Model for the Interparticle Surface Separation in Concentrated Mono- and Polydisperse Suspensions

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The interparticle surface separation in mono- and polydisperse concentrated suspensions of spherical particles is discussed. For monosized particles, it is shown that the "expansion" argument of Frankel and Acrivos (1967) can be extended from cubic to arbitrary packing geometries. This argument is then further extended to polydisperse suspensions, resulting in an equation of the same form, but incorporating the surface mean particle diameter for the interparticle surface separation in terms of the packing fraction of the equivalent packed bed (a packed bed with the same packing geometry as the suspension) and that of the suspension. Another approach to interparticle surface separation in suspensions (the "volume of free liquid" argument) confirms the usefulness of the surface mean particle diameter for polydisperse suspensions. A relation potentially useful for suspensions of nonspherical particles is also given.

Introduction

Interparticle surface separation in concentrated suspensions is of significance in different disciplines. One is the rheology of concentrated particle suspensions, which is important in, among other things, the food industry, the soaps and detergents industry, the paints and coatings industry, and the mining and metal industry.

Most model equations for the rheology of concentrated suspensions of particles contain the particle packing fraction in the suspension, ϕ, and the maximal packing fraction, ϕ_m, which is the packing fraction of a packed bed with the same packing geometry (hereinafter called the "equivalent packed bed"). The argument is that particle–particle interaction plays an ever stronger role in increasing the apparent viscosity of the suspension as ϕ increases toward ϕ_m, finally making the suspension effectively immobile when it reaches this value.

Some models for suspensions rheology are based on the concept of calculating the interparticle surface separation in the suspension and deriving the suspension viscosity from this (Frankel and Acrivos, 1967; Sengun and Probstein, 1989; Probstein et al., 1994). Work aimed at understanding the rheology of colloidal particle suspensions or suspensions of particles coated with polymers (Buscall et al., 1982; Greenwood et al., 1995; Kevelam et al., 1999) also depends on knowledge of the surface separation.

Two expressions giving the particle surface separation D as a function of the packing fraction ϕ are used in the literature. Both are based on comparison with the equivalent packed bed. One expression is

$$D = d_p\left[\left(\frac{\phi_m}{\phi}\right)^{1/3} - 1\right] \tag{1}$$

(Frankel and Acrivos, 1967). Here d_p is the particle diameter. The second expression will be considered in a separate section toward the end of the article. Frankel and Acrivos arrive at Eq. 1 by an "expansion argument," expanding a cubic packing of monosized particles. They assume Eq. 1 also applies to other packing geometries of monosized particles.

In the context of an investigation into the rheology of sterically stabilized colloidal suspensions, the question arose if a predictive equation for the surface separation in suspensions

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containing polydisperse spheres could be found, and which mean particle diameter, if any, could be used. The aim of this work is to answer these questions.

First we give an account of a derivation of Eq. 1, which extends its range of applicability.

Derivation of Eq. 1

The maximum packing fraction ϕ_m of a face-centered cubic or hexagonal close packing of monosized spheres is 0.74. With these packing geometries, therefore, any packing fraction below 0.74 means that the particles no longer are touching, but have a surface separation, D. For a cubic packing, on the other hand, the particles are in contact at the much lower packing fraction of 0.52.

Thus the particle surface separation is not a unique function of the packing fraction. In order to derive a relation for $D(\phi)$, the packing geometry must be kept constant, so that we consider a suspension in comparison with a packed bed with the same packing geometry as the suspension: the "equivalent packed bed."

