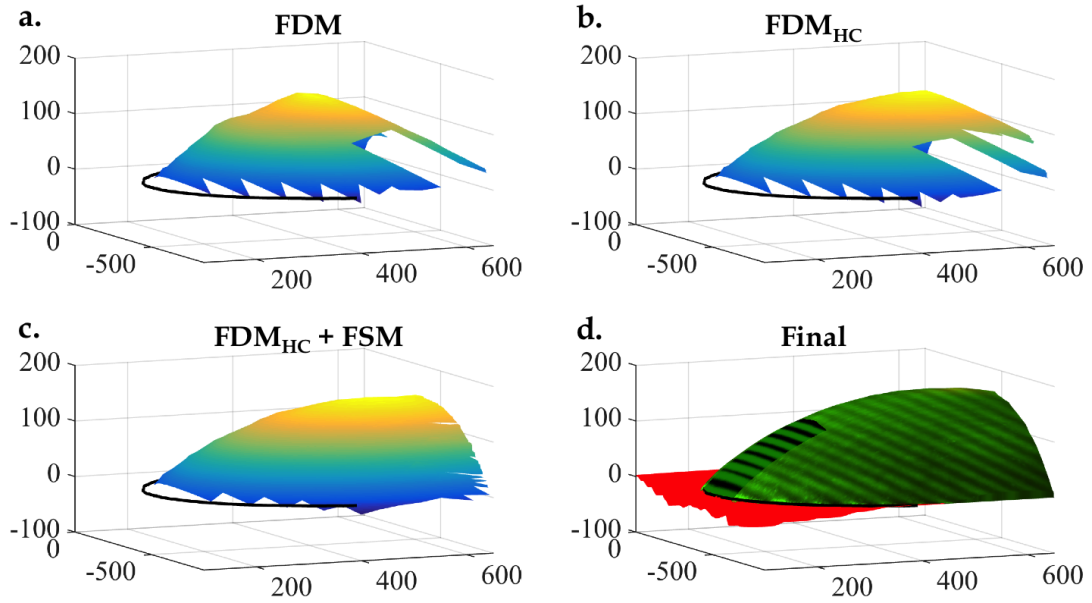


Figure 6.11: (a) The surface after FDM-analysis of each individual fringe. Surface colouring is based on height. (b) The FDM surface after height-correcting (HC) each fringe based on FSM-analysis of one image slice. (c) The surface after incorporating FSM data into the FDM_{HC} data for all sample points. (d) The surface after fitting and interpolating down to the contact line, and rendered with the original photograph. The curved black line in all plots is the contact line, as detected from the scan. All dimensions are in pixels.

Fitting the Meniscus to the Contact Line: Here we explain Step 4 in more detail, where the nearly-complete surface is interpolated down to the contact line. The interpolation function needs to be carefully chosen. Simple meniscus pertur-

bations decay exponentially [2–4],⁵ whereas an unperturbed meniscus more likely decays linearly over small distances. The choice of interpolation function depends on:

- The local shape of the contact line—perturbed/erratic (exponential interpolation) or unperturbed/smooth (linear interpolation)?
- Meniscus curvature in the vicinity—non-zero curvature (exponential interpolation) or near-zero curvature (linear interpolation)?
- Reconstructed surface noise—a linear function is more robust in a noisy environment

The present study uses linear interpolation at all points along the contact line (the contact line is smooth and the interpolation gap is small relative to the curvature of the meniscus).

Smoothing the Final Surface: It is usually advised to mathematically smooth the reconstructed meniscus after reconstruction. As explained in the next section, high-frequency noise is typical in the final surface. This can be eliminated by smoothing with a 2D moving average filter.⁶ Care must be taken when smoothing, so that true meniscus features are not distorted.

After smoothing, the final surface is as shown in Figure 6.11d and again in Figure 6.12, rendered with the scan image for greater realism and spatial dimensions converted to micrometers.

Summary: Figure 6.13 presents a flow chart summarising the algorithm. The above description is only an overview. For a detailed description the reader is referred to the Matlab code, which is replete with in-code comments.

Whilst snapshots of the 3D meniscus are of use, a greater suite of information is available when we take repetitive scans of the meniscus throughout a meaningful event, such as pinning and depinning from a cavity. Time-resolved data can be easily attained by recording a video of the liquid in the 3D scanning environment, and

⁵Kralchevsky et al. [3] cite a meniscus decay function described by a modified Bessel equation. This is an exponentially decaying function.

⁶The droplet shown above has been smoothed with 9 passes of a moving average filter of window size 5×5 pixels² ($14 \times 14 \mu\text{m}^2$).

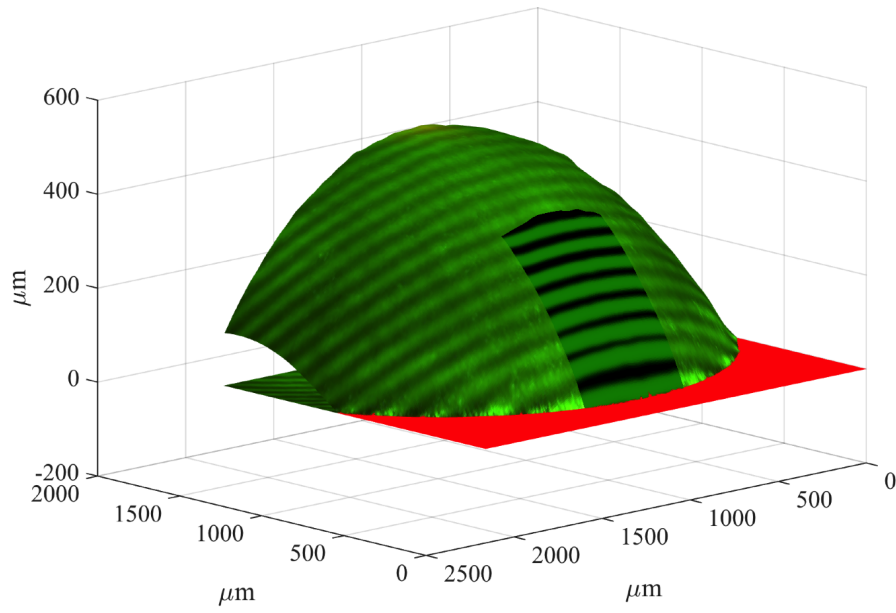


Figure 6.12: The reconstructed portion of a sessile droplet, rendered with the original scan image for realism.

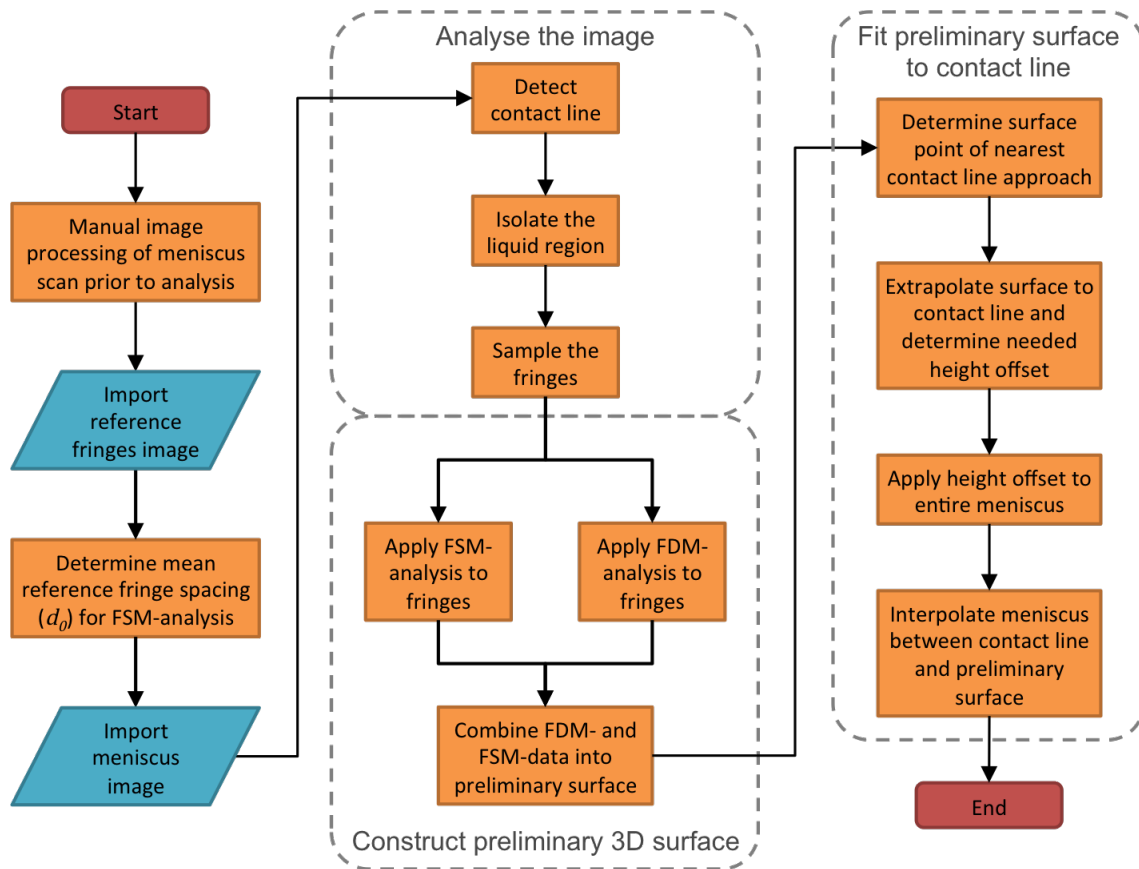


Figure 6.13: A flow chart summarising the 3D reconstruction algorithm.

then reconstructing meniscus surfaces from sequential video frames. This method is applied in the next two chapters to quantify pinning dynamics and estimate the development of local convective flows during assembly.

In the next sections we will assess the accuracy and limits of resolution in the reconstructed meniscus.

6.5 Assessing the Accuracy and Resolution of Reconstruction

Having demonstrated meniscus reconstruction, it is necessary to look at the source and impact of errors (Section 6.5.1) and to assess the accuracy of the reconstruction (Section 6.5.2). (Theoretical limits of scan resolution are in Appendix 6.D.)

6.5.1 Errors in Surface Reconstruction

The Source of Error: Since nanoparticles form the scattering medium, inhomogeneities in particle concentration give fringes a mottled appearance, confusing the detection of fringe centrelines (Figure 6.14). Noisy fringes translate to roughness in the reconstructed surface.⁷

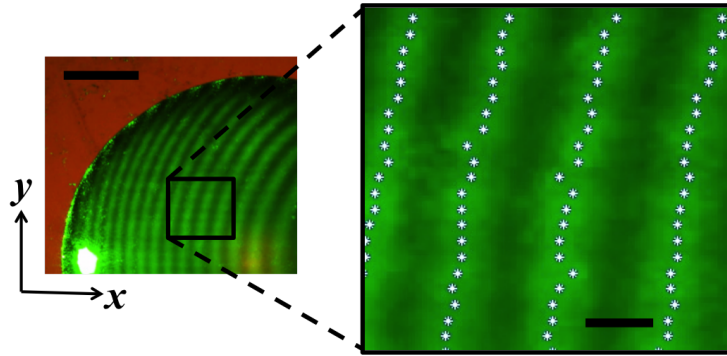


Figure 6.14: Close inspection of the liquid surface shows a mottled appearance, which causes the detected fringe centrelines (white markers) to be erratic and noisy compared to their ideal smooth paths. Scale bars are $450\ \mu\text{m}$ and $60\ \mu\text{m}$ for the left and right images, respectively.

⁷We can safely assume the camera resolution is sufficient to mitigate substantial errors from pixelation.

The Impact of Fringe Error: Working from Equation 6.1 (FSM-analysis), an error in fringe spacing (δd) is added into the equation:

$$h \pm \delta h = (d_0 - (d \pm \delta d)) \tan(\theta_p) \quad (6.15)$$

$$= (d_0 - d) \tan(\theta_p) \mp \delta d \tan(\theta_p) \quad (6.16)$$

This quantifies the error in height as

$$\delta h = \delta d \tan(\theta_p) \quad (6.17)$$

and is solely dependent on the angle of projection (θ_p). The same equation can be derived from FDM-analysis.

To characterise this error we return to the prior case study of a sessile droplet. For a droplet with a circular base, the fringes wrapping over the droplet surface ought to appear as elliptical contours when viewed from above. The raw fringe data is shown in Figure 6.15a, with an elliptical fit applied to each fringe separately. The elliptical fits are expected to very closely match what we would expect from ideal fringes.

The difference between the raw fringe data and the elliptical fits is shown by the probability density function (PDF) in Figure 6.15b. Applying Equation 6.17 to the envelope of the PDF yields the magnitude of noise in the reconstructed surface, shown in Figure 6.15c. The projection angle makes a noticeable difference in the probability of error in the surface.

Reducing the Error: As would be expected, the error can be lessened by smoothing either the reconstructed surface or the fringes prior to reconstruction. The smoothing function⁸ removes much of the high frequency noise without altering the broader surface contours. The PDF in Figure 6.15d shows the fringe spacing error after smoothing with noticeably more clustering around zero. The PDF of the noise distribution in the resulting surface is improved approximately by a factor of two (Figure 6.15e). Smoothing the output is a straightforward way to substantially reduce the impact of scatterer inhomogeneity.

A Note on Generalising the Error PDFs: Note that the error PDFs in Figure 6.15 are strongly tied to the fringe spacing. Tighter fringes means more sharply

⁸Nine passes of a moving average filter of window size 5×5 pixels

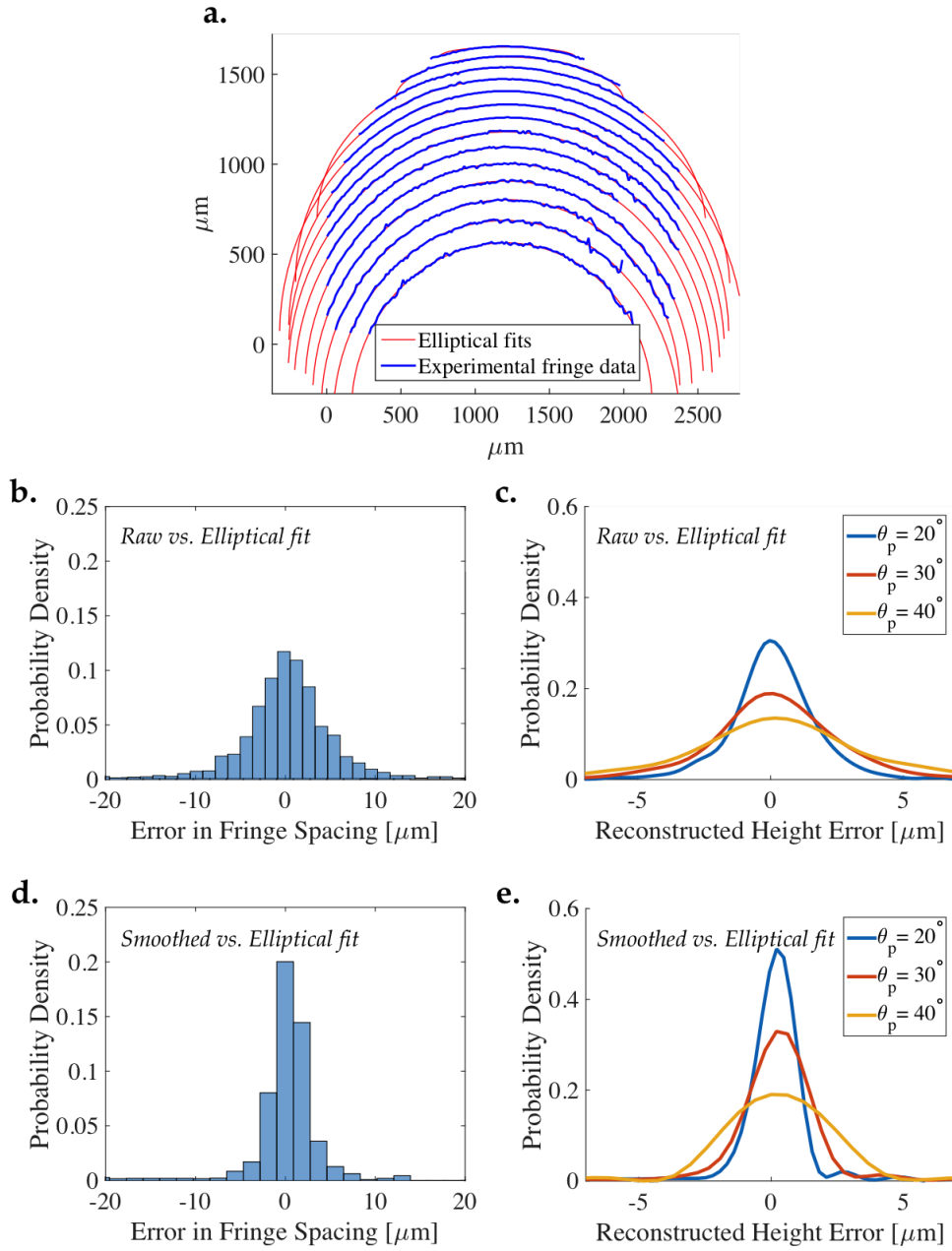


Figure 6.15: (a) The raw fringe data with elliptical fits applied to each fringe. (b) A probability density histogram of fringe error relative to the elliptical fits. (c) The resulting error in reconstructed surface height, based on the the error histogram and projection angle (θ_p). Plots (d) and (e) are akin to plots (b) and (c) after smoothing the fringe data with 9 passes of a moving average filter to remove high frequency noise. The elliptical fits were recalculated after smoothing.

defined fringes, and this narrows the PDF of fringe error. In general, if the fringe spacing is halved (leading to a higher resolution scan), the PDF of fringe error is expected to halve in its width, and the resulting error in surface height will likewise halve. The widths of the PDFs in μm therefore apply to this specific case study and are not indicative of the error magnitude in all experiments.

6.5.2 Assessing Sessile Droplet Reconstruction Accuracy

With the above introductory treatment of error, we will now assess reconstruction accuracy by comparison with the theoretical surface.

The Theoretical Surface: The theoretical droplet shape is an oblate spheroid.⁹ To calculate the theoretical droplet shape we require three measurements: the droplet radius, the droplet height and the mean contact angle.

The droplet radius ($r = 1254 \mu\text{m}$) is obtained from the circle of best fit to the contact line in the region of interest (ROI). (Note: the droplet base is not perfectly circular, and the radius of best fit in the ROI is 4.7 % different from the radius of best fit of the full droplet. This discrepancy is minor but will impact on our error analysis later.)

The droplet height must be estimated from the reconstruction itself ($h = 465 \pm 5 \mu\text{m}$). This is the only parameter that is dependent on the reconstructed surface, so the theoretical surface is still taken to be calculated largely independent of the reconstruction. A good fit between theoretical and reconstructed surfaces in other aspects will confirm this.

The mean contact angle is obtained from independent contact angle measurements of sessile water droplets on SU8. The angle ($\theta = 48.5^\circ \pm 0.2^\circ$) is taken at the equivalent time during the evaporation process as is the droplet we are reconstructing.¹⁰

⁹The droplet size (2.86 mm) is larger than the capillary length of water, so gravity flattens the droplet slightly from a spherical cap. An oblate spheroid is an ellipsoid with its two horizontal axes of equal length. Think of it as a sphere that has been squashed vertically.

¹⁰This is the measured contact angle at 6 minutes and 35 seconds after droplet placement on the substrate, which is the same time at which the scan used in the reconstruction was taken. In both cases it is before the contact line begins receding, so the contact angles ought to correlate between the two scenarios. The substrate temperature in both cases was the same range above

The horizontal and vertical axes lengths of the oblate spheroid are calculated as

$$l_{horiz} = \frac{r(s-h)}{\sqrt{s(s-2h)}} \quad (6.18)$$

$$l_{vert} = \frac{h(s-h)}{s-2h} \quad (6.19)$$

where,

$$s = r \tan(\theta) \quad (6.20)$$

The z offset to position the spheroid to match the height of the droplet is

$$z = \frac{h^2}{s-2h} \quad (6.21)$$

Figure 6.16 shows the full oblate spheroid surface.

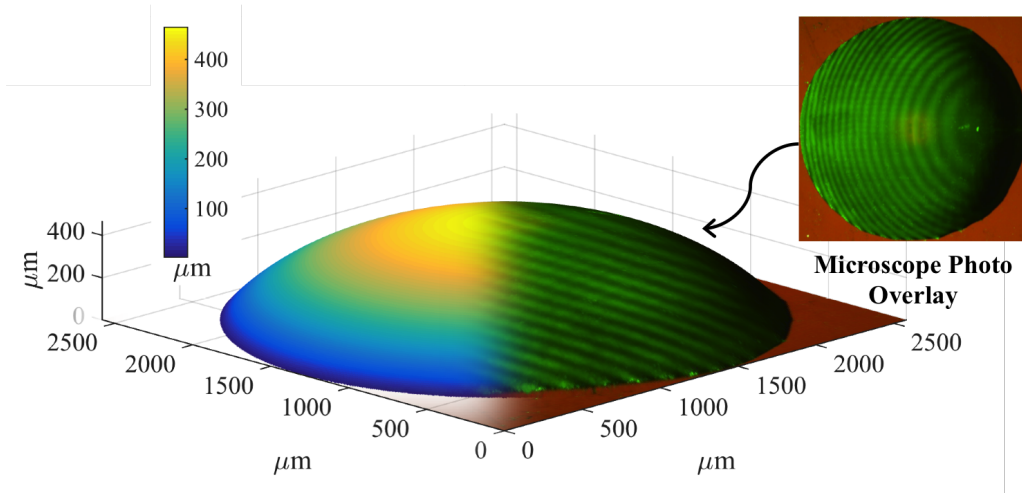


Figure 6.16: The theoretical sessile droplet surface modelled as an oblate spheroid. The left half is rendered by height, the right half is overlaid with the original scan to demonstrate its coordination with the photo.

Comparing the Theoretical and Reconstructed Surfaces: The theoretical and reconstructed surfaces in the ROI are plotted together in Figure 6.17. A very good match is seen by eye, but it's necessary to quantify the differences.

Figure 6.18 shows the difference in height between the two surfaces, as projected onto the horizontal plane. Since the difference in μm would scale with the size of the droplet, the difference is given as a percentage of the droplet height to obtain a

the dew point temperature.

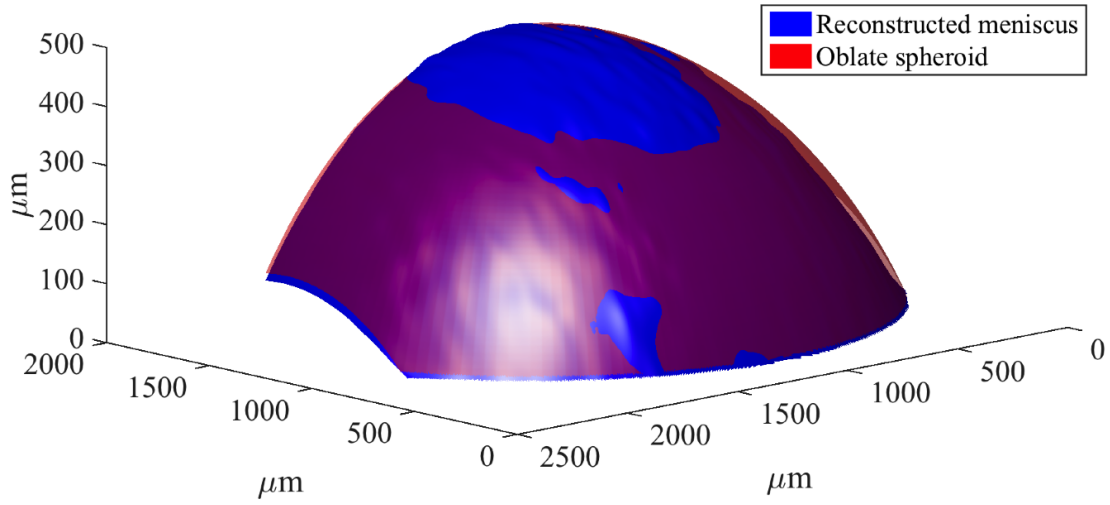


Figure 6.17: The theoretical and reconstructed sessile droplet surfaces plotted together in the ROI. A good fit is evident, with minor discrepancies. (See Figure 6.12 for a realistic-looking image of the reconstructed surface used here.)

more generalised characterisation. Half the reconstructed surface fits the theoretical surface to within 2 % of the droplet size, and most of it fits to within 5 %. The greatest deviation is around 10 %. These deviations may be from two sources: (1) inaccuracy in the reconstruction, and (2) inaccuracy in the theoretical surface.

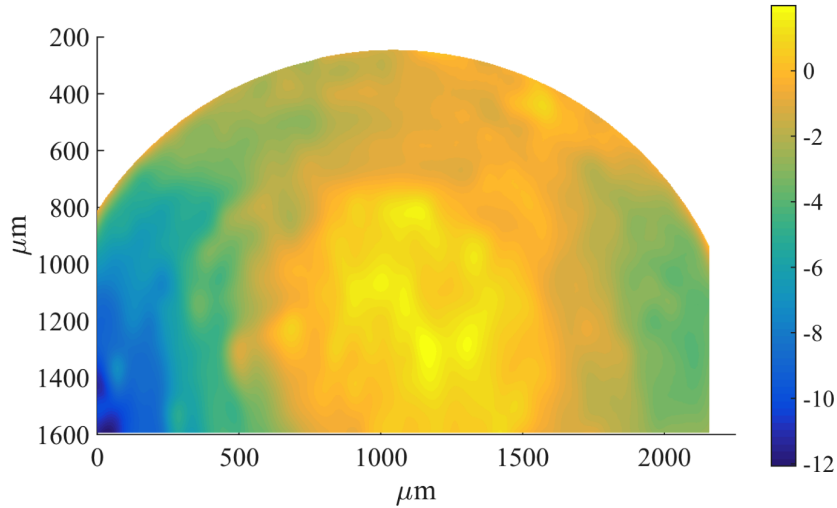


Figure 6.18: The difference in height between the theoretical and reconstructed sessile droplet surfaces, plotted as a percentage of droplet height. The contact line is the circular top edge of the shape. The theoretical surface is taken as the reference surface.

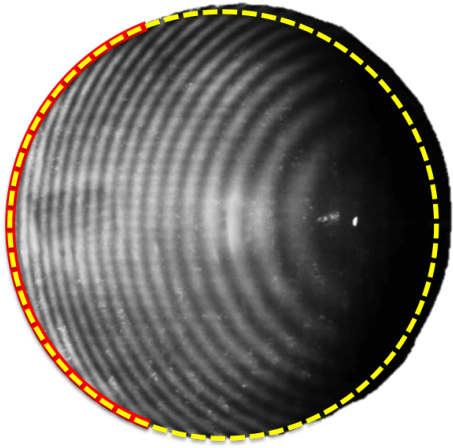


Figure 6.19: The circular fit (yellow line) to the contact line in the ROI (red line), from which the theoretical droplet surface is calculated, does not properly match the whole droplet dimensions, as the droplet base is not precisely circular.

Considering the accuracy of the theoretical surface, note that it presumes a perfectly circular droplet base. This is not the case (see Figure 6.19) and the theoretical surface is therefore expected to increasingly diverge from the true droplet surface towards the edges of the ROI. This likely accounts for the increasing alleged errors approaching the left and right ROI boundaries.

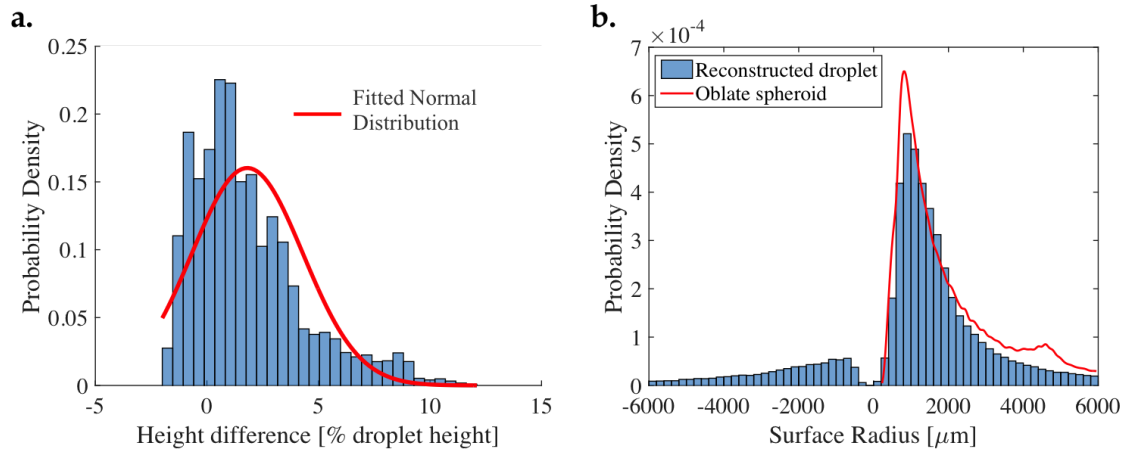


Figure 6.20: (a) The probability density histogram of the difference between the theoretical and reconstructed droplet surfaces. It can be approximately described by a normal distribution. (b) The probability density histogram (or envelope) of the radius of curvature of the theoretical and reconstructed surfaces. The negative radii of curvature represent roughness in the reconstructed surface.

Considering the accuracy of reconstruction, the mottled appearance of Figure 6.18 reveals that the reconstructed surface has roughness. Neither the theoretical or true droplets have any roughness, leaving roughness as indicative of reconstruction errors. Figure 6.20a plots a histogram of the height difference, with a mean close to

zero and a 2σ interval (95 % confidence) of ± 5 %.¹¹ This is taken to quantify the magnitude of surface roughness to be no greater than a few percent of the surface height. Errors larger than 5 % are concentrated at the edges of the ROI, and so are suspected to be from the growing mismatch there between the theoretical and true droplet surfaces, not necessarily due to reconstruction error.

Having quantified the magnitude of error, it is worth quantifying its prevalence. Errors may be within a few percent of the droplet height, but how common are such errors? For this we refer to Figure 6.20b. The histogram of the reconstructed surface radii has a very good match with an oblate spheroid, except for the presence of the negative surface radii.¹² The negative radii of curvature reflect the roughness, and based on their probability density integral they constitute no more than 15 % of the data.¹³ It is therefore determined that roughness after smoothing does not appreciably deviate the surface from its correct form.

To summarise, the larger discrepancies (>5 %) near the ROI boundaries are likely due to the theoretical shape not matching the true droplet shape. The smaller discrepancies (<5 %) are likely the true reconstruction error, exhibited as surface roughness. We hence conclude that the reconstruction can be accepted with a high degree of certainty, often to within 2 % of the full meniscus height, and up to 5 %.

That completes our description and analysis of the meniscus profilometry method. To conclude this chapter we examine methods to extract thermodynamic information, which are relied upon in later chapters.

6.6 Thermodynamic Information from Meniscus Reconstructions During CFA

In this concluding section we present the theory and modelling to take the study of pinning events far beyond meniscus geometry. Evaporative information is par-

¹¹The validity of this confidence interval depends on the data being approximated by a normal distribution, which the fitted normal distribution shows to be sufficiently true.

¹²Negative surface radii don't exist for a smooth ellipsoid.

¹³Note that this is after the surface has been smoothed. With half as much smoothing the proportion of negative surface radii increases to 27 %. Smoothing is therefore important and effective.

ticularly pertinent to pinning dynamics. Here we show how this and other thermodynamic information can be extracted from the 3D meniscus. This section therefore examples the greater experimental potential of this meniscus profilometry method.

6.6.1 Sample 3D Form of a CFA Meniscus

The algorithm has been demonstrated on a sessile droplet, but we can theoretically apply the method to nearly any meniscus shape. Figure 6.21 shows the reconstruction of a CFA meniscus pinned on a $500 \times 500 \mu\text{m}^2$ cavity in 50 nm of SU8 on Si.¹⁴ A small region of this reconstruction around the pinned feature will be the focus of the rest of this chapter.

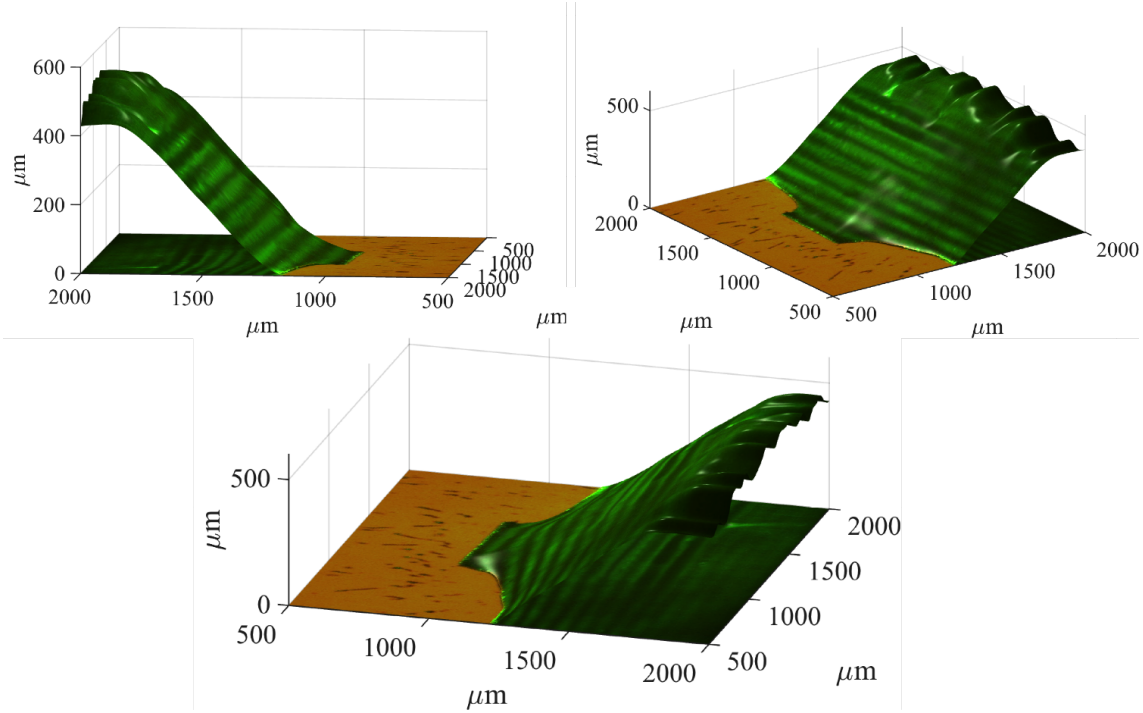


Figure 6.21: An example meniscus reconstruction of a pinned meniscus, shown from various angles. Geometrically analysing the meniscus, particularly in a time-resolved fashion, can yield helpful information about the liquid/thermo- dynamics that are in operation.

¹⁴The scattering medium is deionised water bearing gold nanorods ($44 \text{ nm} \times 107 \text{ nm}$, $\sim 10^{11}$ particles/mL) capped with sodium polystyrene sulfonate (Na-PSS, 70 kDa) ligands.

6.6.2 Liquid Dynamics: Instantaneous Laplace Pressure

Laplace pressure (or interfacial pressure) is the jump in pressure that exists across a liquid-gas interface. It is defined by the surface tension and the curvature of the interface as

$$\Delta p = 2\gamma H \quad (6.22)$$

where γ is the liquid-gas surface tension (0.072 N/m for water) and H is the mean surface curvature. The mean curvature of the surface $S = f(x, y)$ can be calculated according to

$$H = \nabla \cdot \left(\frac{\nabla S}{\sqrt{1 + |\nabla S|^2}} \right) \quad (6.23)$$

$$= \frac{\left(1 + \left(\frac{\partial S}{\partial x}\right)^2\right) \frac{\partial^2 S}{\partial y^2} + \left(1 + \left(\frac{\partial S}{\partial y}\right)^2\right) \frac{\partial^2 S}{\partial x^2} - 2 \frac{\partial S}{\partial x} \frac{\partial S}{\partial y} \frac{\partial^2 S}{\partial x \partial y}}{\left(1 + \left(\frac{\partial S}{\partial x}\right)^2 + \left(\frac{\partial S}{\partial y}\right)^2\right)^{3/2}} \quad (6.24)$$

In Figure 6.22 the portion of the meniscus that is pinned over the cavity is shown, and it is coloured by the Laplace pressure, in units of Pascals (Pa). The variation in Laplace pressure is extremely small, with a minimum far above the tensile strength threshold of water (which is below -100 MPa [5, 6]). This implies that the distorted meniscus is in no way threatened by spontaneous rupturing due to negative pressure build up. (Much of the variation in pressure is expected to be an artefact of persistent roughness in the reconstructed surface)

6.6.3 Wetting Dynamics: Instantaneous Surface and Contact Angles

Wetting dynamics are often contained in surface/contact angle information. To that end, if we define the vector normal to the surface as $\mathbf{n}$, then the angle of the surface (relative to horizontal) at any point on the surface is given by

$$\theta_s = \cos^{-1} \left(\frac{\mathbf{n}_z}{|\mathbf{n}|} \right) \quad (6.25)$$

where the z subscript refers to the z -axis component. Figure 6.23 shows the reconstructed meniscus coloured by surface angle in degrees.

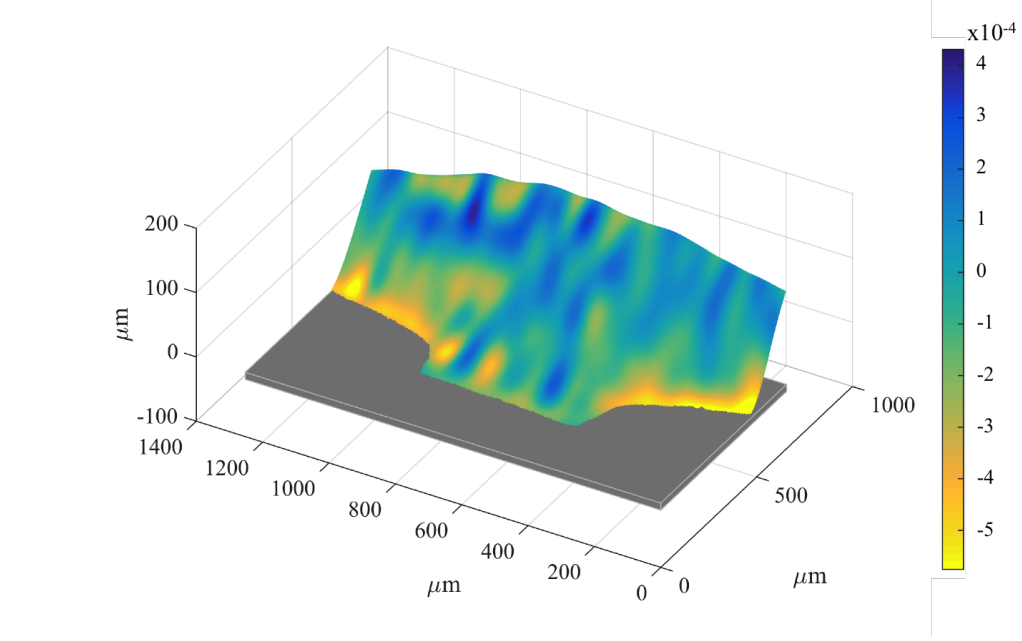


Figure 6.22: A meniscus reconstruction coloured by Laplace pressure (Pa). The grey plane is the substrate.

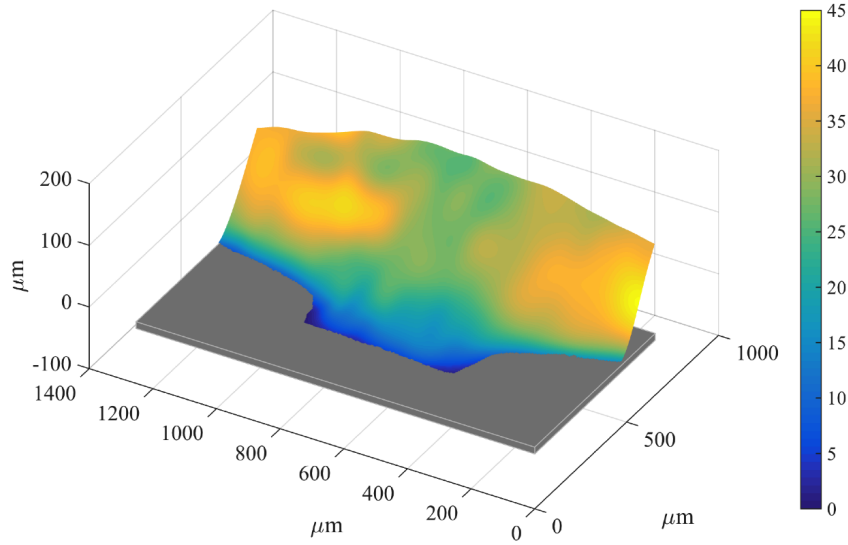


Figure 6.23: A meniscus reconstruction coloured by surface angle (degrees).

It is apparent that the surface angle approaches zero in the pinned corners. We can extract the surface angle as we traverse the contact line to yield the contact angle (Figure 6.24a). Figures 6.24b and 6.24c show correlations between the contact angle and (1) the meniscus geometry, and (2) the amount of nanoparticle deposition, respectively.

