Correction of Wall Adhesion Effects in the Centrifugal Compression of Strong Colloidal Gels.

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Introduction

Flocculated and coagulated colloidal suspensions gel when sufficiently concentrated and form compressible sediments, filter-cakes, drying films and green bodies. Strongly cohesive particulate gels, by which is meant systems where the interparticle attraction is large enough to arrest activated processes such as coarsening, creep and delayed collapse on any time-scale of interest, show self-limiting sedimentation and filtration; the formation of sediments etc. with a stable density profile. The scaled well-depth $-U_{\min} / k_B T$, the negative of which can be taken to be the activation energy for particle escape and diffusion, can be very large for strongly-flocculated and

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coagulated colloidal particles, easily of order 10^2 or more for, say, mineral suspensions, for example, hence it is found that sediments and cakes can be stable for many years. Under such circumstances it is meaningful to say that the particulate network has a well-defined ‘equilibrium’ compressive strength and it is then possible to calculate the compressive strength as a function particulate volume-fraction (ϕ) from curves of equilibrium filter-cake volume (or sediment volume) versus load (or centrifugal acceleration)^{1-9, 14-16}, or from the equilibrium concentration profile itself^{8, 23-29, 30-32, 34}.

The most direct method in concept is pressure-filtration, whereby the equilibrium filter-cake volume is measured for a series of increasing applied pressures in a carefully-controlled and instrumented pressure-filter¹⁻⁸. The analysis of this test is trivial, in the absence of adhesion of the network to the side-walls, since then the equilibrium pressure P has to be uniform and the equilibrium cake should have the same volume-fraction $\phi(P) = \phi_0 V_0 / V(P)$ everywhere, where subscript ‘zero’ denotes the starting conditions.

The effect of wall adhesion was considered first by Michaels and Bolger⁹ in the context of sedimentation, who found more generally that adhesion can be ignored when the scaled ratio of wall shear to bulk compressive strength $\frac{4h\tau_w(\phi_0)}{P_y(\phi_0)D} \ll 1$: here τ_w is the adhesive shear strength at the wall, P_y is the compressive strength, h and D are the thickness and diameter of the cake respectively, supposing it to be cylindrical for the sake of argument, and where the starting volume fraction is above the gel-point. τ_w here is the yield stress associated with debonding and slip at the walls, hence

it can be determined independently, in principle, using a suitable shear rheometer fitted with smooth tools constructed of material exactly similar to that used to make the filtration cell. Alternatively, one could, perhaps, simply take the true yield stress of the suspension, τ_y , to be an upper bound value, given that the sample would yield very near the wall anyway, were $\tau_w > \tau_y$ ^{8,10-13}.

Various other methods used commonly rely on sedimentation-equilibrium in one way or another:

- (i) Measure the equilibrium sediment height in a series of batch settling columns of increasing height under normal gravity^{1,8,14-16}.
- (ii) Measure the equilibrium height in a suitable laboratory centrifuge for a series of accelerations^{1,8, 10, 16-22} (the centrifuge should be fitted with a swing-out rotor, preferably, since otherwise the net resultant acceleration is not in the plane of the tube axis except asymptotically at high 'g').
- (iii) Determine the equilibrium concentration versus depth profile under gravity in a column tall enough to produce significant compression towards the bottom^{8,23-29,30-32}.
- (iv) As (ii) but with direct determination of the concentration profile, as in (iii)³⁴.

In each case the default analysis assumes that the unbuoyed self-weight at any height point z in a sediment of total equilibrium height h_{eq} , viz.,

$$w(z) = \Delta\rho g \int_z^{h_{eq}} \phi(z') dz' ,$$

is balanced by the compressive strength at that level, $P_y(\phi\{z\})$: in the above $\Delta\rho$ is the suspension inter-phase density difference, g , the magnitude of the gravitational or centrifugal acceleration and $\phi(z)$ the local volume-fraction. The above only holds exactly in the absence of wall adhesion, of course, whereas in its presence a vertical force balance^{9,33} gives,

$$\frac{dP}{dz} = \Delta\rho g \phi - \frac{4\tau_w}{D} , \quad (1)$$

which shows that otherwise wall effects can only be ignored or neglected when the second term on the RHS is negligible compared to the first, that is, when,

$$\frac{4\tau_w(\phi)}{D\Delta\rho g \phi} \ll 1 \quad (2)$$

This differs from the condition obtained by Michaels and Bolger⁹ inasmuch that it applies locally in any sediment, whereas the former, which can be deduced from eqn 2, applies only to the initial uniform suspension.

Methods (i) and (ii) are very similar in basis, clearly. In case (i) the raw data, which comprises a set of values for h_{eq} as a function of h_0 , can be inverted exactly in the absence of adhesion, to obtain $P_y(\phi)$, whereas one of the corresponding pair of equations used to invert centrifuge data, that for the pressure, is only approximate because of the complication introduced by the radially varying acceleration. The usual approximation made¹⁸ is good to within ca. 5% in the pressure, typically. It turns out however to be possible to do better, simply by using a different pre-average, as will be seen below.

