Invited paper

Theory for stabilization of magnetic colloid in liquid metal

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Abstract

This work suggests that van der Waals attraction of small colloidal particles to large colloidal particles can establish a cloud of the small particles that tends to shield the larger ones from agglomerating to each other. With consideration of the finite size of the small particles the system is analyzed thermodynamically with interest in stabilizing dispersions of magnetic particles in liquid metallic media. © 1999 Published by Elsevier Science B.V. All rights reserved.

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1. Introduction

Past attempts to produce colloidal magnetic fluid that remains stably dispersed in metallic liquid in the presence of applied magnetic field have been unsuccessful [1–3]. A dispersion of ferromagnetic particles in the size range of a few nanometers is readily formed, e.g. by electrolytic deposition at a liquid metal cathode. The particles remain suspended for long periods of time in gravitational field without the benefit of an additive dispersing agent. However, the dispersion phase-separates rapidly when magnetic field is applied. It appears that the metal in liquid metal colloids are almost stable and require a little additional help. The steric repulsion mechanism is not available as organic surfactants are insoluble in liquid metals. Transfer of electronic charge at the metal–metal interface produces a short range repulsion and is small in magnitude [4]. This work considers stabilization that may be conferred using a bimodal distribution of particle sizes, e.g. single domain iron particles with size in the range of 10 nanometers dispersed in a liquid metal such as mercury containing a large number of smaller particles. It is supposed that the small particles form a cloud at the surface of the large particles rather than chain to each other. The present analysis examines whether overlap of the clouds when the surfaces approach one another produces a repulsion force.

2. Basic relations

Limiting forms of Hamaker's expression for the van der Waals interaction between macroscopic spheres of different sizes are found in Ref. [5] with

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the potential of closely spaced spheres at surface to surface separation distance D is given by

$$W_1 = -\frac{A}{6D}\left(\frac{RR'}{R+R'}\right) \quad (R, R' \gg D), \quad (1)$$

where A is the Hamaker constant and R and R' the radii of the spheres. Eq. (1) yields the following limiting forms.

$$W = -\frac{AR}{6D}, \quad R' \gg R, \quad (2a)$$

$$W = -\frac{AR}{12D}, \quad R' = R. \quad (2b)$$

Eq. (2a) gives the interaction potential between a plane surface and a sphere, and Eq. (2b) the potential between equal size spheres. It is seen that attraction to a surface exceeds that of particles to one another by a factor of 2. As a result, clustering of small particles near a surface is favored over clustering of the small particles to one another, and in the following the particle–particle interaction is neglected. For a particle located at a point between two plane surfaces the potential is the sum of two terms.

$$W = -\frac{AR}{6}\left(\frac{1}{D_1}+\frac{1}{D_2}\right). \quad (3)$$

With y defined as the distance from the midplane between the surfaces to the center of a particle, the separation distance between the left surface and the particle surface is $D_1 = (L/2) - R + y$ and the distance from the right surface is $D_2 = (L/2) - R - y$.

The free energy F of particles per unit volume is now formulated as the sum of an entropic term representing the free energy of a monatomic gas [6,7] adjusted for the finite volume of the particles plus the van der Waals term:

$$F = kTn_g\left[\ln\left(\frac{n_g v_0}{1-n_g v_0}\right) - 1\right]$$
$$-\frac{AR}{6}\cdot\frac{(L-2R)n_g}{\left(\frac{L}{2}-R\right)^2 - y^2}. \quad (4)$$
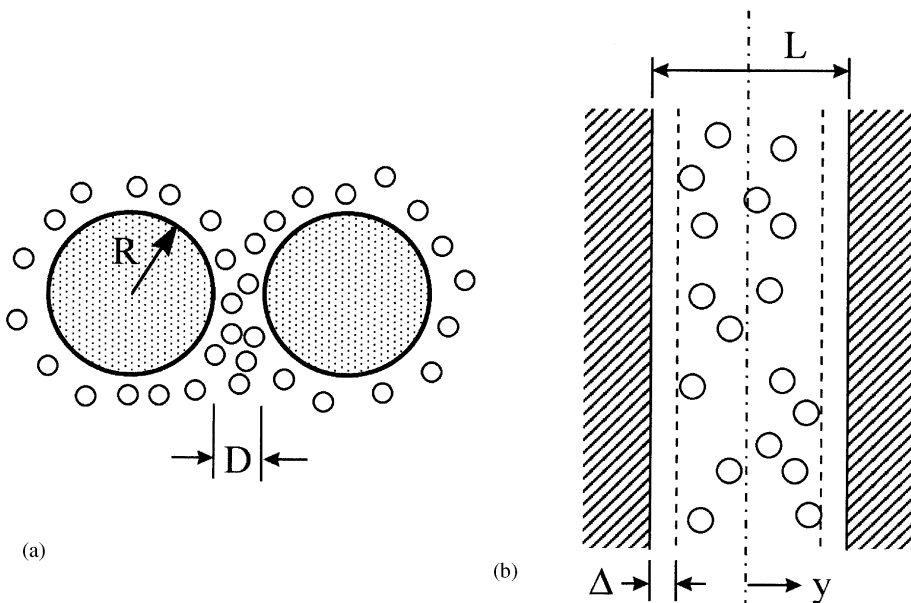