Consider a cube of side length unity containing a randomly packed bed of spherical particles with packing fraction ϕ_m. The coordinates of the center of the ith particle are (x_i, y_i, z_i) in a coordinate system with origin in a corner of the cube. The center-to-center interparticle distance is $\frac{1}{2}(d_{p,i} + d_{p,j})$. Expand the cube to make the side length $\xi > 1$, maintaining the relative position of the particles, changing the coordinates of their centers to $(\xi x_i, \xi y_i, \xi z_i)$ and the center-to-center distance to $\frac{1}{2}\xi(d_{p,i} + d_{p,j})$. The surface separation, D, of two particles i and j, which were touching in the packed bed, becomes:

$$D = \frac{1}{2}\xi\left(d_{p,i} + d_{p,j}\right) - \frac{1}{2}\left(d_{p,i} + d_{p,j}\right). \tag{2}$$

The packing fraction of the particles becomes:

$$\phi = \frac{\phi_m}{\xi^3},$$

giving

$$\xi = \left(\frac{\phi_m}{\phi}\right)^{1/3}. \tag{3}$$

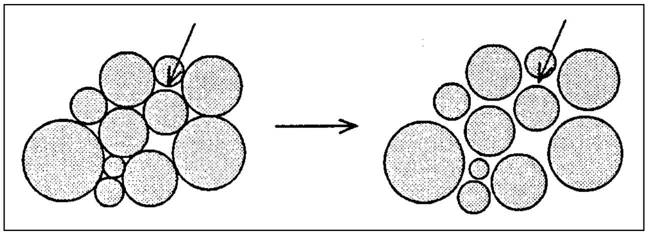

Figure 1. Expansion argument for polydisperse suspensions.

Substituting Eq. 3 in Eq. 2 gives

$$D = \frac{1}{2}\left(d_{p,i} + d_{p,j}\right)\left(\left(\frac{\phi_m}{\phi}\right)^{1/3} - 1\right). \tag{4}$$

This gives Eq. 1 for monosized particles. This justifies Frankel and Acrivos' assumption that Eq. 1 applies to all packing geometries of monosized particles.

Derivation of a Relation for the Interparticle Surface Separation in Suspensions of Polydisperse Spheres

Expanding a polydisperse packed bed, the resulting surface separations between particles that made contact in the packed bed depend on the particle size (see the 2-dimensional sketch in Figure 1).

A particular problem, which arises when applying the expansion argument to polydisperse suspensions, is that at higher voidages the distances between small particles, which were close but not touching in the packed bed (arrowed in Figure 1), will become less than that between large particles that did make contact. This throws open the entire question of which surface separations to include when calculating the mean and which not. Application of the expansion argument is therefore restricted to suspensions so concentrated that only the distances between particles that were in contact in the packed bed need to be included. How severe this restriction is depends on the width of the particle-size distribution (the measure of width should remain unchanged when the particle assembly is scaled), and can be estimated in the following way. Say two of the largest particles touching in the equivalent packed bed make a surface separation of L upon expansion. We reject the model argument if the number of surface separations less than L in the expanded bed of the character arrowed in Figure 1, n, exceeds a certain percentage of the number of surface separations resulting from particle contacts in the equivalent packed bed. The number of separations, n, can be calculated roughly, assuming that the particles small enough to contribute to n are distributed with a uniform probability throughout the bed. The number of contacts in a cubic equivalent packed bed of linear dimension $1/\xi$, N, can be calculated as half of the total number of particles in the assembly multiplied by the average coordination number. These calculations were performed for a lognormal distribution:

$$f(d_p) = \frac{1}{d_p \sigma\sqrt{2\pi}} \exp\left[-\frac{1}{2}\left(\frac{\ln d_p - \langle \ln(d_p)\rangle}{\sigma}\right)^2\right], \tag{5}$$

taking the largest particle as the 98% mark on the cumulative surface distribution, the average coordination number as six, and requiring that n is only 2% of N. The width of a lognormal distribution, σ, which is the same for number, surface, and volume distributions, can be estimated from the 16 and 84% marks on the cumulative distribution as: $1/2 \ln(d_{p,84}/d_{p,16})$. Figure 2 shows the limiting value of $(\phi_m - \phi)$ as a function of σ, taking ϕ_m as 0.65. The plot does not change very much when varying ϕ_m within the relevant range.