In method (iii), concentration-profiling, integration of the concentration profile gives the pressure at any height z above the base of the column, in the absence of adhesion,

$$\Delta\rho g \int_z^{h_{eq}} \phi(z') dz' \rightarrow P_y(\phi[z]). \quad (3)$$

This particular method is however very sensitive to any adhesion to the tube walls^{27, 28}, to the point where it is possible to exploit that sensitivity and invert raw data acquired using two or more columns of differing diameter²⁷ to determine both the compressive and the wall shear strength functions with good accuracy. The exact method of inversion²⁷ is way too involved to be of routine use, but it has subsequently proved possible to develop a very simple but accurate approximate scheme that is very straightforward to implement³³. The same approach renders the modelling of sedimentation dynamics with wall adhesion tractable too (Lester et al. – to be published), whereas this would be a very formidable challenge otherwise.

The essential problem with the profiling method is that adhesion reduces the magnitude concentration gradient $d\phi/dz$ everywhere, with the result that the relative difference between the concentration at any depth $h_{eq} - z$ and that which would prevail in the absence of adhesion increases with depth, causing the resulting error in $P_y(\phi)$ to increase rapidly with ϕ ²⁷. The reason for this can be understood by inspection of eqn 2. The shear yield strength τ_w in the numerator is expected to increase with ϕ much faster than ϕ , given that it derives from particle-particle interactions (e.g. naïve particle level models give ϕ^2 and experiments more like ϕ^3), thus the ratio on the RHS must increase with ϕ and hence with depth in the column. This means that in a tall column of modest diameter, one for which $4H_0/D \gg 1$, eqn 2 will always be violated below some critical height, z_c , causing the compressive strength calculated from eqn 3 to appear to diverge at $\phi(z_c)$. The upshot is that the apparent compressive strength deduced from the concentration profile in a tall but narrow column will appear to diverge well below the jamming volume-fraction when there unacknowledged adhesion²⁷. Furthermore, the tubes need not be all that ‘narrow’ in laboratory terms, as in Lester et al.²⁷ it was necessary to go to tube diameters of $\sim 100\text{mm}$ in order to render the influence of the walls small. The basic problem with the profiling method (iii), then, is that in order to determine $P_y(\phi)$ over a significant range of concentration, the column needs to be tall in order produce substantial compression, except that this tends to encourage working at large $4h_{eq}/D$ in practice, except that this just amplifies any errors coming from adhesion and defeats the object. Method (i), whereby the sediment is compressed stepwise by increasing h_0 suffers from the essentially same problem, as increasing the column height just increases the total bounding surface area. By contrast, in method (ii), centrifugation, the acceleration is

increased step-wise at fixed h_0 and for this reason alone wall effects tend to be less serious, everything else being equal, as will be seen. In a centrifuge, any errors coming from the neglect of adhesion do not accumulate going up the apparent $P(\phi)$ curve, as they do in profiling in terrestrial gravity, simply because the sediment is shrinking, causing the area in contact with the wall reduce. The same is true for pressure-filtration. The other very significant advantage of the centrifuge method is its large dynamic range, since four or even five decades of acceleration, and thus pressure, can be covered using fairly standard laboratory centrifuges (the range of ca. $10^2 < g = \omega^2 R < 10^6 \text{ ms}^{-2}$ is accessible using standard centrifuges fitted with swing-out rotors; where R distance from the axis of rotation to the bottom of the centrifuge tube). Its main disadvantage is that it can be difficult to run at accelerations much below 10^2 ms^{-2} with most standard laboratory centrifuges, because of problems of speed control, and this translates into meaning that it is not normally possible to work near the gel-point. A similar problem arises in pressure-filtration because of the problem of applying and controlling small pressures. Because of that, gravity sedimentation methods are commonly used to complement either centrifugation and pressure filtration. Squat tubes should be used where possible though in order to avoid the amplification of wall effect errors.

A word needs to be said about adhesion versus cohesion perhaps. There are ten or so different types of interparticle attraction known (e.g Van der Waals, depletion, liquid-bridging, incipient flocculation, charge-patch, polymer-bridging, and so on³⁰). Some are indiscriminate inasmuch that they can be expected to produce an attraction between particles and any bounding surface too, albeit one that will depend upon the nature of the bounding material in some cases (cf. Van der Waals), if not others (e.g.

depletion). The Derjaguin approximation³⁰ suggests that the particle-wall force should be ca. *twice* the particle-particle force (for spheres), everything else being equal. This could be taken to imply, perhaps, that the adhesive shear strength could even be larger than the bulk shear strength, perhaps, except this has never been observed in experimentally to the best of our knowledge^{8,10-13}. Both shear strengths can be measured rheometrically, in principle, by determining the shear yield stress twice, first, using appropriately chosen smooth shearing surfaces, to obtain the wall yield stress, and then again with suitably roughened tools, so as to obtain the true or bulk yield stress¹³. Such little data as there is in the literature suggests that $0.2 \leq \frac{\tau_w}{\tau_y} \leq 0.7$ could be typical, perhaps, supposing that the very limited published data is reasonably representative^{8,10-13, 34}.