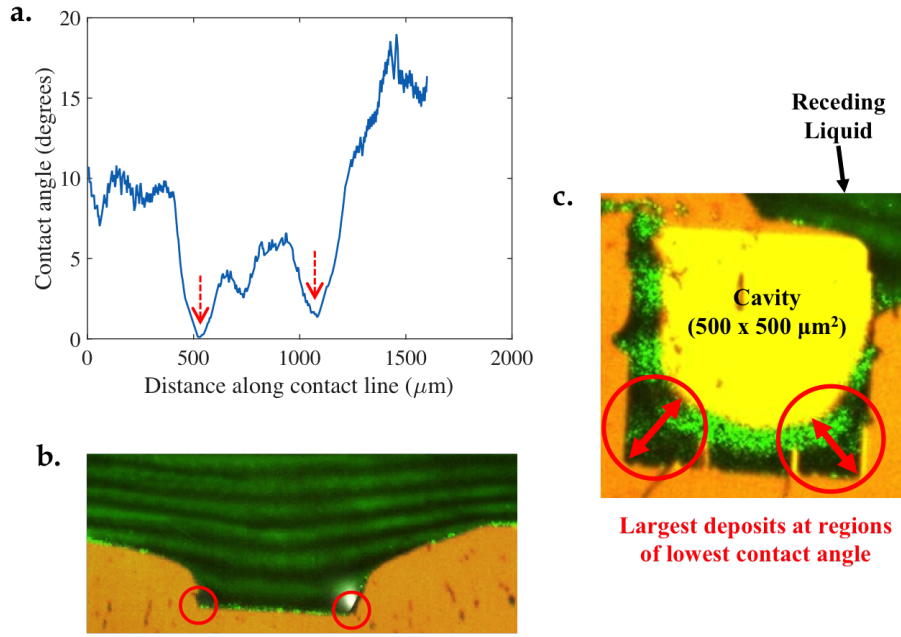


Figure 6.24: (a) A plot of the meniscus contact angle (degrees) derived from the 3D reconstruction. The points of lowest contact angle (red arrows) correlate with the pinned corners of the meniscus in (b). In (c) we observe that the amount of nanoparticle deposition correlates well with the contact angle profile in (a).

Figure 6.24 suggests that a thin film forms as the meniscus pins on the cavity. The near-zero contact angle around the pinned edge implies a region of strong evaporation. This would lead to stronger nanoparticle deposition, which is attested to in Figure 6.24c. The heavy deposition is anticipated to be solely due to local convective flows. This conforms well to the pinned-convective model and is explored more in Chapter 8.

6.6.4 Evaporative Dynamics: Evaporation Rate, Surface Temperature, Thermal Marangoni Flows and Convective Flow Patterns

The final type of thermodynamic information to demonstrate from 3D profilometry is evaporative dynamics. This will directly yield surface temperature, evaporation rates, and thermally-mediated surface tension, with convective flow patterns to be inferred from these.

Evaporation of small liquid bodies in the absence of forced air flows is a vapour

diffusion-limited process. The atmosphere at the liquid interface quickly reaches its saturation vapour concentration, and the ability for evaporation to continue is then metered by the rate at which vapour can diffuse away from the liquid body into the ambient environment.

The dynamics of evaporation constitutes a complex phenomenon involving a feedback loop between surface temperature, evaporative cooling and saturation vapour concentration (which varies with surface temperature), all combining to establish the evaporation rate. A partial differential equation (PDE) model to numerically solve evaporative dynamics emerged in 2015 [7, 8]. The equations are equivalent to an electrostatics problem, allowing for straightforward implementation in PDE-solving software like COMSOL.

The power of this set of PDEs is that they inherently incorporate the thermodynamic feedback loops by unifying all the relevant properties into a universal equivalent temperature field. The cited papers apply the model successfully to spherically-capped sessile droplets. In this thesis we apply it to a pinned CFA meniscus. Further explanation can be found in Appendix 6.E. To solve for CFA evaporation rates, the slider-CFA apparatus is modelled in COMSOL with the reconstructed 3D meniscus and suitable atmospheric conditions. Appendix 6.F details the COMSOL implementation.

The following data can be derived from the evaporative model:

- Atmospheric vapour concentration distribution
- Temperature distributions in the substrate, liquid and slider (including all surface temperatures)
- Evaporation rates across the liquid surface

From these one can also derive the thermally-modified interfacial surface tension. According to the Eötvös rule the surface tension of pure water within 0 to 100 °C scales with temperature by

$$\gamma = 0.07275(1 - 0.002(T_K - 291)) \quad (6.26)$$

where T_K is the temperature in Kelvin. This yields important information about the direction and relative intensity of thermal Marangoni flows.

Figure 6.25 demonstrates some of the data output from this model applied to the pinned meniscus in a full slider-CFA environment (though only a small region

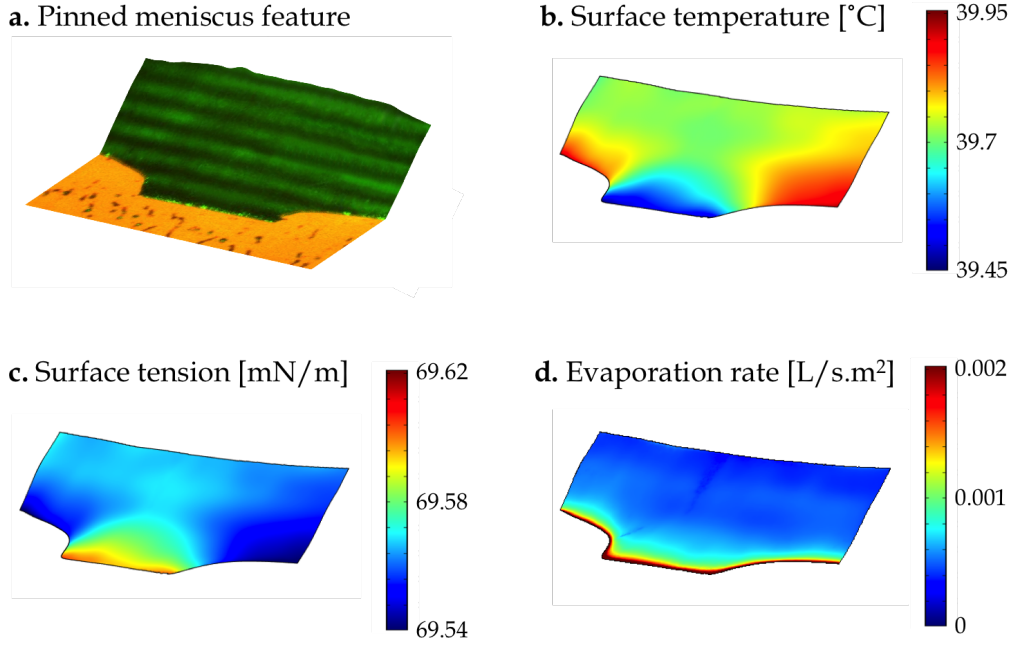


Figure 6.25: Example plots of evaporative dynamics derived from numerical modelling based on the 3D reconstruction. Figure (a) shows the region of interest of the original meniscus reconstruction (a meniscus part way through a pinning event). Remaining figures show thermodynamic data on that portion of the meniscus (a full CFA context was modelled, not shown here). The substrate in these simulations is $300\text{ }\mu\text{m}$ of PMMA on Si, with a base Si temperature of $42\text{ }^{\circ}\text{C}$.

of interest is shown in the Figure). With information like that above we will seek to learn about convective dynamics during pinning.

6.6.5 Application to Nano-CFA

The profilometry method has been demonstrated on the microscale. We must use scaling laws to apply it in the nano regime. This is acceptable if the same forces apply. Section 1.4.2 shows that pinning dynamics scale down to the nanoscale, with an emphasis on surface tension as the dominating force. Surface tension scales linearly with distance, making our application to nano-CFA straightforward. It will be twice confirmed in Sections 7.5 and 8.3.7 that surface tension is indeed the governing force, verifying that linearly scaling microscale meniscus structure into the nano-regime is warranted.

6.7 Conclusions

To explain meniscus dynamics in nano-CFA, it is imperative that we know the liquid's behaviour as it pins and depins from a cavity. To that end, this chapter and its appendices explain a new and powerful method for 4D meniscus profilometry. The method is highly versatile, being able to scan a wide variety of meniscus morphologies, resolving microscale features with ease.

By projecting the interferometric pattern onto the liquid surface, and with a suitable choice of liquid (a plasmonic nanoparticle solution), the structured light pattern is rendered and its appearance is inverse-mapped to yield the 3D form of the meniscus. This can be repeated at a sufficiently high scan rate to enable time-sequenced meniscus reconstructions throughout a meniscus pinning event. The algorithm to reconstruct the meniscus form has been presented, along with a case study to assess reconstruction accuracy.

Closing off this chapter we brought the discussion back to the central goal of gleanig vital information about nano-CFA dynamics. Methods to extract vital thermodynamic information have been presented. In the coming two chapters we use these methods to quantify pinned-convective dynamics.

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Appendices

<i>A Survey of Existing Meniscus Profilometry Methods ...</i>	<i>Appendix 6.A</i>
<i>Interferometer Design for Micro-4D Scanning ...</i>	<i>Appendix 6.B</i>
<i>Derivation of Equations for the Interferometer in Appendix 6.B ...</i>	<i>Appendix 6.C</i>
<i>A Partial Differential Equation Model for Evaporation ...</i>	<i>Appendix 6.D</i>
<i>Evaporative Model Implementation in COMSOL ...</i>	<i>Appendix 6.E</i>

Appendix 6.A A Survey of Existing Meniscus Profilometry Methods

Section 6.2 of the main text detailed the requirements for meniscus profilometry. Reasons are given below as to why meniscus profiling techniques are unsuitable for the present task.

Electrical Conductance Methods

Liquid has a measurable conductance, which can be used to infer liquid depth. Some electrical conductance methods are only workable with flat films. More versatile methods are intrusive (and so distort the meniscus we're seeking to map micro defects in) and they are slow, noisy, and have low resolution (minimum 2 μm resolution) [1, 2]. A slight variation on electrical conductance methods is to measure the capacitance of the liquid [3], but this too works only for flat films.

Laser-Induced Fluorescence

By loading a fluid with a fluorescent dye, the power of the fluorescing signal is theoretically dependent on the number of dye molecules in the light path [4, 5]. Fluorescence intensity can be translated into liquid depth. This technique has low resolution ($10\text{ }\mu\text{m}$), but more notably assumes relatively uniform dye concentration. This cannot be assumed in nano-CFA which is highly convective, and where particle concentration rapidly varies. It also works best on flat films, not meniscus regions with highly variable gradients, as in CFA. A slight variation on this approach is to measure the absorption of light passing through the liquid [6, 7]. This can reportedly have a sensitivity of just $5\text{ }\mu\text{m}$, but it suffers from similar issues above.

Interferometry

Interferometric techniques use the reflectance of the upper and lower liquid interfaces to generate overlapping phase-shifted beams [8, 9]. The phase shift depends on the path length, which is most notably affected by the liquid depth. This technique is used often to measure thin films, and it has been used to study meniscus profiles during pinning and rupturing events [10]. Interferometric techniques have high resolution, but they are limited to thin films (only several μm thick) and films with very shallow surface gradients. Refraction blurs the interference pattern when these conditions are not met, as in Figure 6.26. Indeed, fringes are rarely seen in CFA.

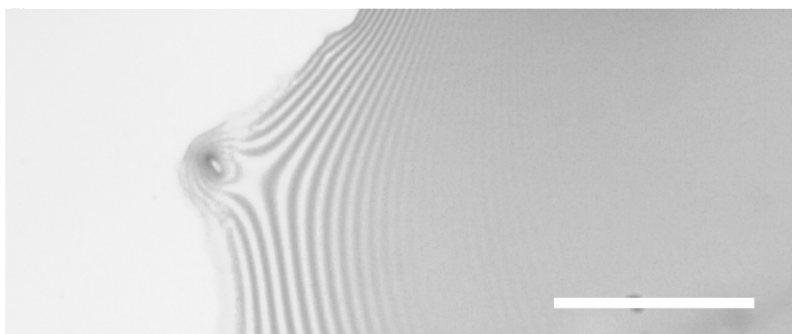


Figure 6.26: Micrograph of interference fringes emerging in an evaporating thin liquid film. The fringes blur out and disappear then the thickness becomes too large. Scale bar is $900\text{ }\mu\text{m}$.

Two variations employed to study evaporating droplet profiles [11, 12] don't

share these limitations, but their microscopy setups do not interface well with a CFA apparatus or a standard microscope platform. One method also requires a transparent substrate which is often not practical for nano-CFA.

External/Internal Reflection of Light

By utilising the reflectance of a liquid-gas interface, the surface slope and liquid depth at a test point can be obtained by analysing the direction of externally reflected light [13]. The current resolution ($10\text{ }\mu\text{m}$) is low, it measures only a single test point (unsuitable for dynamic studies like CFA), and it does not interface well with a CFA microscopy platform. Total internal reflection (TIR) of light has also been used to derive depth and surface gradient information simultaneously [3, 14, 15]. It is limited to transparent substrates and a narrow range of liquid surface gradients.

Summary

Existing meniscus profiling methods are restricted to either thin films, thick films, low surface angles, no contact line or static meniscus shapes. To reliably profile CFA menisci, it is therefore necessary to develop a new profilometry technique. The profiling method detailed in this chapter allows rapid time-resolved reconstruction of a nearly *arbitrarily* shaped liquid body over a wide area with micrometer resolution.

Appendix 6.B Interferometer Design for Micro-4D Scanning

A novel optical interferometer is integral to the present profilometry method. In this Appendix, the interferometer is described and modelled to understand its capabilities and its limitations. The interference pattern projected onto the microscope stage matches excellently with the results from modelling. We close this section with a discussion about optimising the interference pattern for high-resolution 3D scanning.

The Optical Setup

The most reliable way to generate a closely-spaced pattern of bright and dark regions is by optical interference (interferometry). When a steadily increasing phase shift is applied to a beam of light relative to a reference beam, the superposition of the two beams oscillates between constructive and destructive interference, thus creating bright and dark fringes when imaged. Depending on the setup, bright and dark fringes are often either straight parallel bands or concentric rings. For the ease of inverse-mapping the pattern, parallel bands is chosen.

To create a high-contrast interference pattern it is necessary to use a narrow range of illuminating wavelengths. Due to the additional need for *visible* microscopy, a 532 nm continuous wave laser is used as the light source (500 mW, diode-pumped solid state laser, Shanghai Dream Lasers, Model: SDL-532-DL-150T). The laser is passed through a beam expander to create a full beam waist of 2.5 cm. A wide beam waist is beneficial for generating the interference pattern, as explained below. From there the beam passes through a series of mirrors so that it is directed vertically downwards onto the interference pattern generating apparatus, which lies next to the microscope stage.

General Requirements

There are many interferometers in existence,¹⁵ and whilst they share the same core principles of inducing a phase shift between two overlapping beams, each is nonethe-

¹⁵For example, see: https://en.wikipedia.org/wiki/List_of_types_of_interferometers

less designed for a particular purpose (be it for microscopy, quantum cryptography, measuring light wavelengths, or measuring the flatness of an optical surface, to name but a few applications). The present interferometry method is likewise designed according to the application at hand, bearing the following requirements:

1. The interference pattern ought to be uniform and regular over the microscope's field of view, otherwise the inverse-mapping algorithm rapidly grows in complexity. This precludes a variety of interferometers producing non-uniform or non-linear fringes.
2. The pattern will be projected beneath the microscope objective onto the stage at an acute angle. Different positions on the stage will therefore be different distances from the light source. To ensure the stage portrays a uniform pattern the pattern's dimensions must not vary with distance from the source.
3. The pattern repetition should be on the scale of tens of micrometers for sufficient 3D scanning resolution. This typically precludes interferometers that do not allow very fine setting of the interference parameters.
4. The pattern must have strong contrast over the entire field of view. This precludes interferometers producing fringes whose brightness quickly decays with distance from a central constructive interference peak.
5. The interferometer must not interfere with operation of the microscope or the CFA apparatus on the stage.
6. It is desirable that the interference pattern have easily adjustable dimensions, so it can be set according to the scale of the meniscus features we wish to resolve. This precludes interferometers that use unadjustable elements.

The Optical Interference Apparatus

Parallel bands of bright and dark fringes are well-known in interference studies. Newton interferometry provides a useful starting point, whereby a partial mirror (or a glass flat) is placed at an angle on top of a flat mirror, as shown in Figure 6.27a. The full mirror is a standard circular optical mirror of 2.5 cm in diameter. Due to the large size needed for the partial mirror, it was made by sputtering 7.3 nm of

silver onto a glass microscope slide.¹⁶

Description of the Interferometer

The interferometry method uses the Newton interference apparatus (Figure 6.27b) but operates in a substantially different manner to Newton interferometry. When illuminated by a vertical beam of collimated light, the smoothly varying distance between the two mirrors forms an angular spread of multiple reflected beams. If the incident light is properly perpendicular to the plane of the base mirror, then the primary beam ($n = 0$) will emanate out vertically along the path of incidence. Additional beams ($n = 1, 2, 3, \dots$) will propagate at increasing angles from the primary beam. The beams vary in intensity with the primary beam being the most intense, and each subsequent beam having a reduced intensity. The exiting angles of the beams are:

$$\theta_n = \frac{\pi}{2} - 2n\theta_m, \text{ where } n = 0, 1, 2, \dots \quad (6.27)$$

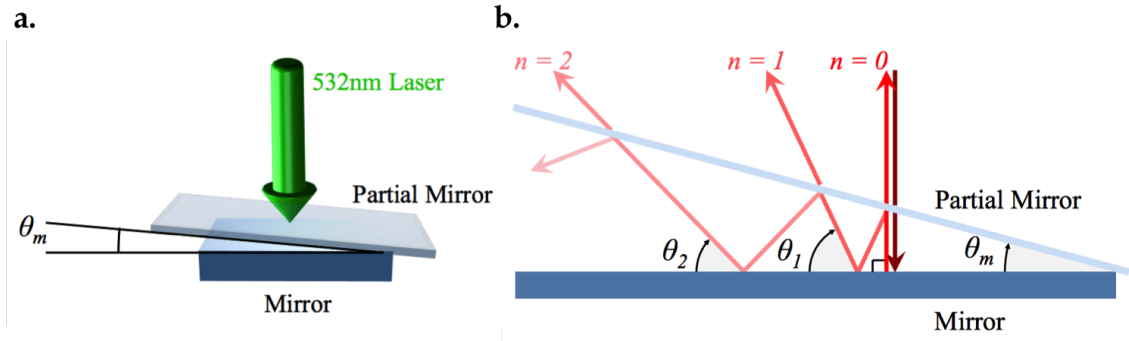


Figure 6.27: (a) The planar Newton interference setup involves a partial-mirror atop a full mirror at an angle, θ_m . (b) In contrast to the textbook Newton interference method, we leverage the spread of emanating beams created by multiple internal reflections from the Newton interference setup.

The spread of beams exiting the mirrors is directed onto the microscope stage by means of a half-mirror in the illuminating beam path (Figure 6.28). By increasing the angle θ_m between the Mirrors 1 and 2, the beams can be spread sufficiently such that only the zeroth and first order reflected beams ($n = 0, 1$) overlap under

¹⁶Glass slide wiped clean with acetone and ethanol, and dried under N₂ flow before sputtering. Sputtering done in a Emitech K575 sputter coater, at 40 mA for 30 seconds. Film thickness is based on expected sputtering rates.

the microscope's field of view. At this point we see a clear interference pattern between these two beams, observed as a repetition of uniform bright and dark parallel fringes.¹⁷ As θ_m is changed, only beams $n > 0$ move on the stage; the $n = 0$ beam remains fixed.

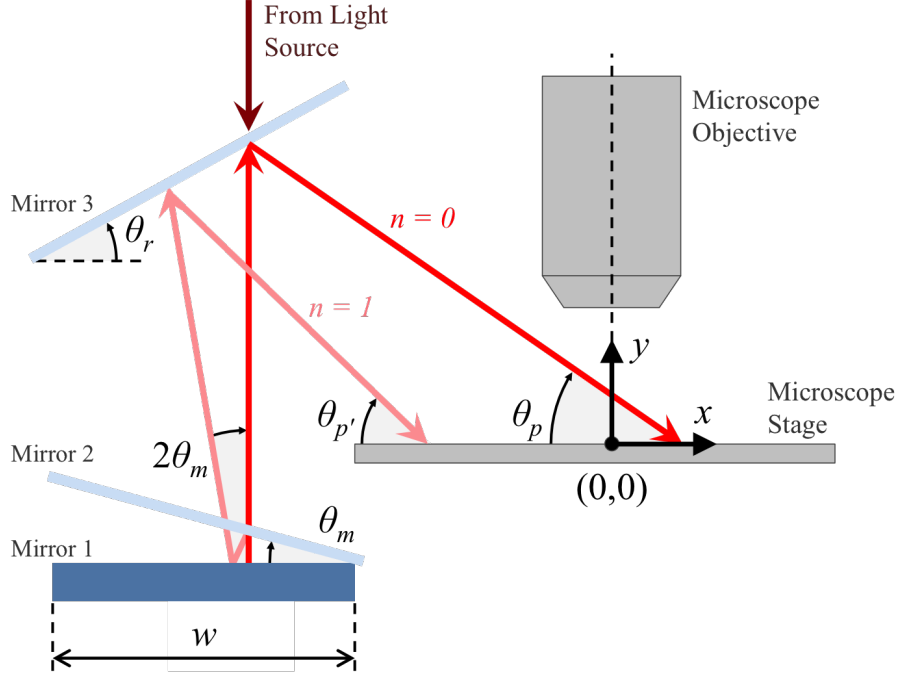


Figure 6.28: The full interference pattern generating setup. The first two reflected orders are shown projected onto the microscope stage. The beam paths shown represent the centre of each beam. The width of the beams leads to a region of overlap between both beams, even though the beam centres are offset from each other. The interference pattern is created when the two beams overlap on the stage, due to their differing path lengths. The coordinate system's origin is on the stage, centred beneath the microscope objective. Angles and dimensions are not drawn to scale.

To determine the interference pattern we must determine the variation in path length between the two beams at all points on the stage within the microscope's field of view. Under 2x magnification, the field of view is 36 mm, so we wish to analyse the region over $x = \pm 0.18$ cm ($y = 0$ cm). Path lengths are measured from the first reflection off Mirror 1 (the last common point of all reflected orders).

The relevant equations can be derived by trigonometry. Due to the length of the derivations, and since this interferometry setup is not described in other works,

¹⁷When more than two reflected orders overlap beneath the imaging objective, a superposition of multiple interference patterns is created, which is too sparse and irregular for reliable 3D scanning.

they are presented in Appendix 6.C. To aid in understanding the equations, Figure 6.29 presents information additional to that of Figure 6.28.

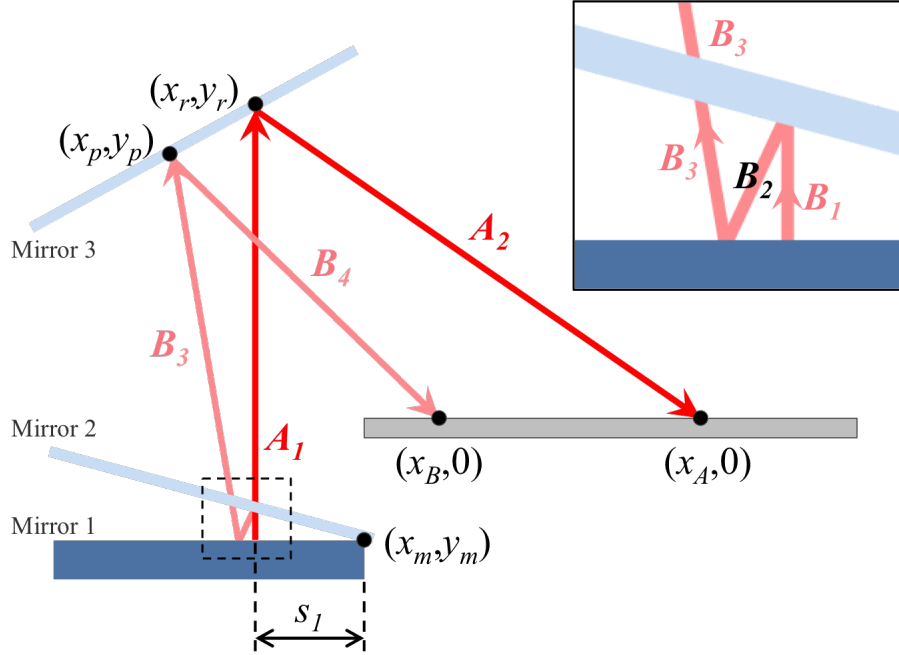


Figure 6.29: The interference pattern apparatus showing the various beam sections (A_1 , A_2 and B_1 to B_4) that combine into the total path lengths. Here the paths drawn need not be the beam centres, they can be any part of the beam since the beams illuminate the entire Mirror 1 area. Coordinates x_A and x_B mark any position on the stage illuminated by the $n = 0$ and $n = 1$ beams, respectively. Distance s_l describes any point of reflection off the full mirror, relative to (x_m, y_m) . The inset enlarges the boxed area of the Newton interference mirrors. Angles and dimensions are not drawn to scale.

The path length of the zeroth reflected order is (see Figure 6.29)

$$L_0 = A_1 + A_2 \quad (6.28)$$

where

$$A_1 = x_A \left(\frac{\tan(\theta_p) \tan(\theta_r)}{\tan(\theta_p) + \tan(\theta_r)} \right) - x_r \tan(\theta_p) - y_m \quad (6.29)$$

$$A_2 = \frac{x_A}{\cos(\theta_p)} \left(\frac{\tan(\theta_r)}{\tan(\theta_p) + \tan(\theta_r)} \right) - \frac{x_r}{\cos(\theta_p)} \quad (6.30)$$

The angle of Mirror 3 (θ_r) is related to the projection angle by

$$\theta_r = \frac{\pi}{4} - \frac{\theta_p}{2} \quad (6.31)$$

Similarly, the path length of the first reflected order as it first leaves Mirror 1 is (see Figure 6.29)

$$L_1 = B_1 + B_2 + B_3 + B_4 \quad (6.32)$$

Section lengths B_1 to B_4 are

$$B_1 = s_1 \tan(\theta_m) \quad (6.33)$$

$$B_2 = \frac{s_1 \tan(\theta_m)}{\cos(2\theta_m)} \quad (6.34)$$

$$B_3 = \frac{(x_P - x_r) \tan(\theta_r) + x_r \tan(\theta_p) - y_m}{\cos(2\theta_m)} \quad (6.35)$$

$$B_4 = \frac{y_P}{\sin(\theta_p + 2\theta_m)} \quad (6.36)$$

where s_1 is

$$s_1 = \frac{(y_m + 2x_r \tan(\theta_p)) \tan(2\theta_m) + x_r + w/2 - x_P(\tan(\theta_r) \tan(2\theta_m) + 1)}{\tan(\theta_m) \tan(2\theta_m) + 1} \quad (6.37)$$

The coordinates (x_P, y_P) define any position on Mirror 3 illuminated by part of the first reflected order:

$$x_P = \frac{x_B \tan(\theta_p + 2\theta_m) + x_r(\tan(\theta_r) + \tan(\theta_p))}{\tan(\theta_p + 2\theta_m) + \tan(\theta_r)} \quad (6.38)$$

$$y_P = (x_P - x_r) \tan(\theta_r) - x_r \tan(\theta_p) \quad (6.39)$$

The equations thus far describe the path lengths of the zeroth and first reflected orders in terms of any illuminated position on the stage (x_A or x_B) and the physical parameters of the setup (x_r , y_m , w , θ_r , θ_m and θ_p).

Simulating the Interference Profile

To simulate the interference pattern we model the path length difference between the $n = 0$ and $n = 1$ beams at all points within the microscope's field of view, converting that into regions of constructive or destructive interference.

By setting $x_A = x_B$ we analyse points of overlap between the two beams. By scanning these x values over the microscope's field of view ($x = \pm 0.18$ cm) we can analyse the path length difference (ΔL_x) at all visible illuminated points on the stage by

$$\Delta L_x = L_{0,x_A} - L_{1,x_B}, \text{ where } x = x_A = x_B \quad (6.40)$$

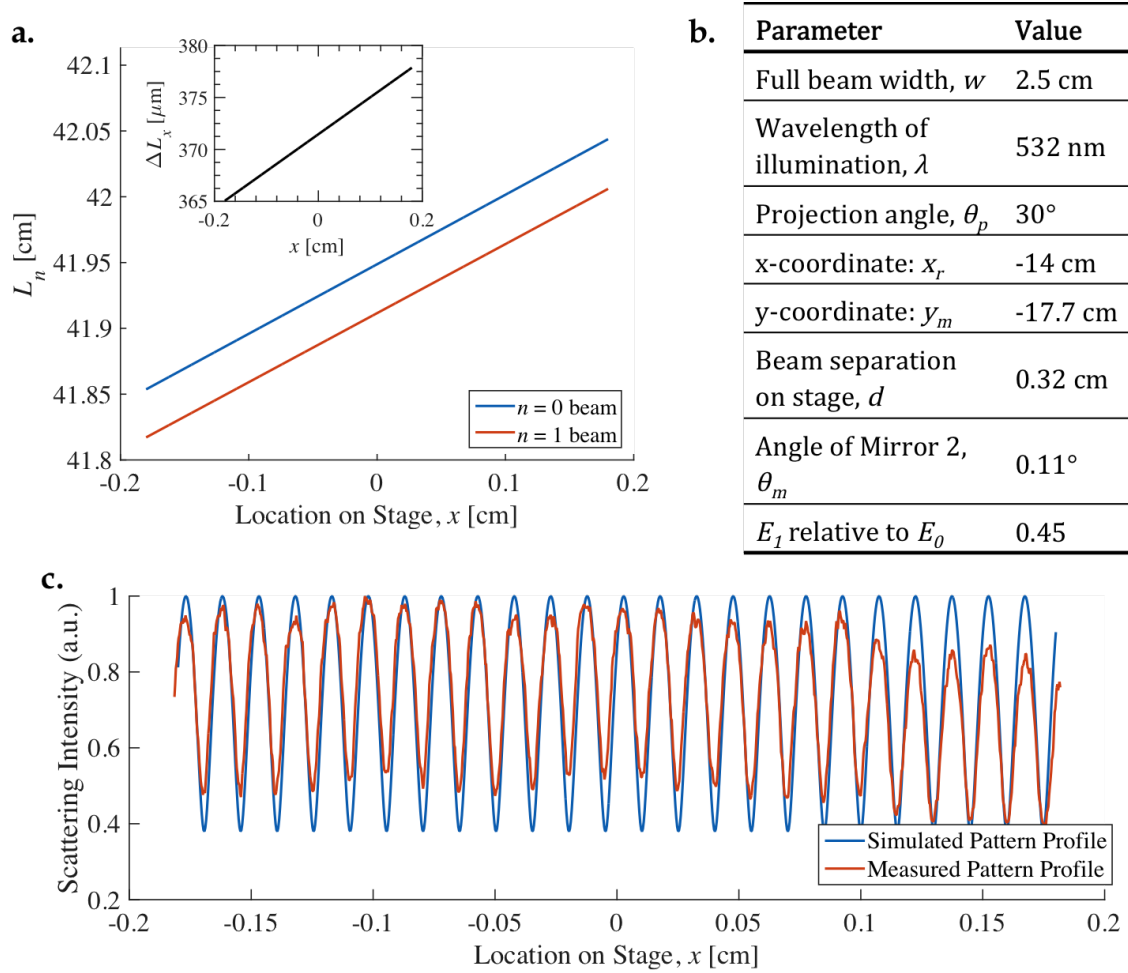


Figure 6.30: (a) Path lengths of the zeroth and first reflected orders at all points within the microscope’s field of view, and the resulting path length difference (inset plot). In (b) is a table of parameters used to produce these results, including the results in (c) showing the simulated interference pattern. A measured interference pattern is also shown in (c), giving a good match to the simulated pattern. Measuring the pattern is discussed in the next section.

The path lengths of each beam vary linearly across the microscope’s field of view. Figure 6.30a shows an example based on the setup parameters in the table in Figure 6.30b.

The interference pattern depends on the phase shift between the beams at each point on the stage. The phase shift of the $n = 0$ beam relative to the $n = 1$ beam is

$$\phi_x = \frac{2\pi}{\lambda} \text{frac} \left(\frac{\Delta L_x}{\lambda} \right) \quad (6.41)$$

where $\text{frac}(\Delta L_x/\lambda)$ refers to the fractional (i.e. non-integer) portion of the division.

The wavelength of operation is $\lambda = 532$ nm.

A uniform banded interference pattern requires the path length difference (ΔL_x) to vary linearly, inducing a phase difference profile oscillating between $[0, 2\pi]$ in regular intervals across the stage. The inset of Figure 6.30a shows this is the case in the model.

From the phase difference profile we calculate the normalised net electric field magnitude (E_x) from the magnitude of the first order beam (E_1) relative to the zeroth order beam (E_0):

$$E_x = \sqrt{E_0^2 + E_1^2 + 2E_0E_1 \cos(\phi_x)} \quad (6.42)$$

The simulated intensity profile of Figure 6.30c is produced.

The fringe spacing (s_f) in the interference pattern can be determined by considering that for every full fringe width on the stage, the difference in path length (ΔL_x) equals one full wavelength of light. Therefore, the fringe spacing is related to the gradient of the path length difference by

$$s_f = \frac{\lambda}{\left(\frac{d(\Delta L_x)}{dx}\right)} \quad (6.43)$$

This equation is too complex to analyse intuitively for how s_f varies with θ_m and θ_p , but it is shortly analysed computationally.

Measuring the Interference Profile

To observe the real interference pattern, a flat and highly scattering surface (such as white paper) is placed on the microscope stage. A photograph of the microscope image is shown in Figure 6.31a, based on the parameters used above (Figure 6.30b). The pattern is seen to have high contrast and uniformity, as required for 3D scanning. The image speckle is due to scattering surface roughness, and wobbles in the fringes are due to slight undulations in the scattering substrate.

The green colour channel can be extracted along horizontal cross-sections of the image and the pixel intensity measured at each point. A sample single cross-section colour profile is shown in Figure 6.31b. Imperfections in the substrate show as high-frequency noise (blue trace) and variation in peak intensities. High-frequency noise

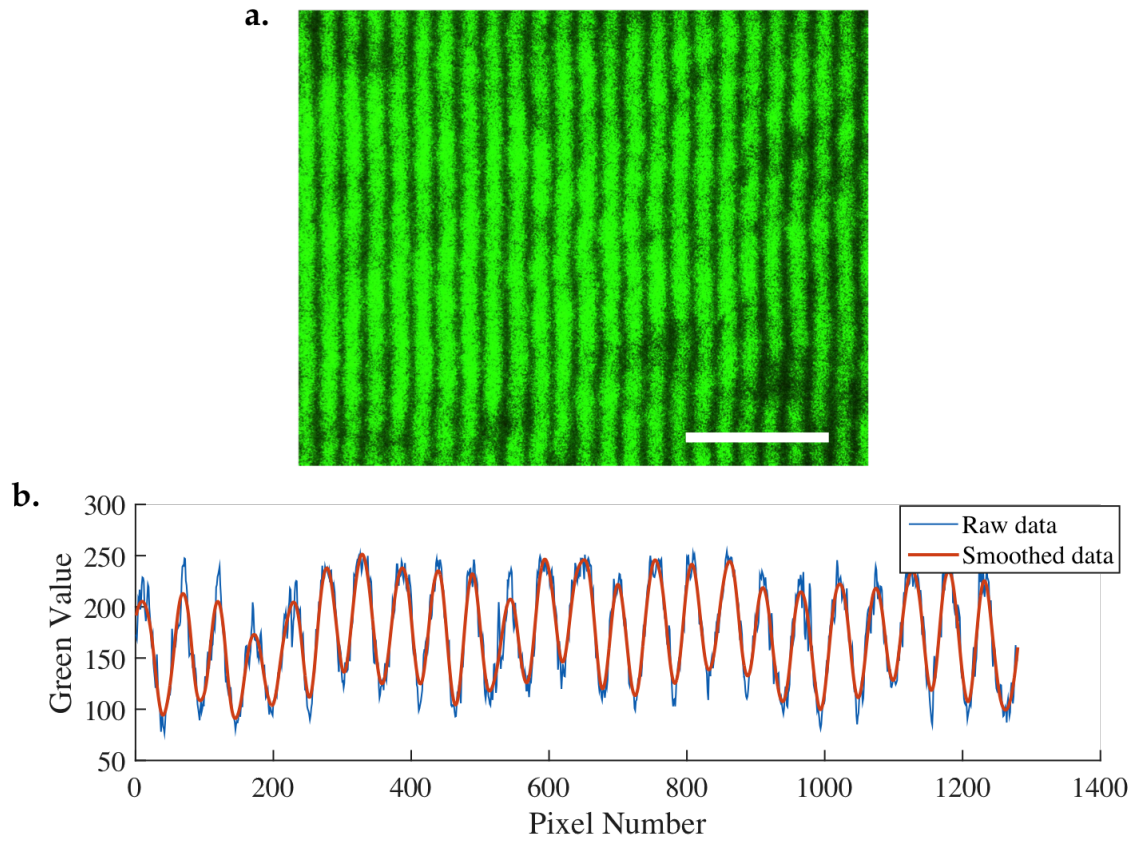


Figure 6.31: (a) Microscope photograph of a reference pattern imaged on white card that was moved while capturing the image to blur out speckle effects. The band spacing is $d_0 = 149 \mu\text{m}$ at a projection angle of 30° . The wobbles in the fringes are due to slight undulations in the substrate. Image acquired under 2x magnification. The scale bar is $900 \mu\text{m}$. (b) A sample green colour profile of a cross-section through the image.

can be removed with a moving average filter (red trace), but that still leaves a very irregular signal.

To remove all artefacts caused by substrate imperfections we average the raw (unsmoothed) data from many cross-sections. Averaging 95 cross-sections reproduces the interference pattern as if a nearly ideal scattering surface were used. The result is shown in Figure 6.30c against the simulated pattern profile, giving an excellent match. This confirms that the true interference pattern conforms exceptionally well with the simulated pattern, and all deviations from the ideal case are due to imperfections in the substrate itself, not in the pattern generating apparatus.

The fringe spacing of the photographed pattern (peak-to-peak distance) is measured as $149.9 \pm 5.4 \mu\text{m}$ (95 % confidence interval), compared to the simulated fringe

spacing of $149.6\text{ }\mu\text{m}$. The high correlation suggests that the large error margin of $\pm 5.4\text{ }\mu\text{m}$ is primarily due to imperfections in the substrate (introducing slight distortions into the pattern), not an inhomogeneous optical pattern.

In the next section we will discuss the means and limitations of reducing the fringe spacing for greater 3D scanning resolution.

Optimising the Optical Pattern

Finally, we consider here how the pattern density can be increased, and the limitations to such optimisation. In this regard there are two points to note. First, to get an optical pattern the zeroth and first order beams must overlap on the microscope stage. If the angular spread ($2\theta_m$) between these two beams becomes too large, they will separate too much on the stage and cease to overlap.

Second, for 3D scanning, the fringe spacing should be roughly half (or less) of the feature size that we wish to resolve. We therefore wish to also know how the fringe spacing is tuned by parameters of the setup.

Ensuring Beam Overlap on the Stage

To elucidate the first requirement, we relate the amount of beam overlap with the two main variables of the setup—the angles of Mirror 2 (θ_m) and Mirror 3 (θ_r).¹⁸ To simplify the situation, we note that the value of θ_m is present mathematically in the angle subtended by the two beams (which is $2\theta_m$). We also note that the angle of Mirror 3 can be expressed in terms of the projection angle of the zeroth reflected order (θ_p) via Equation 6.31.

Thus in a diagram of the full apparatus we can remove all the mirrors and straighten out the light paths without losing any information, as shown in Figure 6.32. In place of the Newton interference mirrors we simply have two beams originating from the same point in space. All parameters are mathematically equivalent to the more detailed diagrams presented earlier (except for path length L_1 : the

¹⁸There are other variables, such as the beam width and the distance between Mirror 1 and the stage, but once the setup is complete these variables are generally fixed and cannot be used to tune the optical pattern. We will therefore treat them as constants in our analysis.

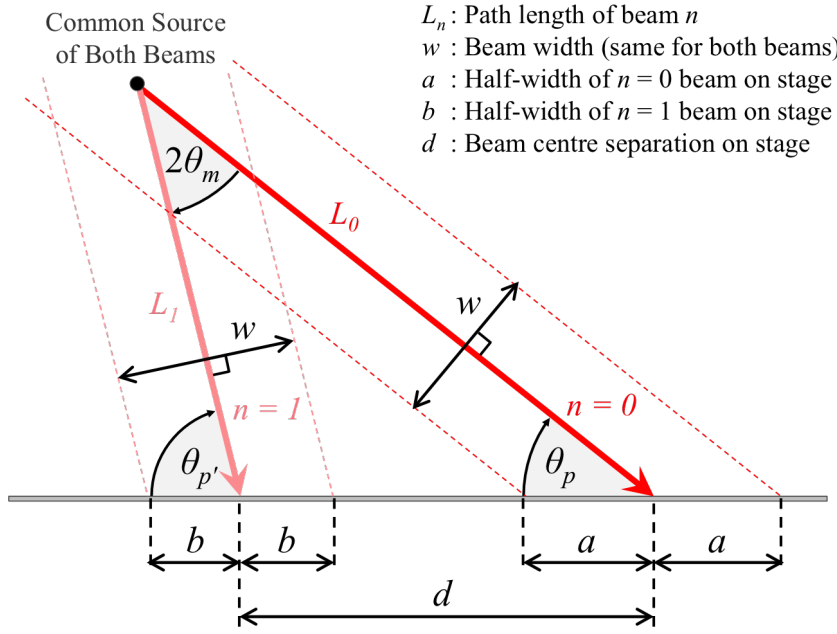


Figure 6.32: A simplified diagram of the zeroth and first order beams illuminating the microscope stage. We have removed the mirrors to ease the mathematical analysis.

straight-line version shown in this diagram is very slightly shorter than the real path length, though the difference is negligible).