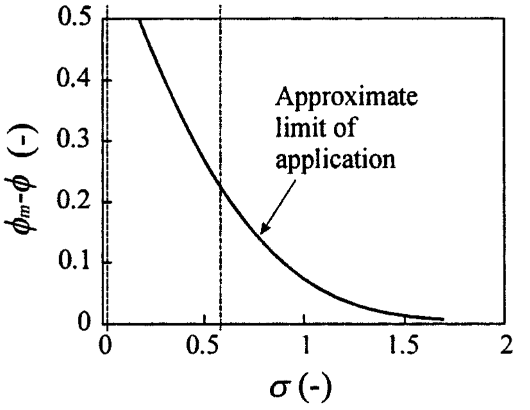

Figure 2. Approximate limit of application of the expansion argument for a lognormal distribution (——) and range of widths for most particulate materials (----).

For many particulate materials σ is in the range 0.03 to 0.6. This range is also indicated in the figure.

Since surface separations depend on particle size, the size of the particles in contact in the packed bed have to be considered to calculate the distribution of surface separations after expansion. We assume that the number of contact points in the packed bed for a given particle is proportional to its surface area: πd_p^2. This aspect is discussed in the Appendix. The total number of contact points in the packed bed involving particles of diameter $d_{p,i}$ is then proportional to $f_N(d_{p,i})d_{p,i}^2\pi$, where $f_N(d_p)$ is the number density distribution function. The joint probability density that a given contact between two particle sizes i and j is then:

$$p(d_{p,i},d_{p,j})\,\alpha f_N(d_{p,i})\,d_{p,i}^2\pi \times f_N(d_{p,j})\,d_{p,j}^2\pi\alpha f_S(d_{p,i}) \times f_S(d_{p,j}), \quad (6)$$

where $f_S(d_p)$ is the surface density distribution function for the particles.

Equation 4 shows that when expanding the system, the resulting surface separation is only a function of the sum of the two particle diameters. We can therefore state that the probability density of surface separations D is given by

$$p\left[D = \frac{1}{2}(d_{p,i} + d_{p,i})(\xi - 1) = \frac{1}{2}Z(\xi - 1)\right] = \int_0^\infty f_S(d_p)\,f_S(Z - d_p)\,d(d_p) = f(Z). \quad (7)$$

The integral is the convolution of $f_S(d_p)$ with itself. By a change of variable and normalization, $f(Z)$ gives the probability density distribution function of the surface separations in the expanded particle assembly, $f_D(D)$:

$$f_D(D) = \frac{2}{(\xi - 1)} f(Z(D)). \quad (8)$$

Note that $f_D(D)$ does not reflect an actual distribution of particle separations in a physical system. There is no reason to assume a dependence of D on d_p like the one given earlier in a physical system. This is simply a calculation method used to estimate the mean particle surface separation in the concentrated polydisperse suspension.

The mean surface separation can be found as the first moment of $f_D(D)$ around zero:

$$\langle D\rangle = \int_0^\infty D f_D(D)\,dD = \int_0^\infty \frac{Z(\xi-1)}{2}\left(\frac{2}{(\xi-1)}f(Z)\right)\frac{dD}{dZ}\,dZ = \int_0^\infty Z f(Z)\frac{(\xi-1)}{2}\,dZ = \frac{(\xi-1)}{2}\int_0^\infty Z f(Z)\,dZ. \quad (9)$$

The integral in the last expression is the mean of the convolution function $f(Z)$, which is simply equal to the sum of the means of the two functions from which it was formed (see, for instance, Pfeiffer, 1978, p. 177), in this case twice the first moment of $f_S(d_p)$ around zero, which is twice the surface mean diameter, $d_{p,S}$.

Finally, we then obtain the expression

$$D = d_{p,S}(\xi - 1) = d_{p,S}\left(\left(\frac{\phi_m}{\phi}\right)^{1/3} - 1\right), \quad (10)$$

which is the same form as Eq. 1, but with d_p replaced by the surface mean diameter, $d_{p,S}$. This is the final equation for the surface separation in polydisperse suspensions of spherical particles.