Constitutive relationships and modelling

Quantitative constitutive relationships were needed in order to generate synthetic sedimentation-equilibrium data for subsequent analysis. The continuum model used here to generate raw ‘experimental’ data, that described in detail by Lester et al.²⁷, requires the compressive yield stress and wall shear functions $P_y(\phi)$ and $\tau_w(\phi)$ to be specified as input. Following Lester et al.²⁷, the representative functional form used for $P_y(\phi)$ was,

$$P_y(\phi) = k \left[\left(\frac{\phi}{\phi_g} \right)^n - 1 \right]; \quad \phi > \phi_g \quad (4)$$

This form captures the experimentally-observed rapid increase in compressive strength just above gel-point, along with the progression towards power-law behaviour seen typically at higher concentrations. A power-law index of $n \approx 4.0 \pm 0.5$ seems to be typical of electrolyte-flocculated and coagulated systems^{8,10, 16-22, 33,34}, whereas the strongly polymer-flocculated CaCO_3 used by Lester et al.^{27,28} showed a somewhat higher value of ca. 5. In consequence, numerical data were synthesised for both $n = 4$ and $n = 5$, by way of example. Eqn 4 neglects the expected divergence of the compressive strength at high volume-fraction. This feature could have been built in readily, if required, but we did not do so, simply because the corrections coming from adhesion cease to be important at high volume-fraction (in centrifugation) and hence the region near to jamming was not of interest. It might however be noted for the sake of completeness that experimental data for coagulated alumina suspensions³⁴

suggest a more complete form like, $P_y(\phi) \propto \left[\left(\frac{\phi}{\phi_g} \right)^{n'} - 1 \right] (\phi_{\max} - \phi)^{-m} ; \phi > \phi_g$.

Again, following Lester et al.²⁷ and guided by experimental data¹¹, it was taken as axiomatic that $\tau_w(\phi) \leq \tau_y(\phi) = \gamma_c G(\phi)$, where G is the linear (small strain) shear modulus, taken to be related to the bulk modulus of the particulate phase K by $G(\phi) = 5/3 K(\phi) = 5/3 dP_y(\phi)/d\ln\phi$ for the sake of definiteness, and γ_c is the apparent shear strain at yield. It should be emphasised that, here, γ_c , the *apparent* yield strain is merely a parameter since it is defined by the relationship $\gamma_c \equiv \tau_y / G$. The only reason for parametrising thus is that experimental data suggest that γ_c , so defined, varies relatively weakly with ϕ ^{8,10-12,19-21,34}, which makes it a convenient way of quantifying the intrinsic adhesive strength of the model gels. Hence in the simulations here, the amount of wall adhesion was varied by changing the value of the γ_c . Again, from

experimental data^{8,10-12,19-21,34}, it seems that γ_c varies widely from one material to another; e.g. for electrolyte aggregated systems values from 0.00005 to 0.025 have been reported^{8,10-12,19-21, 34} with, 0.0001 to 0.002 being more typical perhaps, whereas larger apparent critical strains of ca. 0.02 have been seen for strongly polymer flocculated suspensions; larger values reflecting the elasticity of the bridging polymer perhaps. Values of this order, ~ 0.01 , give rise to wall effects in gravity-settling that are just detectable in tubes as large as 110mm internal diameter and to very strong effects in columns with diameters more similar to laboratory test tubes²⁷. The apparent critical strain needs to be $\ll 0.001$ before adhesion effects cease to be significant on the latter scale^{27,28}. From a consideration of the nature of colloidal inter-particle forces, the apparent critical strain would be expected to vary inversely with particle size, and weakly with volume-fraction, viz. to first order or less: published data are reasonably consistent with these notions, in so far as they go^{8,10,11,21, 34}.

The functional forms used here combine to cause the ratio $\tau_w(\phi)/P_y(\phi)$ to decay rapidly from unity at the gel-point to an asymptotic value of $\frac{2}{3}\gamma_c$ at high volume-fraction, as shown in fig.1. The rate of decrease is such that the ratio of shear to compressive stress is not far from constant over much of the volume-fraction range and this too is consistent with what has been seen in experiments, approximately-speaking^{10,11,21, 34}. The ratio $\tau_w(\phi)/P_y(\phi)$ is however always expected to rise to unity at the gel-point^{11,27,29,31,33,34}, with the result that wall effects can be expected always to dominate there, given any adhesion at all^{27,28}. Finally, it might be noted that the constitutive forms used here are not abstract since they are exactly those that were used earlier to fit experimental data for CaCO_3 particles flocculated using three different polymeric flocculants^{27, 33}.

