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Sedimentation in bidisperse and polydisperse colloids

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Abstract

We introduce a simple force and flux balance model for sedimentation and creaming in high volume fraction, polydisperse colloidal suspensions. The model is set alongside monodisperse and bidisperse sedimentation data for latex spheres, and we suggest that the broadening of the larger species sedimentation profile observed in the bidisperse case is linked to the particle pressure gradient arising from the smaller species. The model gives a satisfactory qualitative description of real emulsion creaming data, but implies either that the effective droplet radius is larger than the measured droplet radius, or that the effective background viscosity is reduced. Increasing the particle pressure gradient results in interface broadening at short times. We propose that the smallest emulsion droplets contribute to this broadening.

Keywords: Sedimentation; Creaming; Polydisperse; Bidisperse; Burgers' equation; Emulsion; Concentrated colloid

1. Introduction

Particles heavier than the fluid in which they are suspended sink, or sediment, over time. This theoretically interesting and industrially important process, called sedimentation, has been studied extensively. The starting point is sedimentation of monodisperse spheres at infinite dilution. In this case, the dispersed particles move downwards at a rate determined by the Stokes velocity, and particles are so far apart that they do not interact with each another.

However, real sedimentation scenarios include two obvious complications. One concerns the volume fraction of the dispersed particle phase, which is typically so large that sedimenting particles do not behave independently. Instead, particle motions are strongly correlated through hydrodynamic interactions. The second complication, appropriate for many real systems, arises because the sedimenting entities are not all the same size: the system is then described as polydisperse rather than monodisperse. These two issues have been addressed by Batchelor in a series of classic papers [1–4] and by others [5–7] but the full description of the sedimentation for high volume fraction, highly polydisperse systems continues to present challenges.

Food dispersions include both those in which the dispersed phase sediments, and others that are based on droplets, often oils, which are lighter than the suspending fluid. These systems, called emulsions, tend to cream. The droplets retain their integrity, via some stabilizing agent present at the droplet surface, and rise through the system over time. Usually, food emulsions are highly polydisperse and in applications typically have high droplet volume fractions.

In the present work, we introduce a simple "engineering" model that works equally well for both sedimentation and creaming, which so far as the model is concerned simply differ by the direction of the external field. The model is geared to both high volume fractions and polydispersity. In particular, we extend an existing force- and flux-balance model to accommodate an arbitrary degree of polydispersity. The model is framed in terms of average velocities, so ignores the interesting issue of velocity fluctuations, and is blind to surface and shape effects. There is no particle or droplet aggregation in the present implementation.

Below, we begin by outlining the previously published monodisperse version of the model, then go on to discuss

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the polydisperse implementation in some detail. Next, we present the monodisperse model with a particular parameter set and compare with some real sedimentation data. As a step towards full polydispersity, we then consider a bidisperse version of the model alongside bidisperse sedimentation data. The experimental system considered is quite unusual, in that the particle sizes are very different. We then consider the full polydisperse version of the model against some real emulsion creaming data.

2. The model

The basic model to be developed in the present study has been introduced elsewhere [6,8–10]. Here, we begin by summarizing the model as applied to monodisperse sedimentation.

Consider a particle sedimenting in a vertical column of fluid for which the positive z direction is upwards. Relative to the container walls, let the average speed of the particle be $u = u(\phi)$, where for medium to high dispersed phase volume fractions, ϕ, the particle speed is a function of volume fraction only. Then $\underline{u} = -u\hat{\underline{z}}$. The average speed of the fluid displaced by the sedimenting particles, relative to the container walls, is $w = w(\phi)$ with $\underline{w} = +w\hat{\underline{z}}$. The downward gravitational force per unit volume is $-\Delta\rho\varphi g\hat{\underline{z}}$, where $\Delta\rho = (\rho_{\text{dispersed phase}} - \rho_{\text{continuous phase}})$ is the density difference between the particles and the suspending fluid. This force is opposed by viscous drag on the moving particles. In addition, Brownian particles are subject to a stochastic Brownian force.