Parameters a and b describe the half-widths of the illuminated cross-sections of the zeroth and first order beams on the stage, respectively. Parameter d describes the centre-to-centre separation distance between the beams.

Derivations yield:

$$a = \frac{w}{2 \sin(\theta_p)} \quad (6.44)$$

$$b = \frac{w}{2 \sin(\theta_p')} = \frac{w}{2 \sin(\theta_p + 2\theta_m)} \quad (6.45)$$

$$d = \frac{L_0 \tan(2\theta_m)}{\sin(\theta_p) + \cos(\theta_p) \tan(2\theta_m)} \quad (6.46)$$

The easiest parameters to measure are d and θ_p , along with the other variables needed to calculate the path length L_0 . L_0 can be calculated from Equations 6.28 to 6.31 by setting $x_A = 0$, as this denotes the $n = 0$ beam projected into the centre of the microscope's field of view.

Since θ_m is difficult to measure directly, we can rearrange Equation 6.46 to make θ_m the subject based on other known variables. This is how the angle θ_m given in

the table of Figure 6.30b was determined.

$$\theta_m = \frac{1}{2} \tan^{-1} \left(\frac{d \sin(\theta_p)}{L_0 - d \cos(\theta_p)} \right) \quad (6.47)$$

With these equations we can begin analysing how the beam overlap varies with angles θ_m and θ_p . The first relevant result is how the beam centre-separation varies with θ_m . This is plotted in Figure 6.33a for a variety of projection angles. The other variables are as per the table in Figure 6.30b.

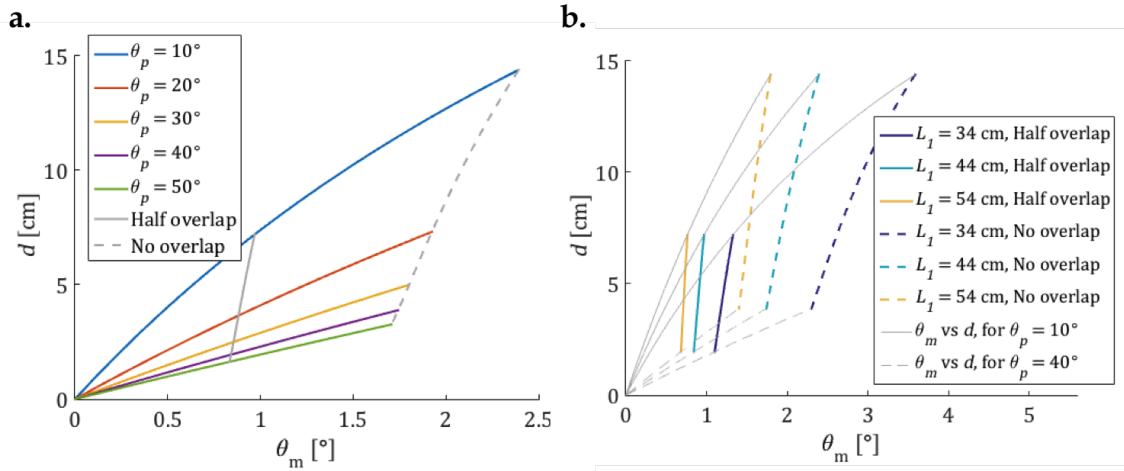


Figure 6.33: (a) The variation of the centre-to-centre beam separation with angle θ_m . (b) The variation of the half-overlap and no-overlap points between the $n = 0$ and $n = 1$ beams.

In the plot it is seen that as the angle of Mirror 2 (θ_m) increases very slightly, the beam separation markedly increases, particularly when low projection angles (θ_p) are used.

When the beams only half overlap on the stage, $d \approx a$, and when they cease to overlap at all, $d \approx 2a$. These key points are marked on the plot by the grey solid and dashed lines, respectively.

When lower projection angles are used, the illumination cross-sections (a and b) are much larger, and we can accommodate greater beam separations (higher θ_m) before overlap ceases. This translates into greater path length differences between the beams, and so smaller fringe spacings.

To observe how beam separation varies with the total path length (L_0), Figure 6.33b shows us that designing the entire setup to give shorter path lengths allows substantially greater angles of Mirror 2 to be accommodated before beam overlap

ceases. We can therefore maintain beam overlap at higher angles of Mirror 2 (leading to lower fringe spacings) when we use shorter overall path lengths and lower projection angles.

Optimising the Fringe Spacing

The main variable parameters of interest to study the fringe spacing are still θ_m and θ_p . Figure 6.34 presents how the fringe spacing varies with these parameters.

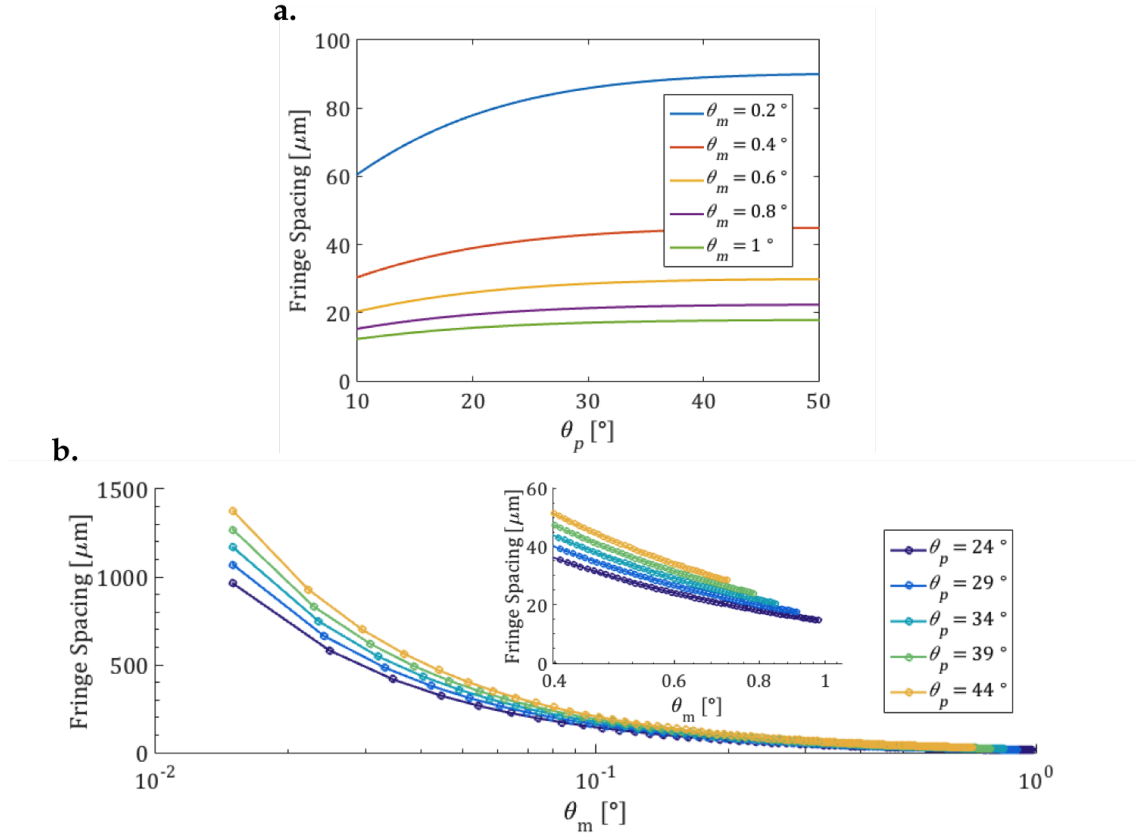


Figure 6.34: (a) The variation of the fringe spacing with angle θ_p . The fringe spacing improves increasingly for lower θ_p , though at high θ_m the fringe spacing is largely insensitive to dramatic changes in θ_p . (b) The variation of the fringe spacing with angle θ_m . The fringe spacing rapidly diminishes with increasing θ_m , though it plateaus at no more than about $7 \mu\text{m}$, giving a minimum limit to fringe spacing.

A practical range of θ_m to study is that up to where the beams reach the ‘half overlap’ point (this is the range of the plot). This is chosen since the $n = 0$ beam is fixed beneath the microscope objective, so when the beams half overlap the optical pattern is disappearing out of the field of view.

When the two-beam interference pattern appears, the fringe spacing is initially hundreds of micrometers (θ_m near 0). The lateral resolution of the 3D scan is comparable to the fringe spacing as seen on the microscope stage, so for true microscale scanning we must reduce the spacing. This can be achieved by increasing θ_m , whereby the fringe spacing can easily be reduced by over an order of magnitude, down to tens of micrometers. Surprisingly, there is not a major difference seen from changing the angle of projection when lower fringe spacings are achieved (see inset of the plot). If we use beams of greater width, then beams remain overlapping at greater separations, which would allow us to move to even higher angles θ_m .

If we move θ_m to much higher angles and ignore the need to retain beam overlap, we find that the fringe spacing does not asymptote to zero but reaches an absolute minimum of about 7 μm . This would suggest that the smallest feature we can reliably 3D scan is one about 14 μm in size.

Practical Optimisation

Achieving the lower limit of fringe spacing requires careful optimisation of the light path. The light incident on Mirrors 1 and 2 must be precisely perpendicular to the plane of Mirror 1, such that the zeroth reflected order returns exactly along the path of incidence. Any deviation from this gives a greater angular spread in the output light beams at lower values of θ_m , which means beam overlap ceases at lower values of θ_m , translating to a higher minimum fringe spacing.

In practice, the minimum fringe spacing that could be achieved was 20 μm , using a projection angle of $30^\circ \pm 3^\circ$. This was attained with the beams just beyond the ‘half overlap’ point. This result is in good agreement with the theoretical value in Figure 6.34b at the ‘half overlap’ mark (the end of the plot) for the same projection angle.

The brightness of the fringes reduces with increasing beam separation (due a Gaussian beam intensity profile), and although the pattern at the minimal fringe spacing could be seen by eye in a very dark room, it was too faint for reliable 3D scanning at a sufficiently high scan rate for use in this work. Using a brighter light source, and optimising the reflectance of Mirror 2 would help retain adequate contrast at such high pattern resolutions.

Summary

We have now concluded the presentation of the optical pattern used for micro-4D scanning—how it is generated and optimised. It is seen that the pattern resolution can be brought down to as low as $7\text{ }\mu\text{m}$ theoretically, though for the setup used in this study the practical minimum was $20\text{ }\mu\text{m}$ if a high-intensity light source is used. There is excellent agreement between theoretical and measured interference pattern data.

Appendix 6.C Derivation of Equations for the Interferometer in Appendix 6.B

Derivation of Equation 6.27

Derivation of the equation describing the angular spread of beams emanating from the Newton interference mirrors.

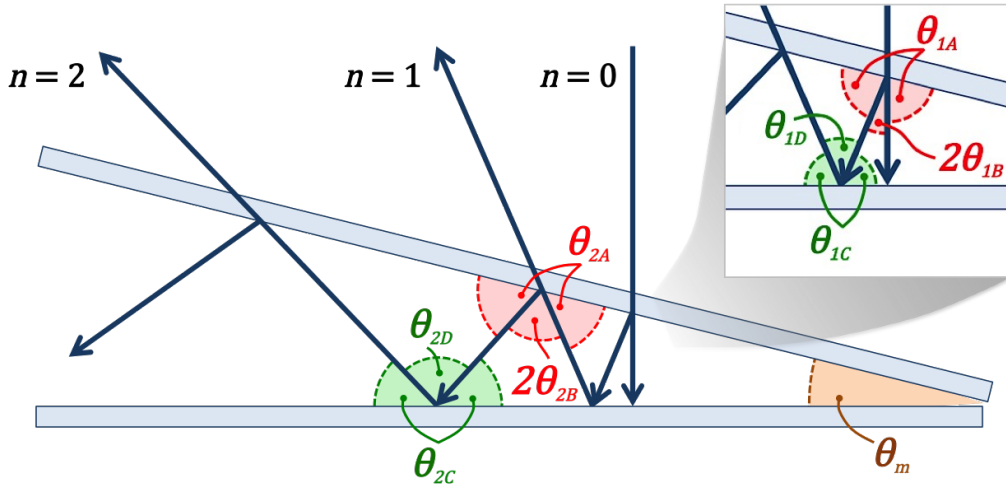


Figure 6.35: The Newton interference mirrors showing the angles for the derivation of the equation describing the angular spread of emanating orders.

The zeroth order emanates away at 90° to the horizontal. The first order emanates away at θ_{1C} , where

$$\begin{aligned} \theta_{1A} &= \frac{\pi}{2} - \theta_m \\ \theta_{1B} &= \frac{\pi}{2} - \theta_{1A} \\ &= \theta_m \\ \theta_{1C} &= \frac{\pi}{2} - 2\theta_{1B} \\ &= \frac{\pi}{2} - 2\theta_m \\ \theta_{1D} &= \pi - 2\theta_{1C} \\ &= 4\theta_m \end{aligned}$$

The second order emanates away at θ_{2C} , where

$$\begin{aligned} \theta_{2A} &= \pi - \theta_{1A} - \theta_{1D} \\ &= \frac{\pi}{2} - 3\theta_m \\ \theta_{2B} &= \frac{\pi}{2} - \theta_{2A} \\ &= 3\theta_m \\ \theta_{2C} &= \pi - 2\theta_{2B} - \theta_{1C} \\ &= \frac{\pi}{2} - 4\theta_m \\ \theta_{1D} &= \pi - 2\theta_{2C} \\ &= 8\theta_m \end{aligned}$$

And so the pattern continues up the beam orders, to yield the angle of propagation for beam order $n = 0, 1, 2, 3, \dots$ as

$$\theta_n = \frac{\pi}{2} - 2n\theta_m$$

Derivation of Equation 6.47

Equation 6.47 describes the angle between mirrors 1 and 2, and also half the angle subtended between the zeroth and first order beams:

$$\theta_m = \frac{1}{2} \tan^{-1} \left(\frac{d \sin(\theta_p)}{L_0 - d \cos(\theta_p)} \right)$$

To derive it we refer to Figure 6.32, which is reproduced below as Figure 6.36.

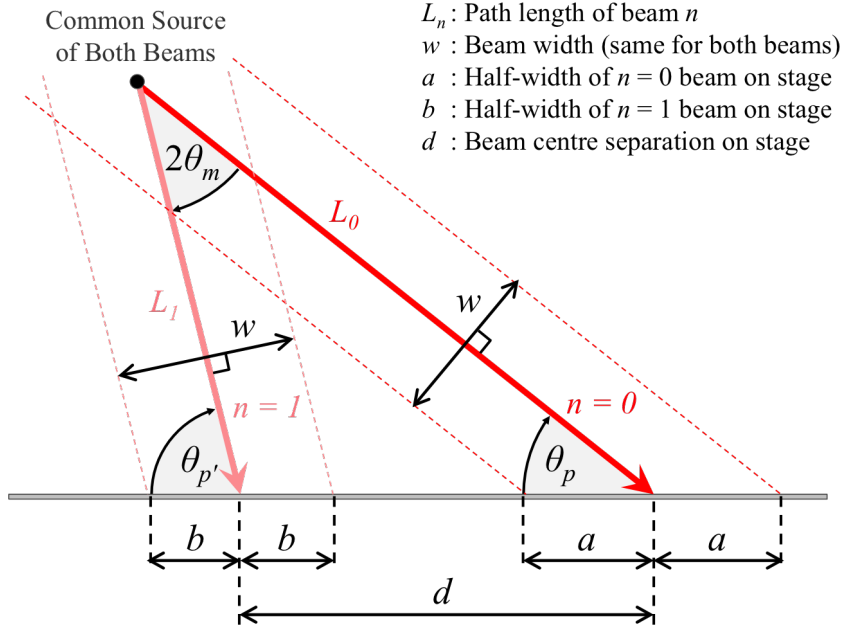


Figure 6.36: A simplified diagram of the zeroth and first order beams illuminating the microscope stage. We have removed the mirrors to ease the mathematical analysis.

Let, $\theta_1 = \pi - \theta_{p'} = \pi - 2\theta_m - \theta_p$, and therefore, by the law of sines:

$$\frac{d}{\sin(2\theta_m)} = \frac{L_0}{\sin(\theta_1)} = \frac{L_0}{\sin(\pi - 2\theta_m - \theta_p)}$$

$$\therefore d \sin(\pi - 2\theta_m - \theta_p) = L_0 \sin(2\theta_m)$$

Since $\sin(\pi - \alpha) = \sin(\alpha)$,

$$d \sin(\theta_p + 2\theta_m) = L_0 \sin(2\theta_m)$$

By the double angle identity,

$$\sin(\theta_p + 2\theta_m) = \sin(\theta_p) \cos(2\theta_m) + \sin(2\theta_m) \cos(\theta_p)$$

and hence,

$$\begin{aligned} L_0 &= d \left(\sin(\theta_p) \frac{\cos(2\theta_m)}{\sin(2\theta_m)} + \cos(\theta_p) \right) \\ \therefore L_0 &= \left(\frac{\sin(\theta_p)}{\tan(2\theta_m)} + \cos(\theta_p) \right) \\ \therefore \frac{\sin(\theta_p)}{\tan(2\theta_m)} &= \frac{L_0}{d} - \cos(\theta_p) = \frac{L_0 - d \cos(\theta_p)}{d} \\ \therefore \frac{d \sin(\theta_p)}{L_0 - d \cos(\theta_p)} &= \tan(2\theta_m) \\ \therefore \theta_m &= \frac{1}{2} \tan^{-1} \left(\frac{d \sin(\theta_p)}{L_0 - d \cos(\theta_p)} \right) \end{aligned}$$

Derivation of Equations for the First Order Beam (Equations 6.33 to 6.39)

The full path of the first order beam is shown in Figure 6.37. First a few preliminary notes, each of which is represented in Figure 6.37:

- The origin of the chosen coordinate system is on the microscope stage beneath the centre of the objective lens.
- The apex of Mirrors 1 and 2 is at the coordinates (x_m, y_m) .
- The size of Mirror 1 dictates the size of the reflected orders (in other words, the incident beam covers the entire surface of Mirror 1). Therefore the centre of the zeroth order beam is in the centre of Mirror 1, and the beam width (w) describes the size of Mirror 1.
- The incident and zeroth reflected order beams are perfectly vertical. The point on Mirror 3 in the exact centre of these beams is at coordinates (x_r, y_r) .
- θ_r is the angle that Mirror 3 makes with the horizontal plane.
- Mirror 3 is angled such that the centre of the zeroth order beam is reflected to strike the microscope stage at coordinates $(0, 0)$, thus also fixing the projection angle, θ_p .
- Angles θ_1 and θ_2 describe the reflection of the zeroth order beam off Mirror 3.

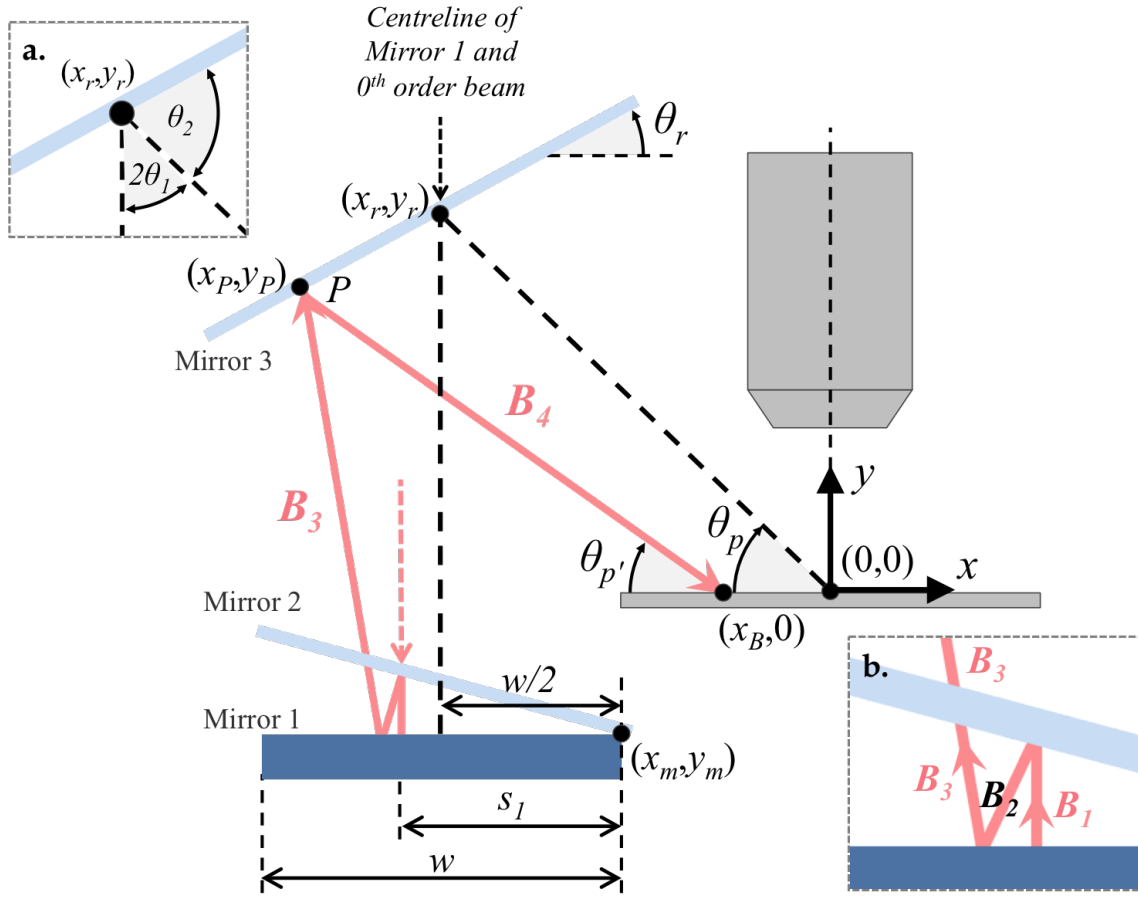


Figure 6.37: A diagram highlighting a sample ray path of the first order beam, with its segments B_1 to B_4 . Inset (a) shows the angles at point (x_r, y_r) on Mirror 3, and inset (b) enlarges the path segments between Mirrors 1 and 2. Point P denotes any position on Mirror 3 that is illuminated by a ray from the first order beam.

- All of the above coordinates and angles are fixed by the physical setup.

By geometry it's helpful to establish that,

$$\begin{aligned}
 2\theta_1 &= \frac{\pi}{2} - \theta_p \\
 \therefore \theta_1 &= \frac{\pi}{4} - \frac{\theta_p}{2} & y_r &= -x_r \tan(\theta_p) \\
 \theta_r = \theta_1 &= \frac{\pi}{4} - \frac{\theta_p}{2} & x_m &= x_r + \frac{w}{2}
 \end{aligned}$$

To derive the length of path sections B_1 and B_2 , let s_1 be the distance from the apex of Mirrors 1 and 2 to any point in the incident beam. By geometry,

$$\begin{aligned}
 B_1 &= s_1 \tan(\theta_m) & B_2 &= \frac{B_1}{\cos(2\theta_m)} \\
 & & &= \frac{s_1 \tan(\theta_m)}{\cos(2\theta_m)}
 \end{aligned}$$

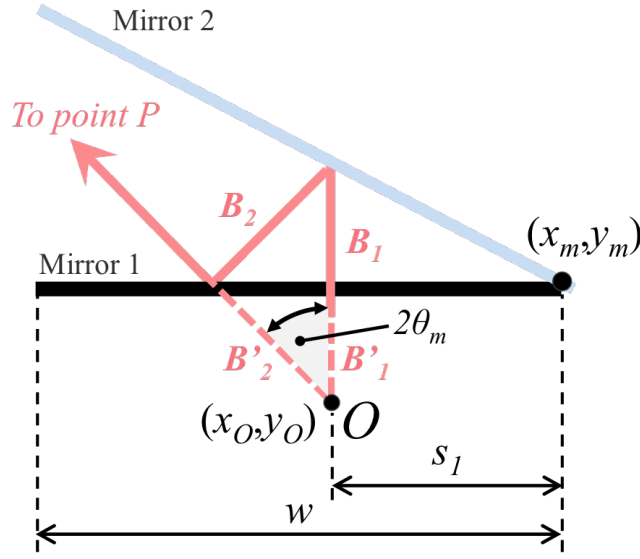


Figure 6.38: A diagram of the virtual counterparts of segments B_1 and B_2 . The point of intersection of the virtual segments is denoted as O . The segment OP is therefore identical mathematically to segments $B_2 + B_3$.

To derive the expression for B_3 , we first redraw B_1 and B_2 in their virtual form below Mirror 1, denoted as B'_1 and B'_2 , as seen in Figure 6.38. Their lengths and the angle subtended ($2\theta_m$) are unchanged. We label the intersection of B'_1 and B'_2 as point O , and the intersection of B_3 with Mirror 3 as point P . Thus, the net path length $B_2 + B_3$ is the linear distance OP . The coordinates of O are:

$$\begin{aligned}
 x_O &= x_m - s_1 \\
 &= x_r + \frac{w}{2} - s_1 \\
 y_O &= y_m - B_1 \\
 &= y_m - s_1 \tan(\theta_m)
 \end{aligned}$$

To find the coordinates of P (x_P, y_P), we first construct two linear equations describing the path of OP and the plane of Mirror 3, and then we find the expression for the intersection of these two equations. The equation for the beam line OP takes the general form, $y = mx + c$, where

$$\begin{aligned}
m &= -\tan(\pi/2 - 2\theta_m) \\
c &= y - mx \\
&= y_O + \tan(\pi/2 - 2\theta_m)x_O \\
&= y_m - s_1 \tan(\theta_m) + \tan(\pi/2 - 2\theta_m)(x_m - s_1) \\
\therefore y &= \tan(\pi/2 - 2\theta_m)x + y_m - s_1 \tan(\theta_m) + \tan(\pi/2 - 2\theta_m)(x_m - s_1) \\
\therefore y &= (x_m - s_1 - x) \tan(\pi/2 - 2\theta_m) + y_m - s_1 \tan(\theta_m)
\end{aligned}$$

The equation for Mirror 3 takes the same general form:

$$\begin{aligned}
m &= \tan(\theta_r) \\
c &= y - mx \\
&= y_r - \tan(\theta_r)x_r \\
\therefore y &= \tan(\theta_r)x + y_r - \tan(\theta_r)x_r \\
\therefore y &= (x - x_r) \tan(\theta_r) + y_r
\end{aligned}$$

Find the expression for the intersection by equating the y and x coordinates in both linear equations:

$$(x - x_r) \tan(\theta_r) + y_r = (x_m - s_1 - x) \tan(\pi/2 - 2\theta_m) + y_m - s_1 \tan(\theta_m)$$

Rearranging, and letting $x = x_P$ (to denote any illuminated position on Mirror 3) yields,

$$x_P = \frac{y_m - s_1 \tan(\theta_m) - 2y_r + (x_m - s_1) \tan(\pi/2 - 2\theta_m)}{\tan(\theta_r) + \tan(\pi/2 - 2\theta_m)} \quad (6.48)$$

We can therefore use this directly in the simplest equation for y_P :

$$y_P = (x_P - x_r) \tan(\theta_r) + y_r$$

The vertical height difference between O and P is $y_P - y_O$, and since the angle of the path OP is $2\theta_m$, it follows from trigonometry that the net path length of $B'_2 + B_3$ is

$$\begin{aligned}
B'_2 + B_3 &= \frac{y_P - y_O}{\cos(2\theta_m)} \\
&= \frac{(x_P - x_r) \tan(\theta_r) + y_r - y_m + s_1 \tan(\theta_m)}{\cos(2\theta_m)}
\end{aligned}$$

Subtracting from this the expression for B'_2 (the same as B_2) yields

$$B_3 = \frac{(x_P - x_r) \tan(\theta_r) + x_r \tan(\theta_p) - y_m}{\cos(2\theta_m)}$$

To derive the expression for B_4 we note that the projection angle of the first order beam onto the stage is $\theta_{p'} = \theta_p + 2\theta_m$. Again by trigonometry,

$$\begin{aligned} B_4 &= \frac{y_P}{\sin(\theta_{p'})} \\ &= \frac{(x_P - x_r) \tan(\theta_r) + y_r}{\sin(\theta_p + 2\theta_m)} \end{aligned}$$

At this point all the path length segments (B_1 to B_4) of the first order beam are written in terms of constants relating to the physical setup, and s_1 , which is the position of illumination on Mirror 1. We wish to transform these equations so they are in terms of the illuminated position on the microscope stage (the x coordinate of which we denote as x_B for the first order beam). We begin this process by writing an expression for x_B in terms of the first order beam. By geometry it follows that

$$\begin{aligned} x_B &= x_P + B_4 \cos(\theta_{p'}) \\ &= x_P + \frac{(x_P - x_r) \tan(\theta_r) + y_r}{\tan(\theta_p + 2\theta_m)} \end{aligned}$$

Making x_P the subject yields

$$x_P = \frac{x_b \tan(\theta_p + 2\theta_m) + x_r \tan(\theta_r) - y_r}{\tan(\theta_p + 2\theta_m) + \tan(\theta_r)} \quad (6.49)$$

We now have two equations for x_P —one in terms of s_1 (Equation 6.48) and one in terms of x_B (Equation 6.49). By equating these expressions and rearranging to make s_1 the subject, we deliver an expression for s_1 in terms of the physical setup's parameters and x_B .

$$s_1 = \frac{(y_m + 2x_r \tan(\theta_p)) \tan(2\theta_m) + x_r + w/2 - x_P(\tan(\theta_r) \tan(2\theta_m) + 1)}{\tan(\theta_m) \tan(2\theta_m) + 1} \quad (6.50)$$

Thus we can now determine the path length of any portion of the first order beam for any illuminated position on the microscope stage, x_B .

Derivation of Equations for the Zeroth Order Beam (Equations 6.29 and 6.30)

The full path of the zeroth order beam is shown in Figure 6.39. Using a similar process to the first order beam we can derive the path length much more easily than the first order beam's, owing to the fact that the zeroth order propagates vertically

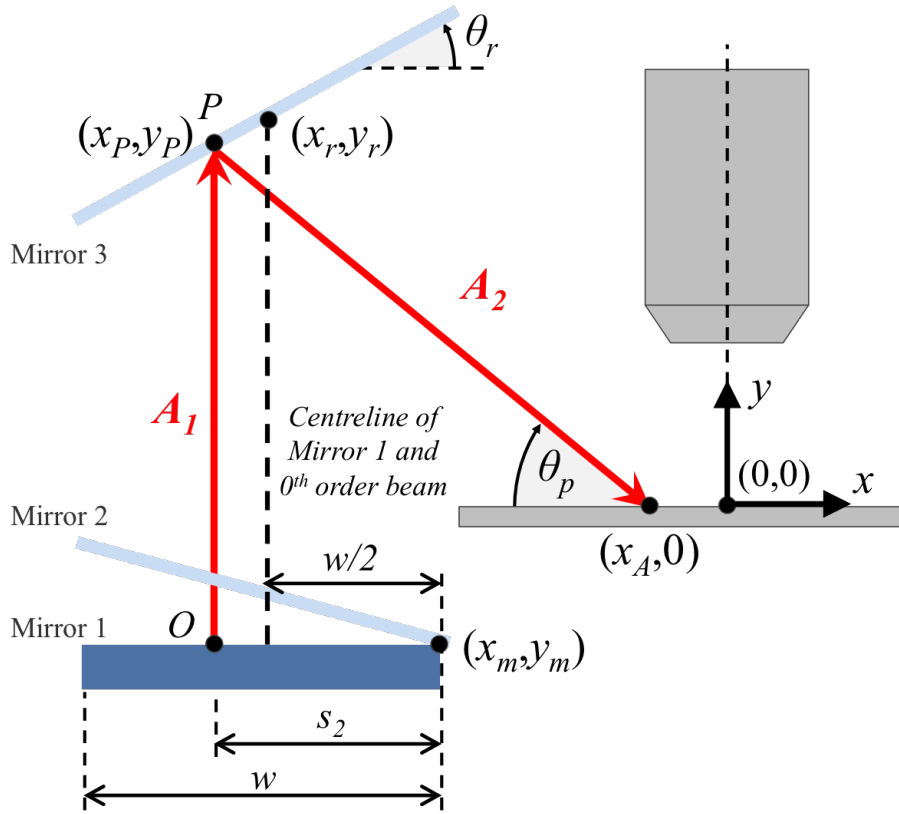


Figure 6.39: A diagram highlighting a sample ray path of the zeroth order beam, with its segments A_1 and A_2 . Points O and P denote any position on Mirrors 1 and 3, respectively, that is illuminated by a ray from this beam.

upwards from Mirror 1. Using the same notation convention to that used with the first order beam, we note that,

$$A_1 = OP = y_P - y_m$$

Recalling the equation for the plane of Mirror 3, the coordinate y_P is found by setting $y = y_P$ and $x = x_P = x_m - s_2$:

$$\begin{aligned} y &= (x - x_r) \tan(\theta_r) + y_r \\ \therefore y_P &= (x_m - s_2 - x_r) \tan(\theta_r) - x_r \tan(\theta_p) \\ &= (w/2 - s_2) \tan(\theta_r) - x_r \tan(\theta_p) \end{aligned}$$

Thus the equation for A_1 becomes

$$A_1 = (x_m - s_2 - x_r) \tan(\theta_r) - x_r \tan(\theta_p) - y_m$$

The equation for A_2 is easily derived by trigonometry as being

$$A_2 = \frac{x_A - x_P}{\cos(\theta_p)}$$

where x_A is any position on the microscope stage illuminated by the zeroth order beam.

Again we face the issue of having some of the beam section length defined in terms of the illumination position on Mirror 1 (variable s_2). We must express s_2 in terms of x_A . We can write,

$$x_P = x_r + (w/2 - s_2)$$

and noting from trigonometry that

$$\tan(\theta_p) = \frac{y_P}{x_A - x_P}$$

we substitute in for x_P and y_P , and rearrange to make s_2 the subject:

$$s_2 = \frac{w}{2} - x_A \left(\frac{\tan(\theta_p)}{\tan(\theta_p) + \tan(\theta_r)} \right)$$

Resolving A_1 and A_2 in terms of x_A and the physical setup's parameters gives

$$A_1 = x_A \left(\frac{\tan(\theta_p) \tan(\theta_r)}{\tan(\theta_p) + \tan(\theta_r)} \right) - x_r \tan(\theta_p) - y_m$$

$$A_2 = \frac{x_A}{\cos(\theta_p)} \left(\frac{\tan(\theta_r)}{\tan(\theta_p) + \tan(\theta_r)} \right) - \frac{x_r}{\cos(\theta_p)}$$

This completes the derivation of the path length of the zeroth order beam for any position on the stage that is illuminated by that beam.

Appendix 6.D Reconstructed Surface Resolution

The resolution of the reconstructed surface is determined by the resolution at which we can sample the image. This varies between the three spatial dimensions.

6.D.0.1 Resolution in the x -Dimension

Our sampling in the x -axis is limited to where we find fringes, and hence the x -resolution of our scan is entirely dependent on the fringe spacing over the surface.

It is reasoned that to reconstruct a surface feature in a minimal sense, one would want at least two sample points over the feature to ascertain the feature's average surface gradient. Presuming we only sample bright or dark fringes, the minimum feature size that can be scanned in the x -dimension ($R_{x,min}$) is therefore twice the reference fringe spacing (d_0):¹⁹

$$R_{x,min} = 2d_0 \quad (6.51)$$

This is a rule of thumb only, not an inflexible rule. The actual fringe spacing in any region depends on the local surface gradient in the x -axis. For a steep positive surface gradient, many fringes might appear in a region smaller than $2d_0$, and our equation for $R_{x,min}$ must reflect this fact.

So by rearranging Equation 6.4 we can relate the local fringe spacing to the average surface gradient ($\langle \partial S / \partial x \rangle$) and state the minimum resolvable²⁰ feature size in the x -dimension as

$$R_{x,min} = \frac{2d_0}{1 + \left\langle \frac{\partial S}{\partial x} \right\rangle \cot(\theta_p)} \quad (6.52)$$

This rightly collapses to Equation 6.51 when $\langle \partial S / \partial x \rangle = 0$.

If we sample bright and dark fringes together, then $R_{x,min}$ reduces by a factor of two.

¹⁹Depending on how the fringes are positioned over the feature to be scanned, it is possible to have two sample points on a feature that is nearly as small as d . This requires the fringes to be at the two ends of the feature. To allow for fringes that are positioned anywhere over the feature (not necessarily at the ends) it is necessary that the feature be at least $2d$ to ensure that two fringes are present over the feature, and therefore two sample points as well.

²⁰Where 'resolvable' means there are at least two sample points over the feature.

6.D.0.2 Resolution in the y -Dimension

In the y -axis we are sampling along individual fringes, and we can sample the fringes as densely or sparsely as we deem appropriate, limited only by the camera resolution. We could sample every pixel or every tenth pixel. This maps directly to the minimum resolvable feature size in the y -dimension ($R_{y,min}$) being equal to the twice pixel size²¹:

$$R_{y,min} = 2d_{pix}(n + 1) \quad (6.53)$$

where d_{pix} is the size of one pixel and n is the number of rows between each sampled row.

6.D.0.3 Resolution in the z -Dimension

The z -dimension is reconstructed from the x - and y -dimension data. The FSM relies on detecting the centreline of fringes and measuring their separation ($d - d_0$). This separation is converted directly into a change in height (a surface gradient) between the two points (Equations 6.1 and 6.3). Assuming perfect fringe centreline detection, the resolution of fringe separation is the pixel size (d_{pix}). This is the smallest difference in fringe spacing that can be measured.

The FDM relies on detecting the centreline of a fringe and measuring its deviation (δd). Again, assuming perfect centreline detection, the smallest fringe deviation that can be measured is the pixel size.

This limit of measurement for both methods translates to a consistent minimal z -axis feature size of

$$R_{z,min} = d_{pix} \tan(\theta_p) \quad (6.54)$$

The resolution of the reconstructed height profile is therefore very high, but this does not ensure an *accurate* reconstructed surface. Precision is never the same as accuracy, and whilst the precision may be high, we discussed in Section 6.5 the errors that reside in the reconstructed surface, which overshadow the theoretical precision limit spoken of here.

²¹Again assuming we need at least two sample points over a feature to call it minimally ‘resolvable’

6.D.0.4 Resolution in the Temporal Dimension

Sufficiently high temporal resolution allows the 3D scanning technique to expand into 4D. The temporal resolution is limited by the image capture rate. For time-resolved studies, it is necessary that frames are not dropped by the recording software, and this depends on the computing power available. Consequently, a very high frame rate may require a reduction in image resolution, which presents a trade-off for spatial versus temporal resolution.

Appendix 6.E A Partial Differential Equation Model for Evaporation

The Model

In this Appendix we present an overview of the partial differential equation (PDE) model of evaporation used in this thesis. Some of the information presented here is more detailed in the source papers [19, 20], so the reader is referred there for more information. The section titled *Mapping to an Electrostatic Analogy* is additional to the source papers.

Figure 6.40 presents the PDEs of this model, as they apply to different regions and interfaces. Laplace's equation is satisfied within each phase, and Neumann conditions explain the interfaces.

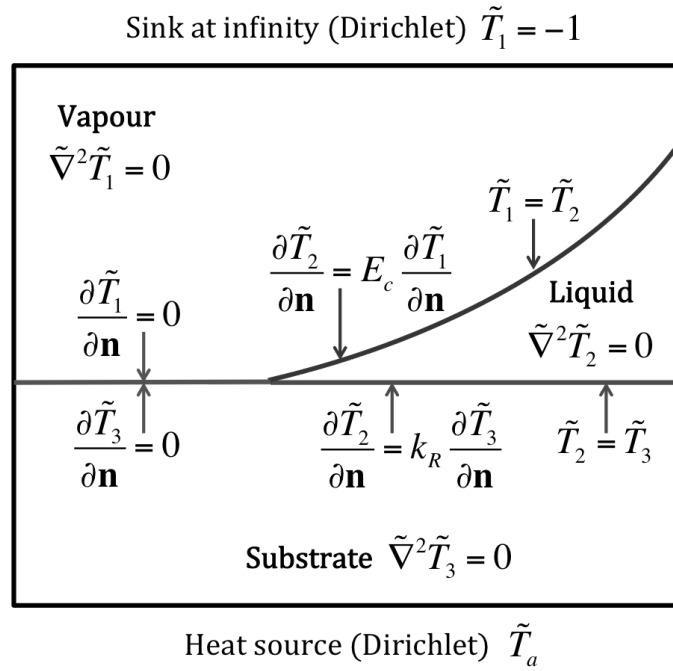


Figure 6.40: Diagram showing the partial differential equations that apply to the various phases and interfaces of the evaporation model. The equations are in terms of the dimensionless temperature field, $\tilde{T}$. This field satisfies Laplace's equation in each phase, with Neumann conditions applying at each interface.

As discussed below, the physical parameters in the model include the ambient relative humidity (H), the thermal conductivities of the substrate (k_S) and liquid

(k_L), the room temperature (T_0) and substrate base temperature (T_a), the latent heat of evaporation (H_L), and the coefficient of diffusion of vapour in the atmosphere (D).