[Fig. 1 near here]

Synthetic sedimentation curves were generated for apparent critical strain values of $\gamma_c = 0, 0.0002, 0.002$ and 0.02 . The gel-point and starting volume-fractions were taken to be 0.1 : the initial column height h_0 was 0.075m and the tube diameter was taken to be 10mm in most of the runs, these dimensions being fairly typical of centrifuge testing.

[Fig. 2 near here]

In any real centrifuge the magnitude of the acceleration $g = \omega^2 r$ varies with radial distance away from the axis of rotation and hence it varies down and, to a lesser extent, across the column of suspension. It is useful to define maximum and mean values of the magnitude of the acceleration thus, (cf. Fig. 2) ,

$$g_{\max} = \omega^2 R; \quad \bar{g} = g_{\text{mean}} = \omega^2 (R - h_{\text{eq}} / 2), \quad (5)$$

The first represents an upper bound to the mass average acceleration in any real particulate network, whereas the latter represents a lower bound.

The task of developing simple but robust means of data inversion that acknowledge wall adhesion can be largely carried out in the uniform g limit, since the case of spatially-varying acceleration can be handled in the same way.

In the base case of both uniform g and negligible wall adhesion, the equilibrium curve of h versus g can be inverted to give the pressure and the volume-fraction at the bottom of the tube exactly, using the formulae¹⁸,

$$P_y(\phi_b) = \Delta \rho g h_0 \phi_0; \quad \phi_b = \frac{h_0 \phi_0}{h_{eq} + dh_{eq} / d \ln g} \quad (6)$$

The pressure itself can be seen to depend upon g plus three known constants only, hence any scatter in the raw data of $h_{eq}(g)$, together with any errors of numerical or graphical differentiation, affect only the volume-fraction to be associated with it to give $P_y(\phi)$.

The case of radially varying g is slightly more complicated inasmuch that the data can only be inverted approximately even in the absence of adhesion, unless, that is, iteration is employed¹⁸. The approximation suggested by Buscall & White¹⁸ and used by most workers to date reads,

$$P_y(\phi_b) = \Delta \rho \bar{g} \phi_0 h_0 \quad (7)$$

$$\phi_b = \frac{\phi_0 h_0 \left[1 - \frac{1}{2R} \left(h_{eq} + \frac{dh_{eq}}{d \ln g_{max}} \right) \right]}{\left[\left(h_{eq} + \frac{dh_{eq}}{d \ln g_{max}} \right) \left(1 - \frac{h_{eq}}{R} \right) + \frac{h_{eq}^2}{2R} \right]}$$

It can be seen that the eqn for the pressure is now approximate, since it contains the mean acceleration defined in eqn 5. It would be more accurate to say that it contains ‘a mean acceleration’, since there is no best way of averaging the acceleration a priori in the absence of details of the concentration profile. There is an error associated with

any arbitrary averaging and hence the inversion should be iterated, ideally, in order to improve upon the accuracy of the pressure at the bottom of the tube, although this never seems to be done in practice. Eqns 7 were derived by acknowledging the radial increase in the magnitude of g down the tube axis, but by supposing otherwise that the $\mathbf{g}$ vectors within the tube are parallel to the tube axis and walls, and hence identical at any height z . This “parallel- $\mathbf{g}$ ” approximation, valid for $D/2\pi R \ll 1$, simplifies the analysis of the test very considerably by rendering the analysis 1-dimensional. $D/2\pi R$ is of order 0.01 in a typical benchtop centrifuge and so the error introduced by the use of the parallel- $\mathbf{g}$ approximation is expected, from the geometry, to be of order $1 - \cos(D/R) \sim (D/R)^2$. It will be confirmed later via a direct comparison of simulated data for ‘parallel - $\mathbf{g}$ ’ versus true vector $\mathbf{g}$, that the error is indeed negligible for small $D/2\pi R$ and of the expected order. Furthermore, if both $D/2\pi R \ll 1$ and $h_{eq}/R \ll 1$, then the acceleration can be regarded as both parallel and approximately uniform (as per eqn 5), allowing eqns 6 to be applied to centrifuge; the validity of this approximation for small but finite $(D/2\pi R)$ will be tested also.