Fig. 1. (a) Snapshot of magnetic particles surrounded by diffuse cloud of smaller particles. (b) Cloud of small particles between parellel surfaces. Δ is a cut-off distance representing surface roughness.

The finite volume correction may be verified by computing the pressure from the thermodynamic relationship $p = -(\partial FV/\partial n_g)_T$, where V is the molar volume. This recovers the gas law in the form $p = kTn_g/(1 - n_gv_0)$ where k is the Boltzmann constant, T the temperature, and v_0 measures the particle volume.

3. Particle cloud in an isolated gap

The system is illustrated in Fig. 1 where Δ represents a cutoff distance to prevent the occurrence of singular values of van der Waals interaction; Δ may loosely be regarded as surface roughness. At equilibrium the total free energy F_t of the system is minimum subject to the constraint that the total number of particles N_t in the gap is fixed. The mathematical problem is stated compactly as

$$\delta F_T = 0, \tag{5a}$$

$$\delta N_T = 0, \tag{5b}$$

where, assuming unit area of surface,

$$F_T = \int_{-(L/2)+\Delta+R}^{(L/2)-\Delta-R} F \, dy, \tag{6a}$$

$$N_T = n_0 L = \int_{-(L/2)+\Delta+R}^{(L/2)-\Delta-R} n_g \, dy. \tag{6b}$$

This defines a variational problem as the distribution $n_g = n_g(y)$ is not yet known. The constraint is incorporated into the problem by introducing a Lagrange multiplier λ which is independent of y. The variational problem is then expressed as

$$\delta \int_{-(L/2)+\Delta+R}^{(L/2)-\Delta-R} (F - \lambda n_g) \, dy = 0. \tag{7}$$

Denoting the integrand as $G = F - \lambda n_g$ and noting that the derivative of n_g with respect to y is absent from G, the associated Euler equation is simply $\partial G/\partial n_g = 0$. This yields $\lambda = \partial F/\partial n_g$ and identifies the multiplier as the chemical potential μ.

To obtain an appreciation for the concentration distribution in a simple way it will be assumed for the moment that the small particles possess

negligible volume such that $R \ll L/2$ and $n_gv_0 \ll 1$. G then takes the following form:

$$G = kTn_g[\ln(n_gv_0) - 1)]$$

$$-\frac{AR}{6} \cdot \frac{Ln_g}{(L/2)^2 - y^2} - \lambda n_g. \tag{8}$$

Computation of $\partial G/\partial n_g$ yields

$$n_g = \frac{1}{v_0} \exp\left(\frac{\mu}{kT}\right) \exp\left(\frac{AR}{6kT} \cdot \frac{L}{(L/2)^2 - y^2}\right). \tag{9}$$

Introducing this expression for n_g into Eq. (6b) and recognizing that μ is spatially constant, after rearrangement yields the desired expression for concentration distribution.

$$\frac{n_g}{n_0} = \frac{\exp\left(\dfrac{\gamma/\varphi}{(1/2)^2 - z^2}\right)}{\int_{(-1/2)+(1/\psi)}^{(1/2)-(1/\psi)} \exp\left(\dfrac{\gamma/\phi}{(1/2)^2 - z^2}\right) dz} = \frac{\varepsilon_g}{\varepsilon_0}. \tag{10}$$