Regional PDEs

Wang et al. [20] explain that in a quasi-steady condition, the heat transfer in a small liquid body is essentially conductive. The liquid velocity diverges immediately at the contact line, increasing the contribution of convective heat transfer locally, but conduction remains the dominant heat transfer mechanism overall. Moreover, convective flows to the contact line tend to be along the base of the liquid body, which is largely isothermal. This further limits the role of convection. Studies that use this evaporative model show that neglecting convective heat transfer yields experimentally accurate evaporation rates for sessile droplets.

Vapour transport in the air (in the absence of forced air flow) is by diffusion, and at the surface of the liquid body the vapour concentration rapidly adjusts to maintain saturation vapour concentration. All this entails that the air vapour concentration (c), the liquid temperature (T_L) and substrate temperature (T_S) each conform to Laplace's equation:

$$\nabla^2 c = 0, \nabla^2 T_L = 0, \nabla^2 T_S = 0 \quad (6.55)$$

These constitute the basis for the regional PDEs, though in the model they are used in their equivalent non-dimensional temperature form (see below).

Dimensionless Temperature Field

The evaporation model recognises that the substrate and liquid temperature profiles, and the vapour concentration profile, can all be transformed into one continuous dimensionless temperature-like field. Let $\tilde{T}_1$, $\tilde{T}_2$ and $\tilde{T}_3$ be akin to the dimensionless temperatures in the air, liquid and substrate, respectively. $\tilde{T}_a$ is the dimensionless temperature of the substrate's base. The dimensionless forms are given by

$$\tilde{T}_1 = \frac{c - c_0}{c_0(1 - H)}, \tilde{T}_2 = \frac{b(T_L - T_0)}{c_0(1 - H)}, \tilde{T}_3 = \frac{b(T_S - T_0)}{c_0(1 - H)}, \tilde{T}_a = \frac{b(T_a - T_0)}{c_0(1 - H)} \quad (6.56)$$

where c_0 is the saturation vapour concentration (c_{sat}) at room temperature (T_0) and b is the gradient in c_{sat} with T in the vicinity of T_0 ($b = dc_{sat}/dT$). At infinity (or

sufficiently far from the liquid), $c = c_0 H$ and $\tilde{T}_1 = -1$. This sets the atmospheric boundary condition. The substrate boundary condition is simply $\tilde{T}_a$.

The final step of transformation involves non-dimensionalising distances, by invoking a characteristic length scale, R , such that

$$\tilde{x} = \frac{x}{R}, \tilde{y} = \frac{y}{R}, \tilde{z} = \frac{z}{R}, \tilde{\nabla} = \left(\frac{\partial}{\partial \tilde{x}}, \frac{\partial}{\partial \tilde{y}}, \frac{\partial}{\partial \tilde{z}} \right) \quad (6.57)$$

Interfacial PDEs

The dimensionless temperature is continuous across all interfaces, except for the solid-gas interface (by virtue of the Neumann conditions imposed there). The solid-liquid and liquid-gas interfaces have proportionality constants for their normal gradients, being k_R and $1/E_c$, respectively. These are essentially the ratio of the thermal conductivities of each region:

$$k_R = \frac{k_S}{k_L}, \frac{1}{E_c} = \frac{k_L}{H_L D b} \quad (6.58)$$

The parameter, E_c , denotes the evaporative cooling number. It indicates how significant the negative feedback effect of temperature reduction at the contact line is, due to evaporation, causing a lower evaporation rate in that area.

This, then, completes the evaporative model presented in Figure 6.40.

Evaporation Rates

The diffusion-limited evaporation rate is given by

$$J = -D \nabla c \cdot \mathbf{n} \quad (6.59)$$

By noting that $c = \tilde{T}_1 c_0 (1 - H) + c_0$, $\nabla c_0 = 0$ and $\nabla = \tilde{\nabla}/R$, this is put in terms of the dimensionless model as

$$J = \frac{-D c_0 (1 - H)}{R} \tilde{\nabla} \tilde{T}_1 \cdot \mathbf{n} \quad (6.60)$$

Indeed, the dimensionless evaporation rate is given in the source papers as

$$\tilde{J} = -\tilde{\nabla} \tilde{T}_1 \cdot \mathbf{n} \quad (6.61)$$

The units of J are kg/s.m². This can be converted to L/s.m² by multiplying by $1000/\rho_L$, where ρ_L is the liquid density.

Mapping to an Electrostatic Analogy

The evaporation model can be numerically solved in its present form, or by treating it as an electrostatic problem. The dimensionless temperature equations equate in their form to being equations for electrostatic potential (ϕ) with thermal conductivities of each phase being exchanged with dielectric constants (ϵ_n). Gradients in $\tilde{T}_n$ are by analogy the electric field ($\mathbf{E}$). Laplace's equation for each region corresponds to Poisson's equation for electrostatic potential with no free charge ($\nabla^2 \phi_n = 0$). The gradient conditions at the solid-gas interface ($\partial \tilde{T}_1 / \partial \mathbf{n} = \partial \tilde{T}_3 / \partial \mathbf{n} = 0$) correspond to the normal electric field being zero ($\mathbf{E}_z = 0$), which means a surface with zero surface charge ($\sigma = 0$). Thus the evaporative model can be fully defined in terms of an electrostatic analogy.

Appendix 6.F Evaporative Model Implementation in COMSOL

The COMSOL Model and Parameters

The model in COMSOL was built with the CFA apparatus as shown in Figure 6.41. The reconstructed meniscus is the lower-centre segment of the tilted liquid front in the Figure. It is imported as a STL file produced from the Matlab meniscus reconstruction code. The meniscus was extruded equally out on either side to avoid edge effects interfering with the computed evaporative dynamics of the pinned meniscus segment. It was likewise extruded backwards a sufficient distance to eliminate those edge effects as well. The model was built using the dimensionless units $(\tilde{x}, \tilde{y}, \tilde{z})$, where the characteristic length ($R = 515.2717 \mu\text{m}$) was chosen, that being the depth of the reconstructed meniscus segment.

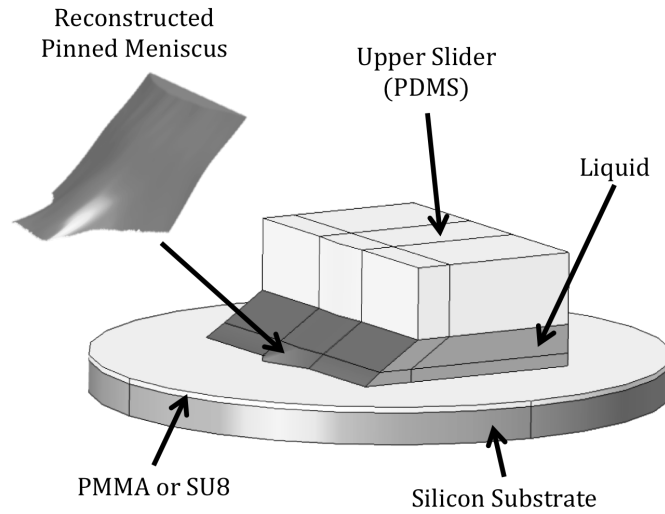


Figure 6.41: Diagram of the CFA apparatus in the COMSOL model, showing its different components and materials. The reconstructed meniscus is only the lower-centre segment of the tilted liquid front. The substrate extends out much further than what is shown.

The substrate is a Si wafer (thermal conductivity 148 W/m.K) overlain with a thin film of PMMA or SU8 (thermal conductivity 0.2 W/m.K). The Si thickness has a real-world equivalent of $540 \mu\text{m}$, and the thin polymeric film thickness was given

a variety of values (5, 20, 80, 150, 300 and 500 μm). (Due to the large expanse of the model, film thicknesses smaller than 5 μm could not be implemented.) Thus the films correspond to the case of a template fabricated by nano-imprint lithography (μm -thick films). The heat source was simulated as being on the base of the Si wafer.

The upper slider was built as a block of PDMS (thermal conductivity 0.23 W/m.K). The liquid-filled gap had a height in real-world units of 600 μm , which is what the real apparatus uses.

Figure 6.42 shows how the CFA apparatus is embedded in the larger model. Figure 6.42a shows the CFA apparatus enclosed by a hemispherical shell to delineate the region of extremely fine meshing (minimum mesh size of 0.005 units—1 unit is the size of the pinned meniscus segment). In Figure 6.42b this is shown enclosed by a larger hemispherical shell with a radius of 200 units. This region is meshed on the ‘normal’ size setting. The substrate extends out to the boundary of this shell, but not further. The substrate extent had to be limited in this way so that a very thin film could be modelled (COMSOL has limitations on the size difference between the smallest and largest geometrical features in a model). Figure 6.42c shows the final hemispherical shell, which denotes the effective ‘infinity’ boundary. The radius of this shell is 500 units, and this region is meshed more coarsely again.²²

Simulation Parameters

The model was setup using the electrostatic analogy with appropriate boundary conditions. The Si substrate was simulated with heating from beneath at a variety of temperatures (22, 27, 32, 37, 42, 47 and 51 °C).

Room temperature (T_0) was set to 22 °C. A value of 0.609 W/m.K was used for the thermal conductivity of water (k_L) at 27 °C,²³ and 2.45 MJ/kg for the latent heat of evaporation (H_L). The coefficient of diffusion of water vapour in air

²²Simulation results did not change when the outer-most shell radius was increased to 1000 units, nor when the meshing size of the CFA apparatus was reduced to 0.0025 units, suggesting our former values were sufficient for optimum accuracy.

²³http://www.engineeringtoolbox.com/thermal-conductivity-liquids-d_1260.html

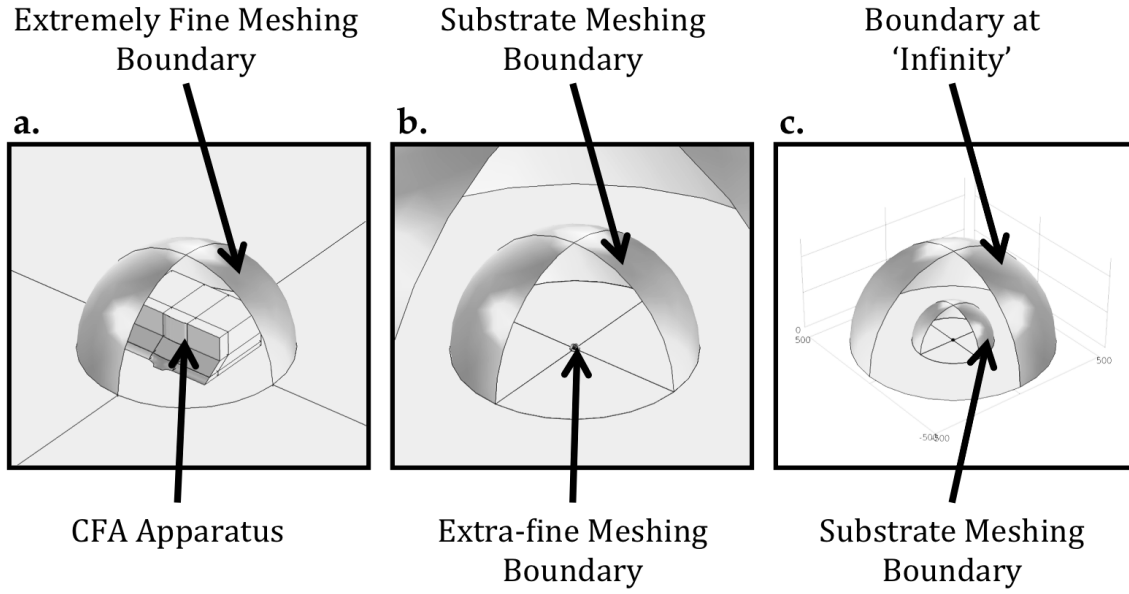


Figure 6.42: Diagrams of the COMSOL model at different zoom factors to show model details and extent. Image (a) shows the CFA apparatus within a hemispherical boundary delineating the region of extremely fine meshing resolution. Image (b) shows the boundary of the next reduction in meshing resolution, with the content of (a) barely visible in the centre. Image (c) shows the full extent of the model with the outer boundary far enough away to emulate conditions at an infinite distance from the CFA apparatus.

($D = 2.49 \times 10^{-5} \text{ m}^2/\text{s}$) is calculated at atmospheric pressure by²⁴

$$D = -27.75 \times 10^{-7} + 44.79 \times 10^{-9}(T_0 + 273.16) + 16.56 \times 10^{-11}(T_0 + 273.16)^2 \quad (6.62)$$

The ambient saturation vapour concentration ($c_0 = 0.0194 \text{ kg/m}^3$) is determined by²⁵

$$c_0 = 0.2166 \times 6.1121 \exp \left(\frac{18.678 - \frac{T_0^2}{234.5(257.14 + T_0)}}{T_0 + 273.16} \right) \quad (6.63)$$

The gradient of saturation vapour concentration with temperature ($b = 0.00118$

²⁴http://www.cambridge.org/us/engineering/author/nellisandklein/downloads/examples/EXAMPLE_9.2-1.pdf

²⁵http://www.engineeringtoolbox.com/water-vapor-saturation-pressure-air-d_689.html

kg/K.m³) is calculated by

$$b = \frac{0.2166 \times 6.1121}{2(T_0 + 273.16)} \left[\exp \left(18.678 - \frac{2(T_0 - 1)}{234.5(257.14 + (T_0 - 1))} \right) - \exp \left(18.678 - \frac{2(T_0 + 1)}{234.5(257.14 + (T_0 + 1))} \right) \right] \quad (6.64)$$

The relative humidity was 0.4 and the density of water set at $\rho_L = 998$ kg/m³.

Calculating Results

Here we give some of the COMSOL expressions to calculate pertinent results from the model.

When using the electrostatic analogy to implement the model, the voltage V is the electric potential, equating to the dimensionless temperature $\tilde{T}$. The true temperature across any surface in the model can be obtained by the expression

$$T \Rightarrow V * c_0 * (1 - H) / b + T_0$$

The dimensionless evaporation rate at each point on the liquid-gas interface can be calculated from the electric field at that surface using the expression

$$\tilde{J} \Rightarrow \text{up}(\text{es.Ex}) * n_x + \text{up}(\text{es.Ey}) * n_y + \text{up}(\text{es.Ez}) * n_z$$

This computes Equation 6.61 at each point on the surface, since gradients in $\tilde{T}_n$ are analogous to the electric field in the electrostatic implementation. The dimensionless evaporation rate can be converted into the true evaporation rate (kg/s.m²) by multiplying by $Dc_0(1 - H)/R$.

Finally, the temperature-dependent surface tension can be calculated from the true temperature at each surface point using the expression

$$\gamma \Rightarrow 0.07275 * (1 - 0.002 * ((V * c_0 * (1 - H) / b + 273.16 + T_0) - 291))$$

This expression assumes the liquid is pure water, which may not be the case, but the resulting profile will nonetheless indicate the surface tension gradients that evaporation will lead to. Only the actual surface tension values will be different for a different liquid.

Verifying the Implementation

To verify that the implementation is correct according to the source papers, the COMSOL modelling was applied to spherically-capped sessile droplets with the intention of reproducing key results from the published papers. Figure 6.43a shows the droplet in the COMSOL model (this image is akin to Figure 6.42a, with the rest of model as shown in Figures 6.42b and 6.42c). Figure 6.43b shows an example of the droplet surface rendered according to some of the data output from computing the evaporative model.

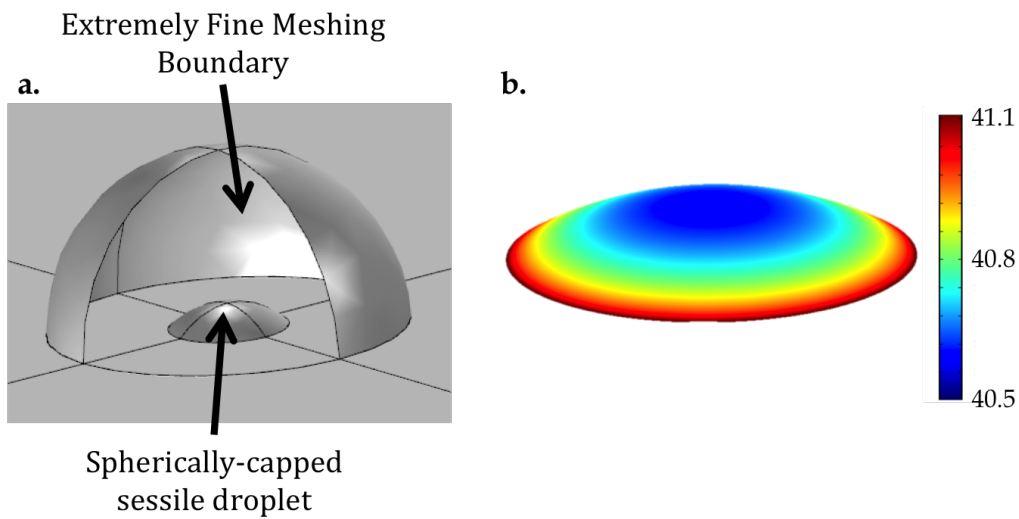


Figure 6.43: (a) The spherically-capped droplet within a hemispherical boundary delineating the region of extremely fine meshing resolution. (b) An example of the data output from computing the model. The liquid surface is shown rendered by the true temperature profile (in °C) of the droplet on a glass substrate whose base is heated to 42 °C.

Verification of the COMSOL implementation was sought particularly for the following aspects: calculation of the dimensionless evaporation rate at all points over a droplet; correct handling of air, liquid and substrate thermal conductivities; correct derivation of evaporative cooling effects; and correct determination of the total true evaporation rate from entire droplets of various liquids and sizes.

Comparisons between the COMSOL model and the source papers are presented in Figures 6.44, 6.45 and 6.46. In each Figure, the left-hand plot shows the data produced from this COMSOL model, and the right-hand plot is that from the source paper(s). The COMSOL model is seen to be in excellent agreement with the pub-

lished data in all cases (including with experimental data), giving confidence that the evaporative model has been correctly implemented.

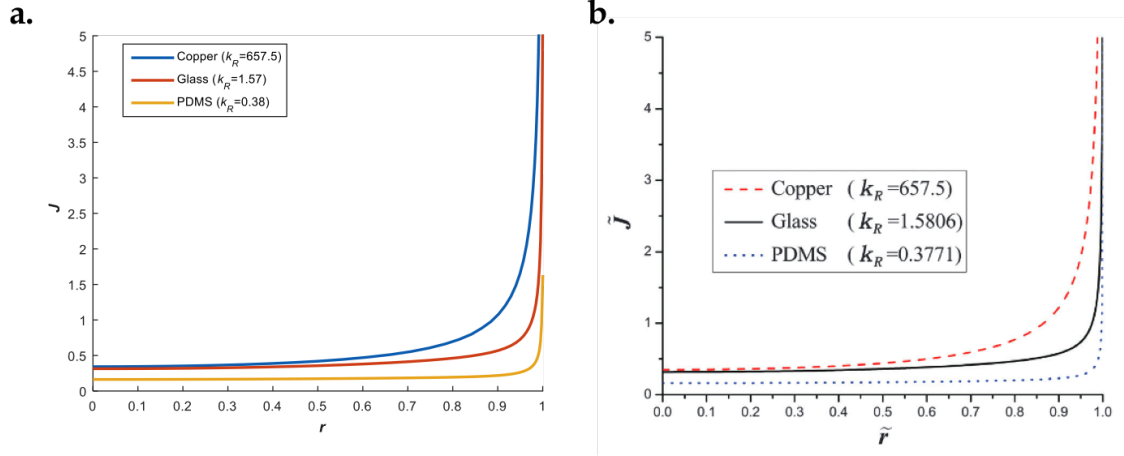


Figure 6.44: Non-dimensional evaporation rate from droplet centre ($r = 0$) to contact line ($r = 1$) on different substrates. Own data (a) matches precisely with data published by Wang et al. [20] (b).

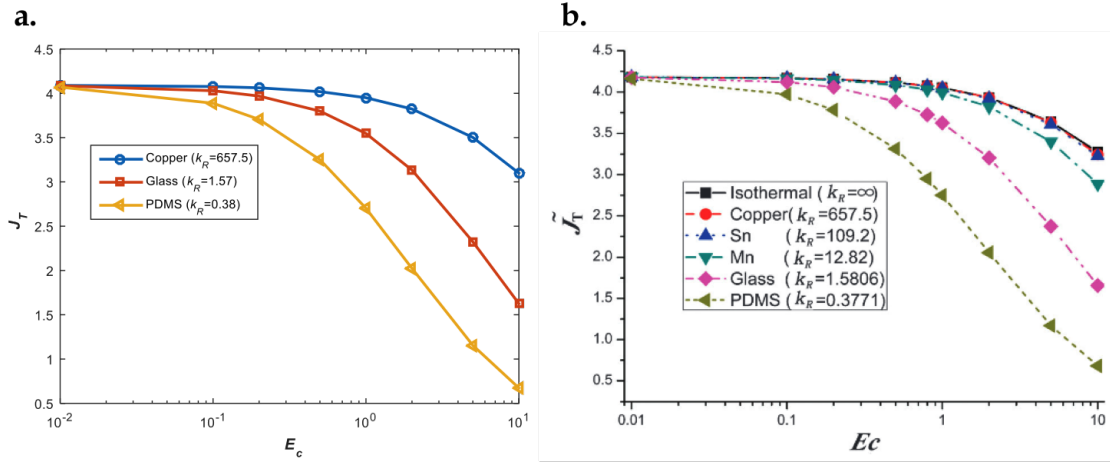


Figure 6.45: Total non-dimensional evaporation rate on different substrates and with different evaporative cooling factors. Own data (a) matches precisely with data published by Wang et al. [20] (b).

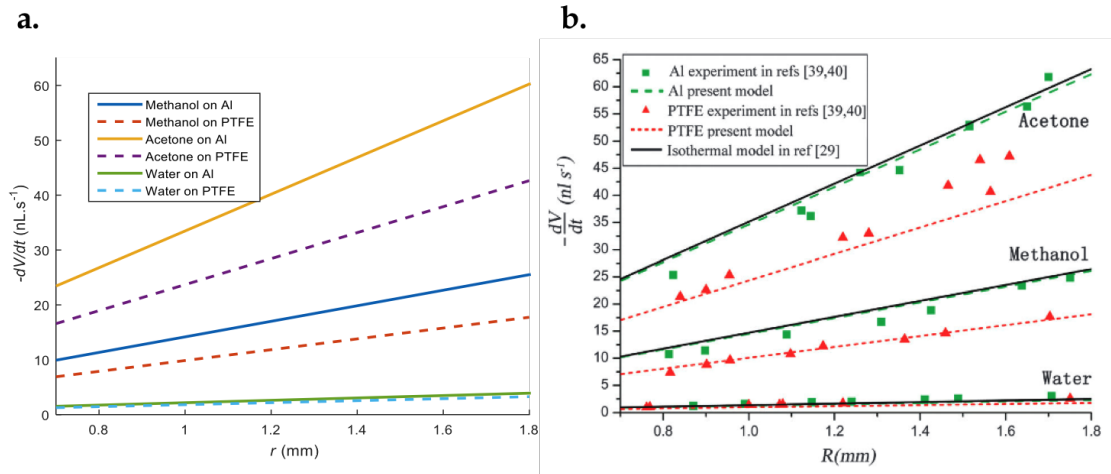


Figure 6.46: Net true evaporation rate from droplets of different liquids. Droplets are of various sizes and on different substrates. Own data (a) matches precisely with data published by Wang et al. [20] (b).

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Quantifying Pinning Dynamics for the Pinned-Convective Model

7

It is necessary that the pinned-convective model be experimentally characterised and quantified. This chapter accomplishes half of that in quantifying pinning dynamics on micro- and nano-cavities. Clamping dynamics and thin-film formation during pinning are demonstrated. A model is also derived by which the meniscus form can be predicted over a range of square cavity sizes at any stage during a pinning event.

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7.1 Introduction

We turn our attention now to quantifying the pinned-convective model of nano-CFA. In this chapter we will characterise pinning and clamping dynamics. In the following chapter we characterise the resulting convective dynamics. This chapter therefore serves two purposes: (1) it provides an in-depth understanding of pinning trends, which appear vital to nano-CFA, and (2) it produces a predictive framework to model a meniscus during pinning on a range of cavity sizes. This predictive meniscus model is key to deriving trends in convective flows during pinning (the next chapter).

The work presented here begins to address a distinct absence of literature about meniscus dynamics over nano-cavities (or an array of nano-cavities). The closest studies available concentrate on microscale contact line motion over arrays of micro-posts (super-hydrophobic surfaces) [1–9] or other micro-features rising out of the substrate [10–13]. These studies primarily seek to understand ultra-low wettable surfaces, and none investigate meniscus or convective behaviour over cavities.

In another attempt to identify relevant literature we may adopt the view that an array of cavities is essentially a nano-rough surface. Studies of dynamic wetting in this regard are few, and quantitative investigations have not yet been reported. A theoretical treatment serves us none the better, as researchers are inconclusive about how much to apply hydrodynamic theory over molecular kinetic theory in the nano-regime [14].

In a final attempt to locate literature we can note that an isolated cavity can be studied as a single defect on an otherwise flat substrate. Here we find some studies dealing with contact line behaviour around single macroscale defects protruding out of the surface (not cavities) [15, 16]. Moreover, very few studies have probed meniscus behaviour during pinning events, and none have discussed how pinning might alter convective flow patterns in the vicinity of the defect. No studies have sought the relationship between pinning dynamics and local nanoparticle motion.

It has therefore been necessary to design basic experiments to begin characterising meniscus behaviour in these respects. The results presented in this chapter bridge micro- and nano-scales. Time-resolved reconstructions of the three-dimensional meniscus structure during a pinning event are also reported (leveraging the experimental setup described in the previous chapter). Despite the relevance of

this work to the more general field of dynamic wetting on micro- and nano-structured surfaces, it is presented here explicitly in the context of nano-CFA.

The studies here are on single cavities, with the dynamics on an array being similar. On an array, contact line distortions from neighbouring cavities begin to overlap. Cavity density thus induces greater overall resistance to the contact line, reducing the eccentricity of the dynamics, but not changing their nature. A first-principles study of nano-CFA dynamics must begin with isolated cavities, and can be adequately applied to an array.

We also limit our studies to aqueous media. Organic solvents (such as hexane) are rarely used in nano-CFA. Nonetheless, the dynamics here would apply phenomenologically to organic solvents. Different liquid properties (relative to water) would alter the scaling of meniscus dynamics but not their primary form.

After covering the basic experimental setup (Section 7.2), analysis begins with a study of the eccentricity and duration of pinning on cavities (Section 7.3). From there we discuss depinning mechanisms and outline some pertinent outstanding questions (Section 7.4). Surface tension is demonstrated to be the dominant force guiding pinning, allowing inertial forces to be neglected (Section 7.5). This leads into an analysis of how cavity shape and aspect ratio affect pinning dynamics (Section 7.6) and then observation of the predicted meniscus clamping dynamic (using 4D meniscus reconstruction) and thin-film formation (Section 7.7). Finally, we study the profile of the contact line during pinning (Section 7.8), and derive the pinning force (Section 7.9). From the trends in each of these areas we will be in a position to predict the meniscus and contact line form for a variety of cavities throughout pinning events.

7.2 Experimental Setup

The experimental results of this chapter were obtained using the template presented in Figure 7.1 within a slider CFA apparatus. The template cavities are 200 nm deep in SU8 on Si, with Si forming the base of each cavity.

A slider CFA apparatus was connected to a modified dip coater arm, which was used to force contact line motion upwards of 1 mm/min ($16.7 \mu\text{m/s}$). The height of the slider was set to 600 μm . The apparatus was positioned on a microscope stage

for continuous monitoring. Pinning events have been studied via either 2D video-microscopy, or via the 4D meniscus reconstruction method given in the previous chapter.

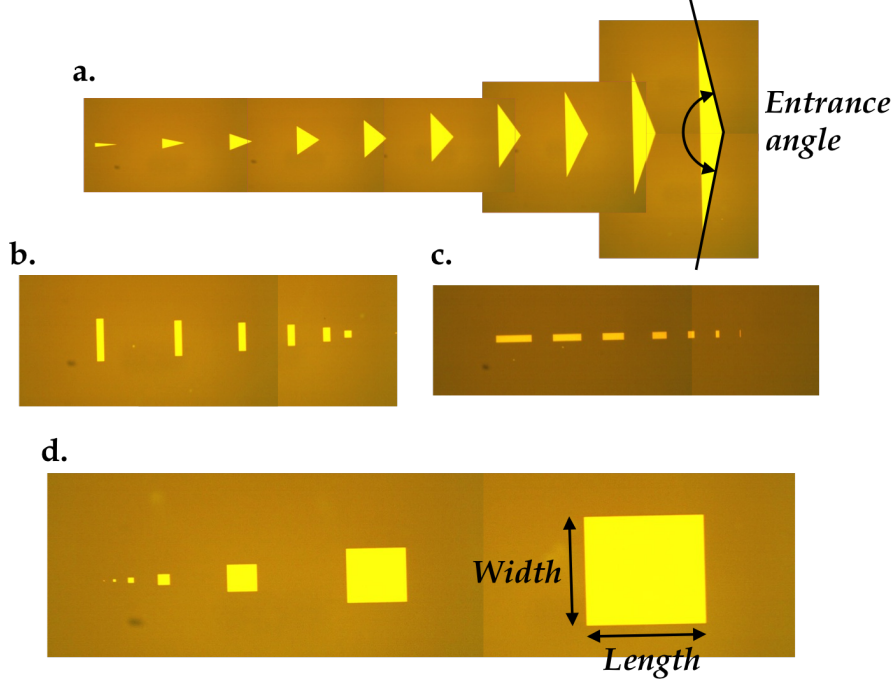


Figure 7.1: Microscope photographs of the main template features used to study pinning dynamics. In all cases the contact line recedes from right to left. Images are not to the same scale. Dimensions denoted by ‘width’ and ‘length’ are as shown in (d) (‘width’ is parallel to the contact line, ‘length’ is perpendicular to the same). The triangles in (a) are of length $500\ \mu\text{m}$ with varying entrance angles (10° to 140°). The cavities in (b) have fixed length ($100\ \mu\text{m}$) and varying width (100 to $600\ \mu\text{m}$). The cavities in (c) have fixed width ($10\ \mu\text{m}$) and varying length (1 to $50\ \mu\text{m}$). The cavities in (d) are squares of varying side lengths (10 to $1000\ \mu\text{m}$). Not shown are arrays of $200\ \text{nm}$ cavities with varying periodicity. The templates are $200\ \text{nm}$ of SU8 on Si.

It is anticipated (and confirmed in Sections 7.5 and 8.3.7) that surface tension governs pinning dynamics in the micro- and nano-regimes. On this basis it is appropriate for us, where necessary, to study dynamics on micro-cavities and suitably scale the results into the nano-regime.

Unless otherwise stated, mathematical expressions in this chapter are chosen for visual approximation to the data trend, and are then optimally fitted to the data. The expressions are intended to capture trends for modelling purposes only, not to convey physical laws.

7.3 Characterising Pinning Eccentricity and Duration

The first aspects of pinning we wish to characterise are the pinned length and lifetime. Pinned length is the distance between the start of a cavity and bulk contact line, at the moment of depinning (see Figure 7.2). Pinned length is of interest because it reflects the intensity of meniscus distortion, and would reasonably determine (in part) local convective flow intensity into the cavity.

The pinned lifetime is the duration of the pinning event, from the moment the contact line touches the cavity to the moment of depinning. The pinned lifetime would reasonably affect assembly. We must be cautious, however, as until we demonstrate a suitable assembly force to hold particles in a cavity during pinning, a prolonged pinned lifetime might in fact allow greater time for particles to *diffuse out* of the cavity, negating assembly. At this point, therefore, the impact of pinned lifetime remains uncertain.

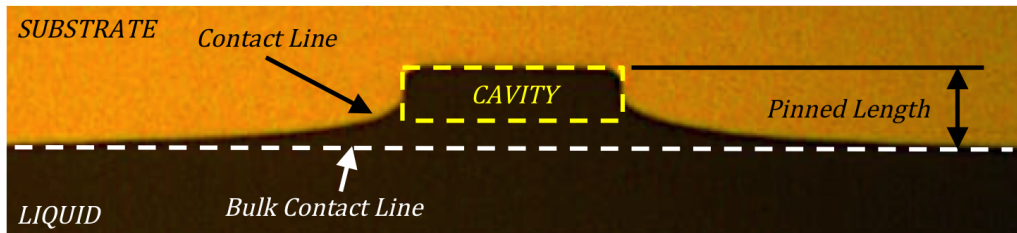


Figure 7.2: An explanation of pinned length being the distance between the start of the cavity and the bulk contact line, measured just prior to depinning.

The pinned length and lifetime were studied for cavities ranging in size from 200 nm to 1000 μm , and over speeds of 1, 2, 4 and 6 mm/min, barring 200 nm cavities studied at 0.018 mm/min. All cavities have a depth of 200 nm.

The pinned length was measured by counting pixels, and therefore is limited by the image resolution. The pinned lifetime was obtained by counting the video frames covering the pinning event, and is thus limited in resolution by the frame rate. In both respects the measurement uncertainty is sufficiently less than the measurement to not warrant error bars on the data plots.¹

¹This holds for all but the 200 nm cavities. However, for these cavities the actual error is demonstrated in Section 7.3.3 to be very small, much smaller than the measurement resolution, and so the measurement resolution bars are omitted for that reason.

From our anticipated dependence on surface tension, which scales linearly with distance, we predict a linear relationship between pinning measurements and cavity size, at least as far as surface tension dominates the interaction.

7.3.1 Pinned Length

Figure 7.3a shows pinned length data. We observe that for cavities $< 50 \mu\text{m}$, the pinned length progresses linearly with cavity size (plot inset) and for cavities $> 200 \mu\text{m}$ the measurement plateaus at approximately $250 \mu\text{m}$ (main plot). Later it will be demonstrated that a thin-film forms over a cavity as the pinning event progresses. Noting this, the limiting threshold in pinned length indicates a maximum thin-film size that can be sustained over 200 nm deep cavities, up to 500 to 1000 times the film depth (this would vary with cavity depth). Cavities of side length below $200 \mu\text{m}$ show a reduction in pinned length that progresses to a linear relationship against cavity size, with a ratio of 1.7 . The linear form is more evident in the inset plot. This leads to the two limiting equations for the pinned length (L_p):

$$L_p = \begin{cases} 1.7d, & \text{for } d < 50 \mu\text{m} \\ 250 \mu\text{m}, & \text{for } d > 200 \mu\text{m} \end{cases} \quad (7.1)$$

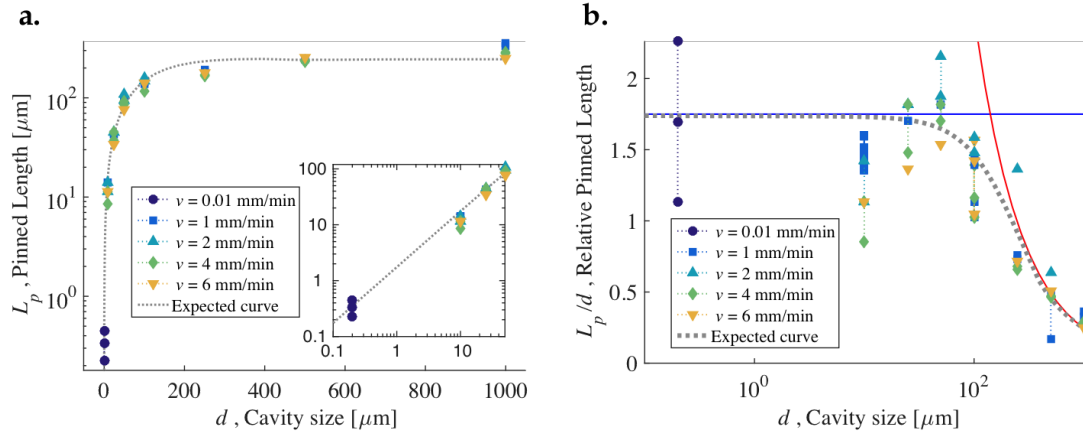


Figure 7.3: Data showing how the aqueous pinned length (a) and relative pinned length (b) vary with square cavity size. The pinned length plateaus for cavities larger than $\sim 100 \mu\text{m}$ owing to their shallow depth (200 nm). The relative pinned length data is fitted well by the two proposed bounding cases, as denoted by the red and blue curves, and discussed in the main text.

Figure 7.3b plots a modification of this data as the *relative* pinned length—the ratio of the pinned length to the cavity size. The limiting equations thus become

$L_p = 1.7$ for $d < 50 \text{ } \mu\text{m}$, and $L_p = 250/d$ for $d > 200 \text{ } \mu\text{m}$. These equations are the blue and red curves in the Figure, respectively, to which the data fits well, showing a region of transition between these characteristic curves. The simplicity and constancy of these fitted regions allow us to reliably predict the pinned length for even small nano-cavities. The data is not expected to diverge from the fitted curve until we approach the molecular scale of water (Knudsen number ~ 0.1), which means cavities 2-3 nm in size.

The grey dashed curve in Figure 7.3b is a best fit curve that well approximates both limiting cases. It is given by

$$h = \frac{1.7 \times 18790 + 0.1542d^{1.788}}{18790 + d^{1.788}} \quad (7.2)$$

The curve in Figure 7.3a is simply hd .

7.3.2 Pinned Lifetime

The pinned lifetime data is plotted in Figure 7.4a. It shows pinned lifetimes plateauing for larger cavities. The cavity size for the onset of plateauing appears to increase with lower contact line speeds, suggesting that slower speeds produce slightly more stable menisci on average. This is befitting of the pinned length data, which shows an onset of plateauing fixed at a given cavity size. The inset plot again shows a linear relationship for cavities smaller than $100 \text{ } \mu\text{m}$. (Note that the data from 200 nm cavities is far removed from the rest because the speed is dramatically slower, a necessity in order to gather data over such small cavities.)

To confirm no unexpected behaviour is present, the relative pinned lifetime is plotted in Figure 7.4b. It shows the ratio of the pinned lifetime to the time taken for the bulk contact line to traverse the cavity, given the fixed bulk contact line speed. As expected, it follows the same limiting curves presented from the pinned length, plateauing at a relative pinned lifetime of 1.7.

7.3.3 Measurement Accuracy

Since the pinned length is taken by counting pixels, and the pinned lifetime is taken by counting frames, we have two independent measurements of essentially the same phenomenon—the amount of pinning. From the pinned lifetime and the bulk contact

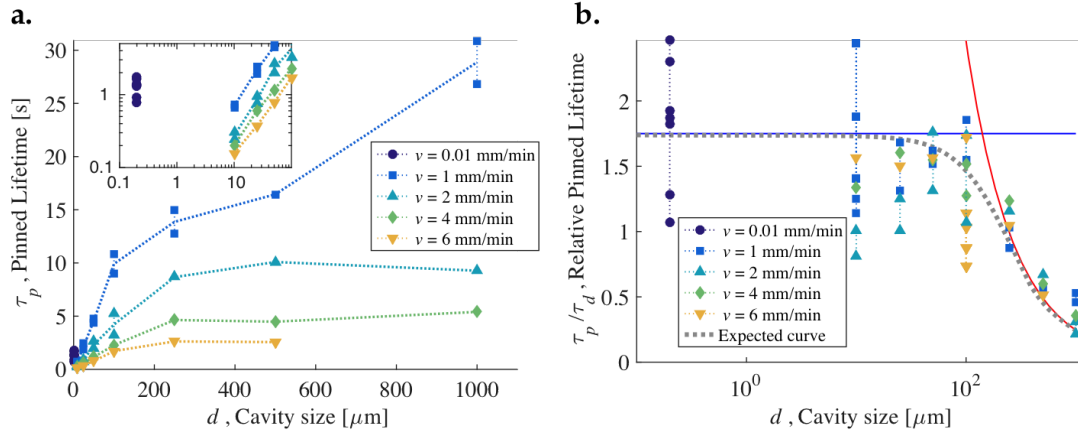


Figure 7.4: Data showing how the aqueous pinned lifetime (a) and relative pinned lifetime (b) vary with square cavity size. The pinned lifetime diverges from a linear relationship for cavities larger than $\sim 100 \mu\text{m}$ owing to their shallow depth (200 nm). The relative pinned lifetime data is fitted well by the two proposed bounding cases, as denoted by the red and blue curves, and discussed in the main text.

line speed we can derive an inferred pinned length based on the video frame count. To assess the accuracy of our measurements, Figure 7.5 plots the measured pinned length with the inferred pinned length. A one-to-one relationship is expected from accurate measurements, and the data indeed clusters around the one-to-one line, giving us confidence in the data.²

7.4 Depinning Mechanisms and Variance in Pinning Data

It is seen that pinning data, whilst conforming to trends, can have a large variance. This can be attributed to the unstable nature of dynamic micro- and nano-wetting in general. The cause of depinning from a cavity can be either (1) dissociation of the meniscus from the cavity wall, (2) rupturing of the thin film that forms over the cavity in the latter stages of pinning, or (3) formation of a new meniscus contact point at the trailing edge of the cavity.

²There is some divergence towards the larger cavity sizes, however this is due to an underestimated measure of the pinned length, due to the limited field of view in the camera (the bulk contact line position had to be estimated in some instances, as it could not be seen in the field of view).