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The numerical calculations required to generate synthetic sedimentation-equilibrium curves in centrifugation, i.e. $(P_y(\phi), \tau_w(\phi)) \rightarrow (h_{eq}, \bar{g})$, can be executed efficiently using plasticity theory to resolve the deviatoric stresses below the yield stress, although the usual problems associated with spurious slip-lines are encountered²⁷. Because of this, it is preferable to assume solid-like viscoelasticity sub-yield. For materials brittle in shear, viz. those that have a small critical shear strain γ_c in the current terms, and for the present purposes, the results are totally insensitive to the precise details of the viscoelasticity assumed and so small-strain linear elasticity suffices to regularize the solutions given by plasticity theory, as has been shown and

discussed at length elsewhere²⁷. The reader is referred to that work²⁷ for full details of the method employed to simulate the equilibrium sedimentation curves. The values of the various constants and variables used are shown in table 1 below.

[Table 1 near here]

True radial versus parallel versus uniform acceleration.

[Fig. 3 near here]

Simulated equilibrium height versus acceleration curves calculated for true vectorial $\mathbf{g}$ and constant parallel- g are plotted together in fig. 3 for $D/2\pi R = 0.009$ ($D=10\text{mm}$), $h_0/R \sim 1/3$ and a power-law index $n=4.0$. It can be seen that even for h_0/R as large as $1/3$, the radial variation of acceleration makes little difference to the predicted equilibrium curve; provided, that is, that the heights from the vector simulation are plotted against the mean magnitude of the acceleration defined in eqn 5 and not its maximum value. This implies that for $\frac{h_{eq}}{R} \leq \frac{1}{3}$ the simpler eqn (6) can be used to invert real centrifuge data instead of (7), even if both are equally easy to use. The main difficulty in the application of either of these equations to experimental data is the calculation of the slope $dh_{eq}/d\ln g$, which needs to be evaluated as accurately as possible. Fortunately, for typical dependencies of $P_y(\varphi)$, the curvature of h_{eq} as a function of $\ln(g)$ tends to be rather weak (as a result of the approximate power-law behaviour of $P_y(\varphi)$ away from the gel-point) and this facilitates 1st order piece-wise fitting for the purpose of smoothing and differentiating real experimental data. Given

that uniform g and true vector $\mathbf{g}$ differ only slightly, then parallel $\mathbf{g}$ and true vector $\mathbf{g}$ can only differ by an even smaller amount, as is confirmed in Fig. 4. The error introduced by the parallel- $\mathbf{g}$ approximation is negligible, clearly, and $\sim (D/R)^2$ as expected from scaling. In spite of criticisms of its use^{35, 36}, it is abundantly clear from the simulated data in fig. 4 that the parallel- $\mathbf{g}$ assumption is a very accurate approximation for real laboratory centrifuges, and a negligible source of error.

[Fig. 4 near here]

Effect of adhesion

Synthetic equilibrium height data for $n=5$ and $n=4$ and three different critical strains are shown in fig. 5. While the effect of increasing the critical strain from 0.0002 to 0.002 is barely discernible, that of going from 0.002 to 0.02 is more substantial. For the suspension constitutive model used here, the corresponding yield stress ratio, $\tau_w(\phi)/P_y(\phi)$, decreases rapidly from ca. unity at the gel-point toward the asymptotic value of $5/3\gamma_c$ at high concentrations, where it is thus always small. A $\tau_w(\phi)/P_y(\phi)$ ratio does not of itself equate to a small effect of adhesion, necessarily though, since, from eq. 5, wall effects are amplified by a geometric factor of $\sim 4h_{eq}/D$, and hence they can still show in long narrow tubes^{9, 27}.

The synthetic data were inverted using (6) and some sample output for $n=5$ is plotted in fig. 6. It can be seen that the large error introduced by neglect of adhesion near the gel-point decreases rapidly with increasing volume-fraction. This decrease has two

components: it comes in part from the decrease in the surface area of the compressed gel in contact with the walls and in part from the constitutive behaviour assumed, whereby the wall-adhesion to compressive strength ratio decreasing rapidly with volume-fraction (cf. fig.1), this type of behaviour being consistent with the various experimental data available^{11, loc. cit, 27} and consistent too with the idea that, whereas cohesive particulate networks are short in shear, they exhibit ratchet poroelastic and strain-hardening in compression^{11,31-34}. Similar results for $n = 4$ are shown in fig. 7. The same pattern can be seen, viz. large errors due to the neglect of adhesion for a critical strain of 0.02 near the gel-point, but with convergence towards the correct result at higher concentration.