$\psi = L/\Delta$, $\varphi = L/R$, $\gamma = A/6kT$ and it is recognized that $\varepsilon_g = n_gv_0$ and $\varepsilon_0 = n_0v_0$ where ε is particle volume fraction. A plot of this relationship for the
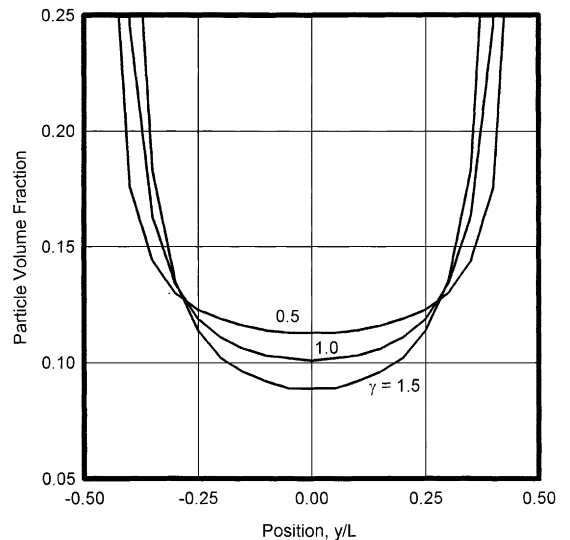

Fig. 2. Concentration profiles in an isolated gap. Initial volume fraction $\varepsilon_0 = 0.1$, $\gamma = A/6kT$, A is the Hamaker constant and T the temperature ($R = 2.5$ Å, $\Delta = 2$ Å, $L = 20$ Å, $\varepsilon_0 = 0.1$).

concentration distribution in an isolated gap is shown in Fig. 2. Concentration near both surfaces exceeds the initial uniform value and, as would be expected, larger values of Hamaker constant, hence larger values of γ, yield higher concentrations near the boundaries. At the midsection the concentration is reduced below the initial value when the Hamaker constant is relatively large, the particles having moved towards the boundaries. The cutoff zones are free of particles but are assumed to contain carrier fluid. As a result the concentration of particles in the midsection tends to become greater than the initial concentration at the lower values of the Hamaker constant.

Fig. 3. Concentration in gap for colloid in equilibrium with the bulk solution. R, Δ, L, ε_0 are the same as in Fig. 2.

4. Particle cloud in equilibrium with bulk solution

In a colloidal suspension the particles in the clouds are free to move in and out of the bulk solution and hence the gap fluid equilibrates with the bulk fluid. Again, the influence of finite particle size plays a role and will limit the volume fraction of particles to be less than one anywhere.

Consider therefore that the gap communicates with the bulk fluid regarded as a reservoir of large extent. Potential W is uniform in a differential volume element located between positions y and $y + dy$. The free energy density F_g of the particles in the volume element is given by Eq. (4) and the free energy F_0 of particles in the bulk where W is zero is given from Eq. (4) by

$$F_0 = n_0 kT \left[\ln\left(\frac{n_g v_0}{1 - n_g v_0}\right) - 1 \right]. \tag{11}$$

At equilibrium the chemical potential is the same in both regions. Thus,

$$\mu = \mu_0 \tag{12a}$$

or

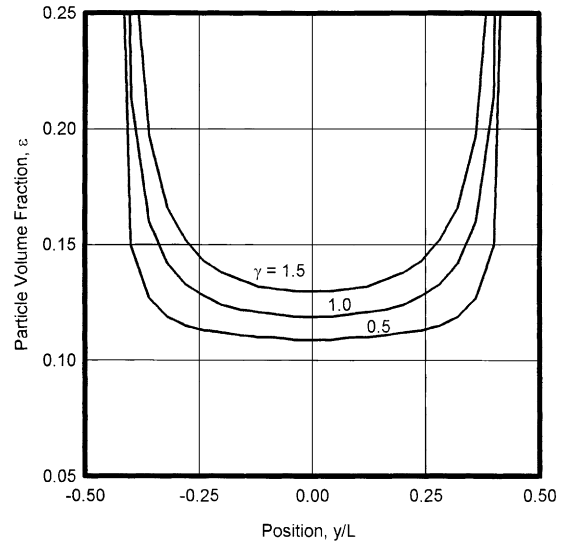$$\frac{\partial F_g}{\partial n_g} = \frac{\partial F_0}{\partial n_0}. \tag{12b}$$