"Volume of Free Liquid" Argument

In this section we briefly consider the other approach to interparticle surface separation in the literature:

$$\frac{D}{2} = \frac{\phi_m}{S}\left(\frac{1}{\phi} - \frac{1}{\phi_m}\right) \quad (11)$$

(Mori and Ototake, 1956, as quoted in Tsutsumi et al., 1994). Here S is the total surface area of the particles in unit volume of the equivalent packed bed. Equation 11 is derived by considering the interstitial liquid in the packed bed as "bound" liquid, and the extra liquid in the concentrated suspension as "free" liquid, which is then wrapped around the particles in a uniformly thick layer of thickness $D/2$. Equation 11 is less rigorous in its derivation than Eq. 1, but claims the advantage of having a wider range of application. For monosized spherical particles it becomes

$$\frac{D}{2} = \frac{d_p}{6}\left(\frac{1}{\phi} - \frac{1}{\phi_m}\right). \quad (12)$$

Comparing Eq. 1 and Eq. 12, we recognize the linear dependence on the particle diameter d_p in both, but a different dependence on ϕ.

Injecting more liquid into a unit cube containing particles packed at a fraction ϕ_m, expanding it to one with the side

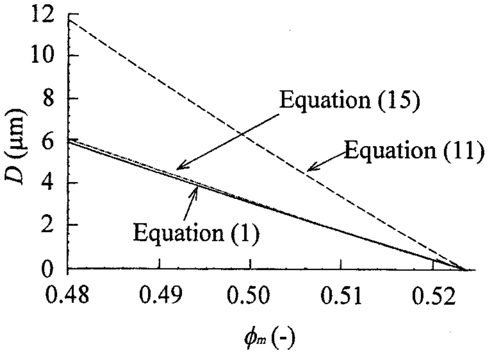

Figure 3. Interparticle surface separation as a function of packing fraction for a cubic packing geometry.

length $\xi > 1$ with a packing fraction of ϕ gives for the volume of free liquid, V_f:

$$V_f = \xi^3(1-\phi) - (1-\phi_m) = \xi^3 - 1, \tag{13}$$

since the volume of solid remains the same: $\xi^3\phi = \phi_{\mathrm{m}}$.

Wrapping this liquid around the particles, which have a total surface area, S, gives for the thickness of the free-liquid layer, which is equal to $D/2$,

$$\frac{D}{2} = \frac{V_f}{S} = \frac{\phi\xi^3}{S}\left(\frac{1}{\phi} - \frac{1}{\phi_m}\right) = \frac{\phi_m}{S}\left(\frac{1}{\phi} - \frac{1}{\phi_m}\right), \tag{14}$$

which reduces to Eq. 12 for monosized, spherical particles. Figure 3 shows the predictions of Eqs. 1 and 12 for an example of particles of 200 μm in a cubic packing arrangement.

The agreement between the two can be improved by amending Eq. 12, realizing that the free liquid should be wrapped around the particle *and its associated bound liquid* (see the 2-dimensional sketch in Figure 4) rather than only the particle itself. Doing this, S, the surface area of the particles in the bed, should be replaced by S', the surface area of the particles and bound liquid together in Eq. 11:

$$\frac{D}{2} = \frac{V_f}{S'} = \frac{\phi_m}{S'}\left(\frac{1}{\phi} - \frac{1}{\phi_m}\right). \tag{15}$$

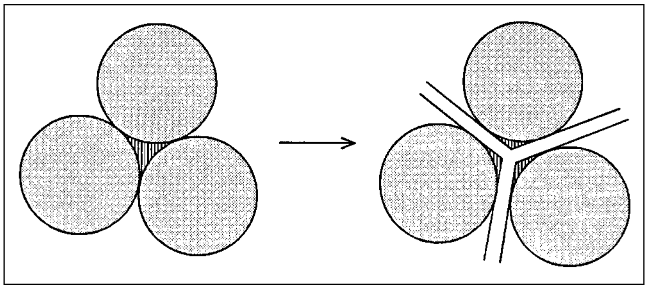

Figure 4. Volume of free-liquid argument similar to that of Tsutsumi et al. (1994).