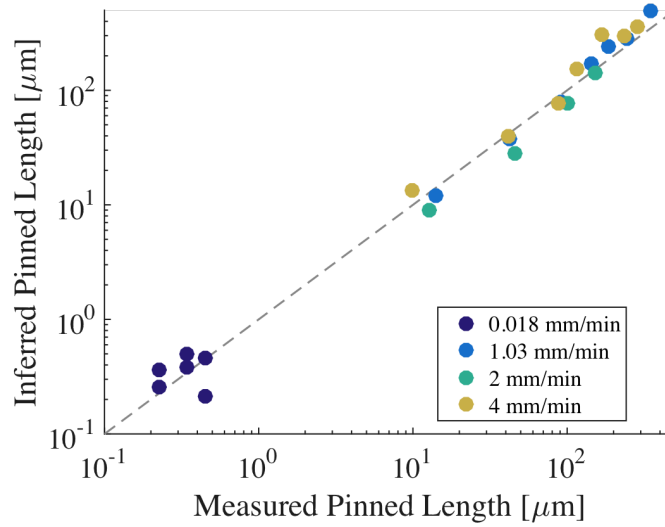


Figure 7.5: Pinned length plotted against the inferred pinned length, to demonstrate the accuracy of measurements. A one-to-one relationship is expected and evident.

Meniscus Dissociation: Early meniscus detachment can occur at any time during a pinning event. Its cause is difficult to isolate, though it's suspected to be from nano-defects or contaminations on the cavity wall. These may induce nano-bubble formation or create an instability from very tight meniscus curvature on sharp nano-defects. Once meniscus detachment is initiated, the rest of the meniscus quickly peels off the remainder of the cavity. In general, Mapperson observes that a cavity that initiates meniscus dissociation will do so repeatedly, and will less often allow sufficient pinning for a thin film to form and rupture. Also, cavities that do not depin prematurely are unlikely to do so. This suggests that the susceptibility to premature depinning is largely permanent, and thus part of the cavity itself.

Moreover, Mapperson observes that occasionally a strongly-pinning cavity will for no apparent reason no longer hold a meniscus and early dissociation becomes the norm. This suggests that contamination can be a cause for early depinning. Contamination on the wall may lead to small air pockets in the liquid-wall interface which locally becomes a poorly wettable surface (essentially a patch wetting in a Cassie state), prompting early separation of the liquid from the wall at that point.

Thin-Film Rupture: When a thin-film forms over a cavity its rupture is not guaranteed at a specific time or film extent. Thin-film rupture occurs by instabilities created by a superposition of thermal waves over the film surface, which can at any

point induce strong film corrugation and rupture the film [17]. This may explain variation in results due to the statistical nature of thin-film rupture. (Thin-film rupture is also a function of substrate and liquid chemistry [18], but in a CFA experiment these tend to not vary across cavities so should not produce highly variable data.)

New Contact Point Formation: As Fang and Amirfazli [19] discuss, when the meniscus lowers down over a cavity it may lower sufficiently to contact the trailing edge of the cavity. This would instantly form a new contact point and initiate depinning. The liquid remaining in the cavity would then rapidly evaporate from its centre. Meniscus oscillations around the meniscus' equilibrium may initiate contact with the cavity's trailing edge before the interface lowers flat. This depinning mechanism may apply when the cavity is not shallow compared to its footprint size (thus preventing earlier thin-film rupture), but it has not been observed on nano-deep microcavities where the other depinning mechanisms appear to dominate. It may apply to nano-cavities, however.

Depinning mechanisms would be an excellent focus of further study, as many industrial processes and material studies involve moving contact lines and subsequent depinning from micro- or nano-defects on the substrate. Variance in depinning time and length data in this present study appears largely unavoidable.

7.5 The Dominance of Surface Tension

From Figures 7.3 and 7.4 there is strong reason to suspect that viscous and inertial forces are negligible and surface tension dominates the pinning dynamics. There is a lack of variance in pinned length with contact line speed, and the pinned lifetimes appear to increase inversely with speed. Surface tension does not vary with speed, but viscous and inertial effects do.

To probe this further, we first normalise the pinned lifetime data to the 1 mm/min data, as shown in Figure 7.6a. The dashed lines are the expected normalised pinned lifetimes for each data set based on speed alone and ignoring viscous or inertial effects. The scaling of normalised lifetimes with speed adheres to the absence of inertial / non-linear speed effects.

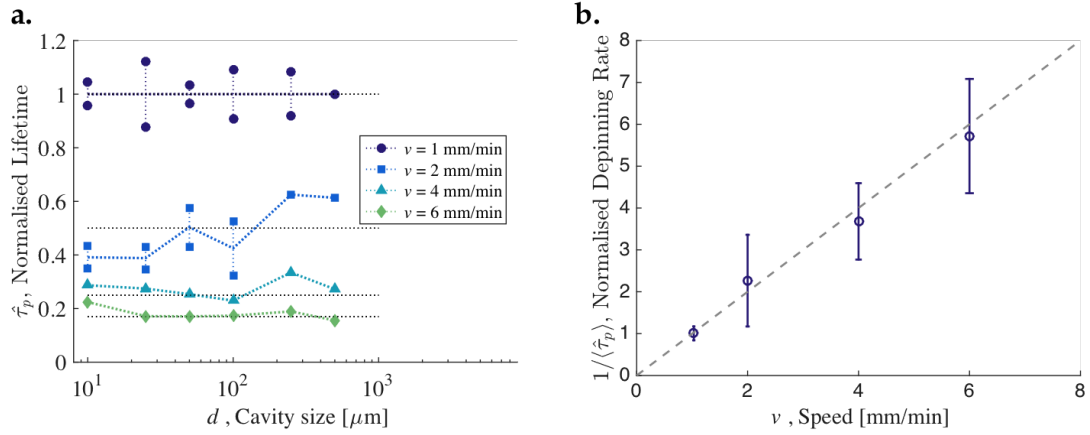


Figure 7.6: (a) The normalised pinned lifetimes. The dashed lines indicate the expected value of each cluster based on speed alone and neglecting any inertial effects. (b) The mean normalised depinning rate, showing a one-to-one relationship with speed, confirming that pinning dynamics scale linearly with speed and viscous forces can be neglected.

We then average the data at each speed across all cavity sizes, and take its reciprocal to yield the mean normalised depinning rate (see Figure 7.6b). It shows a one-to-one relationship with speed, consistent across all cavity sizes. That is, if the contact line speed changes by a factor a , the pinned lifetime changes by $1/a$. This affirms that inertial and viscous forces in the liquid can be neglected, suggesting that surface tension is the dominant factor in these processes. It is unlikely that CFA liquids will have a much greater viscosity than that of water, so this conclusion can be safely generalised to all CFA experiments.

We have demonstrated that hydrodynamic theory explains the trends in the data, at least down to cavities 200 nm in size and 200 nm deep. It is anticipated that the observed trends will continue down to defects just several nanometers in size, possibly smaller. Only when the mean free path of the liquid molecules approaches the size scale of pinning (which would be for cavities a few nanometers in size) is there reason to predict a divergence from hydrodynamic theory.

However, regarding the mystery of depinning, it is as yet unknown whether premature meniscus detachment from a cavity wall finds its explanation in molecular kinetic theory in whole or in part. At this stage, depinning by meniscus detachment must include study of nano-bubbles, thermal instabilities and contact angles / receding contact lines on nano-rough surfaces.

7.6 Pinning Dependence on Cavity Shape

Pinning data presented in the previous section dealt with square cavities. Here we introduce asymmetry to reveal the dependence on the cavity length versus its width.³

7.6.1 Dependence on Cavity Length

The data here is derived from the template region shown in Figure 7.1c, where the cavity width is fixed at $10\text{ }\mu\text{m}$ and the length varies from 1 to $50\text{ }\mu\text{m}$.

Figure 7.7 plots the pinned length on these cavities at the former range of speeds. For reference, the blue dashed line denotes the expected pinned length for square cavities, as shown previously. The grey dashed curve is a data fit giving the anticipated profile.

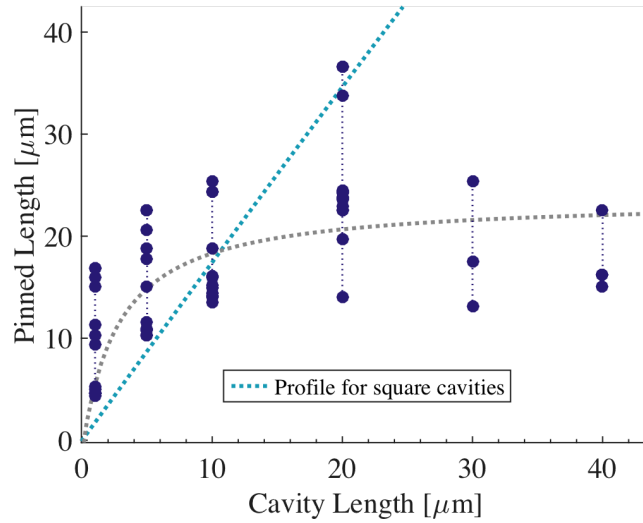


Figure 7.7: Pinned length data from cavities fixed at $10\text{ }\mu\text{m}$ wide and varying in length from 1 to $50\text{ }\mu\text{m}$. The pinned length profile of square cavities matching the given cavity length shows a marked divergence from the data, suggesting that cavity length is not the primary pinning determinant.

The cavity length varies from 0.1 to 5 times the cavity width. It is seen that the data intersects the square cavity trend when the length equals the width, as

³Recall that cavity length is defined as the cavity dimension perpendicular to the bulk contact line, and cavity width is parallel to the contact line.

expected. For cavity lengths below this intersection point, the cavity width is greater than the length, and this produces an increase in the pinned lifetime (relative to the square cavity trend line). When the cavity's length increases beyond its width (i.e. to the right of the intersection point), the pinned lifetime essentially plateaus. These trends suggest that cavity width is more dominant in determining pinned length than is the length. These trends naturally translate to the pinned lifetime as well.

7.6.2 Dependence on Cavity Width

The data here is derived from the template region shown in Figure 7.1b, where the cavity length is fixed at 100 μm and the width varies from 100 to 600 μm .

Figure 7.8 plots the pinned length on these cavities. The blue dashed line again displays the trend line for square cavities.

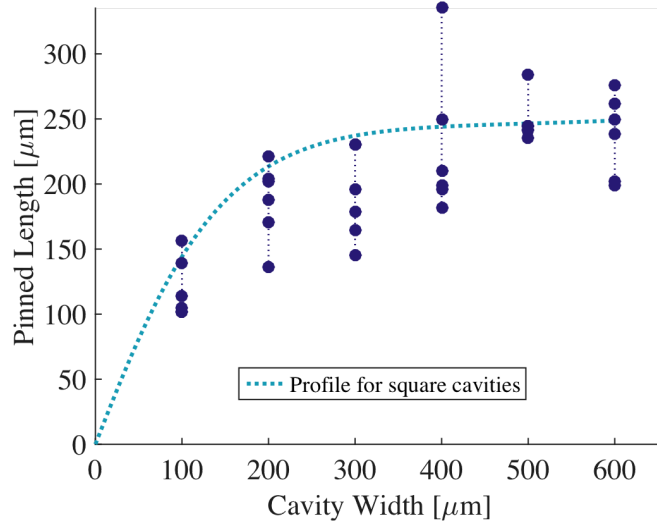


Figure 7.8: Pinned length data from cavities fixed at 100 μm long and varying in width from 100 to 600 μm . The pinned length profile of square cavities adheres well to the data, suggesting that cavity width is the primary pinning determinant.

As the cavity width increases larger than its length we observe that the extent of pinning conforms reasonably well to the square cavity case. In general, the pinned length either matches the square cavity profile, or is slightly below it (accounting for the obvious variation inherent in the pinning data, as discussed previously). This affirms our prior conclusion that cavity width is the primary factor determining the

extent of pinning. The cavity width is the extent of the pinned portion of the contact line. Thus the experimenter is encouraged to keep in mind the ability to alter the pinned length on asymmetric cavities by how the template is oriented beneath the contact line.

7.6.3 Impact of Cavity Entrance Angle

The final aspect of cavity geometry to study in relation to pinning eccentricity is the cavity's entrance angle. The entrance angle is as shown in Figure 7.1a. For a rectangular cavity oriented with a wall parallel to the contact line, the entrance angle is 180° . The pinning eccentricity is plotted in Figure 7.9 showing a dramatic influence over entrance angles of 80° to 120° . This demonstrates that for optimal assembly under pinned-convective dynamics, the entrance angle should be kept well above 100° . Narrow corners ought to be positioned towards the rear of the cavity, not meeting the contact line head-on. Conversely, if pinning is to be avoided for any reason, small-angle corners should be positioned at the cavity front.

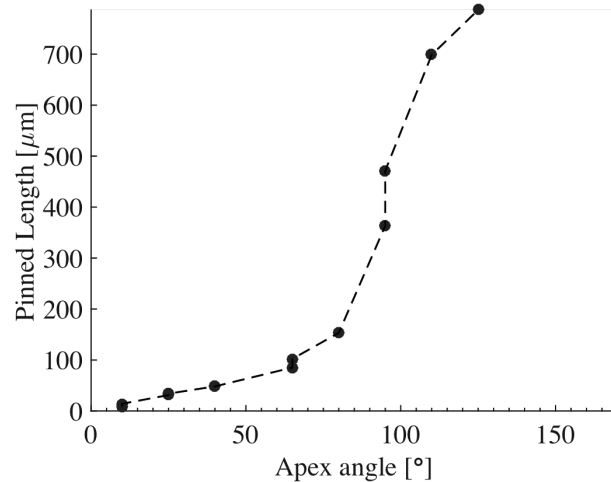


Figure 7.9: The relationship between the pinned length and the entrance angle of a cavity relative to the contact line. The most dramatic change in pinned length occurs for intermediate angles.

Note that the entrance angle must be considered together with the length of the pinned perimeter. For example, rotating a rectangular cavity to have the entrance angle anywhere between 90° and 180° will not see a statistically meaningful variation in the pinned length. This is due to the change in the perimeter of the pinned front

when the cavity is rotated, which offsets the change in entrance angle, as shown in Figure 7.10. The cavity orientation to yield the smallest entrance angle also presents the longest pinning perimeter (effectively like pinning on a larger cavity) and the two effects largely cancel each other in the case of a square cavity. This applies to single cavities. When an array of cavities is present, however, rotating the *array* does alter the amount of macro-scale contact line distortion over the array (as covered in Section 3.7).

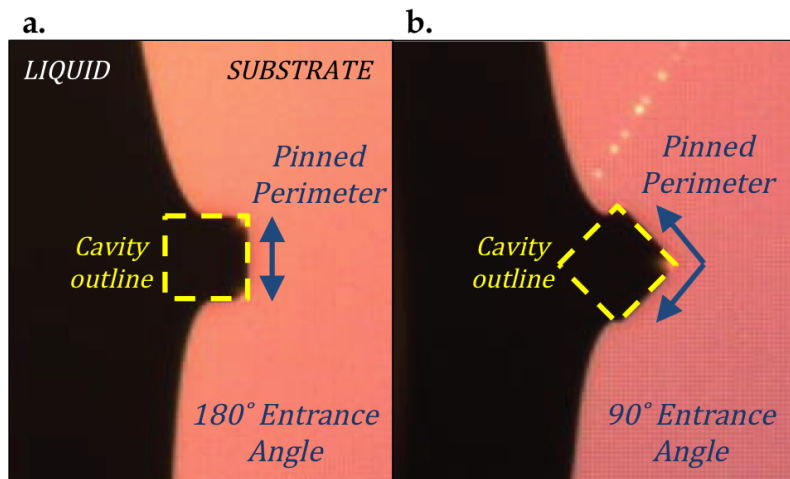


Figure 7.10: Rotating a square cavity to introduce a different entrance angle does not alter the pinned length because of the change in size of the pinned perimeter. Lower entrance angles have a larger pinned perimeter, and this offsets the reduced pinned length normally expected from lower entrance angles.

7.6.4 Intermediate Summary of Pinning Dynamics

To summarise the key points thus far, we have demonstrated that pinning is linearly dependent on the cavity size for small cavities. Whilst the duration of pinning has some variance, it is possible to reasonably predict the extent of pinning on square and rectangular cavities in most situations. We have also shown that pinning is essentially a surface tension effect, and as such it scales linearly with contact line speed. We will now move into studying more aspects of pinning, including the predicted meniscus clamping dynamic.

We now extend our study to derive trends about the 3D meniscus morphology and the contact line during pinning. Reconstructing the meniscus form in 3D reveals key information relating to meniscus clamping and thin-film formation.

More than that, to pursue a study of convective dynamics in the next chapter we must be able to reconstruct the meniscus and contact line forms throughout pinning under a range of experimental conditions. To that end, below we also derive trends about meniscus surface angles, contact line shapes and the pinning force. These are combined in the following chapter to produce a versatile model of pinned menisci, which are then subject to evaporative simulations and convective flow analyses.

7.7 Meniscus Morphology During Pinning

The pinned-convective model predicts a strong meniscus clamping dynamic. It also surmises that a thin-film forms over the cavity, dramatically increasing local convective flow rates. Here we employ the micro-4D meniscus reconstruction technique detailed in the previous chapter to confirm these predictions.

7.7.1 Clamping Dynamics

A $500\text{ }\mu\text{m} \times 1000\text{ }\mu\text{m}$ cavity, at 200 nm deep, was used with gold nanorods in water.⁴ The rods were synthesised with CTAB ligands and later coated in sodium polystyrenesulfonate to allow repeated washing (to restore the surface tension to that of water). The rods were $44\text{ nm} \times 107\text{ nm}$, at $\sim 10^{11}$ particles/mL, as needed for micro-4D scanning.

The large cavity that was used ensures high resolution in the 4D reconstruction, given that previously derived scaling laws enable us to extrapolate the derived reconstruction down to any desired cavity size. The same scaling laws apply to the full 3D meniscus shape because we have shown that surface tension governs the pinning dynamic over micro- and nano-cavities.

The nanorod solution was recorded as it progressed through pinning and depinning from the cavity. 3D reconstructions were not needed from every single video frame, so only frames every 435 milliseconds were reconstructed. This provides ample temporal resolution, yielding fifteen 3D snapshots over the pinned lifetime. A sample 2D snapshot and reconstructed 3D meniscus are shown in Figure 7.11.

⁴Template made by EBL in PMMA on Si. PMMA has a very similar wettability to SU8.

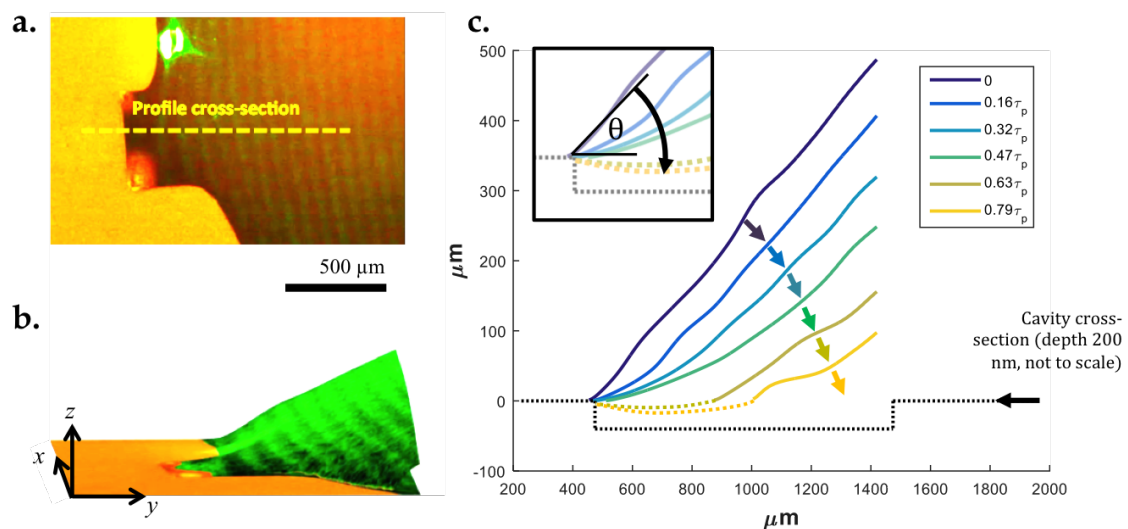


Figure 7.11: (a) A photograph of a gold nanorod solution pinning on a cavity 500 μm wide. (b) The reconstructed 3D meniscus of (a). (c) Profiles of the meniscus along the cross-section marked in (a), at various moments of the pinned lifetime. A thin-film is seen to form over the front of the cavity in the latter moments of pinning.

The profile of the meniscus in the y - z plane down the centre of the cavity was taken from various snapshots. 2D profiles are plotted in the Figure, denoted by their respective fractions of the pinned lifetime (τ_p) at which they occur. It is seen that as the meniscus lowers, a thin film is formed at the front of the cavity in the latter third of the pinned lifetime. The formation of a thin film equates to a strong clamping dynamic. The meniscus angle progresses over the cavity from the receding contact angle down to zero, essentially lying flat over the cavity opening.

The conventional CFA model assumes a capillary immersion force is nearly constantly operating, but the only time this will realistically occur is when the meniscus has clamped down to be lower than the particle height. At that point the particle is trapped against the substrate with the meniscus receding down over it. At all times preceding this the meniscus force will be highly transient (as was explained in Section 1.5.2). This confirms a key aspect of the pinned-convective model, whereby particles are not pushed into place by a receding meniscus (as in the conventional CFA model), rather they are trapped in the cavity by a lowering meniscus.

The Brownian diffusion rate of nanoparticles is much faster than the clamping dynamic, and this begins to explain why nano-CFA can often seem like a hit-and-miss endeavour. Without a strong force to simultaneously drive particles into the

cavity, assembly becomes a much less probable outcome.

7.7.2 Thin-Film Formation

By correlating the 3D reconstructions with the colour photographs, the point at which a thin-film forms can be recognised by a sudden brightening at the head of the cavity. Figure 7.12 shows this well. By studying a variety of cavities and cavity sizes, the thin-film lifetime, as a percentage of the pinned lifetime, can be determined. This lifetime denotes how long the thin-film survives before rupturing. Data is plotted in Figure 7.12c, which shows a mean thin-film lifetime of 12 % (standard deviation approximately 2.5 %).⁵ This data will be useful for modelling evaporative dynamics over nano-cavities in the coming chapter.

7.8 Contact Line Profile During Pinning Events

Here we will examine the contact line behaviour around a cavity during pinning events. This has had limited discussion in prior work for defects rising out of the substrate [15, 16], but has not received attention for cavities. This will assist us in modelling the meniscus on and around a cavity.

This section consists of describing the contact line profile as it varies in time (Section 7.8.1), in space (Section 7.8.2) and with cavity size (Section 7.8.3).

7.8.1 Contact Line Progression in Time

Figure 7.13 presents the meniscus outlines around variously sized square cavities, at every tenth of the pinned lifetime. It is seen that the majority of contact line movement occurs towards the end of the pinned event.

As seen in the upper-left diagram of the Figure, during pinning the contact line meets the cavity at some intermediate point along the cavity perimeter (the

⁵Larger cavity sizes were avoided as they diverge from the linear pinning scaling trend, and smaller cavity sizes could not be adequately observed, as the slider CFA apparatus prohibited greater than $2\times$ magnification. The large error bars on some data points is due to insufficient frame rate to resolve the thin-film lifetime more accurately, and they apply only to the smaller cavities that have a very short pinned lifetime.

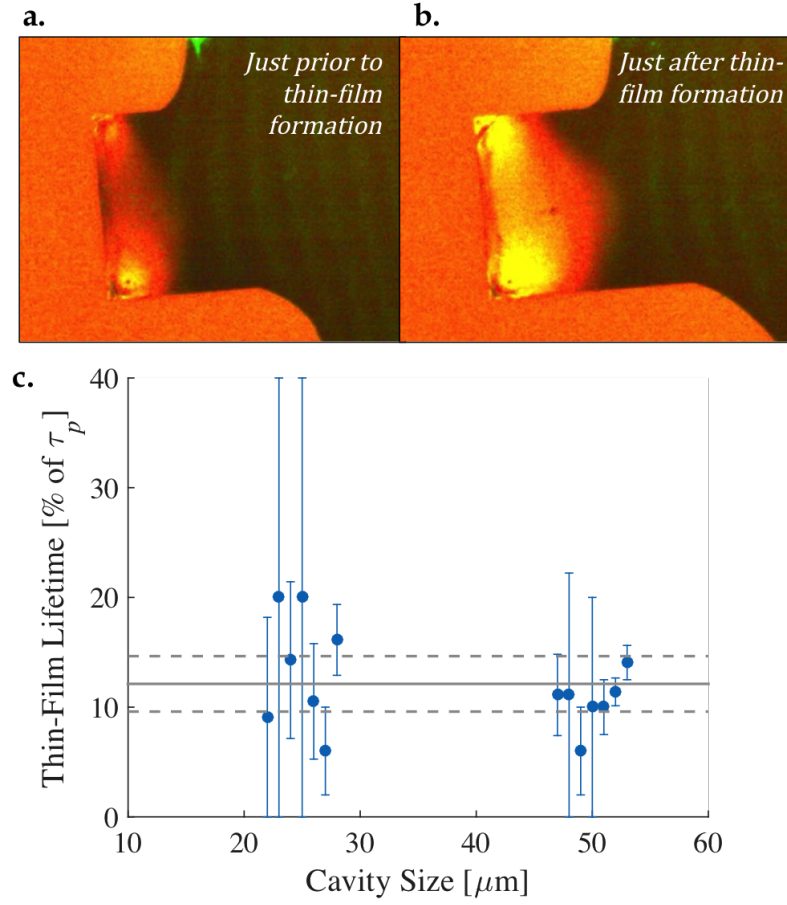


Figure 7.12: Photographs of the meniscus immediately prior to thin-film formation (a) and after thin-film formation (b). The thin-film is evidenced by the bright region appearing at the head of the cavity. In (c) is plotted the lifetime of the thin-film, shown for two cavity sizes and given as a percentage of the pinned lifetime. The mean is 12 %, with a standard deviation of approximately 2.5 %.

yellow dot in the Figure) and then makes a sharp turn to follow the cavity wall up to the front of the cavity. This represents a discontinuity in the curve of the contact line where it meets the cavity boundary. The contact line within the cavity region follows the cavity perimeter.

To characterise this unique contact line profile, there are two parameters of most interest. The first is the intersection angle (θ) that the contact line makes with the side wall of the cavity. The second is the retraction distance, which denotes how far along the cavity side perimeter the contact line intersects with the cavity, as measured from the front of the cavity. These are portrayed in the Figure.

Cavities ranging from 25 to 200 μm were studied. Figures 7.14a and 7.14b

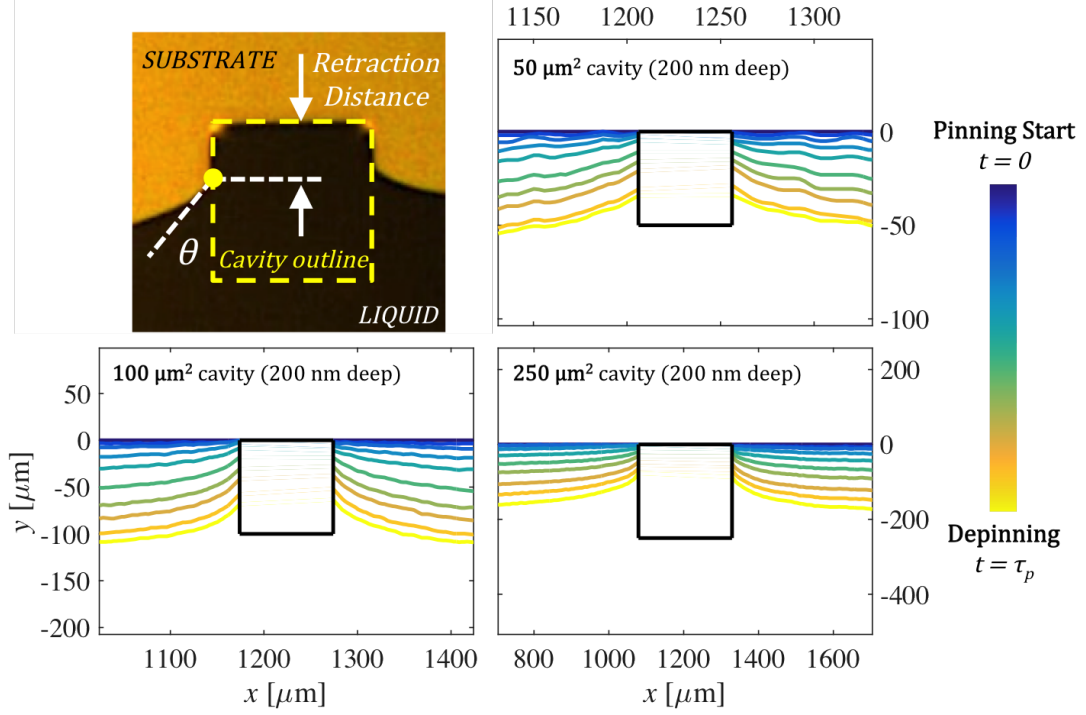


Figure 7.13: Profiles of the contact line around variously sized cavities throughout pinning events. The upper-left diagram depicts key parameters used to characterise the contact line profile. Data from a 25 μm cavity has been omitted, as it is similar to the other cavities presented.

present data from four such cavities, demonstrating how these parameters vary over the pinned lifetime.⁶ The contact line retraction distance is given as a percentage of the cavity size. The contact line retracts gradually down the side of the cavity at first, and then accelerates. The bulk contact line is moving at a constant speed throughout. The dashed line is a parabolic fit that approximates the trend.⁷

This trend is explained by observing the progression of the angle the contact line makes with the cavity side perimeter. The angle begins at 90° , meaning the contact line is straight and parallel with the front of the cavity. The angle then has an accelerating reduction in size until it levels out at $\sim 40^\circ$ in the latter half of the

⁶More than four cavities were studied, giving similar trends to those shown. Data from additional cavities is not plotted as it would overcrowd the plot without adding any new information.

⁷The data is not strictly a parabolic fit, as the retraction rate is roughly linear in the latter third/half of the pinned lifetime. However, due to the inherent spread in the data, and for ease of modelling, a parabolic fit is very adequate.

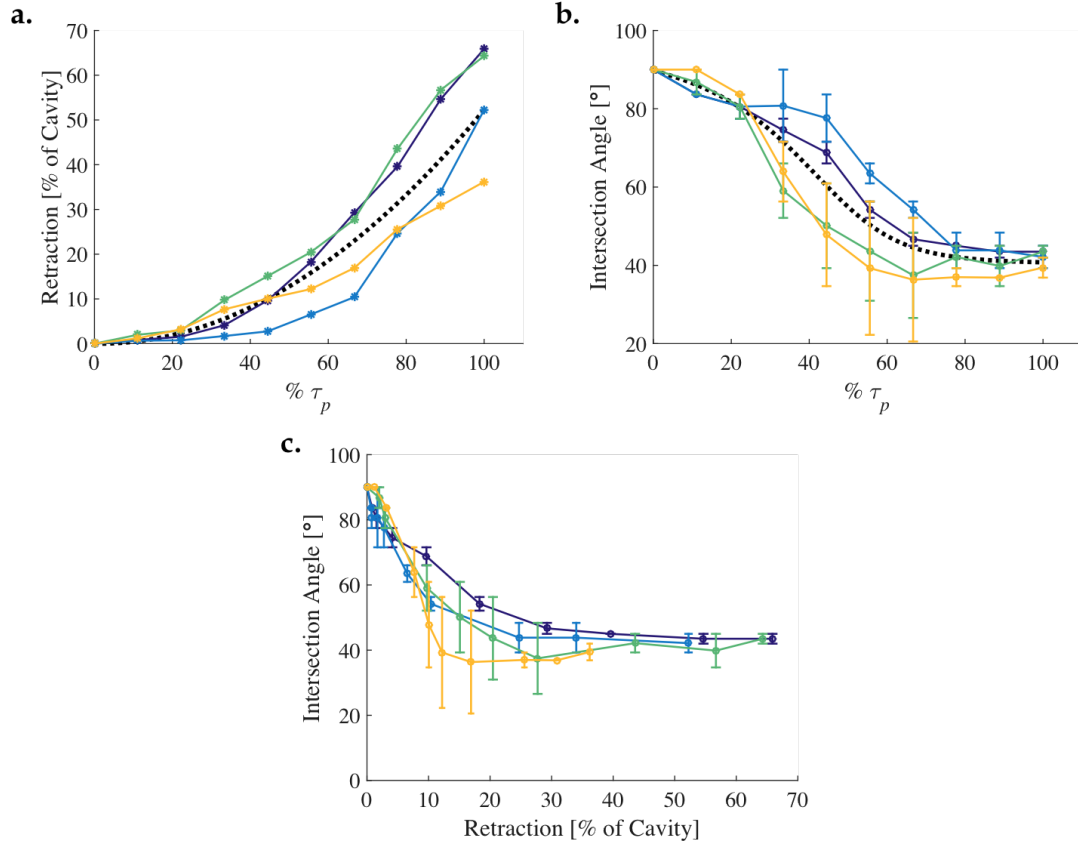


Figure 7.14: (a) Data showing the accelerating retraction of the contact line during a pinned lifetime. (b) Data showing the reduction and then plateauing of the intersection angle during pinned lifetime. (c) Data showing that the retraction of the contact line primarily occurs when the intersection angle has reduced to its minimum value.

pinning event. The dashed line is a sigmoid fit to the data, following the form

$$a + c \left(1 + \frac{50 - x}{\sqrt{b + (50 - x)^2}} \right)^2 \quad (7.3)$$

The trend can be interpreted in terms of balancing forces. At all times the contact line pulls outwards from the cavity in the direction of the intersection angle. This is initially perpendicular to the direction of bulk contact line motion, when the angle is close to 90° . The energy from the stretching of the contact line at this time is expended in stretching the meniscus over the cavity more and more as the pinned length increases. This results in a reduction of the intersection angle.

There is a certain resistance to a discontinuity forming in the contact line at the cavity boundary. We might call this the discontinuity force threshold. The contact line prefers to maintain a smooth flowing profile, not one with sudden bends and

turns.

As the intersection angle reduces, the elastic contact line force pulls with an increasingly large component parallel to the direction of recession. Once this component of the force exceeds the discontinuity force threshold, an abrupt discontinuity forms and the contact line begins to retract along the side of the cavity while it still remains pinned across the front of the cavity. The energy of the elastic contact line is now expended in dragging the contact line discontinuity point, and the intersection angle ceases to reduce any further.

This is seen clearly in Figure 7.14c, where we plot the angle of intersection as it varies with the retraction distance. The majority of retraction evidently occurs once the angle has reduced to its minimum value, and the angle remains there until depinning.

Interestingly, the data shows the threshold angle is independent of cavity size. This further supports our prior conclusion that the meniscus profile scales linearly proportional to the cavity size, indicating surface tension dominates the interactions.

It is during the retraction phase of the pinning event that the thin film forms, in the latter portion of that phase. As the point where the contact line joins the cavity slides along the cavity boundary, the meniscus that is still pinned at the front of the cavity is pulled lower and lower. Eventually the meniscus snaps down to form a thin film. From that time on, as the pinned length continues to increase, the thin-film grows in its extent over the cavity.

7.8.2 Contact Line Progression in Space

Having seen how the contact line progresses temporally, let us examine how it progresses spatially. Nadkarni [15] and others have derived that the contact line profile distorted around a defect rising out of an otherwise smooth substrate follows a modified Bessel function of the second kind, zeroth order. (This approximates to a natural log function close to the defect.) Applying the same theory to the contact line extending out from a recessed cavity gives an excellent fit, as shown in Figure 7.15. The fitted functions continue to match the contact line profiles much further from the cavity than shown in the Figure.

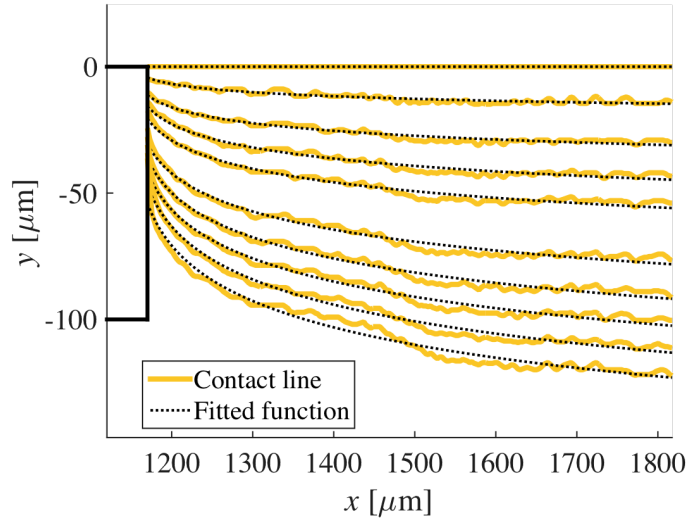


Figure 7.15: Example contact line profiles outside a micro-cavity, overlaid with an excellent fit from a modified Bessel function as predicted by theory.

The fitted equation is

$$y = f_p K_0(|x - x_d|/\kappa) - y_d \quad (7.4)$$

where κ is the capillary length (2700 μm for water at room temperature), y_d is the contact line retraction distance, and x_d is the horizontal offset of the point which the contact line force acts through (the centre of the fitted Bessel function). It is found that a good fit to the data is consistent when x_d is a distance of $d/4$ in from the cavity boundary, where d is the cavity width. This was affirmed for cavities of width 25, 50, 100 and 250 μm .

Fitting the equation to the data was done with Matlab using y_d and f_p as the only fitting variables. The variable f_p is the pinning force function, given by

$$f_p = \frac{F_p}{\pi \gamma_{lv} \theta_{REC}^2} \quad (7.5)$$

where F_p is the magnitude of the pinning force, γ_{lv} is the liquid-vapour surface tension, and θ_{REC} is the standard receding contact angle.

This affirms that pinning due to raised defects follows the same profile as pinning from recessed defects (cavities). It is also a first step in modelling the contact line around a cavity.

7.8.3 The Influence of Cavity Size

To further model the contact line we must characterise how the retraction distance varies with cavity size (we have already established that the contact line intersection angle does not vary with cavity size, and nor does the form of the spatial fit as a modified Bessel function).

The contact line retraction distance before thin-film formation does indeed vary with the cavity size. The data is given in Figure 7.16. The solid line is a data fit of a function of the same form as Equation 7.2 used for the relative pinned length and relative pinned lifetime. The dotted line is an extrapolation of this function down to nano-cavities. No data could be collected for nano-cavities due to limited camera resolution, however there is no reason to expect the trend to differ from the fitted function, which plateaus for cavities $10\text{ }\mu\text{m}$ in size and smaller.

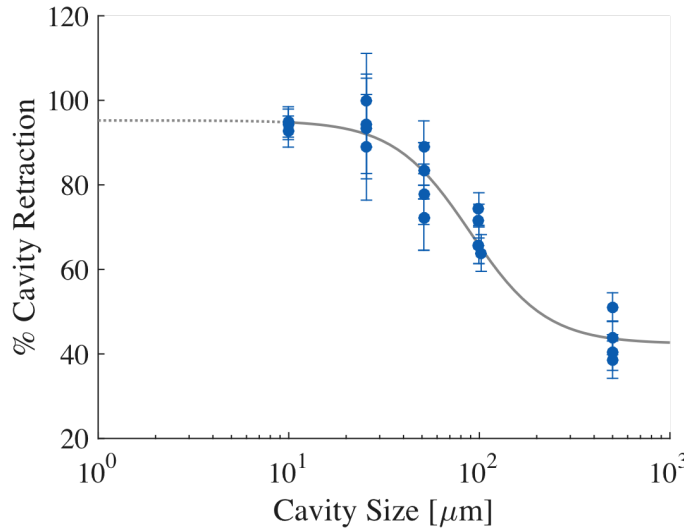


Figure 7.16: Data showing what percentage of the cavity length the contact line retracts over before a thin-film is observed to form at the head of the cavity (depinning occurs moments later). The data indicates a constant retraction distance prior to thin-film formation for cavities smaller than $100\text{ }\mu\text{m}$. The fit form matches that of the relative pinned length and lifetime data.

As a sanity check, we can confirm that a thin-film does indeed form over nano-cavities. A sudden brightening of the meniscus over the front of nano-cavities can be observed, despite the poor camera resolution at that size scale. This indicates thin-film formation.

More conclusive evidence, however, is the observation that particles assembled into nano-cavities are routinely separated evenly to the cavity extremities upon drying. The only explanation for this is that a thin-film is formed and ruptures near the centre of the cavity, pulling particles to the cavity perimeter evenly on all sides as the ruptured film rapidly evaporates to the cavity walls. On this basis we comfortably extrapolate the above data into the nano-regime.

7.9 Characterising the Pinning Force

Based on the contact line fit provided by Equation 7.4, it is possible from Equation 7.5 to derive the force exerted by the pinned contact line at various times throughout a pinning event. This has been done for sample cavities from 25 to 250 μm in size, and the results are shown in Figure 7.17, plotted against fractions of the pinned lifetime.

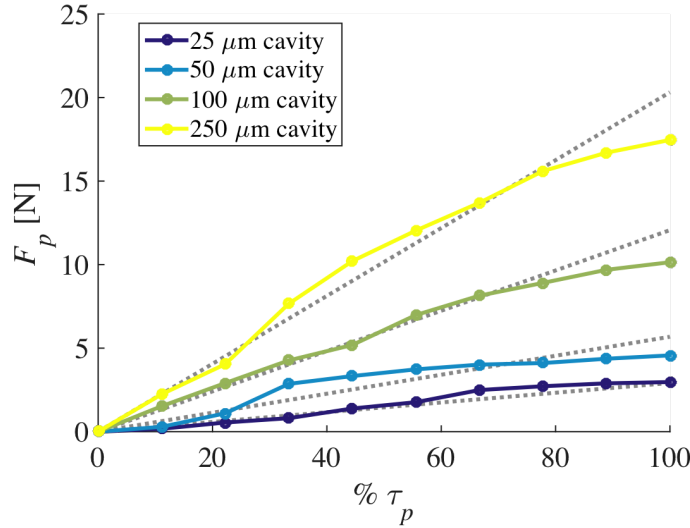


Figure 7.17: The pinning force derived from equation fits to contact line profiles on cavities of various sizes throughout their pinned lifetimes. The force plateaus slightly at the end of pinning, but overall is well approximated by linear fits.

