Depletion Stabilization by Semidilute Rods

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The entropic depletion force in colloids arises when large particles are placed in a solution of smaller ones and sterically constrained to avoid them. We calculate the interaction between two hard spheres (of radius R) in a semidilute solution of hard rods of length L and diameter D ($D \ll L \ll R$) to second order in rod concentration. In addition to the well-known attractive force for separations less than L, we find a repulsive force between the spheres at larger separations. For semidilute rods, the resulting barrier can be large compared to k_BT, permitting kinetic stabilization.

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Recently, suspensions consisting of colloid-polymer and colloid-colloid mixtures have attracted considerable attention as a result of their rich phase behavior [1]. The phase transitions in these systems arise from the nonadditivity of the excluded volumes leading to the so-called depletion interaction. This depletion interaction was first recognized and formulated for a number of cases by Asakura and Oosawa [2,3]. In Ref. [3] they showed that both the range and the absolute value of the depletion interaction can increase when rodlike macromolecules are used instead of spherical ones as the depletant. Bolhuis and Frenkel [4] presented a numerical study of the phase diagram of a mixture of spherical and infinitely thin rodlike colloids using simulations and first order perturbation theory. Their work suggests in addition to the fluid-solid transition the possibility of a fluid-fluid phase separation. Experimentally, however, no depletion phase separation induced by rodlike macromolecules or particles has been observed [5,6]. This raises an important issue of principle, whether the depletion interaction might, in this case, give rise to kinetic stabilization rather than depletion flocculation or phase separation. A hint as to why this might happen is provided by recent calculations of the depletion interaction between large spheres (radius R) due to the presence of small ones with volume fraction ϕ, where at second order in ϕ a repulsive *barrier* appears in the depletion potential [7,8].

In this Letter we consider the depletion interaction between two large spheres (of radius R) caused by mutually avoiding thin hard rods of length L, diameter D ($D \ll L \ll R$), and bulk number density n_b. Our second order calculation, given below, is formally valid only for small values of the reduced density $c_b = n_b D L^2$. However, we believe that the physical mechanism leading to the repulsive barrier that we find should persist throughout the semidilute regime.

Our calculation method parallels that of Ref. [8]. We first find the depletion force, $f_p(h)$ per unit area between two infinite parallel plates, at separation h; the force f_s between two large spheres of radius $R \gg L$ then follows by the Derjaguin approximation [9]:

$$f_s(h) = -\pi R \int_\infty^h f_p(h')\,dh'. \tag{1}$$

To calculate f_p to second order in rod concentration we invoke the "pressure sum rule" [10], which expresses p, the (osmotic) pressure exerted on a hard wall by a solution of thin rods, as $p = k_BTn_e(\infty)$ where $n_e(\infty)$ is the density of rod ends in contact with the wall. For hard rod particles, this relation is exact to all orders in bulk concentration; it is the analog of Henderson's formula for the pressure in terms of the contact density for hard spheres [11], and may be proved rigorously (for rods *in vacuo*) by elementary kinetic theory.

For two hard parallel plates immersed at separation h in a solution of depletant, the force per unit area on one of the plates is simply the differential pressure on its two sides:

$$f_p(h) = k_BT[n_e(h) - n_e(\infty)], \tag{2}$$

where $n_e(h)$ is the density of rod ends in contact with a plate, separated by h from another. To second order in (reduced) density, this can be written in the form

$$n_e(h) = n_b\left(1 + \frac{\pi c_b}{2}\right)[E_1(h/L) - c_bE_2(h/L)], \tag{3}$$

where $E_{1,2}(h/L)$ are a pair of dimensionless functions whose calculation we defer to the end of this Letter. The depletion force $f_p(h)$ for general separation h follows immediately from Eqs. (2) and (3); from this, the force $f_s(h)$ between spheres of radius R can be found by the Derjaguin approximation. To second order in c_b, the interaction energy between two such spheres is given by one further integration and takes the form

$$W_s(h) = \int_h^\infty f_s(h')\,dh' = k_BTc_b\frac{R}{D}[K_1(h/L) + c_bK_2(h/L)], \tag{4}$$

where $K_{1,2}(h/L)$ are a further pair of dimensionless functions, considered in detail below.