The bound liquid is striped.

The volume of the particles plus bound liquid is unity, and if the shape of the particles with bound liquid is assumed cubic (in a cubic packing), we get for monosized particles

$$\frac{D}{2} = \frac{d_p}{6}\phi_m^{2/3}\left(\frac{\pi}{6}\right)^{1/3}\left(\frac{1}{\phi} - \frac{1}{\phi_m}\right) \qquad \left(= \frac{d_p}{6}\left(\frac{1}{\phi} - \frac{1}{\phi_m}\right)\right). \tag{16}$$

This equation is also shown in Figure 3, and effectively coincides with Eq. 1. The residual deviation is due to the simple "wrapping" process not accounting for edges and corners of the cube (if the volume of free-liquid argument is completely rigorously applied to a cubic packing, Eq. 1 results).

The geometrical argument leading to Eq. 16 only applies to cubic packing. If the packing is, for instance, hexagonal close packed, the shape of the particle/bound liquid region is somewhere between cubic and spherical.

The result is that a geometric factor, k_G, should be applied, which should vary with ϕ_m (at least for spherical particles, see the "Discussion and Conclusions" section below), taking on the value $(\pi/6)^{1/3}$ for $\phi_m = 0.52$ and going toward unity for $\phi_m \to 1$:

$$\frac{D}{2} = \frac{d_p}{6}\phi_m^{2/3}k_G\left(\frac{1}{\phi} - \frac{1}{\phi_m}\right). \tag{17}$$

It may be fruitful to use the volume of the free-liquid argument to derive an equation applicable also to nonspherical particles, perhaps using a geometrical factor as a semiempirical constant, fitting it by comparison with experimental data.

This approach gives further information about the mean particle size to be used in polydisperse suspensions. The appropriate choice of mean diameter for a polydisperse suspension in Eqs. 12 and 14 is clearly the diameter giving the same surface/volume ratio as the polydisperse powder: the surface/volume mean diameter. This is identical to the surface mean diameter determined as the first moment of the surface-density distribution function that we arrived at in the previous section, $d_{p,S}$. If both the particles and the particles with bound liquid are assumed spherical, and bound liquid is assigned to each particle in proportion to its volume (which is reasonable), then S is directly proportional to S', and the appropriate choice of mean particle diameter is $d_{p,S}$ also in Eq. 15. This supports the use of $d_{p,S}$ for polydisperse suspensions.

Discussion and Conclusions

One problem that may arise in applying equations like Eqs. 1, 10, and 11 to the rheology of dynamic suspensions is that the suspension microstructure may be influenced by imposed flow, for instance, by the formation of aggregates (e.g., Bossis et al., 1993).

It is often desirable to be able to estimate ϕ_m on the basis of the particle properties. There are no relationships available for this directly applicable to suspensions. Hoffmann and Finkers (1995) derived a semiempirical relationship for the voidage fraction, $\epsilon = 1 - \phi_m$ of randomly packed beds of "dry" powders (assuming the powders to have a lognormal size distribution) in terms of the:

- mean particle size,
- the spread in the particle-size distribution, and
- the particle shape (expressed as a sphericity).

Their relationships for loose and tapped packed beds can probably serve as a first indication of the range of ϕ_m, bearing in mind that the interparticle forces causing very loosely packed beds for small particle sizes generally are very much less important in suspensions than for dry powders. In any case, fitting their empirical constants to data for ϵ in suspensions should yield a usable equation.