We observe that the pinned force for each cavity size approximates to a linear progression. This is appropriate given a constant bulk contact line speed which would linearly increase the pinned length with time. The order of magnitude of the forces agrees well with data from [15] where raised defects were studied.

Whilst a linear fit is approximate, it can be seen that each force progression curve actually begins to plateau slightly towards the end of pinning. The exact cause of this is uncertain. It may have a correlation with the intersection angle of the contact line, or may be due to thin-film formation, or simply due to a contact line that is free to drag along the side of the cavity whilst still being pinned at the front of the cavity.

Using the linear approximations, the gradient of each cavity size's force progression is plotted in Figure 7.18. Here it is seen that the rate of increase in pinning force for each cavity size of 100 μm and smaller forms a linear trend leading back to the origin, with a gradient of 0.1169 N/% τ_p . The force gradient of the 250 μm cavity diverges from this trend, but this is no great surprise. It has been shown previously that cavities larger than 100 μm (for the given cavity depth of 200 nm) do predictably diverge from all linear trends that exist for smaller cavities.

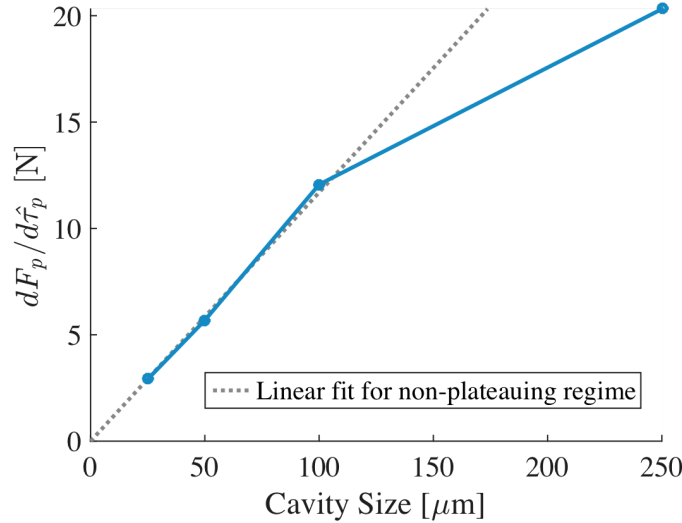


Figure 7.18: The gradient in the pinned force progression throughout a pinning event, based on cavity size. Cavities smaller than 100 μm show a linear trend in accordance with other pinning dynamics that also show linear trends for small cavities.

Based on these findings, we can estimate the gradient in the pinned force throughout a pinning event for any cavity size ($d < 100 \mu\text{m}$) by the simple equation

$$\frac{dF_p}{d\hat{\tau}_p} = 0.1169d \quad (7.6)$$

where d is the square cavity size in micrometers. From this the actual pinned force

at any moment in the pinned lifetime can be estimated by

$$F_p(\% \tau_p) = 0.1169d(\% \tau_p/100) \quad (7.7)$$

This result is important as it allows us to then predict the value of f_p , the pinning force function. That in turn feeds into the mathematical profile of the contact line, with all other variables known (x_d is set at $d/4$ in from the cavity side wall, and y_d is the retraction distance). We are now in a position to compute the contact line profile at any stage in a pinning event for any square cavity of size $< 100 \mu\text{m}$.

7.10 Conclusions

We have now sufficiently characterised pinning dynamics, showing that they scale linearly with the size of the cavity for small cavities. We have also shown that trends in micro-cavities apply equally well to nano-cavities.

By applying the new technique of micro-4D meniscus profilometry we have demonstrated that meniscus clamping dynamics are real, and that thin-films are formed over cavities in normal pinning events. These results give important corroboration for the proposed pinned-convective model.

Moreover, characterisation of pinning dynamics has led us to observe and account for all variables in Equation 7.4 describing the full contact line profile. This enables us to predict the contact line shape in the vicinity of any square cavity of size $< 100 \mu\text{m}$, at any moment during pinning. Coupled with the observed progression of the 3D meniscus over the cavity during pinning, we are now in a position to model the full meniscus form over micro- and nano-cavities at any stage throughout their pinned lifetime.

This is an exciting achievement, as it enables us to forge ahead in the next chapter to model convective dynamics during pinning. By leveraging the evaporative simulations, we will soon derive the magnitude and reach of local convective flows that are setup momentarily over a cavity during pinning, showing their suitability as assembly forces. We will thus not only reveal the plausibility of the pinned-convective model, but we will also analyse the impact of several experimental variables on pinned-convective dynamics, allowing educated optimisation of nano-CFA for the experimentalist.

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The Pinned-Convective Model: Quantifying Assembly Dynamics

8

The final aspect of the pinned-convective model to quantify is the convective dynamics, and their resulting impact on nanoparticles in the vicinity of pinning events. This chapter draws together much experimental work to estimate evaporation rates over CFA menisci, and to deduce the convective flow rates at various positions and times during pinning events. This culminates in a simulation of nanoparticle dynamics during pinning, which demonstrates that pinned-convective dynamics are real phenomena and effective for nano-assembly by CFA. Insights are also gained about how various experimental parameters influence the assembly viability.

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8.1 Introduction

In the previous chapter we characterised pinning and clamping dynamics, affirming those aspects of the pinned-convective model and deriving useful trends. In the present chapter we will estimate local convective flows and drag forces on particles, demonstrating the overall viability of the pinned-convective model. No known studies to date have studied pinned evaporative dynamics. The results of this chapter are therefore a pertinent contribution to the field of not just nano-CFA, but of liquid-based deposition and dynamic nano-wetting.

Our route of discovery will follow three main stages, with a final section to tie it all together. The first stage (Section 8.2) involves modelling evaporation from a generic CFA meniscus. From this, generalised principles about evaporation rates in CFA are derived. We also briefly consider the role of thermal Marangoni flows.

The second stage (Section 8.3) focusses on converting evaporation data into estimates of local convective flows during pinning events. The meniscus form can be modelled under various experimental conditions, and convective flow trends analysed. This will be done for multiple snapshots throughout the pinned lifetime, yielding a temporal description of convective flows during pinning.

The third and final stage (Section 8.4) involves mapping nano-assembly viability. Convective flows are used to calculate the spatial extent of assembly dynamics, as well as the energy imparted to particles throughout pinning. This work demonstrates the overall feasibility of the pinned-convective model.

The chapter closes by considering how stochastic processes (Brownian diffusion and particle-particle collisions) influence pinned-convective assembly (Section 8.5).

8.2 Stage I: Evaporative Modelling on CFA Menisci

8.2.1 Substrate Temperature and Thermal Marangoni Flows

The Impact of Substrate Temperature: In Chapter 6 we saw a technique to model CFA meniscus thermodynamics at a snapshot during a pinning event. Using that original meniscus snapshot we vary the substrate temperature to observe the

impact on the evaporation rate, the meniscus temperature and surface tension. Data for these three parameters are shown in Figure 8.1 along the cross-section given in Figure 8.1a.

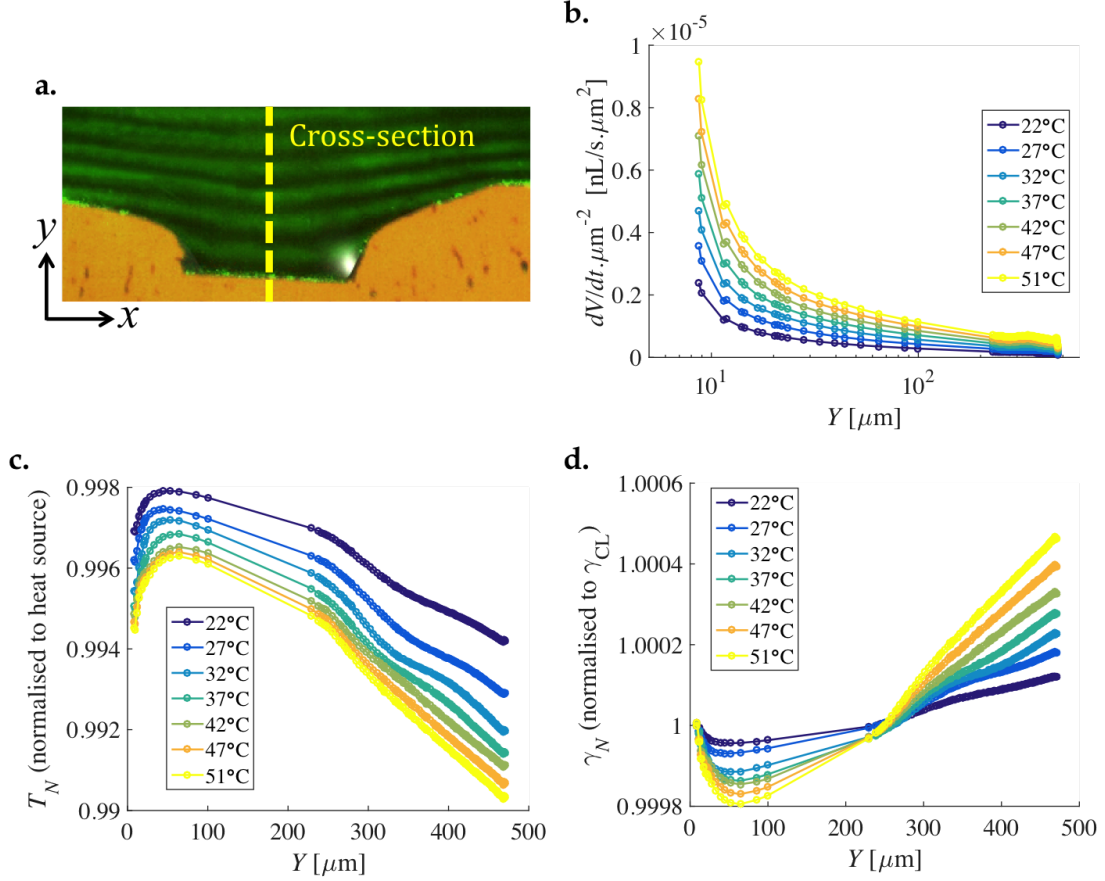


Figure 8.1: (a) A bird's eye view of the meniscus region of interest, showing the cross-section from which data in the remaining plots is taken. The evaporation rate (b), meniscus temperature (c) (normalised to the substrate temperature), and thermally-modified surface tension (d) are as per the tabled substrate temperatures. Strong evaporative cooling is evident near the contact line, and variations in surface tension suggests potential of Marangoni flows.

The evaporation rate along the cross-section conforms to the very common evaporative profile as one approaches a contact line, found in numerous papers (mostly studying sessile droplet evaporation), with a singularity existing at the contact line itself. The proportional change in evaporation rate exceeds the proportional change in temperature for the different cases modelled.

The impact of this is that evaporative cooling becomes pronounced at the contact line, evident in Figure 8.1c. The amount of evaporative cooling increases over

the whole meniscus as the substrate temperature increases, but less and less so with higher substrate temperatures. The peak meniscus temperature occurs not at the contact line but some distance before it—approximately 50 to 70 μm away with substrate temperatures of 22 to 51°C, respectively.

The consequence of evaporative cooling is seen in Figure 8.1(d), where thermally-induced Marangoni flows are intimated by variations in surface tension. The data is normalised to the surface tension at the contact line for each experiment, for comparison purposes. Each curve has a minimum, implying a Marangoni stagnation point at the surface temperature maxima. Xu and Luo [1] found a Marangoni stagnation point approximately 10 μm from the contact line at much lower contact angles (10°), in reasonable agreement with the results here. Marangoni flows, if present, are towards the contact line on the left of the stagnation point, and away from the contact line in the bulk region.

Thermal Marangoni Flows: The Marangoni number (Ma) is a dimensionless number indicating the proportional strength of surface tension forces relative to viscous forces (at $Ma \gg 1$ Marangoni flows start to appear). The thermal Marangoni number is given by

$$Ma = -\frac{d\gamma}{dT} \frac{L}{\eta D_s} \Delta T \quad (8.1)$$

where $d\gamma/dT$ is the rate of change in surface tension with temperature (N/m.K), L is the characteristic length scale (m), η is the dynamic viscosity (N.s/m²), D_s is the thermal diffusivity (m²/s) and ΔT is the change in temperature over the meniscus.

In the region between the contact line and the stagnation point, the Marangoni numbers are approximately 1.3 for the 22°C substrate and 7.6 for the 51°C substrate (using characteristic lengths of 50 μm and 70 μm , respectively). This suggests no influential thermal Marangoni flows near the contact line.

In the bulk liquid region beyond the stagnation point, the change in temperature and the length scale are much larger. The Marangoni numbers for the minimum and maximum substrate temperatures are 35 and 130, respectively. This suggests the potential for Marangoni flows away from the contact line at high substrate temperatures. This is a mechanism by which the concentration of nanoparticles at the contact line may experience a degree of self-limitation, which is useful to prevent aggregated deposition.

These results indicate that the stagnation point shields the assembly region from disruptive Marangoni flows. This is even more true with nano-cavities, as the length scale (L) and temperature variation (ΔT) are much smaller, dramatically reducing Ma . Moreover, Hu and Larson [2] show that very small concentrations of surfactant at the water surface (300 molecules/ μm^2 , or 5×10^{-22} mol/ μm^2) are sufficient to suppress thermal Marangoni flows during droplet evaporation. It is hence predicted that Marangoni flows immediately at the contact line are very unlikely in nano-CFA.

No firm conclusions on the role of thermal Marangoni flows have been drawn in prior literature, making the above findings an important contribution.

8.2.2 Generalising the Evaporation Rate

Modelling evaporative dynamics is very computationally intensive. To efficiently study a wide range of nano-CFA conditions we desire a generalised relationship between the point-wise evaporation rate and meniscus morphology.¹

Figure 8.2a shows that the point-wise evaporation rate appears to correlate well with meniscus height. The plot contains every data point from the meniscus model, and whilst there is a little scatter, it is evenly distributed around the trend lines. The fitted functions are visual best-fit expressions, being two-term exponentials of the logarithm of the meniscus height. That is,

$$E_v = P_1 e^{P_2 \log_{10}(z)} + P_3 e^{P_4 \log_{10}(z)} \quad (8.2)$$

where z is the point-wise meniscus height (μm) and P_1 to P_4 are fitting pronumerals.

To verify that meniscus height is a reliable predictor of evaporation rate on its own, irrespective of local meniscus curvature, Figure 8.2b plots the same data at the lowest and highest substrate temperature settings, where the data over the cavity is distinct from the data not over the cavity. The meniscus over the cavity is characterised by sharp bends in the contact line, very low surface angles and regions of high curvature. The meniscus away from the cavity is much more planar. It is

¹COMSOL Multiphysics is also unable to model extremely divergent size scales (e.g. nano-cavities under a macroscopic CFA apparatus), so a generalised model is also useful in that respect.

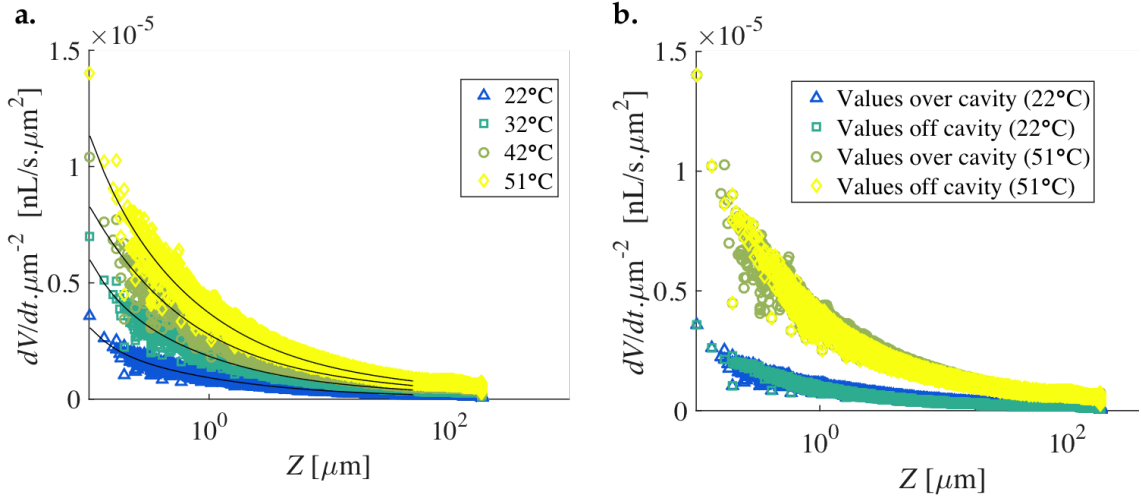


Figure 8.2: (a) The full evaporation rate data set at four substrate temperatures plotted against the point-by-point meniscus height. The solid lines are data fits of Equation 8.2 at each temperature. (b) The same data in (a), excluding the intermediate temperatures, plotted to distinguish the meniscus over the cavity from that off the cavity. The evaporation rates are seen to be irrespective of whether the meniscus is part of the pinned region or not.

seen that both meniscus regions follow the same trend, justifying an evaporative function based solely on height above the heated substrate.²

Support from Existing Models: Comparison with published evaporative models affirms the above conclusions. Evaporation from small liquid bodies is well studied on spherically-capped sessile droplets, whose symmetry allows a first-principles derivation of evaporation rates. There is also much empirical support for such models.

There is a discrepancy, however, in that evaporation from sessile droplets depends on contact angle, not just local meniscus height. This arises because sessile droplets are very small, having a high net curvature, whereas CFA menisci are very planar (pinning perturbations at the contact line constitute an extremely minor change to the overall meniscus shape which remains essentially planar at all times). There is a way to compare the two models, however.

²In Appendix 8.B we note that the four fitting pronumerals (P_1 to P_4) vary predictably with the substrate temperature. We can fit a temperature-dependent function to each pronumeral, allowing us to interpolate the evaporative function (Equation 8.2) at any substrate temperature between 22 to 51°C.

A highly successful droplet evaporative model is given in Equations 8.3 to 8.5 [3]. The model is irrespective of droplet size (R) and only assumes a spherical meniscus. We can use this model to approximate CFA by enlarging the spherical cap enough to be highly planar over the size of a CFA meniscus.³ In the model, r is the radial distance from the droplet centre and θ is the contact angle:

$$E_v = J_0(\theta)(1 - r^2/R^2)^{-\lambda(\theta)} \quad (8.3)$$

$$J_0(\theta) = \frac{Dc(1-H)}{R}(0.27\theta^2 + 1.30)(0.6381 - 0.2239(\theta - \pi/4)^2) \quad (8.4)$$

$$\lambda(\theta) = \frac{1}{2} - \frac{\theta}{\pi} \quad (8.5)$$

where c is the saturation vapour concentration, D is the vapour diffusion coefficient, H is the relative humidity and R is the droplet radius. Based on the contact angle and radial distance, the height z of the spherically-capped meniscus at any point is

$$z = \sqrt{R^2/\sin^2(\theta) - r^2} - \frac{R}{\tan(\theta)} \quad (8.6)$$

Figure 8.3 demonstrates that the spherically-capped evaporation rate, using the spherical CFA-approximation, loses its local contact angle dependence and correlates strongly with the meniscus height alone. Equation 8.2 at 51 °C is given for comparison, showing excellent agreement in form.⁴ The generalised CFA evaporative model is thus supported by extant high-confidence evaporation studies.

Armed with the ability to estimate point-wise evaporation rates over any CFA meniscus profile, we will now move into the second stage of quantifying nano-CFA's convective dynamics: estimating convective flow rates during pinning.

³This is much larger than the capillary length, so such a droplet will not be spherically-capped in reality, due to gravity, but we are leveraging a model which assumes a spherical shape irrespective of droplet size.

⁴Values are $R = 10$ cm, $H = 0.4$, $c = 0.0867$ kg/m³ and $D = 2.91 \times 10^{-5}$ m²/s. Saturation vapour concentration and vapour diffusion coefficient are calculated as at 51°C. Note that the spherically-capped model ('CA' plots) gives the *unscaled dimensionless* evaporation rate, not the correct magnitude like the CFA model. All 'CA' results are therefore consistently scaled by a factor of 7 to match the magnitude of the CFA model. This scaling is arbitrary however, as the key point is that the data is independent of contact angle.

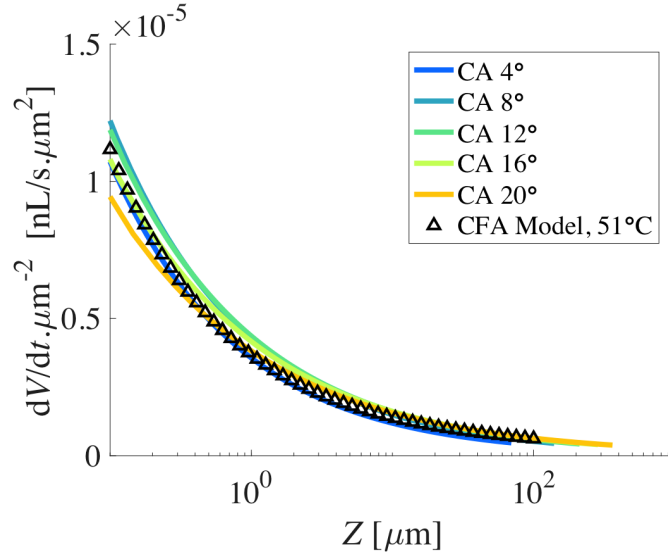


Figure 8.3: Comparison of the CFA evaporation rate model (Equation 8.2) at 51°C with a sessile droplet model (Equation 8.3) at various contact angles (CA). The data affirms that a highly planar meniscus has an evaporation rate that is determined strongly by meniscus height, even with meniscus perturbations near the contact line.

8.3 Stage II: Convective Flows During Pinning Events

The task before us now is to estimate convective flow rates at sequential stages throughout pinning events, and to observe how flows vary with experimental variables. This information will be built on in the subsequent section to simulate assembly dynamics.

8.3.1 A Versatile Meniscus Model

Meniscus models at any moment in the pinned lifetime are required to estimate progressive convective flow rates. Figure 8.4 demonstrates such a model over a 50 μm cavity. Based on experimentally-derived trends (Chapter 7), accurate meniscus profiles can be produced at any instant (t_n) throughout a pinning event ($0 \leq t_n \leq \tau_p$, $n = 1, 2, 3, \dots$). A detailed explanation is in Appendix 8.A. Meniscus modelling is versatile in terms of cavity size, cavity depth, substrate temperature, contact line speed, and receding contact angle. The model is, however, restricted to receding contact angles close to 48°, as the pinned length and lifetime may diverge appreciably from established trends when it changes more than $\pm 15^\circ$. Time did not allow affirmation of all the trends at different receding contact angles.

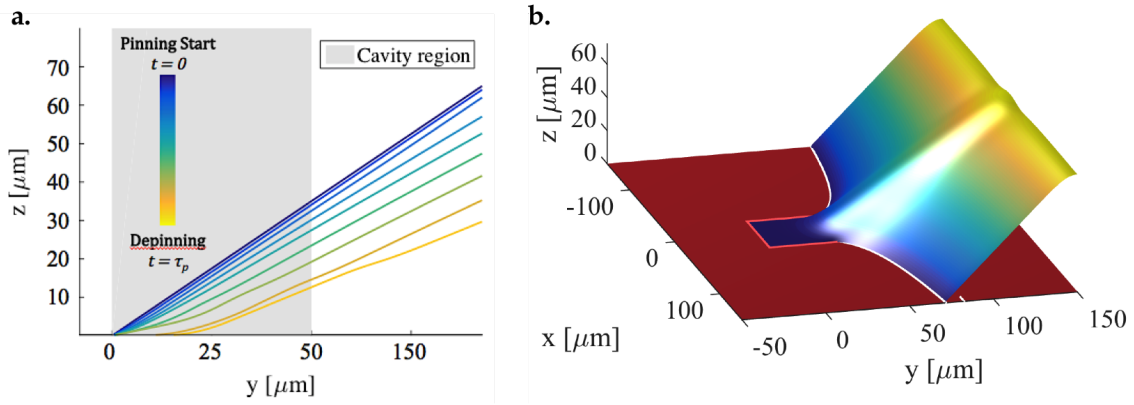


Figure 8.4: (a) Meniscus height profiles over a 50 μm cavity (centre cross-section) coloured by time during the pinned lifetime, based 4D profilometry. (b) A sample meniscus model, coloured by height, near the moment of depinning, based on experimentally-derived trends in morphology. (The full meniscus would in reality extend upwards and outwards from this region of interest. The curvature along the top is an artefact from smoothing the 3D model. It is far removed from the pinned region and does not interfere with the simulation.)

8.3.2 Pinned Meniscus Evaporation

Figure 8.5a shows a sample meniscus snapshot, modelled on a 100 nm cubed cavity (the cavity protrudes beneath the substrate). Figure 8.5b shows the meniscus coloured by evaporation rate, as per Equation 8.2. The evaporation rate progressively lowers towards the cavity centre due to the cavity's depth (Appendix 8.B explains the algorithm to model this).

8.3.3 Calculating Convective Flow Rates

By modelling the meniscus evaporation at two snapshots of a pinning event we are able to estimate the average convective flow rate between those two instants. By dividing the pinned lifetime into many such snapshots, discrete estimates of sequential convective flow rates can be obtained throughout a pinning event. The discussion below describes how flow rates are estimated between any two meniscus snapshots.

Convective flow rates are dependent on the balance of two liquid volume loss mechanisms over a cavity: (1) evaporative loss (V_e , the liquid lost to evaporation) and (2) retraction loss (V_r , the reduction in liquid volume over a cavity due to a

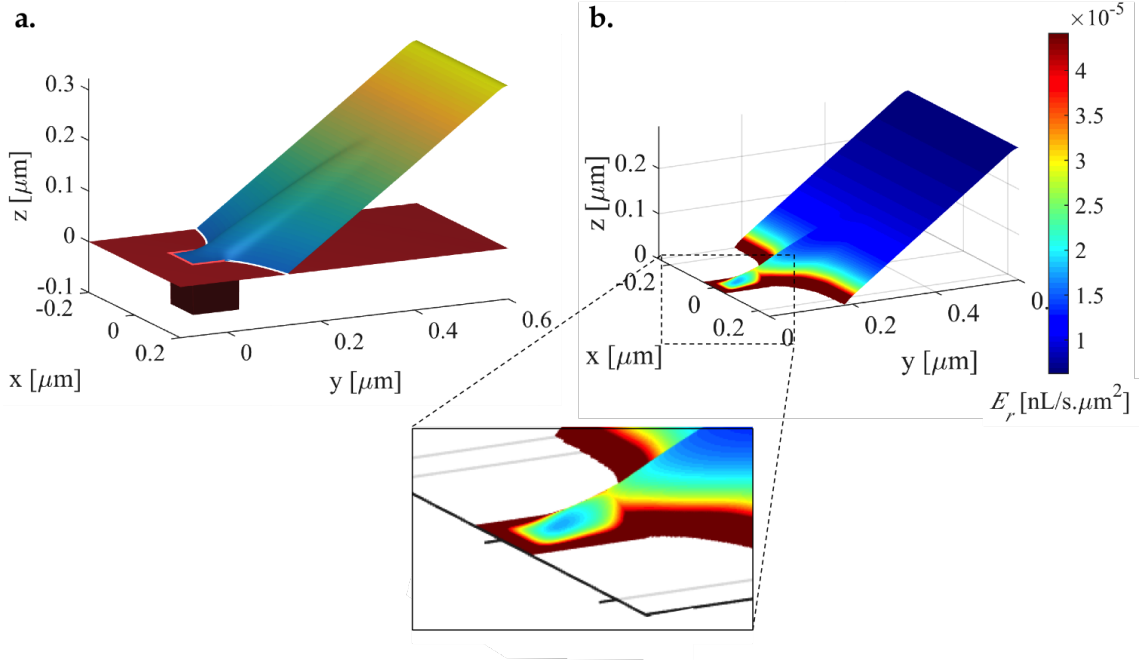


Figure 8.5: (a) A pinned meniscus modelled over a $100 \times 100 \times 100 \text{ nm}^3$ cavity near the end of pinning. (b) The meniscus in (a) recoloured to show evaporation rates. The cavity has a lower evaporation rate due to its depth (see inset).

receding liquid front). The liquid volume, V_c , which convective flows to the contact line must account for is

$$V_c = V_e - V_r \quad (8.7)$$

The retraction loss is easily calculated as the change in volume of one 3D meniscus snapshot to the next. It is calculated in a finite-volume manner for each column of pixels in the x - y plane. The evaporative loss can likewise be determined for each column of pixels in the x - y plane, being dependent on the point-wise evaporation rate (E_r) and the duration between snapshots ($\delta t = t_n - t_{n-1}$). The point-wise evaporation rate used is the average of rates ($\hat{E}_r$) across the two meniscus snapshots that bound the time interval δt . Hence, for each x - y pixel column,

$$V_r = (M_n - M_{n-1})a_p \quad (8.8)$$

$$\hat{E}_r = (E_{r,n} + E_{r,n-1})/2 \quad (8.9)$$

$$V_e = \hat{E}_r(t_n - t_{n-1})a_p \quad (8.10)$$

where a_p is the area per pixel in the x - y plane, and the various 3D meniscus profiles are denoted by M_n .⁵

⁵One must be careful to use consistent volumetric units, as initially V_r is in μm^3 whereas V_e is

A straightforward way to estimate convective flow speeds is to slice the meniscus profile many times in the x - z plane (i.e. vertical slices parallel to the bulk contact line) and calculate the average convective flow volume passing through each slice ($V_c(y)$) in the time δt . The calculated flow rates are really the flow past each y -coordinate averaged over the x - z plane, and also averaged over δt . The results presented later in this chapter divide the pinned lifetime into nine snapshots, giving a temporal resolution of $\delta t = \tau_p/8$ to the flow rate profiles.

It is self-evident that the net convective flow direction will be towards the contact line (i.e. towards smaller y -coordinates in our model's reference frame). Considering a vertical slice at $y = y'$, the volume of convective flow passing the point $y = y'$ must replenish the volume lost to evaporation, less the volume lost to continual retraction of the liquid, for the entire meniscus at $y < y'$. That is,

$$V_c(y') = V_e(y \leq y') - V_r(y \leq y') \quad (8.11)$$

Determining the average convective flow speed through each slice ($v(y)$) is done by dividing the volumetric flow through each slice ($V_c(y)$) by the area of each slice ($A(y)$) and the time interval δt .

$$v(y) = \frac{V_c(y)}{A(y)\delta t} \quad (8.12)$$

The slice area $A(y)$ needs to be carefully chosen at the rear of the cavity. Using the raw substrate profile, one would obtain a step function for $A(y)$ as y moves over the rear wall of the cavity. This is not realistic as a flow profile. Liquid flow over a backwards step follows a sigmoid curve. This is illustrated in Figure 8.6.

A final point to note is that analysis should be restricted to the range of x values over the cavity width. We will refer to this x - y region as the ‘cavity column’, depicted in Figure 8.7. The contact line outside the cavity is only broadly curved and its evaporation profile is near identical to that of an unperturbed contact line. The convective flow to this extra-cavity region is therefore well studied already in the form of ordinary sessile droplet evaporation. There is no need to revisit it here, our focus is solely the convective flows into the cavity. Since our flow estimates are averages in the x - z plane, extending analysis beyond the cavity column will receive extra-cavity flows as well, masking the cavity-region flows. Hence, the analyses to come are restricted to the cavity column.

in nL^3 .

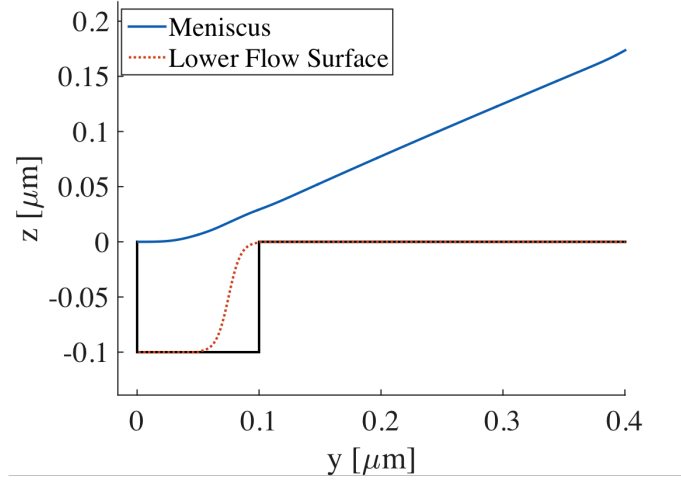


Figure 8.6: An illustration of the upper and lower flow surfaces needed for convective flow speed estimates. Greater realism is obtained with a sigmoid function on the lower flow surface at the cavity rear step.

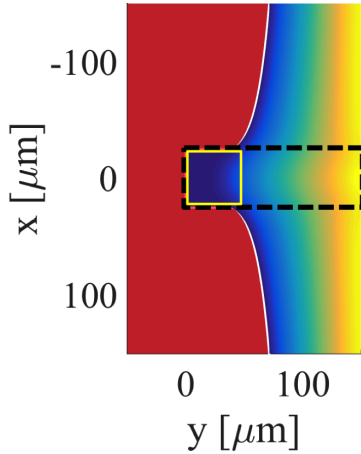


Figure 8.7: A bird's-eye view of a model meniscus (substrate is red; meniscus is blue-to-yellow, coloured by height). The cavity is marked by the solid yellow box. The cavity column encompasses all of the meniscus in the path of the cavity, and is marked by the dashed black line. The right-boundary of the cavity column is simply at the limit of the modelled space, which has been shortened here for display purposes. The cavity column is the region used for convective flow estimates into the cavity.

8.3.4 Simulation Results: Local Convective Flow Speed Estimates

We now discuss simulated local convective flow (LCF) rates.⁶ Figure 8.8 shows modelled LCF rates throughout pinning on a 100 nm cuboid cavity with a bulk contact line speed of 1 mm/min ($17 \mu\text{m/s}$). Each velocity profile has three important parameters: (1) a peak speed, (2) a peak location, and (3) a cut-off point where the

⁶As previously stated, the speeds are averages in x - z slices of the cavity column, also averaged over the indicated intervals of the pinned lifetime (see plot legend).

flow reaches zero at a positive y -coordinate.⁷ y -coordinates equate to distance from the front of the cavity.

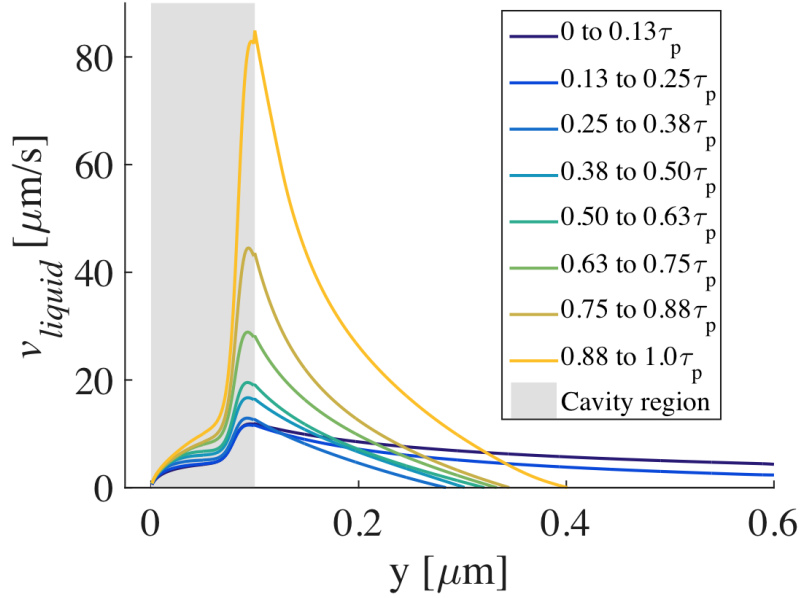


Figure 8.8: Sample LCF speeds throughout the cavity column of a 100 nm cavity. The substrate temperature is 50°C, the receding contact angle is 35° and the bulk contact line speed is 1 mm/min (17 μm/s). It is seen the convective flows extend well beyond the cavity, and that they intensify towards the end of the pinning event.

As pinning commences a moderate convective flow draws particles from far beyond the cavity to the contact line. This is essentially the bulk convective flows of an undeformed meniscus. As pinning progresses, the flow speed increases at the cavity rear and the cut-off point moves to 300-400 nm from the cavity front. The LCF concentrates around the cavity as the contact line perturbs. The flow within the cavity (grey region) changes little, except at the rear. Flows vanish at the cavity front, as expected. This modelling shows flows prior to depinning are approximately 8 times stronger than at the onset of pinning, and they extend well into the semi-crystalline nanoparticle region. These are encouraging results for the proposed pinned-convective model.

Considering the three key parameters that describe LCF patterns ((1) peak flow speed, (2) peak flow location and (3) the reach of the flow beyond the cavity), we

⁷Note that in reality there would not be zero flow beyond the cut-off point. Larger-scale convective flows also operate throughout the bulk liquid body, which are not shown here. What is revealed here is the *additional* and *temporary* flow caused by pinning that would be superimposed over any more permanent flows.

plot in Figures 8.9 and 8.11 how these parameters vary by a range of experimental factors. There are three plots given to each study (plots i, ii and iii), and these are explained in each Figure's caption. Unless specified otherwise, the non-variable parameters in each situation are: cavity depth, 100 nm; cavity footprint, 100×100 nm²; receding contact angle, 35°; substrate temperature, 30°C; bulk contact line speed, 1 mm/min (17 μ m/s).

It should be noted that the following simulations are over nano-cavities only; results from micro-cavities follow different trends, and are not presented for the sake of brevity and our focus on nano-CFA.

Influence of Substrate Temperature (Figure 8.9a): The substrate temperature enhances the intensity and extent of LCFs, as expected, but it does not alter the peak location. The substrate temperature does not greatly alter the flow rate over the cavity itself. This suggests that high temperatures assist primarily in drawing particles close to the cavity.

Influence of Bulk Contact Line Speed (Figures 8.9b and 8.10): Contact line speed dramatically affects the extent of LCFs (see Figures 8.9b.ii and iii). Figure 8.10 presents four additional plots based on contact line speed throughout the pinning lifetime. At speeds of tens of μ m/s flows are irregular over time and of shorter reach. In these cases the optimal flows for assembly are at the end of pinning, making premature depinning detrimental to assembly. At contact line speeds of approximately 0.1 μ m/s, flows become uniform over time and have a consistently greater reach, thus being more forgiving to premature depinning. Assembly speeds <1 μ m/s are desirable.

Influence of Cavity Depth (Figure 8.9c): The cavity depth enhances flow intensity over the cavity itself. This is expected since a shallower depth both increases the evaporation over the cavity and condenses the volume available for convective flows. It has little impact beyond that.