[Fig. 5 near here]

Since rheological characterisation by means of shear rheometry will often involve determination of the either or both of the shear yield stresses, the true (or cohesive) and wall (or adhesive), it is pertinent to ask whether the apparent compressive strength determined by applying eqns (6) or (7) be can be corrected using a set of shear yield stress data measured independently using a suitable rheometer. An overall momentum balance of the type first described by Michaels and Bolger⁹ (cf. eqn 1) motivates the testing of possible corrections of the type,

$$P_{y-corr.}(\phi) = P_{y-app}(\phi) - 4\tau_w(\phi)\frac{h_0}{D}f(h_{eq}) \quad (8)$$

wherein $f(h_{eq})$ represents an approximate or average way of accounting for the facts that the surface area of the sediment in contact with the wall reduces with increasing

acceleration, and thus ϕ or h_{eq} , whereas the mean acceleration increases. Thus, by reference to (8), the following are suggested as possible over-corrections,

$$f_1(h_{eq}) = \frac{h_{eq}}{h_0} \quad \text{or,} \quad f_2(h_{eq}) = \frac{\phi_0}{\phi} \quad , \tag{9}$$

whereas the following pair are likely to be under-corrections

$$f_3(h_{eq}) = \left(\frac{h_{eq}}{h_0}\right)^2 \quad \text{or,} \quad f_4(h_{eq}) = \left(\frac{\phi_0}{\phi}\right)^2 \quad . \tag{10}$$

That this is so should be fairly obvious, since the first pair in eqn 9 would become exact, formally, in the limit of infinite strength (or, equivalently, zero compressibility) whereas the second pair in eqn 10 should become so in the opposite limit of zero strength (or, infinite compressibility). It should be mentioned also perhaps that one of the authors (Lester) has tried hard to derive a set of corrections theoretically by attempting to construct a general but accurate pseudo-1d approximation scheme analogous to that developed earlier for uniform ‘g’³³. This has however proved to be impossible to date as the problem, even for ‘parallel-g’.

[Fig. 6 near here]

The candidate upper and lower bound corrections (9) and (10), were tested by applying them to the simulated data for the largest critical strain of 0.02. The apparent compressive strength so corrected is compared with the true are compared with the

true curve in figs. 6 (for $n=5$) and 7 ($n=4$). The corrected curves bracket the true curve except near the gel-point, where no simple correction term is ever going to eliminate the errors coming from unacknowledged or unsuspected adhesion, given that it becomes dominant there. The corrections fail just below $\phi / \phi_g = 1.5$, where, from fig. 1, the ratio of shear to compressive stress is ca. 0.04, which, given that $4h_0/D = 30$ here, means that the problematic region is where $4\tau_w h_{eq} / DP_y \geq 1$, where adhesion dominates. When however $4\tau_w h_{eq} / DP_y < 1$, then the error due to adhesion becomes fractional and the lower-bound corrections f_3 , or f_4 can be applied to obtain a good estimate of the true compressive strength curve.

[Fig. 7 near here]

[Fig. 8 near here]

A set of uncorrected experimental data for coagulated α -alumina particles, taken from the literature¹⁰, is re-plotted in fig. 8. Also shown are the corresponding yield stress data for the same material in simple shear. The latter were obtained using a cruciform cross-sectioned cylindrical vane in a wide cylindrical cup, hence they represent the true yield stress of the suspension, not the wall stress. The corrections shown, made by using the latter in place of the (unknown) wall or adhesive stress, are thus likely to be over-corrections. They are however relatively small, even so; never much more than ca. 15%, and hence rather insignificant on a logarithmic scale. The implication then, is that the uncorrected or apparent compressive strength is close to the true strength in this case. The reasons the corrections for adhesion are small in this example are as follows: firstly, and more importantly, the lowest volume-fraction is

well away from the gel-point of ca. 0.05 at $\phi / \phi_g \approx 4$ where the ratio of shear to compressive strength is $\ll 1$ (it decreases from ca. 0.1 at $\phi = 0.2$ to ca. 0.01 at the upper end). Second, the centrifuge tubes used¹⁰ had an internal diameter of 26 mm, which is quite large as centrifuge testing goes. Had smaller tubes been used, then the corrections would have been proportionately larger, and hence not ignorable at the bottom end.

What if one does not have a means of generating independent shear-stress data? Or cannot justify or resource the fairly substantial workload involved? An alternative would be to vary the column height and the tube diameter and then to extrapolate each point on the sedimentation curve to $h_0 / D \rightarrow 0$. It should even be possible in principle to determine both the compressive and wall shear stress functions by this means too, although the analysis could well be rather tedious, perhaps, since it would involve iteration by trial and error prediction and correction. The real problem with this method though is that h_0 / D cannot be varied by a factor of more than about five even in the most accommodating of centrifuges, whereas a decade or more would probably be needed in order to extract reliable values for the shear strength as a function of volume fraction. On the other hand, varying h_0 / D by a factor of just two or three can suffice to confirm that adhesion is unimportant, when or where it is, as it can be for many coagulated colloidal particles, e.g. coagulated polystyrene latex¹⁶⁻²⁰.