Computation from Eq. (12b) yields a transcendental equation for the concentration distribution in the open gap:

$$\ln\left(\frac{\varepsilon_g}{1 - \varepsilon_g} \cdot \frac{1 - \varepsilon_0}{\varepsilon_0}\right) + \frac{1}{1 - \varepsilon_g} - \frac{1}{1 - \varepsilon_0}$$
$$- \frac{\gamma}{\phi} \cdot \frac{1 - 2/\phi}{(1/2 - 1/\phi)^2 - (y/2)^2} = 0. \tag{13}$$

For particles of negligible size ($\varepsilon_g \ll 1$, $\varepsilon_0 \ll 1$) the concentration distribution reduces to the following explicit relationship.

$$\frac{n_g}{n_0} = \frac{\varepsilon_g}{\varepsilon_0} = \exp\left[\frac{\gamma}{\phi} \cdot \frac{(1 - 2\phi)}{(1/2 - 1/\phi)^2 - (y/L)^2}\right]. \tag{14}$$

This expression differs from Eq. (10) obtained for particles of negligible size in the isolated gap. Values of concentration computed by numerical solution of Eq. (14) are plotted in Fig. 3. In common with the isolated gap, concentration is larger near the bounding surfaces. However, concentration in the midsection is always larger than in the bulk, consistent with the circumstance that particles from the bulk are attracted into the gap via the van der Waals force fields of the bounding surfaces.

5. Mutual repulsion of the surfaces

Force acting between the surfaces is determined by the change of total free energy (gap plus reservoir) with respect to the surface to surface spacing. The total free energy F_t may be written as

$$F_t = \int_{-(L/2)+R+\Delta}^{(L/2)-R-\Delta} F_g \, \mathrm{d}y + F_0 V_r, \tag{15}$$

where it is assumed that the surfaces are of unit area and V_r is the volume of the reservoir. Because the reservoir is assumed large compared to the gap volume, the free energy density F_0 is sensibly constant. However, V_r varies when the gap spacing changes as the gap fluid is exchanged with the reservoir. Thus,

$$V_r = V_t - V_g, \tag{16}$$

where V_t is the constant total volume of the system. When the gap surfaces are in closest contact $(L = 2\Delta)$ all the fluid resides in the reservoir and the total free energy equals $V_t F_0$ which is constant and large. Eliminating V_r from Eq. (15) with Eq. (16), then subtracting $V_t F_0$ yields the difference in free energy ΔF_t which can be expressed as an integration over the volume of the gap only.

$$\Delta F_t = \int_{-(L/2)+R+\Delta}^{(L/2)-R-\Delta} (F_g - F_0) \, \mathrm{d}y. \tag{17}$$

Substituting for F_g from Eq. (4) and F_0 from Eq. (11) permits ΔF_t to be expressed in the following nondimensional terms:

$$\frac{\Delta F_t}{n_0 kTR} = \int_{-(1/2)+(1/\psi)(1+(1/\xi))}^{(1/2)-(1/\psi)(1+(1/\xi))} \left\{ \varphi \cdot \xi \frac{\varepsilon_g}{\varepsilon_0} \right.$$

$$\times \left[\ln\left(\frac{\varepsilon_g}{1-\varepsilon_g} \right) - 1 \right]$$

$$- \gamma \frac{\varepsilon_g}{\varepsilon_0} \left[\frac{1 - 2/\varphi \cdot \xi}{(1/2 - 1/\varphi \cdot \xi)^2 - z^2} \right]$$

$$\left. - \varphi \cdot \xi \left[\ln\left(\frac{\varepsilon_0}{1-\varepsilon_0} \right) - 1 \right] \right\} \mathrm{d}z,$$

$$(L/2 > \Delta + R), \tag{18}$$

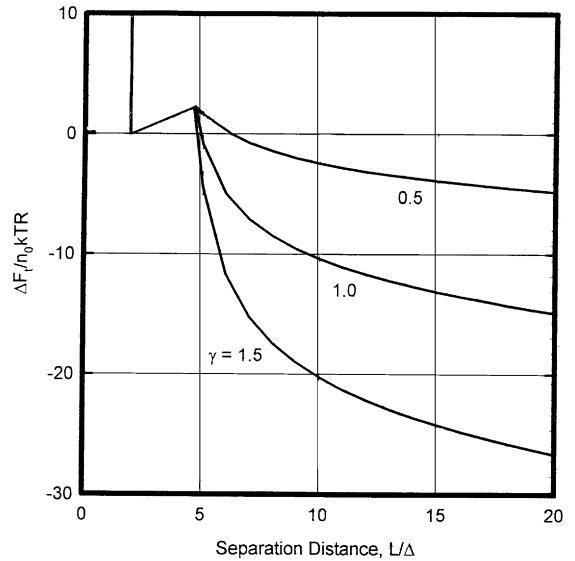where ψ, and γ are the same as defined previously, and $\xi = \Delta/R$. Eqs. (18) and (13) are coupled