The following conclusions can be drawn:

- Equation 1 is valid for monosized spheres irrespective of the packing geometry.
- Equation 12 can be modified to include the bound liquid and the geometry of the particle packing in the derivation to improve its accuracy.
- An equation has been derived for the interparticle surface separation of concentrated polydisperse suspensions of spherical particles:

$$D = d_{p,S}\left(\left(\frac{\phi_m}{\phi}\right)^{1/3} - 1\right).$$

- In the derivation of Eq. 15 no assumptions about the particle shape were made, so this equation may be used for nonspherical particles. The shape of the envelope around the particle and its associated bound liquid will give rise to a geometrical factor. Relating this to ϕ_m is not feasible for nonspherical particles since two packings of the same geometry but with particles of different sphericity will give different values for ϕ_m.

Notation

$Z = d_{p,i} + d_{p,j}$ (Eq. 7)
ξ = Linear dimension of suspension under consideration
$\langle\,\rangle$ = mean

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Appendix: Particle Coordination Number as a Function of Size

The assumption that the number of contact points for a particle (its "coordination number," C) is proportional to its surface area (and thus to d_p^2) should be seen as a first approximation. This is intuitively appealing, and is true at least for large particles. The well-known model of Ouchiyama and Tanaka (1980) implies that the dependence of C on d_p decreases with d_p, starting with a square dependence for large particles.

Figure A1a shows a plot in which Ouchiyama and Tanaka's model has been applied to a binary mixture, calculating the void fraction by the method of the "structural ratio" (Finkers and Hoffmann, 1998). The probabilities for the three possible

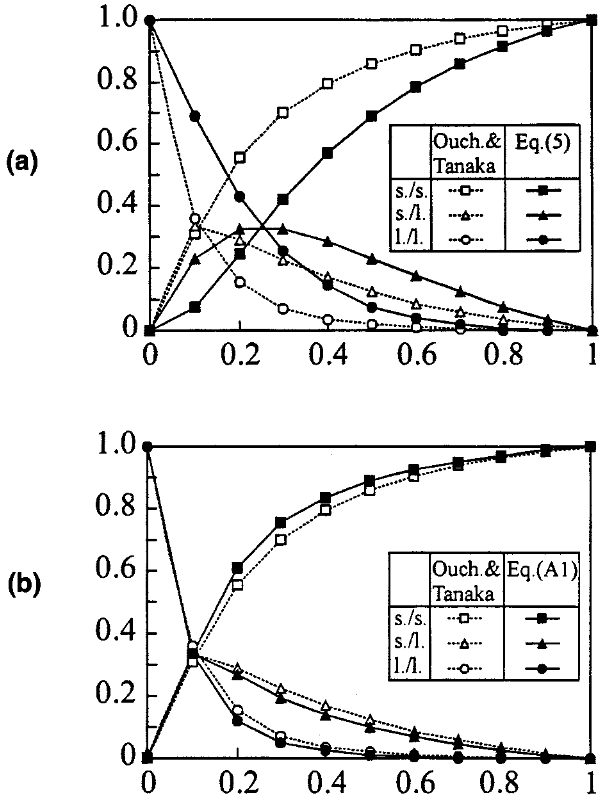

Figure A1. Model predictions of probabilities of the three sorts of particle contacts in binary mixtures as a function of the mixture composition (particle size ratio: 3:1).

types of contact—small/small, small/large, and large/large—are plotted against the volumetric mixture composition. The application of Eq. 6 (a square dependence of C on d_p) to the binary mixture is also shown. The agreement is reasonable for a wide range of diameter ratios.

Excellent agreement with the model of Ouchiyama and Tanaka can, however, be obtained assuming a linear dependence of C on d_p, resulting in

$$p\left(d_{p,i}, d_{p,j}\right) \alpha f_N\left(d_{p,i}\right) d_{p,i}\pi \times f_N\left(d_{p,j}\right) d_{p,j}\pi. \quad \text{(A1)}$$

This is shown in Figure A1b.

Ouchiyama and Tanaka also make assumptions in deriving their model, and they offer no quantitative comparison with experimental data. Until more experimental or theoretical information is available, we assume a square dependence of C on d_p, resulting in Eq. 6 in the text, which is also supported by the volume of the free-liquid argument, as discussed.

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