[Fig. 9 near here]

The simulated effect of diameter is illustrated in figs. 9 and 10 for the most adhesive case studied here of $\gamma_c = 0.02$, and for four different values of tube diameter at fixed

$h_0 = 0.075\text{m}$. The tube diameters were 5, 10, 15mm and infinity. The effect of diameter decreases with increasing acceleration, as expected, and for the two larger accelerations, and hence well away from the gel-point, the extrapolation to $1/D = 0$ is sensibly linear. At the lowest acceleration, of $g_{\text{mean}} = 5$, it is not and there is noticeable curvature away from the abscissa, implying that the use of just three rather narrow centrifuge tubes would likely not be good enough for strongly adhesive suspensions near the gel-point. It is always possible though to augment centrifuge data with gravity-settling data, given that it is much easier to cover a wide a range of tube height to diameter ratios h_0 / D on the bench, supposing, that is, that sample availability is not a problem.

[Fig. 10 near here]

Concluding remarks

The approximate equations used conventionally to calculate the compressive strength of cohesive particulate gels from raw centrifuge data¹⁸ ignore the possibility of adhesion to the walls. Furthermore, they are based on the assumption that the acceleration inside the tube can be considered approximately parallel to the tube axis everywhere in the tube. The validity of these two assumptions has been explored and tested using synthetic raw data, as has the validity of some approximate upper and lower bound correction factors for adhesion suggested by dimensional analysis. Corrections to the “parallel g” assumption are however very unlikely to ever be needed in practice, as this approximation turns out produce negligible error for realistic centrifuge geometries, as is to be expected from scaling arguments.

Furthermore, it turns out also, that for typical centrifuge geometries, by which is meant $h_0/R \ll 1$ and $D/R \ll 1$, it is simpler and more accurate to use eqns 6 of Buscall & White¹⁸, but with $g_{\max}$ replaced by g_{mean} , than it is to use the more complicated but still approximate eqns 7. The reasons for this are two-fold: the first being that the extra terms in eqn 7 are insignificant for sufficiently small h_0/R and D/R , the second that replacing $g_{\max}$ by g_{mean} improves the accuracy of eqn 7.

In the simulations used to generate synthetic raw data, the strength of wall adhesion was parametrised in terms of the apparent critical shear strain for shear yielding, γ_c . This way of parametrising the intrinsic adhesive strength of any particular material is convenient because γ_c is known to vary relatively weakly with volume-fraction, whereas the ratio of the shear yield stress to compressive strength itself varies strongly, near the gel-point at least³⁴. Furthermore, the latter ratio is expected, on theoretical grounds, to asymptote towards a value $\sim \gamma_c$ at high volume-fraction³⁴. Here, values of $\gamma_c = 0, 0.0002; 0.002$ and 0.02 were used in order to cover the range found in the literature, wherein values of $\ll 0.01$ have been reported for many electrolyte coagulated or flocculated suspensions, including polystyrene latex and a range of minerals, whereas larger values of order 0.01 or more have been found reported for mineral suspensions flocculated strongly using high polymer flocculants and to water-treatment sludges (which are ‘polymer flocculated’ in one way or another too, presumably)²⁷.

A particular form for the dependence of the shear and compressive strength on volume-fraction had to be assumed in order to generate the synthetic raw data although this again was motivated by published experimental results²⁷.

Small adhesive to strength ratios alone do not necessarily mean a negligible effect of adhesion in the centrifuge, since the adhesive effects are amplified by the geometric factor $\sim 4h_0/D$ and this factor can be rather large for off-the-shelf centrifuge rotors and tubes. It can be in the range $10 < 4h_0/D < 100$, typically.

Since yielding, be it in the bulk or at a wall, involves breaking bonds, the apparent critical strain can be expected correlate with the equilibrium surface-to-surface separation of the particles (or ‘bond length’) scaled by the particle size. The latter is expected to be small for coagulated particles, in upper colloidal range of size at least, if not for nanoparticles (<100 nm). The simulations herein suggest that adhesion can probably be neglected entirely in centrifuge testing when the lowest volume-fraction point is well above the gel-point, substantially above $2\phi_g$, say, and where the apparent critical shear strain is known to be $\ll 0.01$. More generally, the following tactics might be considered:

1. Measure the adhesive shear strength independently in a rheometer fitted with appropriate tools and apply a correction to (6) or (7) using (8) and (10): noting that corrections for adhesion are always expected to fail *very* near the gel-point, when $4h_0/D > 1$, given any propensity for adhesion at all.

2. Make measurements using several different values of the ratio of initial height h_0 to tube diameter D and extrapolate to h_0/D . This method may or may not be practicable, depending upon the design of the centrifuge. The range of h_0/D covered should be at least three-fold and preferably five-fold, as should the number of data points, although it rather depends upon the strength of the effect found: fewer points are needed to demonstrate that adhesion is insignificant, where it is, than would be needed to perform a good extrapolation, where it is not.
3. Complement the centrifuge data with data from gravity-settling for a set of column chosen so as to vary h_0/D by a factor of at least five and better ten, with h_0 and D each varied by at least three. One could also complement centrifuge data with that coming from an instrumented pressure-filter, in principle, since the construction of these is usually such that h_0/D is small, except that neither does pressure-filtration normally probe the region near the gel-point because of the difficulty in applying the necessary small pressures. This method has however been used to validate and complement the centrifuge method at higher volume-fraction^{8, 10, 21, 23}.