Influence of Contact Angle (Figure 8.11a): The receding contact angle affects the intensity, but less dramatically than temperature. Lower contact angles lead to higher evaporation rates and also constrain the convective flow area more, both

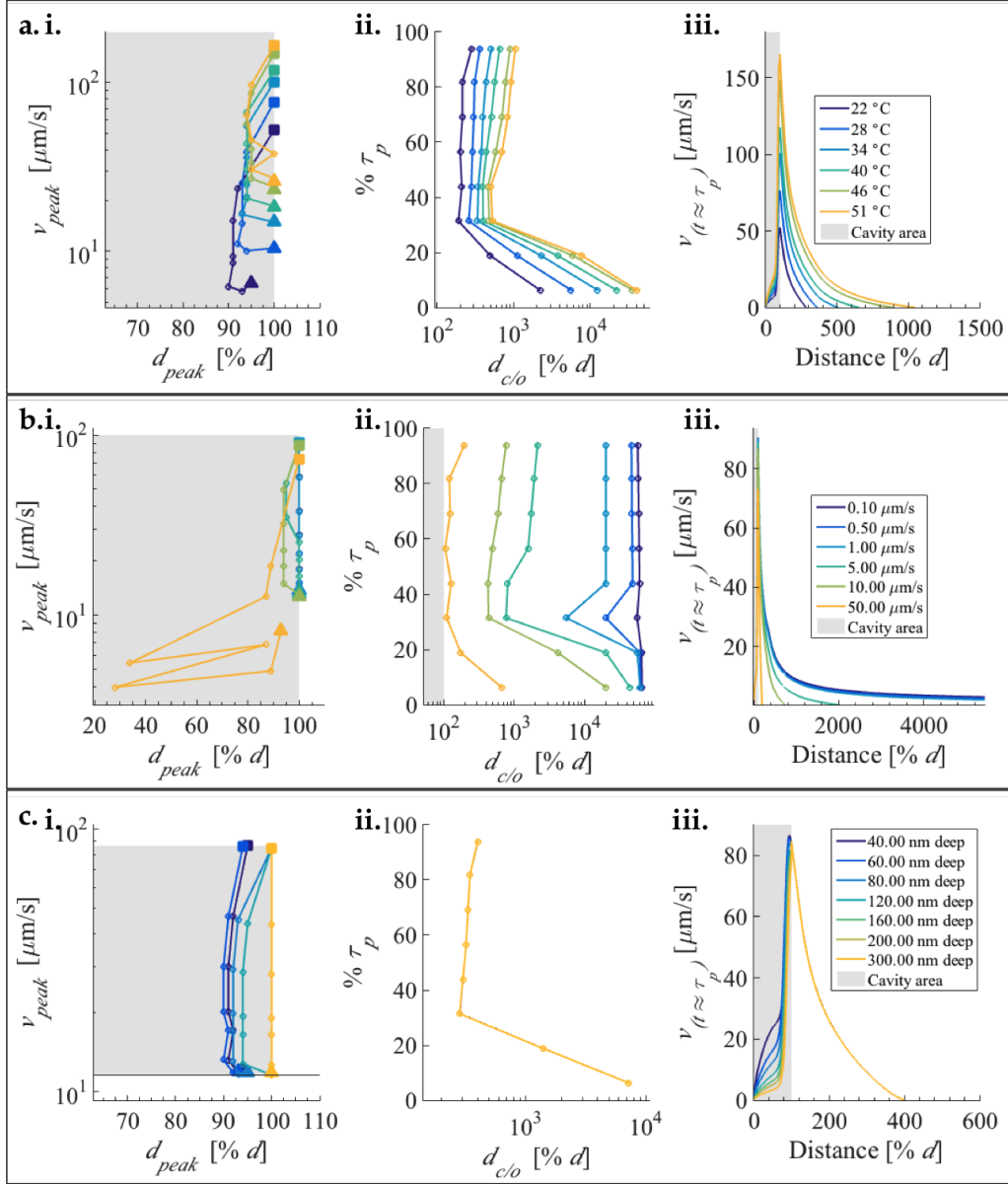


Figure 8.9: Simulation data showing how the LCF from pinning is affected by (a) the substrate temperature, (b) the bulk contact line speed, and (c) the cavity depth. The left-hand plot (i.) of each scenario shows the intensity and location of the peak flow relative to the cavity size (d , where 100 % is the rear edge of the cavity). The triangle on each trace marks the start of pinning and the square marks the end. The centre plots (ii.) show the extent of flows into the bulk phase (the cut-off location) at all stages in the pinned lifetime. The right-hand plots (iii.) show the flow speed profiles just prior to depinning, for comparison purposes.

contributing to higher flow rates. The extent of flows only grows commensurate with the flow intensity. The relatively mild influence of contact angle supports the earlier conclusion that the conventional model incorrectly labels the contact angle

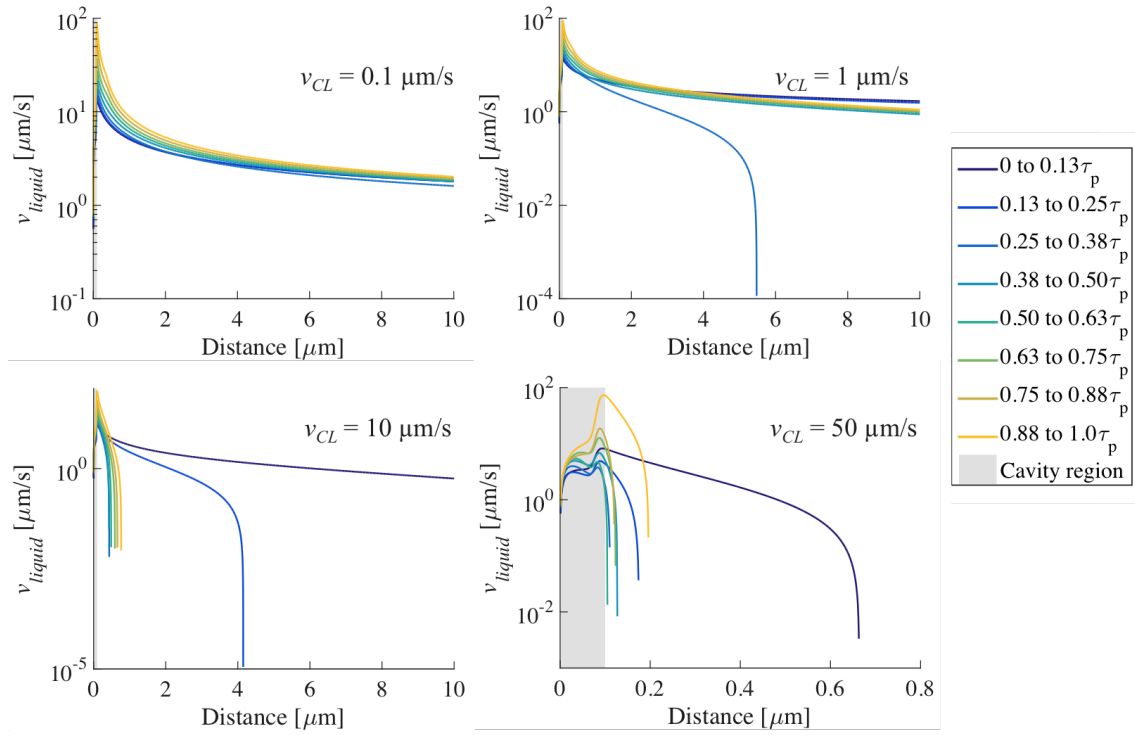


Figure 8.10: Plots showing how contact line speeds below 1 $\mu\text{m/s}$ produce longer and more uniform convective flow profiles. This is thought to aid assembly by reaching further for particles, and providing a more uniform flow environment throughout the entire pinning event.

as critical for assembly (see Section 4.2.4).

Influence of Cavity Size (Figure 8.11b): Cavity size affects the location of the most intense flows, which is at the cavity rear for nano-cavities and at the cavity front for micro-cavities. Intermediate sizes, where the peak flow location moves across the cavity, have the weakest flows overall. Further study shows the weakest flows occur when the cavity length to depth ratio is approximately 1 to 10.

The extent of flow increases steadily with cavity size. It is clear experimentally that larger cavities are easier to assemble in general, and these simulations may help reveal why. (Note that the absolute extent of flow is plotted instead of the relative extent.)

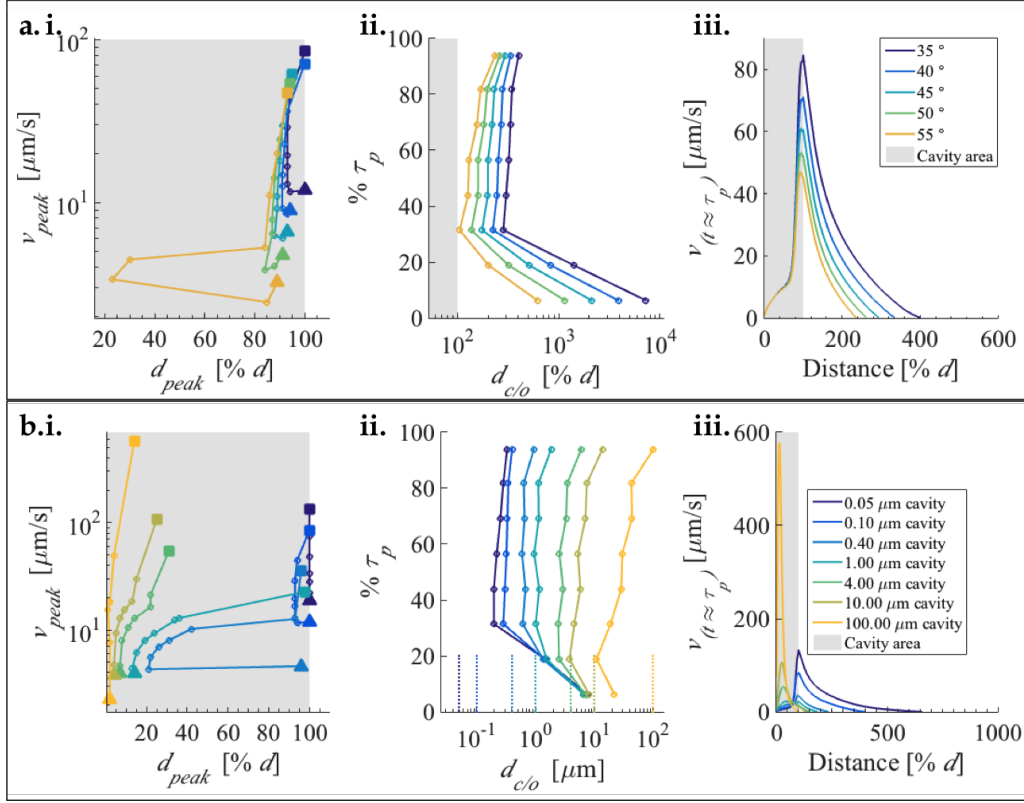


Figure 8.11: Simulation data showing how the local convective flows from pinning are affected by (a) the receding contact angle and (b) the cavity size. Other notes are as per Figure 8.9. Note that Figure b.ii has x -axis units of μm , not $\% d$ like other plots. For reference sake, the rear cavity boundary for each dataset is indicated by a dotted line.

8.3.5 Comparison of Flow Rates with Published Data

It has already been highlighted that published literature on pinned-convective flows is non-existent. We can, however, make some comparisons with extant literature on small evaporating sessile droplets.

Convective Flow Rates in the Early Stages of Pinning: At the start of pinning there is essentially no contact line distortion and flow rates ought to be similar to those in sessile droplets. Data in Figures 8.9 and 8.11 predict initial peak flow rates between $2 \mu\text{m/s}$ and $30 \mu\text{m/s}$, at substrate temperatures between 20°C and 50°C and contact angles between 35° and 55° .

From experimental work, water at 4°C evaporating in a cuvette has flows of $10 \mu\text{m/s}$ to $40 \mu\text{m/s}$ near the contact line [4]. Naturally, flow rates vary based

on various experimental parameters, so order-of-magnitude comparisons are most appropriate, and are well in line with present CFA modelling.

From numerical modelling, estimated flow rates near sessile droplet contact lines are $0.5 \mu\text{m/s}$ to $10 \mu\text{m/s}$ by [2],⁸ $1.5 \mu\text{m/s}$ to $8 \mu\text{m/s}$ by [3],⁹ and $5 \mu\text{m/s}$ to $10 \mu\text{m/s}$ by [5].¹⁰ Order-of-magnitude comparisons are again affirmative.

A more accurate comparison is with Hu and Larson [2] who model a pinned sessile water droplet at room temperature (25°C). At $100 \mu\text{m}$ from the contact line, flows of $0.5 \mu\text{m/s}$ to $10 \mu\text{m/s}$ result at contact angles of 10° to 40° , respectively. We can emulate this scenario with a very low contact line speed (0.1 nm/s) and zero cavity depth (cavity width (the length of contact line we model) is irrelevant and doesn't change the result).

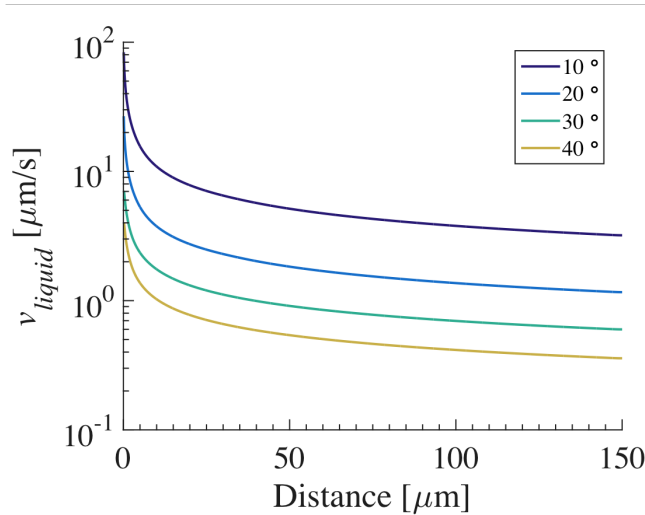


Figure 8.12: Flow rates at the beginning of simulations to emulate a pinned sessile droplet at various contact angles, for comparison with data by Hu and Larson [2].

Our modelled convective flows at the start of pinning are shown in Figure 8.12. As expected for a sessile droplet, the flows peak at the contact line (unlike when a cavity is present) and intensify at lower contact angles. At $100 \mu\text{m}$ from the contact line, flow rates are $0.4 \mu\text{m/s}$ to $3.8 \mu\text{m/s}$, very similar to Hu and Larson's figures. Note also that Hu and Larson's cite the peak flows, whereas our values are height-averaged, so would understandably be slightly lower.

⁸Values are from a simulated 2mm water droplet with a 40° contact angle, where flow rates were estimated at $100 \mu\text{m}$ from the contact line.

⁹Values from a sessile droplet modelled at room temperature.

¹⁰Values from near the contact line on a droplet with contact angle $> 90^\circ$.

Flow rates predicted from the CFA simulations in the early stages of pinning compare well with theoretical and experimental work on sessile droplets.

Convective Flow Rates Throughout the Pinned Lifetime: Considering now the rise in convective flow rates throughout the pinned lifetime, our simulated data indicates rates between $10 \mu\text{m/s}$ and $1000 \mu\text{m/s}$ (depending on experimental parameters). For comparison, we note that the morphology of a meniscus clamping down over a cavity is similar to that of a pinned sessile droplet evaporating down to a thin film. Both cases would predict similar convective flow trends.

The sessile droplet case has been modelled by Barmi and Meinhart [6]. Flows grew to several hundred $\mu\text{m/s}$ when the drop had mostly collapsed, in good agreement with the present CFA simulations.

Of particular note is experimental work by Hamamoto, Christy and Sefiane [7] who found flow rates near the contact line of a sessile droplet evaporating at room temperature (25°C) to progress from $2 \mu\text{m/s}$ to $60 \mu\text{m/s}$ throughout the droplet's lifetime. These figures agree extremely well with our pinned-convective model data of $0.8 \mu\text{m/s}$ to $60 \mu\text{m/s}$, also at 25°C (Figure 8.9a).¹¹

8.3.6 Deposition Concentrated by Convective Flow Profiles

Qualitative experimental validation of convective simulations can be achieved by observing how deposition patterns vary with cavity size. Simulation data (Figure 8.11b.ii) shows convective flows are concentrated (1) at the rear of nano-cavities, (2) at a range of positions for cavities of size $0.5 \mu\text{m}$ to a few micrometers, and (3) at the front of larger micro-cavities. Increasing cavity size is thus like transitioning from cavity-type flows to sessile-droplet-type flows.¹²

Figure 8.13 examples nano-assembly on a variety of cavity sizes. The nano- and small micro-cavities (images (a) and (b), respectively) show even distributions

¹¹These figures are the mean of our data at 22°C and 28°C , to match room temperature of 25°C .

¹²Additional simulations show that cavity-type flows can be present in micro-cavities up to $100 \mu\text{m}$ in size, provided their depth is comparable to their footprint size, making a genuine cavity. Above $100 \mu\text{m}$ in size, the rear cavity boundary is too far from the contact line and the strong evaporation at the contact line keeps the peak flow in the cavity front. If a cavity is very shallow compared to its footprint size, then it ceases to be effective as a cavity and sessile-droplet-type flows result.

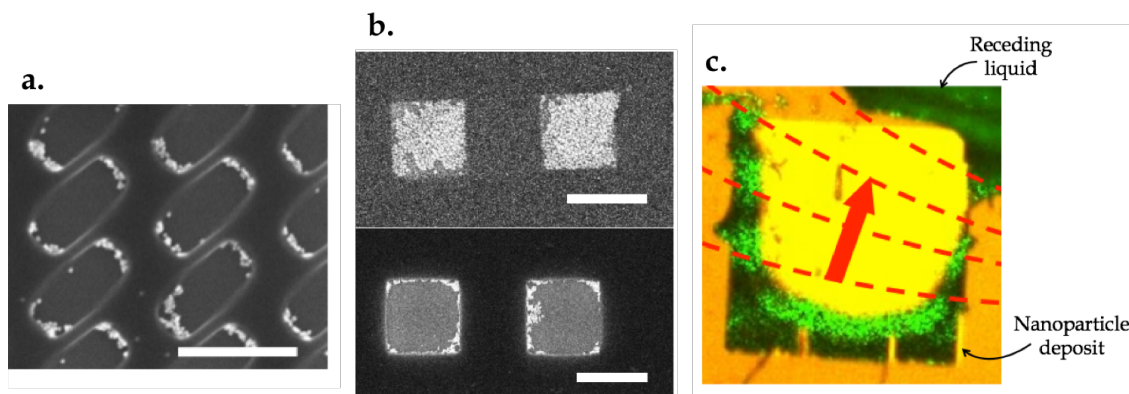


Figure 8.13: (a) Assembly into $150 \times 450 \text{ nm}^2$ cavities by 50 nm gold spheres (scale bar 500 nm). (b) Assembly into $1 \times 1 \text{ } \mu\text{m}^2$ cavities by 50 nm gold spheres (upper) and 20 nm spheres (lower) (scale bars $1 \text{ } \mu\text{m}$). (c) Photograph of nanoparticles deposited into a 200 nm-deep cavity of footprint $500 \times 500 \text{ } \mu\text{m}^2$. Red markings show the asymmetric bulk contact line progression until depinning (green speckle is scattering of a green laser used for micro-4D meniscus profilometry). These results demonstrate how the peak flow location varies with cavity size.

of particles. This implies that peak convective flows did not concentrate particles in a specific location, but pulled particles into the cavity leaving Brownian dynamics to then randomise particle locations prior to depinning. This would occur when the peak flow location is not confined to the cavity front, as predicted for nano- and small micro-cavities. The simulations also predict these cavities to have weak flows over most of the cavity area, allowing Brownian dynamics to effectively randomise locations in the cavity.

This is in stark contrast to assembly on a large micro-cavity (image (c)) showing particles exclusively assembled around the cavity front perimeter. Particles were not pulled in position by the receding contact line since they are on the side opposing contact line motion. Post-pinning capillary forces are not solely responsible, otherwise there would statistically be some particles in other locations. The only remaining dynamic is particles driven by strong convective flows. This implies that flows were concentrated around the cavity front, affirming modelling predictions for this cavity type.

This brief analysis affirms the importance of convective flows in nano-CFA and also affirms the pinned-convective model and simulation. This gives us confidence to pursue nanoparticle kinetic simulations in Stage III below.

8.3.7 Affirming Core Assumptions

Throughout our study we have made several assumptions and conclusions relating to liquid behaviour. We can now test these, using the estimated convective flow rates, which have now also been validated against other works.

The Reynolds number gives the ratio of inertial forces to viscous forces, indicating whether flow is laminar or turbulent. We had assumed the laminar flow, and calculating the Reynolds number (Re) affirms our choice.

$$Re = \frac{\rho v L}{\mu} \quad (8.13)$$

where ρ is the liquid density, v the characteristic velocity, L the characteristic length scale and μ is the dynamic viscosity. For a liquid speed of 1000 $\mu\text{m/s}$ over a 100 nm cavity (which is an exaggeration of the real values, demonstrating the sureness of our conclusion), $Re = 1.05 \times 10^{-4}$, which is $\ll 1$ and the flow is definitely laminar.

The Capillary number gives the ratio of viscous forces to surface tension. For $Ca \ll 1$, surface tension dominates the dynamics.

$$Ca = \frac{\mu v}{\gamma_{lv}} \quad (8.14)$$

where γ_{lv} is the liquid-vapour surface tension. Using the parameters given above for the Reynolds number, $Ca = 1.32 \times 10^{-5}$, affirming our prior conclusion that viscous forces can be neglected from pinning dynamics.

Similarly to the Capillary number, the Weber number is the ratio of inertial forces to surface tension:

$$We = \frac{\rho v^2 L}{\gamma_{lv}} \quad (8.15)$$

The value of We is 1.38×10^{-9} . As this is $\ll 1$, surface tension dominates and inertial forces can be neglected, as concluded experimentally in Section 7.5.

Finally, the Péclet number gives the ratio of convective heat transport to diffusive heat transport.

$$Pe = \frac{v L}{\alpha} \quad (8.16)$$

where α is the thermal diffusivity of the liquid. Based on the above parameters $Pe = 6.99 \times 10^{-4}$ which is $\ll 1$, so heat transfer is essentially by conduction, not convection. This affirms that the evaporation rate is strongly correlated with meniscus height.

We have calculated the above numbers based on a 100 nm cavity. Aside from the Capillary number, each of these ratios scale linearly with length, so even for a 100 μm cavity our interpretations will not change. We therefore comfortably retain all the analyses and conclusions about the pinned-convective model up to this point.

8.3.8 Conclusions from Stage II

The convective flow rates predicted in the above simulations are in good accord with published data from evaporating sessile droplets, insofar as comparisons can be made. This not only validates the present results, but also gives us confidence that the flows during pinning events are sufficient to drive particles, as convectively driven deposition is also seen in sessile droplets as the ‘coffee ring’ effect. We have also examined how various experimental parameters affect LCF rates, and what this might mean for nano-CFA. In the third and final stage of this chapter we model nanoparticle dynamics within LCFs.

8.4 Stage III: Nanoparticle Kinetics in Pinned- Convective Flows

In this Stage III we will convert convective flow profiles into nanoparticle energy profiles, revealing a map of assembly efficacy according to experimental variables. This will conclude our quest to model and quantify the pinned-convective model, and also demonstrate its viability for assembly.

8.4.1 Simulating Particle Motion: Background Information

Describing the Simulation: Section 1.5.4 presents the drag force on a nanosphere in laminar flow as

$$F_d = 3\pi \mu d v \quad (8.17)$$

where μ is the fluid’s dynamic viscosity, d is the diameter of the nanosphere and v is the liquid velocity relative to the particle. Recall also that the LCFs during an entire pinning event are broken down into several LCF profiles, snapshots at different

times. Each profile therefore constitutes a force field that applies for a portion of the pinned lifetime. We calculate the nanoparticle kinetic energy in these flow fields using linear kinematics with the following rules and assumptions:

- Particles are hard spheres (radius r) with the density of gold
- Particles begin at rest at some point within the model space (the model space is sufficiently large to capture the full liquid flow region)
- Successfully assembled particles must reside within the cavity at the end of the pinned lifetime
- A particle residing in the cavity means it is somewhere between a distance of r from the front wall (i.e. touching the front wall) and a distance of $0.5r$ out of the back wall (i.e. at least 75 % of the particle is in the cavity when depinning occurs, to be fully assembled by post-pinning capillary forces).
- Since each convective flow profile exists only for a portion of the pinned lifetime, particles transition from one flow profile to the next, based on how much of the pinned lifetime has transpired.
- Kinetic energy acquired by a particle from the convective drag force is not dissipated; the particle always accelerates as per the convective drag force (Equation 1.14).

A custom finite-difference time-domain simulation has been written in Matlab. The spatial resolution is one hundredth of the cavity length. For example, modelling a 100 nm cavity has a spatial resolution of 1 nm, and every nanometer of a particle's trajectory undergoes a recalculation to determine the force on the particle, the resulting speed of the particle after 1 nm of travel distance, and the time taken to traverse that distance. This is performed incrementally until the pinned lifetime expires, thus indicating the particle's kinematics over the full pinning event. The force is at all times determined from the strength of the convective flow at that point in space, and at that moment in the pinned lifetime.¹³ Additional simulation details are in Appendices 8.C and 8.D.

¹³Appendix 8.C shows that even for a 300 nm nanoparticle starting from rest in a flow field up to 1000 $\mu\text{m/s}$, the particle will reach the flow speed within a fraction of a nanometre of travel. With a model resolution of 1 nm, lag effects become non-existent and the particle velocity can assume the flow velocity at all times.

8.4.2 The Influence of Experimental Factors

Results from particle kinetics simulations are given in plots (i) and (ii) of Figures 8.14 and 8.15 under a range of experimental factors. Unless specified otherwise, the non-variable parameters in each simulation are: cavity depth, 100 nm; cavity footprint, $100 \times 100 \text{ nm}^2$; receding contact angle, 35° ; substrate temperature, 30°C ; bulk contact line speed, 1 mm/min ($17 \text{ }\mu\text{m/s}$); test particle size, 50 nm.

Understanding Plots (i): Plots (i) are based on the annotated diagram of Figure 8.14a. The data in plots (i) shows the size of the region that is available for assembly. It shows the maximum distance (the vertical axis) from the contact line that a particle can begin at, and be drawn into the cavity within the pinned lifetime (thus assuming assembly). These simulations do not include Brownian or collisional effects and model each particle in complete isolation.

The cavity is the grey region. A curve far from the grey region is optimal, meaning a particle starting far from the cavity may be assembled. The horizontal axis shows how far into the cavity the particle will be drawn.¹⁴

Curves that overlap with the grey cavity region mean particles must be over the cavity for the entire pinned lifetime to be assembled at all. This is not a favourable requirement. Under the pinned-convective model particles are held in a semi-crystalline arrangement that does not stay over the cavity during pinning, but it recedes with the bulk contact line as a large semi-rigid structure. Assembly only begins when pinning has deformed the meniscus enough to set up a LCF that is strong enough to extract particles into the cavity. The semi-crystalline structure may have moved well past the cavity by that time. It is most desirable to have the curves in plots (i) as far beyond the cavity rear as possible.

Understanding Plots (ii): The data in plots (ii) shows, for each y -coordinate, how much energy particles will be driven with on average, during the pinned lifetime. It is a map of the average energy available for assembly at each y -coordinate. A greater kinetic energy is presumed to be more favourable to overcome collisional and Brownian effects (these effects are discussed in Section 8.5).

¹⁴This is not a map of assembly position, as Brownian dynamics and post-assembly capillary forces will rearrange particle locations.

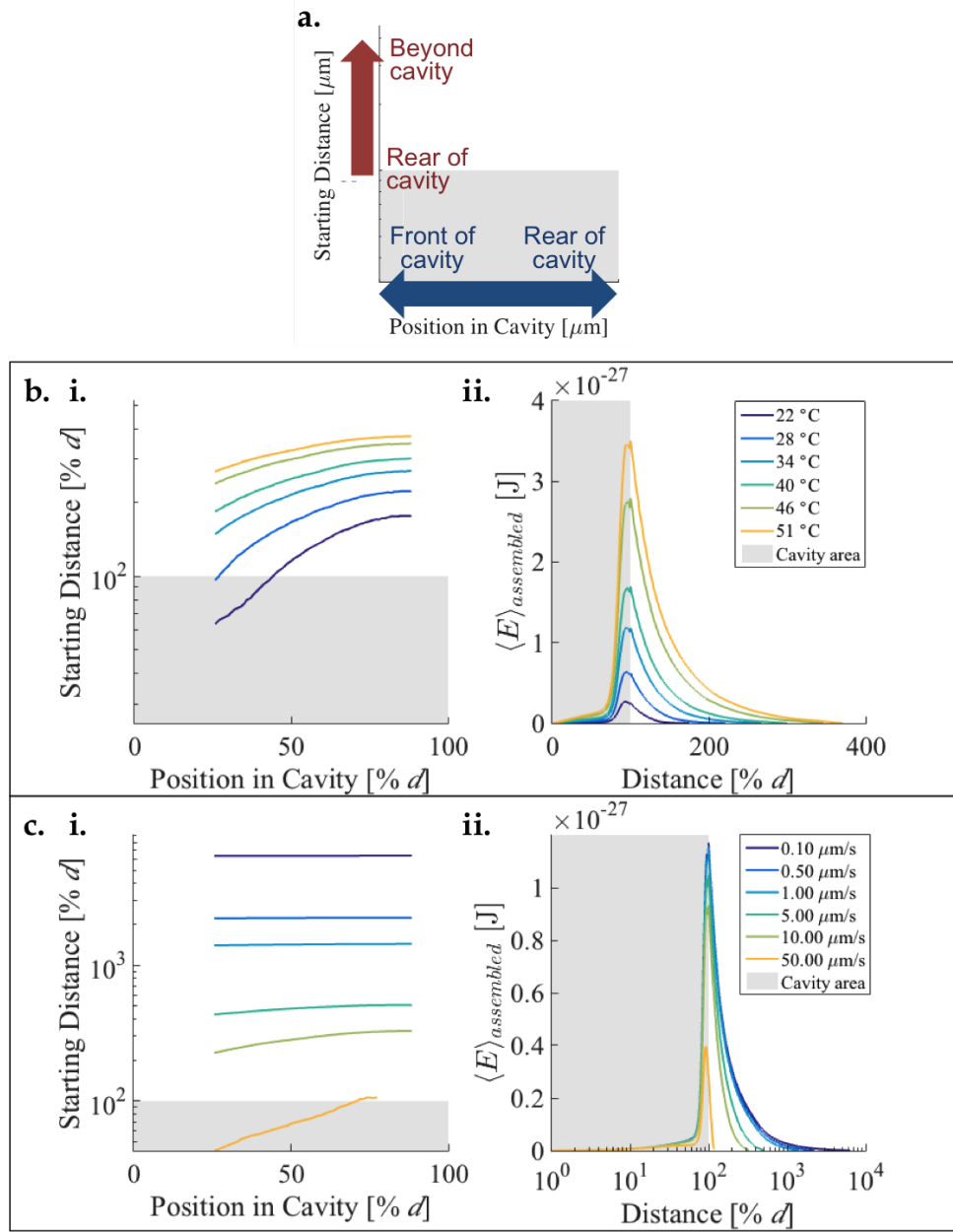


Figure 8.14: Simulation data showing how the particle kinematics in the pinned-convective model are affected by (b) the substrate temperature and (c) the bulk contact line speed. The left-hand plots (i.) show the maximum distance a particle can begin at rest and still end at the specified location in the cavity within the pinned lifetime. The diagram in (a) gives information to help interpret these results (red information relates to the starting position, blue information relates to the ending position). The right-hand plots (ii.) show the mean kinetic energy an assembled particle will receive at various positions within the flow field, at any moment in the pinned lifetime.

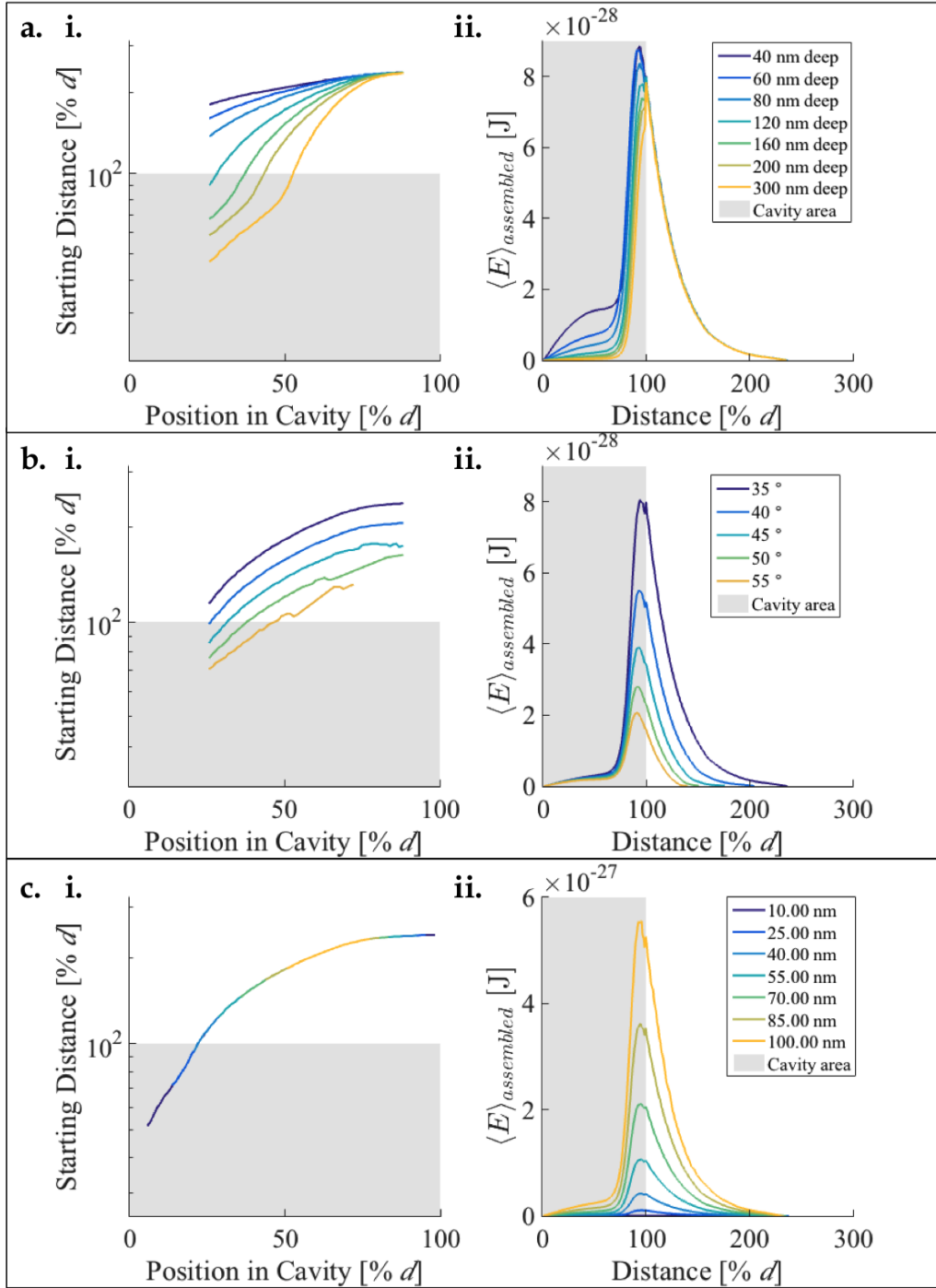


Figure 8.15: Simulation data showing how particle kinematics are affected by (a) the cavity depth, (b) the receding contact angle and (c) the particle size. Other notes are as per Figure 8.14.

Influence of Substrate Temperature (Figure 8.14b): The substrate temperature appreciably enhances the distance available for assembly (plot (i)). Assembly below 28°C appears unlikely as it requires particles to remain over or close to the

cavity at all times.¹⁵ A substrate temperature of 51°C compared to 22°C also gives at least a three-fold increase in assembly energy (plots (ii)). These findings shed further light on why high temperatures are required for nano-CFA, in addition to forming a packed line of colloids along the contact line.

Influence of Bulk Contact Line Speed (Figure 8.14c): Slower contact line speeds increase the amount of energy imparted to particles beyond the cavity but not within the cavity, where the energy remains low at all contact line speeds. The energy imparted beyond the cavity appears to plateau for speeds $< 1 \mu\text{m/s}$, but reducing the speed further will dramatically extend the distance available for assembly. Assembly speed has received little attention in CFA literature, but modelling here shows it to be a significant factor.

Influence of Cavity Depth (Figure 8.15a): The role of cavity depth has never before been explained in nano-CFA, except to say that a cavity must be deep enough to physically hold a particle. Modelling here shows cavity depth to be important *within* the cavity region, but not outside of it (plot (ii)). Shallower cavities are preferred, and they also make assembly more probable (plot (i)).

Influence of Contact Angle (Figure 8.15b): The receding contact angle benefits both the distance available for assembly and the energy imparted to particles, primarily beyond the cavity. Low contact angles may therefore help with bringing particles up to the cavity rear. This is quite a different explanation for the importance of contact angle compared to the conventional model.

Influence of Particle Size (Figure 8.15c): Particle size appears to significantly influence the kinetic energy imparted to particles. There is no difference made to the distance available for assembly, however. It is well-known experimentally that large particles are easier to assemble. This has previously been put down solely to their reduced Brownian motion. We now add to that by saying large particles are also driven with much greater momentum, which may assist their assembly likelihood as well.

¹⁵This assessment is based on the given experimental conditions. As seen below, dramatically lowering the contact line speed may well make assembly at 28°C viable.

This concludes our study of convective dynamics. After a brief discussion on the role of Brownian and collisional effects, we will conclude our study of the pinned-convective model. A concluding discussion about the key experimental parameters for nano-CFA can be found in the next chapter.

8.5 Understanding Nano-CFA in Light of Stochastic Processes

The above findings must now be interpreted in a realistic environment involving Brownian motion and particle-particle collisions.

8.5.1 Brownian Diffusion

Brownian diffusion, as discussed in Section 4.3, is a problem to be overcome in the conventional understanding of nano-CFA. Convective packing of particles at the contact line most likely restrains particles very well, limiting their Brownian motion in a semi-crystalline arrangement. But what of a particle's brief journey out of that packed arrangement and into a cavity?

Extraction of particles out of their packed arrangement is driven wholly by short-lived local convective flows during pinning events. Assembly requires particles to not just enter the cavity but to remain there until capillary forces clamp them in place. The significance of Brownian diffusion in this case is unknown, though it would be greatly retarded by the liquid volume over the pinned feature being so very small.

8.5.2 Particle-Particle Collisions

Another stochastic factor is the high collision rate between particles within the flow region. The particle collision rate may be particularly high during the journey into a cavity.

Recall that the liquid velocity during pinning varies substantially along the direction of flow (see Stage II results, particularly Figures 8.9 and 8.11). This is more true towards the end of pinning. The velocity profile has a strong positive

gradient leading into the cavity, and a strong negative gradient just inside the cavity. Particles will be rapidly accelerated and then decelerated. This produces a high collision rate just inside the rear of the cavity. Does this serve to pack and restrain particles within a cavity, or is the impact so strong that particles are knocked away and compete to just enter the cavity? Does the peak flow at the cavity rear act as an energy barrier preventing particles diffusing out?

8.5.3 Assembly in Light of Stochastic Processes

In tying these effects together, we can note that experimental results on nano-cavities tend to produce no assembly or incomplete assembly. Rarely is dense or over-assembly observed, meaning the conditions for dense assembly are very specific. This trend suggests that Brownian and collisional dynamics are more disruptive to assembly than assistive, and/or that convective flows do not readily extract particles out of their semi-crystalline arrangement along the contact line. The suggested scenario is diagrammatically presented in Figure 8.16.

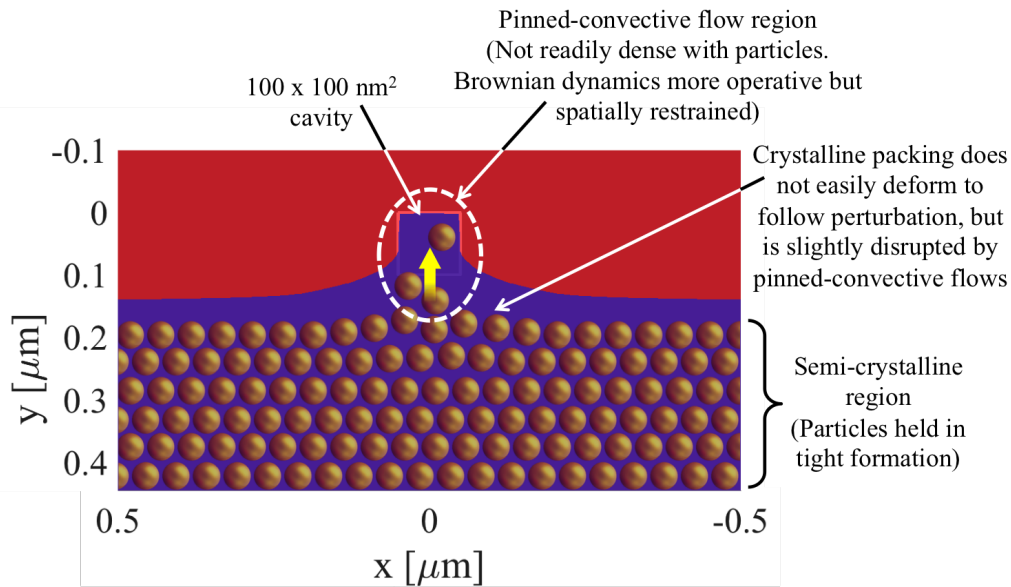


Figure 8.16: A birds-eye illustration of particle behaviour in the pinned-convective model, accounting for local convective flows, Brownian dynamics and semi-crystalline packing which is naturally resistant to disruption.

To summarise, it has long been known that CFA requires dense packing at the contact line before assembly is observed. This is understood as necessary to overcome Brownian effects. The pinned-convective model proposes that this region

acts like a docking station for particles, awaiting a pinning event to enact assembly. It is now likewise suggested that assembly efficacy depends on the efficacy with which particles are extracted out of semi-crystalline packing.

It is highly desirable to investigate this further, specifically to understand how the efficiency of particle extraction from the semi-crystalline phase varies with the magnitude, duration and extent of local convective flows. The pinned-convective model would greatly benefit from modelling that simulates an ensemble of particles. Such simulations would likely reveal the necessary information about extraction dynamics and what is necessary to overcome stochastic disruptions to ensure assembly.

8.6 Conclusions

We thus bring to a close our study of the pinning and convective dynamics in the new nano-CFA model. A detailed study of pinning dynamics, coupled with a novel micro-4D meniscus profilometry technique, opened to us important insights about meniscus behaviour during pinning events. In the present chapter this was then fed into an evaporative model to deduce convective flow profiles, which were converted into a simulation of nanoparticle kinetics. We have approximately quantified the convective flows during pinning events, and the subsequent impact on particles nearby.

This work validates that convective dynamics during pinning are real, and are most likely critical to nano-CFA. We have shown that convective flows during pinning can be an order of magnitude stronger than those of an unperturbed contact line. Additionally, this study reveals which experimental parameters can be expected to enhance assembly, and why that is so. A more thorough description requires detailed simulations of an ensemble of particles in pinned-convective dynamics near a semi-crystalline contact line.

In the final chapter we step back and explore the implications of this work on the bigger picture of nano-CFA. The discussion will also cover how we can best optimise nano-CFA in light of these findings. Opportunities for meaningful future work in this area are presented as well.