For concentrated systems, as opposed to those at infinite dilution, there are two classes of interactions between particles. Indirect interactions occur through hydrodynamics, the movement of any single particle being sensitive to the changing configuration of its neighbors via the suspending medium. This is the origin of the hindering function discussed below. In addition, particles undergo direct interactions with one another. For homogeneous or weakly inhomogeneous systems of Brownian particles interacting as hard spheres, direct interactions, in the form of thermally driven ballistic collisions, give rise to a stochastic force responsible for particle diffusion.

More generally, direct interactions also embrace the case where particles are subject to an additional effective potential (and for hard sphere systems at sufficiently high concentrations steric effects become significant). In such cases, the energy of the system of particles is a function of the particle configuration. For a sedimenting system, the change in vertical configuration leading to the formation of the sediment will give rise to an energy gradient, in other words a force. This force is termed the particle pressure, denoted P. For a gelled system, the particle pressure arises from the stress transmitted through the particle network via direct particle contacts, and the corresponding force is directed in opposition to gravity. In general the particle pressure will be a function of both height and volume fraction, $P = P(z, \phi)$. For an element of sedimenting material, the particle pressure gives rise to an additional term in the force balance represented by the gradient, $\partial P/\partial z$. In the special case of a hard sphere system of Brownian particles, the particle pressure gradient takes a form similar to the osmotic pressure gradient. With an eye to future work on sedimenting flocculated suspensions and to retain generality we present our model in terms of particle pressure.

The force balance is

$$\beta(\phi)|\underline{u} - \underline{w}|\hat{\underline{z}} - \Delta\rho\phi g\hat{\underline{z}} + \left|\frac{\partial P}{\partial z}\right|\hat{\underline{z}} = 0,$$

where $\beta(\phi)$ is a viscous drag coefficient. The first term is the upwards-acting viscous drag force acting on an element of the suspension. The second term is the external downwards gravitational force, and the final term is the upwards-acting particle pressure gradient. Flux continuity can be written

$$\phi\underline{u} + (1-\phi)\underline{w} = 0.$$

The viscous drag coefficient can be expressed in terms of particle velocity by considering sedimentation in the absence of the particle pressure term, i.e. with $|\partial P/\partial z| = 0$. The corresponding sedimentation speed, u_0, can be written in terms of the infinite-dilution Stokes value $u_s = (2r^2 g\Delta\rho)/9\eta$ for a spherical particle, radius r, in a medium with viscosity η, and a semiempirical "hindering function" $h(\phi)$ accounting for indirect hydrodynamic interactions, so that $u_0 = u_s h(\phi)$.

Combining the force and flux balance results yields

$$\frac{\Delta\rho\varphi g u}{u_0} - \Delta\rho\phi g + \left|\frac{\partial P}{\partial z}\right| = 0.$$

The speed of a sedimenting particle is then

$$u = u_0\left(1 - \frac{1}{\Delta\rho\phi g}\left|\frac{\partial P}{\partial z}\right|\right),$$

which, when inserted into the continuity equation for a sedimenting system $\partial\phi/\partial t + \underline{\nabla}(\phi\underline{u}) = 0$ gives, for one-dimensional motion,

$$\frac{\partial\phi}{\partial t} - \frac{\partial}{\partial z}\left(\phi u_0 + \delta(\phi)\frac{\partial\phi}{\partial z}\right) = 0, \tag{1}$$

where

$$\delta(\phi) = \frac{u_0}{\Delta\rho g}\left(\frac{\partial P}{\partial\phi}\right).$$

This expression is the sedimentation result derived by Barker and others [9–12], which also holds for creaming with due attention paid to signs. This result is an extension of the Kynch description [13] following the inclusion of an additional dissipative term controlled by $\delta(\phi)$. The construction contains a number of assumptions, as discussed by Barker [8,9] and others. In particular, the analysis corresponds to a special case for which P has no explicit z dependence, so that

$$\frac{\partial P}{\partial z} = \frac{\partial P}{\partial\phi}\frac{\partial\phi}{\partial z}.$$