Fig. 4. Interaction energy ΔF_t of surfaces shielded by clouds of particles having $R = 2.5$ Å, n_0 is the number concentration of particles in the bulk solution. $\Delta = 2$ Å, $\xi = 0.8$. The depletion region extends to $L/\Delta = 4.5$. Hard core repulsion indicated at $L/\Delta = 2$.

through void fraction ε_g and must be solved simultaneously to determine the dependence of total free energy on the surface separation distance.

Hoon [4] estimates $A = 2.6 \times 10^{-13}$ erg for the Hamaker constant in a metal/liquid metal system. This corresponds to $\gamma = 1.05$ for $T = 298$ K. Numerical integration of Eq. (18) for $\gamma = 0.5$, 1.0, 1.5 yields the plots shown in Fig. 4 where it is seen that the total free energy is a monotonically decreasing function of the surface separation distance *indicating that overlap of the clouds produces repulsion*, as would be required for colloid stabilization.

6. Depletion zone

When the surfaces are close enough together such that $L < 2(\Delta + R)$ there is no room in the gap for a particle to enter and a different treatment is needed. The total free energy consists only that of the reservoir fluid given by $F_r V_r$ where F_r is the free

energy density of reservoir fluid and V_r the volume of reservoir fluid. At minimum spacing of the surfaces $L = 2\Delta$, the total free energy is $F_0 V_t$ where F_0 is the initial free energy density of reservoir fluid when all the fluid in the system is in the reservoir having total volume V_t. Corresponding to the prior treatment wherein the gap contains particles we focus on the difference $\Delta F_t = F_r V_r - F_0 V_t$. From the free energy density introduced previously we have $F_r = n_r kT[\ln(n_r v_0/(1 - n_r v_0)) - 1]$ and $F_0 = n_0 kT[\ln(n_0 v_0/(1 - n_0 v_0)) - 1]$, hence

$$\Delta F_t = N_t kT \ln\left(\frac{V_t}{V_r} \cdot \frac{1 - n_0 v_0}{1 - n_r v_0}\right), \tag{19}$$

wherein the particle conservation relationship $N_t = n_r V_r = n_0 V_t$ is employed. For a large reservoir, n_0 and n_r are closely equal so that

$$\Delta F_t = N_t kT \ln\left(\frac{1}{1 - V_g/V_t}\right), \tag{20}$$

wherein substitution is made of the volume conservation relationship $V_r = V_t - V_g$. Because $V_g/V_t \ll 1$ expansion of the logarithmic factor yields $\Delta F_t = n_0 kT V_g = n_0 kT(L - 2\Delta)$ for unit area of surface. Thus,

$$\frac{\Delta F_t}{n_0 kT R} = \frac{\Delta}{R}\left(\frac{L}{\Delta} - 2\right) = \xi \cdot (\psi - 2),$$
$$\left(\Delta < \frac{L}{2} < \Delta + R\right), \tag{21}$$

where $n_0 = N_t/V_t$ and $\xi = \Delta/R$. The depletion effect is a known result previously obtained in a somewhat different manner in reference to polymer solutions ([5], p. 304). The relationship is plotted in Fig. 4 where the ground energy of ΔF_t from Eq. (18) is redefined to splice the curves together at the edge of the depletion layer where $L = 2(\Delta + R)$. At these small separation distances the surfaces experience attraction to each other, an osmotic effect.

7. Conclusions

This work shows that a diffuse cloud of particles develops near a surface due to van der Waals attraction to the surface mediated by thermal agitation. Overlap of the clouds produces repulsion of opposing surfaces due to entropic effect. At short range, particles of finite size are excluded from the gap and attraction due to osmotic pressure develops. To determine the stability of a colloidal sol it is necessary to transform the relationships developed here for planar geometry to apply to spheres.

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