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Appendices

Building a Versatile Meniscus Model ... Appendix 8.A

Establishing Evaporative Profiles ... Appendix 8.B

Determining Acceleration Distance of Particles in Fluid Flow ... Appendix 8.C

Simulating Nanoparticle Kinematics ... Appendix 8.D

Appendix 8.A Building a Versatile Meniscus Model

The meniscus modelling that follows was done in Matlab. A sample meniscus model is shown in Figure 8.17. It has been built piecewise based on all the correct morphologies of the contact line, the pinned region and a thin-film region over the cavity where applicable during pinning. The combined surface was then smoothed to remove joints and discontinuities between components. Smoothing has been done carefully in such a way as to not distort the intended form.

The present work was conducted by building menisci at multiple snapshots throughout a simulated pinning event. The average convective flow rates that are derived are averages between these snapshots. Figure 8.18 shows some snapshots of a meniscus model at various stages in a single pinned event on a 50 μm cavity. They are shown against photos of the actual scenario for comparison purposes. The models were not modified to match the photos, but were constructed purely from the pinning trends found in Chapter 7.

A range of variables can be specified in the model, including:

- Cavity size—this impacts the pinned length and the onset time of thin-film

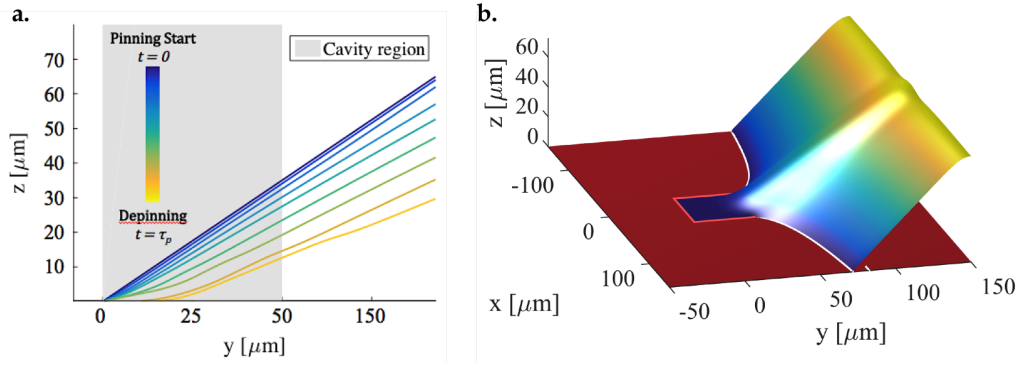


Figure 8.17: (a) Meniscus height profiles over a 50 μm cavity (centre cross-section) progressing through the pinned lifetime. The profiles are modelled from 3D reconstructed meniscus data like that Figure 7.11c. (b) A sample meniscus model, coloured by height, near the moment of depinning, based on experimentally-derived trends in morphology. The 50 μm cavity is outlined in red, and the contact line in white. The full meniscus would in reality extend upwards and outwards from this region of interest. (The curvature at the top of the meniscus is due to the final smoothing operation. It is far removed from the pinned region and does not interfere with the simulation.)

formation

- Cavity depth—this impacts the evaporation rate over the cavity
- Substrate temperature—this impacts the evaporation rate, liquid surface tension and capillary length (the latter two of these are relevant for calculating contact line profile)
- Contact line speed—this impacts the pinned lifetime and hence the amount of evaporation
- Receding contact angle—this impacts the overall model geometry

The meniscus model is therefore very versatile and comprehensive, owing to the breadth of data and trends provided in the previous chapter.

In a complete sense, there are three factors not fully accounted for in the generic pinned meniscus model. They are the influence on the pinned length (and lifetime) of (1) the surface tension, (2) the receding contact angle (θ_{REC}), and (3) the cavity depth. These are absent due to a lack of experimental data in these respects.

Regarding the influence of surface tension, it is known that a lower surface tension results in a longer pinned length. This is, however, not a significant concern

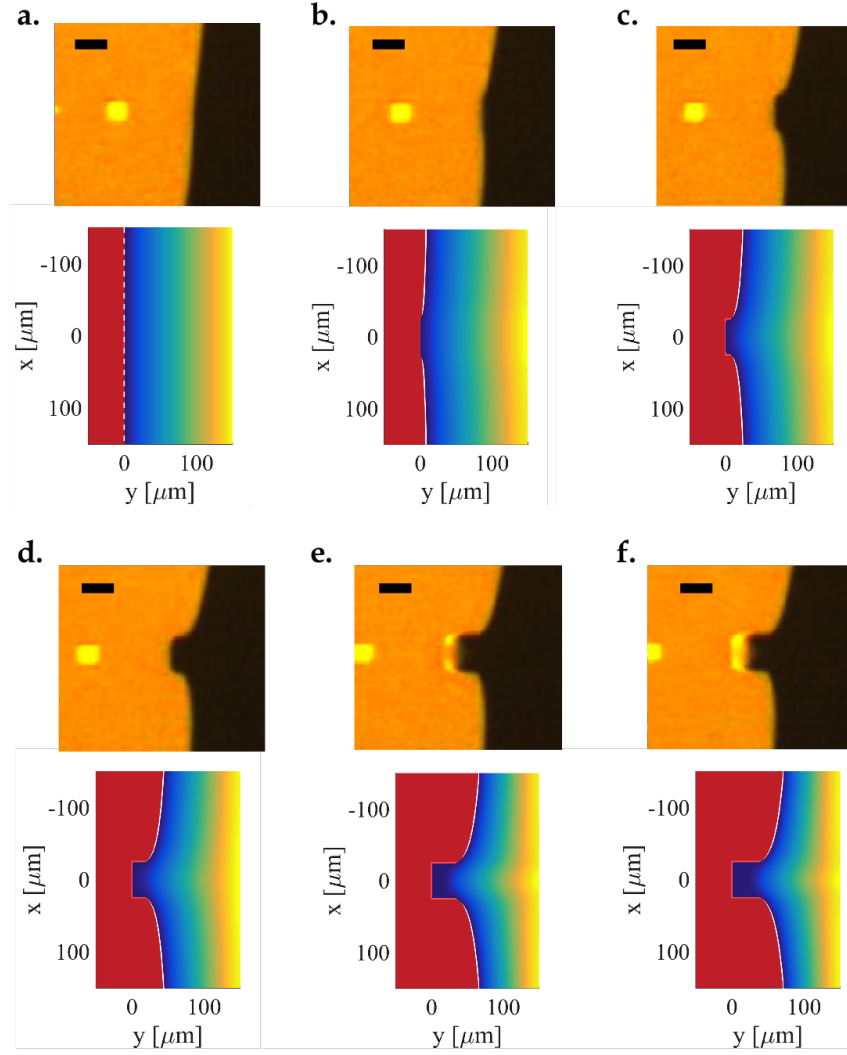


Figure 8.18: Modelling of pinning on a 50 μm cavity, at various moments throughout the pinned lifetime (meniscus is coloured by height). Photos are of actual pinning on a 50 μm cavity. The yellow spot in the photos is a 25 μm cavity that the meniscus has passed already; it slowly moves out of view as the camera is fixed relative to the bulk contact line. Scale bars are 50 μm .

since the present work uses an aqueous solution without surfactants. Thermal modification of surface tension has an insignificant influence on the pinned length on its own.

Regarding the influence of θ_{REC} , it is observed that a very low θ_{REC} produces a slightly longer pinned length, and conversely for a high θ_{REC} . Whilst it would be helpful to study pinned-convective dynamics at a variety of contact angles, it would require a vast amount of additional experimentation, which time has not permitted.

Regarding the influence of the cavity depth, it is not common to vary the depth greatly in nano-CFA. The data was collected at a depth of 200 nm. The pinned length and lifetime may shorten or lengthen with changes in cavity depth, but this relationship requires further study. The simulation results where the cavity depth is varied are thus possibly more indicative than predictive.

Appendix 8.B Establishing Evaporative Profiles

Fitting Parameters

Figure 8.2 in the main text shows that evaporative data can be fitted well by a sum of exponentials as given in Equation 8.2. This function has four fitting pronumerals, P_1 to P_4 , which vary based on the substrate temperature. Modelling evaporation and fitting Equation 8.2 was done at seven temperatures from 22°C to 51°C. The values of each fitting pronumeral are shown below in Figure 8.19.

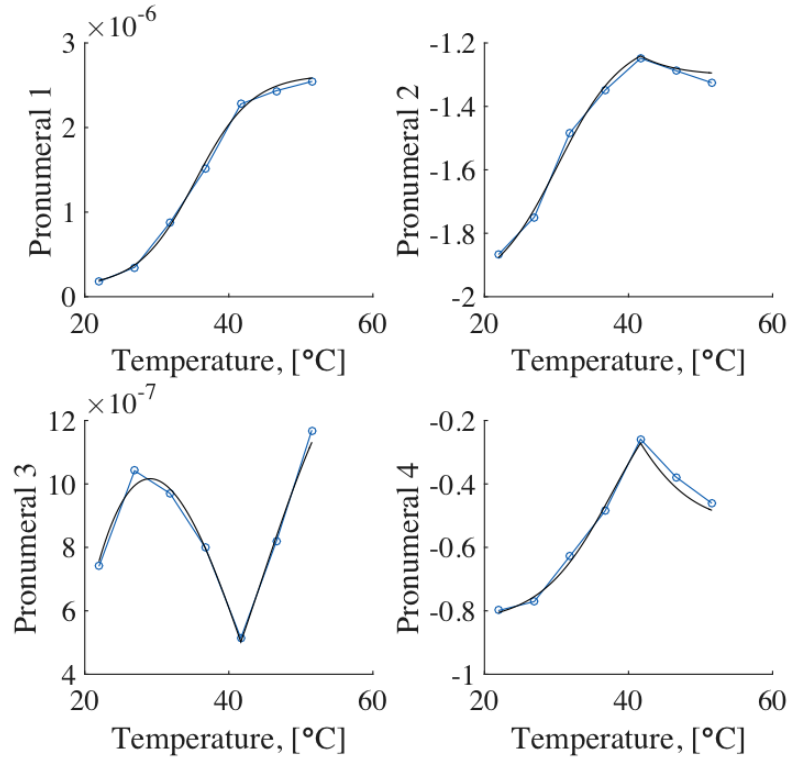


Figure 8.19: Plots of pronumerals P_1 to P_4 used to fit Equation 8.2 to the data in Figure 8.2. The black lines are functions fitted to this data.

Fitting functions to these pronumerals allows us to deduce evaporation rates at any temperature within the range studied, not being restricted to the discrete temperatures that were studied.

It is noticed that pronumerals 2 to 4 follow smooth functions except for an inversion discontinuity at about 42°C. By inverting the data above this temperature, a smooth curve is obtained which can be readily fitted. The fit is inverted again at temperatures above 42°C, and the result is shown as the solid black lines in the Figure. Pronumerals 1, 2 and 4 are fitted with a sigmoid function,

$$P_{1,2,4} = \frac{a}{b + e^{-c(T-34.3)}} + d; \quad (8.18)$$

whereas pronumeral 3 is fitted with a third-order polynomial. Parameter T is the substrate temperature, and a , b , c and d are secondary fitting pronumerals.

Evaporation Rates Over Cavities

Since the evaporative function (Equation 8.2) is dependent on the meniscus height above the heated substrate, we must consider the additional height over the cavity created by the cavity's indentation. Figure 8.20 demonstrates two extreme cases.

Over wide but shallow cavities the cavity's depth makes little difference on the evaporation profile (Figure 8.20a), but when the cavity depth becomes comparable to the meniscus height we must carefully consider how we incorporate the substrate's topography into the evaporative function. The latter case applies to nano-cavities, as their footprint is usually comparable to their depth (Figure 8.20b).

Over broad but shallow cavities, the evaporation rate near the cavity centre can reliably be determined by the total meniscus height, taking into account the cavity's depth. However, since the cavity's walls are also thermally active, this rule breaks down as one approaches the walls. The cavity topography is a step function into and out of the cavity, but the thermal and evaporation profiles are more gradual. This is especially important for nano-cavities whose depth is often comparable to the wall-to-wall distance. In that case the cavity depth relative to the distance to a wall is not large enough to neglect the wall's thermal contribution at any position over the cavity.

We therefore introduce the concept of the *effective height* of the meniscus. This

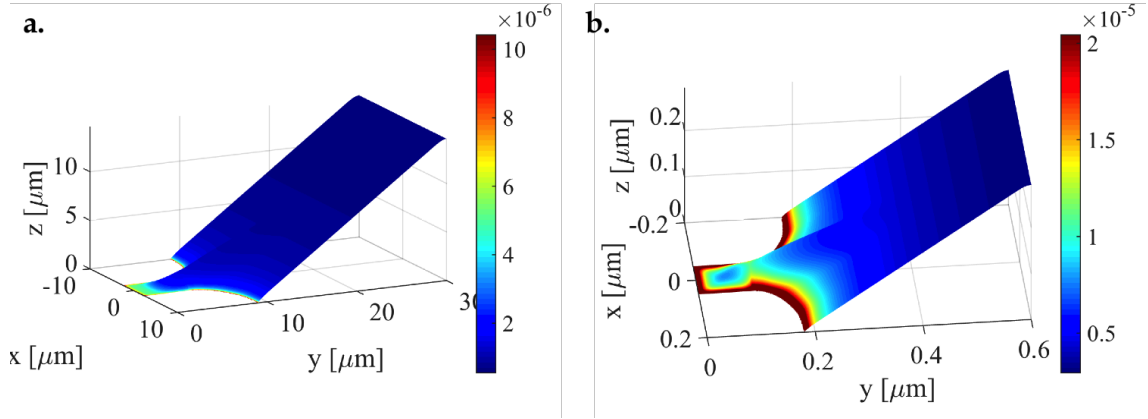


Figure 8.20: Evaporation profiles over menisci pinned on a nano-deep micro cavity (a) and nano-cavity (b). The nano-cavity profile demonstrates the influence of cavity wall proximity on the evaporation rate, which is not noticeable in (a) when the cavity depth is very small compared to its length and width.

is a modification of the actual meniscus height to yield a more accurate evaporative profile near the walls of the cavity. Figure 8.21 illustrates how the effective height is calculated over a cavity. The distance h is the meniscus height if no cavity were present. The distances d_1 to d_5 are the distances to each cavity boundary at a depth of h from the liquid interface.

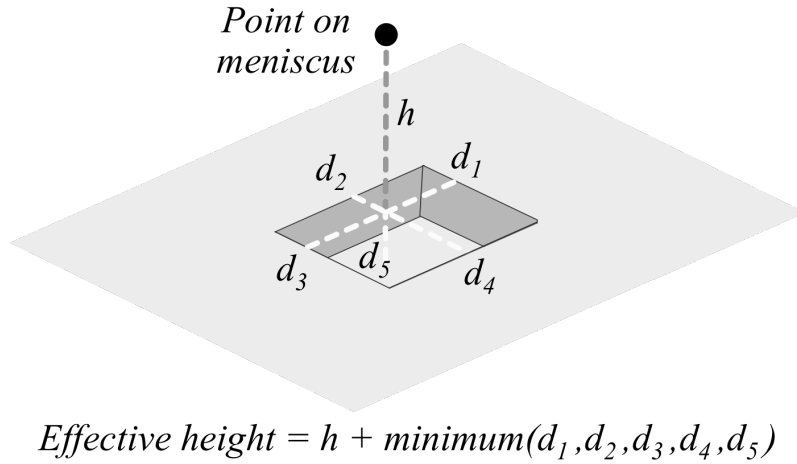


Figure 8.21: A diagram illustrating how the effective meniscus height is determined over a cavity.

The effective height must approach h close to the cavity walls, and must approach $h + d_5$ in the cavity centre (or equal $h + d_5$ in the centre if the walls are sufficiently far away to neglect their contribution). To fulfil these requirements the function chosen to determine the effective height is simply h plus the distance to

the nearest cavity face (the minimum of d_1 to d_5). Thus the effective height blends linearly from the cavity wall towards the cavity centre in all directions, plateauing at $h + d_5$ in the cavity centre if the walls are distant enough. This effective height profile is smoothed and incorporated into the meniscus surface for the purpose of determining the point-wise evaporation rate. For demonstration purposes, the evaporation rate is exemplified in Figure 8.22 showing the influence of the cavity at each modelled stage in the pinning event.

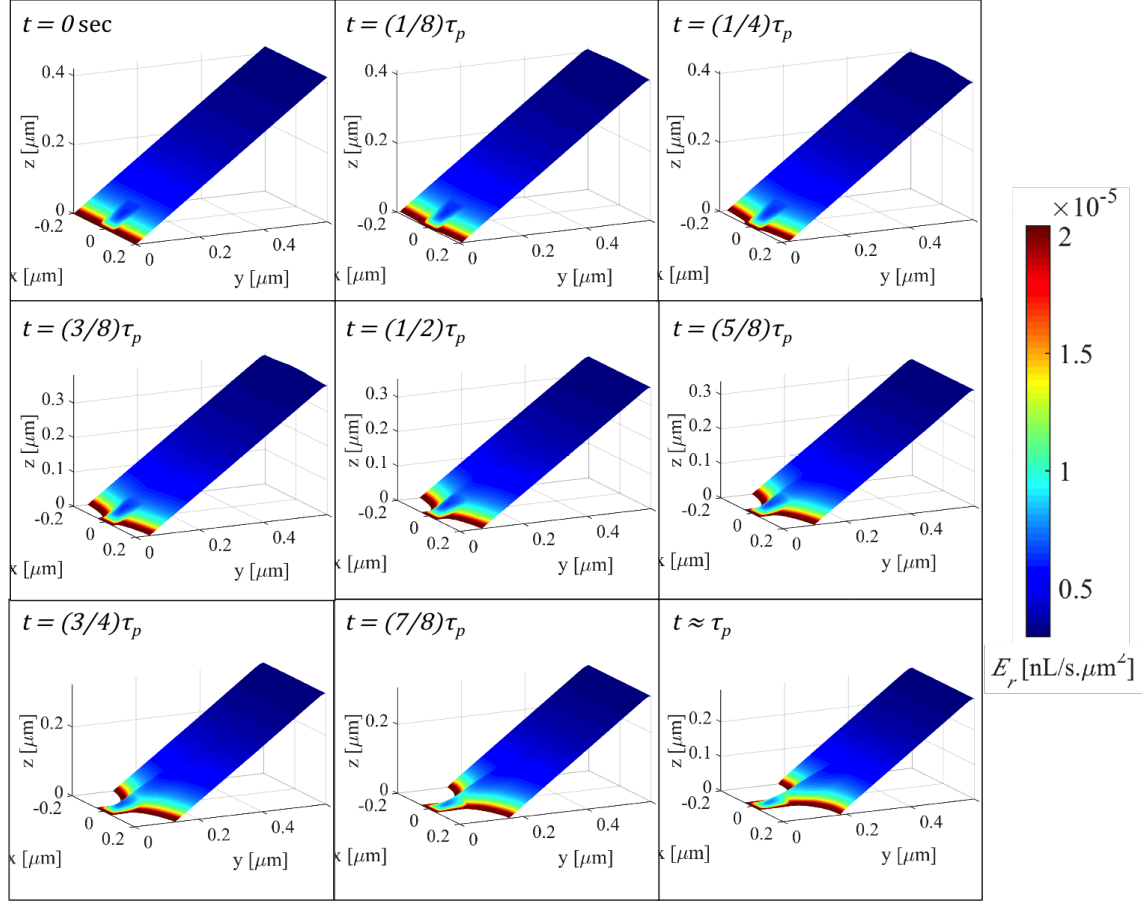


Figure 8.22: Evaporation profiles at different moments throughout a pinning event on a nano-cavity. The cavity is 100 nm in all dimensions, the temperature is 30°C and the receding contact angle is 35°.

Appendix 8.C Determining Acceleration Distance of Particles in Fluid Flow

The simulation of particle motion in the convective flow field recalculates the particle kinematics at every point in the model. The model resolution is set at a hundredth of the cavity length. For a simulation of a 100 nm cavity, the model resolution is hence 1 nm. Over each 1 nm point the flow velocity will be different to the flow velocity in the adjacent 1 nm points. The particle will thus accelerate over each nanometer of model space.

Over each nanometer of space, since the particle is accelerating within a flow field, the velocity differential reduces between particle and fluid as the particle's speed changes. The acceleration hence reduces with time until the particle speed matches the fluid speed, or until the particle traverses the full nanometer of space and transitions into the next model point.

The present model does not account for this reduction in acceleration as the particle accelerates through each nanometer of the model space. The model calculates the acceleration of the particle at its entrance into each nanometer-space, and applies that same acceleration throughout the entire nanometer-space. With this constant acceleration approximation it is found that the particle consistently reaches the flow speed within a nanometer of travel. In other words, there are no lag effects and at each point in the model the particle's speed matches the fluid flow speed.

This Appendix 8.C seeks to answer the question of whether this approximation gives an accurate result. When a more realistic acceleration is used (one that reduces as the particle speed approaches the fluid speed), does the particle consistently reach the fluid speed within one nanometer of travel?

To solve this problem the kinematic equations of particle motion within a fluid field have been solved iteratively with a small time increment. The particle starts from rest and is subject to a flow field of constant and uniform speed. The acceleration of the particle is

$$a = \frac{F}{m} = \frac{3\pi\mu d\delta v}{m} \quad (8.19)$$

where μ is the dynamic viscosity of the liquid, d is the particle size, δv is the velocity differential between the particle and the fluid, and m is the particle mass.

The simulation is iterated at intervals of $\delta t = 1 \times 10^{-11}$ seconds. The changes in velocity and distance traversed by the particle over each iteration are given by

$$\Delta v = a \delta t \quad (8.20)$$

$$\Delta x = \delta t \left(\frac{v + u}{2} \right) \quad (8.21)$$

where u and v are the initial and final velocities of each iteration, respectively. The simulation ceases when the change in particle speed from one iteration to the next is less than 1×10^{-10} m/s. At that moment the particle is seen as sufficiently matching the fluid speed.

Figure 8.23 plots the particle velocity against distance travelled. The simulation was run for particles of three different sizes in different flow speeds from 200 $\mu\text{m/s}$ to 1 mm/s. The particles sizes are 20 nm (thin solid lines), 80 nm (dotted lines) and 300 nm (thick solid lines). It is evident that all particles in all flow fields reached the speed of flow within a fraction of a nanometer of travel.

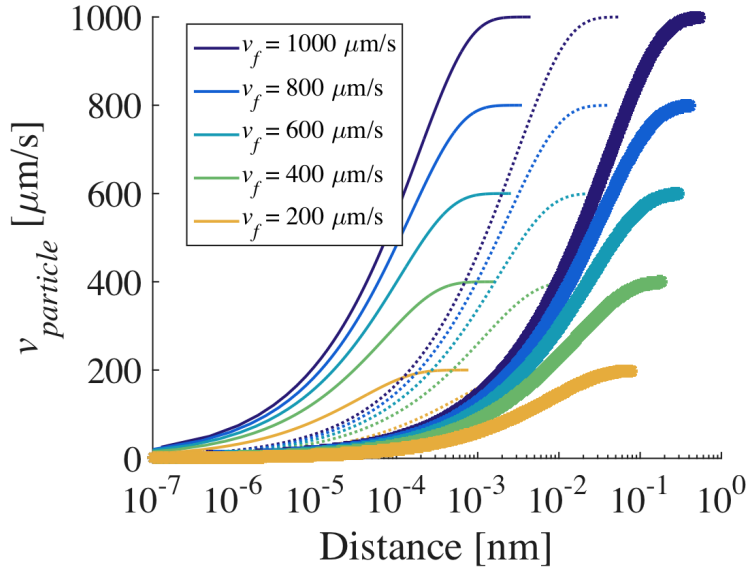


Figure 8.23: Simulation results showing that particles in a flow field rapidly accelerate to match the flow speed. Three different particle sizes are modelled: 20 nm (thin solid lines), 80 nm (dotted lines) and 300 nm (thick solid lines). The flow speed is not a significant determinant of the distance required to attain full speed, but the particle size is. All particles reach the flow speed within a fraction of one nanometer.

The flow field speed is seen to be a minimal factor determining how far a particle must travel to reach the flow speed. A more significant factor is the particle size.

The flow speeds are also greatly exaggerated from reality. These results show that a nanoparticle will attain the flow speed in less than one nanometer of travel even when the jump in flow speed from one nanometer to the next is up to 1 mm/s. That amount of change in flow speed is a large exaggeration of conditions in the pinned-convective model.

This affirms that in all conditions arising from the pinned-convective simulations, having a model resolution of 1 nm is amply sufficient. Over each nanometer of model space the particle speed can simply be matched to the fluid flow speed with no loss in kinematic accuracy.

Appendix 8.D Simulating Nanoparticle Kinematics

In this Appendix are some brief notes and outputs from the nanoparticle kinetics simulations. From the convective flow profiles at each stage in the pinned lifetime (Figure 8.24a) we can determine the kinetic energy of a test nanoparticle at each position in the model space, at each stage in the pinned lifetime (Figure 8.24b, as given for a 50 nm test particle). It is evident that the kinetic energy is orders of magnitude larger in the latter stages of pinning. This is owing the second-power relationship with velocity, and the large increase in flow rate at the end of pinning.

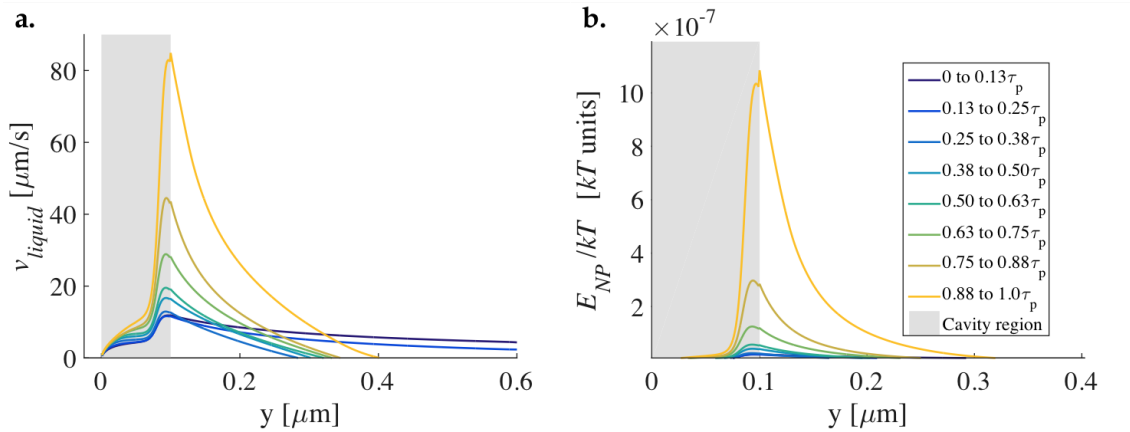


Figure 8.24: Sample simulation outputs showing convective flow profiles (a) on a 100 nm cuboid cavity at different stages of pinning. Figure (b) shows the equivalent 50 nm test particle energy (in units of Brownian energy) at each position in the model and each stage of pinning.

Various outputs from the kinetics simulation are shown in Figure 8.25. In each

plot are two curves that begin at time $t = 0$ and persist until time $t = \tau_p$. The blue represents a test particle that comes to rest at the front of the cavity at time $t = \tau_p$, and the green represents a test particle that comes to rest at the rear of the cavity at time $t = \tau_p$. They represent the two extreme cases of a particle easily being assembled and a particle only just being assembled.

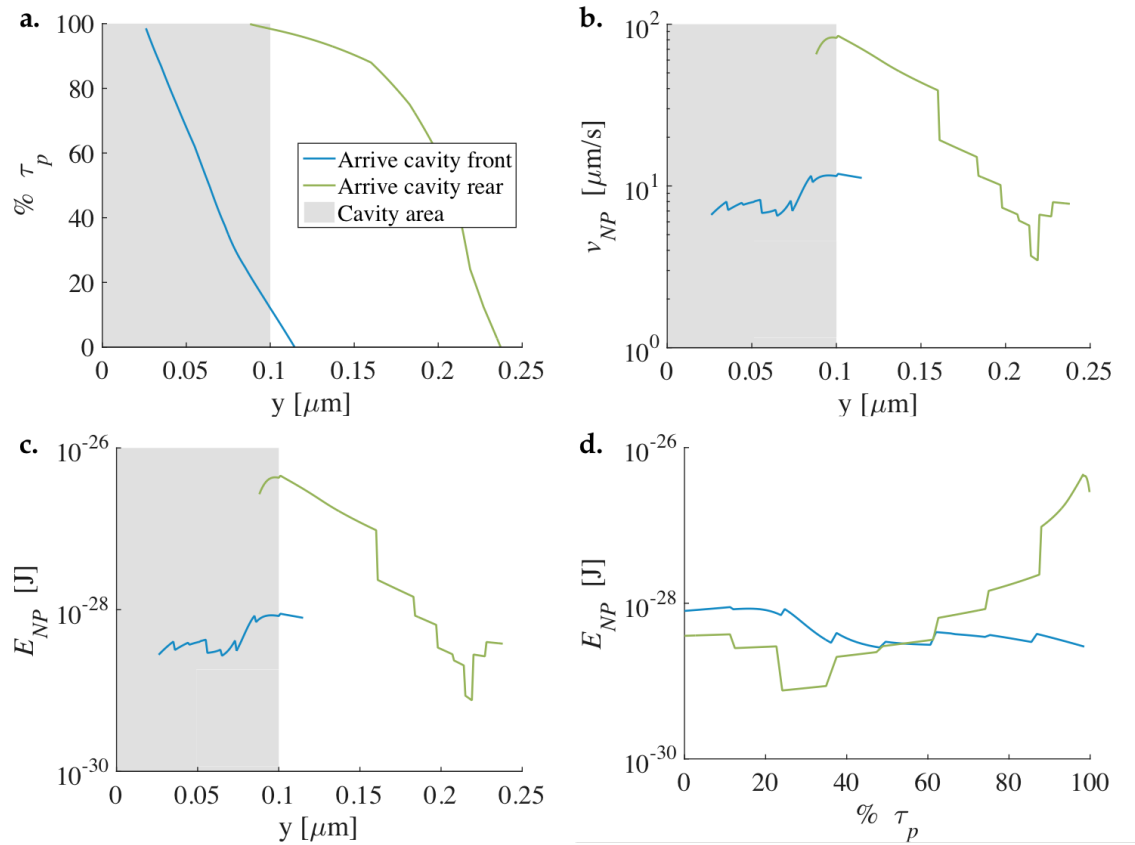


Figure 8.25: Raw simulation outputs showing how test particle kinetics vary with position and time. The jagged nature of some plots is due to the discrete stages of the pinned lifetime used in the model.

Figure (a) shows how the particle positions (y -coordinates in the model space) vary over the pinned lifetime. The blue test particle makes a steady journey to the cavity front, while the green particle makes a more sudden rush at the end of pinning.

Figure (b) shows each test particle's velocity at each position on its path into the cavity. The jagged nature of the curve is due to the discrete time intervals that the pinned lifetime is modelled over. As the particle exhausts the time allotted to one convective flow profile, the simulations applies the next flow profile. Since the entire pinned lifetime is divided into just 8 profiles, and each flow profile is just the

average flow over its allocated time interval, there is a discontinuity in the particle kinetics when transitioning between profiles. The eight stages can be seen as eight steps in the plot. The discontinuities can be smoothed out if necessary, but shown here is the raw simulation output. It is evident that a particle arriving at the rear of the cavity is very much dependent on the final stage of pinning. If the meniscus were to depin prematurely, this test particle would fall far short of the cavity and not be assembled.

Figure (c) shows the test particle energy over its trajectory (the energy begins at zero, but that cannot be shown on a logarithmic scale). The blue test particle receives most of its energy at the start of pinning, but the green particle receives it in the latter half of pinning. Again this shows the ease with which the blue particle can be assembled, whilst the green particle is heavily dependent on a full pinned lifetime. Figure (d) shows similar data to Figure (c), whereby kinetic energy is plotted against time.

Conclusions, the Implications for Nano-CFA, and Suggested Further Work

9

<i>Summary of Work Accomplished ...</i>	<i>9.1</i>
<i>The Key Tuneable Parameters for Nano-CFA ...</i>	<i>9.2</i>
<i>Rethinking CFA ...</i>	<i>9.3</i>
<i>Opportunities for Further Study ...</i>	<i>9.4</i>

9.1 Summary of Work Accomplished

With the goal of seeing plasmonic nanomaterials scaled-up, we set out at the beginning to answer three questions about nano-CFA:

1. Is it feasible to scale-up nano-CFA to make macroscale plasmonic nanomaterials?
2. The mechanism behind nano-CFA has not been well studied or elucidated to date. What are the key mechanisms behind nano-CFA?
3. Nano-CFA is a nano-scale process on very short timescales and so is not readily

observable in detail. How can we probe the mechanisms of nano-CFA and quantify them for a comprehensive model?

The core outcomes of this work are as follows:

- A review of nano-CFA literature to date, revealing two camps of understanding about how nano-CFA operates, both of which are inaccurate for theoretical and experimental reasons (Chapters 1 and 4)
- A demonstration of scaled-up nano-CFA to produce a plasmonic metamaterial (Chapter 3)
- A new model for nano-CFA that more accurately fits wide-ranging experimental results and is derived from first principles (Chapter 5)
- An assessment as to which parameters strongly influence nano-CFA outcomes based on the new model (Chapters 7 and 8)
- A novel 3D instantaneous meniscus profilometry method with micro-scale resolution, and which works on a wide variety of unconventional meniscus shapes (Chapter 6)

A false understanding of nano-CFA dynamics, and of its driving parameters, have hindered nano-assembly optimisation to date. The present work therefore constitutes a solid foundation for experimenters to knowledgeably pursue the greater potential of nano-CFA. A summary and brief discussion of the key variables is given below, as a way of tying together discoveries from Chapters 7 and 8.

9.2 The Key Tuneable Parameters for Nano-CFA

There are two targets for successful pinned-convective CFA: (1) imparting a large amount of kinetic energy to particles, and (2) a sizeable reach of convective flows away from the contact line. The main variables to reach these targets are given below.

Firstly, the amount of convective energy imparted to particles over a cavity is primarily affected by:

- The substrate temperature (higher is better)
- The contact line speed (slower is better)

- The particle size (larger is better)
- The cavity size, in absolute terms (larger is better), but also relative to the cavity depth (a ratio < 1 or > 10 is better)
- A smaller but still meaningful contribution from the receding contact angle (lower is better, provided convective layer deposition does not occur).

Secondly, the reach of the assembly dynamics away from the contact line (greater reach is better) is most affected by:

- The contact line speed (slower is better)
- The substrate temperature (higher is better)
- The cavity size (larger is better)
- A smaller but still meaningful contribution from the receding contact angle (lower is better)

Other parameters exist but are either less tuneable or less influential. Following are discussions about each of the key parameters given above.

Substrate Temperature: The importance of substrate temperature is not surprising to researchers familiar with nano-CFA, yet the reason for its importance has not been confidently demonstrated until now. The conventional model suggests that temperature is important to pack particles at the contact line, and that too high a temperature may detrimentally increase Brownian motion.

The pinned-convective model confronts this with local convective flows in a confined space. Higher temperatures increase contact line packing, restrains Brownian motion and sets up strong local convective flows. There would nonetheless be a maximum useful temperature, above which spontaneous deposition occurs.

Particle Size: The importance of particle size is evident experimentally, but the conventional reasoning is that smaller particles are subject to larger Brownian motion. The present work adds to this by suggesting that smaller particles also receive much less energy from local convective flows.

Contact Line Speed: Simulations show that the contact line speed is significant, and this was not suspected from the conventional model, receiving little attention in

literature (and often not cited at all). Of particular interest is the suggestion that speeds as low as $0.1 \mu\text{m/s}$ are best, but any speed $< 1 \mu\text{m/s}$ may suffice with little difference.

Cavity Size and Depth: The cavity footprint size and depth have never been studied as significant for nano-CFA, except to ensure trapping of particles. The present work shows it may have a greater value in enhancing convective flows over cavities (shallower cavities), and conversely in ensuring that pinning lives out its full lifetime (deeper cavities, though further study is needed to quantify this). The optimum depth is yet to be determined.

Receding Contact Angle: Contrary to the conventional model which predicts contact angle as a critical parameter, the pinned-convective model suggests it to be a minor player. Published CFA works affirm this by showing assembly from a wide and varied range of receding contact angles (see Section 4.2.4, *Disagreement Amongst Recommended Experimental Parameters*).

Nonetheless, researchers do write that there tends to be a range of receding contact angles for which CFA will *not* work, specific to their experiment. This is not a direct outcome from the pinned-convective study given above, and may be explained as follows.

We recall that pinning dynamics were here modelled only at one receding contact angle. The wider importance of the receding contact angle likely stems from its known ability to enhance or inhibit pinning on cavities, a characteristic not part of this present study. This explains why a consistent range of workable contact angles is not found in the literature—the pinned length and lifetime are also greatly affected by other parameters. This means the best range of contact angles depends on a combination of experimental variables and it does not operate in isolation. This needs much further study to characterise the trends and interwoven relationships properly.

In general, it is predicted that the minimum receding contact angle is that at which convective layer deposition begins. The maximum angle is that at which pinning is so limited that subsequent convective dynamics are too diminished to enact assembly.

9.3 Rethinking CFA

Given the above summary of nano-CFA's most important variables, we can begin thinking about how to optimise nano-CFA. It is plausible to optimise CFA by tuning the parameters cited above, but we also ought to consider whether the conventional experimental setup makes the best use of the dynamics and principles in the aforementioned discoveries. Successful implementation of the following suggestions, and a subsequent improvement in results, is an important way of validating the pinned-convective model.

Air Flow Along the Contact Line: Evaporation at the contact is a key driver but it is limited by the diffusion rate of water vapour through the ambient air. The evaporation rate could be dramatically improved by flowing air over the contact line, as Pinedo Rivera and co-workers demonstrate in a fluid cell device [1]. Cavity-level assembly dynamics are also expected to be enhanced when air flow is applied, akin to raising the substrate temperature or lowering the contact line speed. This is useful if temperature and contact line speed are limited by equipment or other reasons.

High-Contrast Wettability On- and Off-Cavities: One could conceive of fabricating templates to enforce a stronger contrast between the on-cavity and off-cavity dynamics. For example, we might imagine cavities that are more hydrophilic than the surrounding template. This would allow higher temperatures without convective deposition, and cavities would pinning more strongly. Chemically coating the template and peeling off the same coating over non-cavity areas may help with this.

Cavity Topography: Additionally, we might envision cavities with a bump or raised portion along their front edge, rising above the unpatterned template. The raised feature would substantially enhance pinning over the cavity alone, amplifying the assembly dynamics for more robust assembly.

Recent work by Flauraud et al. [2] with plasmonic nanorods implement just such a raised structure outside the cavity, bringing assembly yield to 100 % in nearly all cases, over centimetre squared areas (see Figure 9.1). They produced a

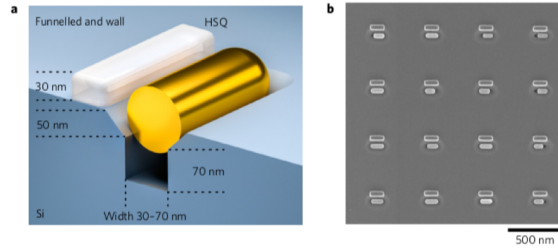


Figure 9.1: An example of cavity topography customised for enhanced pinning dynamics (from Ref [2]). The raised feature and the broadened cavity opening both accentuate pinning, while the narrower cavity base restricts rod placement akin to a smaller cavity.

wide range of nanorod arrangements, showing excellent trapping efficacy. This can be attributed to accentuated pinning (when the raised structure lay on the cavity’s leading edge) or to an enhanced trapping barrier (when the raised structure lay on the cavity’s trailing edge).

Flauraud et al. also implemented another topographical feature, shown as the funnelled cavity opening, and saw a subsequent increase in assembly yield. The funnel profile enhances contact line pinning around the cavity opening but still restricts nanorod placement within the cavity. Thus good rod alignment is retained while simultaneously having a larger pinning perimeter.

These results are strong affirmation of the pinned-convective model in action. These unique templates were made by a complex EBL and etching process, and so the issue of scalable template fabrication remains. It would be well to turn attention to that now that nano-CFA is becoming well-mastered in theory and practise. With additional suggestions below, 100 % assembly may well become routine.

Replacing Cavities with Chemical Patches: An interesting study would be to see whether highly hydrophilic patches could replace cavities. It is known that particles can assemble on chemical patches by diffusion processes [3–6], but combining this with CFA mechanisms may enhance the assembly process.

Patches that are significantly more wettable than the surrounding substrate pin the contact line like a topological deformity. The amount of pinning may be easier to control or enhance with chemical patches compared to cavities where small defects in fabrication can lead to premature depinning. This has been demonstrated with large nanoparticles on large template features already [7], but more work is required

to test the maximum resolution of assembly, the type of features that can be built, and the scalability of the process.

Combining Nano-CFA with Other Assembly Forces A final suggestion is to combine nano-CFA with an additional assembly force. There is no immediately obvious candidate for this, except for chemical-patch assembly, as given above. Highly successful electrophoretic assembly cannot easily be incorporated into a CFA setup.

9.4 Opportunities for Further Study

In addition to the above suggestions for rethinking nano-CFA, further study will be beneficial in:

- How small defects in cavities can lead to premature depinning, and a loss of assembly efficacy, and how these defects might be controlled in fabrication
- How duration of pinning is affected by the receding contact angle, the surface tension and the cavity depth (and what these relationships mean for assembly efficacy)
- How the line of densely packed particles at the contact line behaves on the whole in the presence of a pinning event (i.e. What is its rigidity and ability to flex with a pinned perturbation?)
- How significant the roles of Brownian diffusion and particle-particle collisions are in the small space and time of a pinning event

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