The centrifuge method has been used recently to examine the effect of temperature on the stability of incipiently flocculated polystyrene latices³⁷, albeit without taking the possibility of adhesion into account. It has been used also to measure the compressibility of microgels³⁸, using inclined rotors, which adds complication to the analysis. Wall shear stresses were ignored, which could well be entirely reasonable for microgels in good solvents, perhaps³⁸.

A concise discussion of the essential constitutive behaviour of strong particulate gels can be found elsewhere³⁴. In that work it was shown that if the gel-point is known; from measurement of some other property, say, or from bench settling tests in wide, squat tubes, then the asymptotic ratio of adhesive to cohesive shear yield strengths, α , say, can be found from experimental data similar to that in fig. 8 by correcting the apparent compressional data re-iteratively by using guesses for α and shooting for the known gel point. A value of ca. $\alpha = 1/6$ was deduced for coagulated suspensions of AKP-30 alumina in polycarbonate tubes by such means³⁴.

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Legends to figures:

Fig. 1 Input material functions: compressive strength and wall stress, the latter for three values of the apparent critical shear strain. The ratio of wall stress to compressive stress is plotted for the largest strain. It can be seen that most of the variation is confined to a region close to the gel-point.

Fig. 2 Schematic illustration of the geometry of the centrifuge test.

Fig. 3 Synthesised equilibrium height versus acceleration data for constant g compared with centrifugal acceleration at equivalent mean acceleration $\omega^2(R-h/2)=g$ for $n=4$, $D=15\text{mm}$ and $h_{\text{eq}}/R < 1/3$.

Fig. 3 Synthesised equilibrium height versus acceleration data for constant g compared with centrifugal acceleration at two equivalent mean accelerations of $g_{\text{mean}} = \omega^2(R-h/2)$ and $g_{\text{max}} = \omega^2 R$ for $n=4$, $D=15\text{mm}$ and $h_{\text{eq}}/R < 1/3$.

Fig. 4 Synthesised equilibrium height versus acceleration data for vector centrifugal g compared with the parallel- g for 15mm internal dia. tubes and $n=4$. The figures in brackets show the fractional error of the parallel- g approximation at each end of the curve.

Fig. 5 Synthesised equilibrium height versus acceleration data for constant g , 10mm internal diameter tubes, two values of the power-law index and for three different levels of wall adhesion as parameterised by the critical shear strain. The effect of

adhesion is just discernible at 0.002 and significant at 0.02. The result for zero shear strain (not shown) is indistinguishable from the curve for 0.0002. The inset semi-log plot illustrates the slow change in the gradient term needed in eqns (7) and (6).

Fig. 6 Apparent compressive strength for critical adhesive shear strain = 0.02 obtained by applying eqns 3 to the data in fig. 5 (points) compared with the true curve (heavy line). Also shown are the results of applying the suggested under and over corrections f_1 to f_4 to the points. Approximate corrections of this type cause the result to become negative below ca. 1.3 times the gel-point. Below that only iteration of the data via retrodiction and correction will do and even that scheme will fail if the gel is supported entirely by the walls.

Fig. 7 As for fig. 6 but for a power-law index of $n = 4$. Reducing the power-law from 5 to 4 reduces the errors coming from adhesion a little, but otherwise the picture is much the same.

Fig. 8 Data of Zhou et al. (replotted from ref. 10, see also ref. 8, fig. 3) and corrected according to eqn 6 using correction f_3 from eqn 10 and the fit to the shear data shown. Note that correction f_4 gives very similar results.

Fig. 9 Simulated height data for a critical strain of 0.02 for three tube diameters.

Fig. 10 Extrapolation of simulated height data for a critical strain of 0.02 to infinite tube diameter for three accelerations measured in units of normal gravity g . Here the points for infinite D are known. At the lowest g , near the gel-point, the plot is slightly

convex to the abscissa implying that several tube diameters would be needed in practice for a really good extrapolation.

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Table 1: Values of key quantities used in the simulations

Quantity	Symbol	Value
Initial vol. fraction	$\phi_0 = \phi_g$	0.10
Compressive strength Pre-factor	k	5 Pa
Compressive strength exponent	n	4, 5
Interphase density difference	$\Delta\rho$	2000 kg m ⁻³
Tube diameter	D	5, 10, 15 mm
Initial column height	h_0	0.075m
Centrifuge radius	R	0.175m

Fig. 2 Schematic illustration of the geometry of the centrifuge test.

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