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The scalings of the two contributions to the depletion interaction in Eq. (4) are of great interest. The first order term K_1 influences the depth of the attractive (primary) minimum, which is of order $k_B T n_b R L^2$, and this is the same scaling as for depletion by small spheres whose diameter σ is equal to the *length* of the rods L. For a given $L = \sigma$, however, much larger attractions are possible with rods since the maximum n_b is of order $(DL^2)^{-1}$ (corresponding to $c_b \simeq 1$), which far exceeds that attainable for spheres of order σ^{-3}. The second order contribution in (4), which provides the repulsive barrier, arises directly from the excluded volume interaction among rods, and accordingly is smaller than the first by one power of c_b. The barrier height attains values of order $k_B T R/D$ for c_b values of order unity. It may be confirmed by simple arguments that the third order correction to (4) is smaller than the second by a factor of order c_b, so that $c_b \simeq 1$ lies at the edge of the domain of validity of our theory for the depletion force. (The same remark would not apply to the bulk equation of state where the third order terms remain negligible near $c_b = 1$ for large L/D [12,13].) Although higher order terms will modify our quantitative predictions, we see no physical reason for the qualitative scenario of a large repulsive barrier to change strongly before the Onsager transition is reached at $c_b = 4.2$ [12,13].

These findings may be compared with depletion by spheres [7,8] in which the maximum barrier height (which again arises at the limit of validity of the second order treatment) scales as $k_B T R/\sigma$. Hence, roughly speaking, to obtain a similar barrier height to that obtainable with semidilute rods at $c_b \simeq 1$, spheres of size comparable to the rod *diameter* would be required at a volume fraction of order unity. The resulting barrier would then arise at separations $h \simeq D$ rather than $h \simeq L$, and so be much less robust against attractive contributions from van der Waals forces, surface asperities, and other perturbing effects. We can therefore conclude that the prospects of observing depletion stabilization are very much higher in the rod case.

Our results for the functions $K_{1,2}$ are plotted in Fig. 1; together they allow the second order depletion potential curve to be constructed from (4) for any parameters desired. Representative curves are shown in Fig. 2 for $R/L = 10$, $L/D = 20$, and various c_b. The case $c_b = 2$ corresponds to a rod volume fraction of only around 8%, but the height of the repulsive barrier is already $25 k_B T$. Of course, a quantitative use of the theory is unjustified for this value of c_b, but the result nonetheless suggests that kinetic stabilization of colloids could feasibly be achieved under practical conditions by suspending them in a semidilute solution of high-aspect-ratio rodlike particles. In Fig. 3 we plot, for a given $R/L = 10$, the volume fraction of rods required to attain a given barrier height of $20 k_B T$ as a function of the aspect ratio of the rods. This highlights the efficacy of long thin rods for stabilization purposes. Also shown is the volume fraction at which the barrier height is equal to the thermal energy. This marks the onset of significant departures from the conventional scenario of attractive depletion forces; note, however, that in principle there is no concentration below which the barrier completely disappears, since the function K_2 is of longer range than K_1 (see Fig. 1).

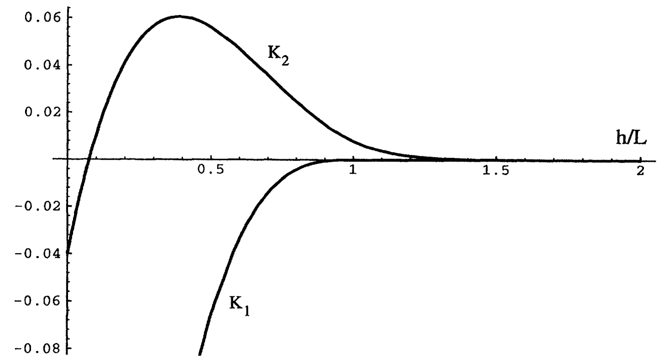

FIG. 1. The dimensionless functions $K_{1,2}$, allowing the determination of the depletion potential to second order for arbitrary parameters.

We now summarize the arguments that allow us to calculate the functions $E_{1,2}(h/L)$ and $K_{1,2}(h/L)$ defined above. (For related work on rods near a *single* plate, see Ref. [14].) Our calculation of $n_e(h)$ to second order in n_b rests on the same idea as lies behind the potential distribution theorem due to Widom [15,16]. Suppose we put our system of rod particles and parallel plates in contact with a hypothetical reservoir in which rods are exempt from mutual excluded-volume interactions. We first calculate the relation between the particle density in the reservior n_{res} and the bulk density n_b. Imagine an infinitesimal volume centered at position r in the bulk solution in which we consider placing (the midpoint of) a rod of orientation $\Omega_1 = (\theta_1, \phi_1)$. This would exclude from a volume $v_{\text{exc}}(\Omega_2) = 2DL^2|\sin\theta_2|$ the midpoint of another rod with relative orientation $\Omega_2 = (\theta_2, \phi_2)$ defined with respect to coordinate axes in the first rod. (We define our angular coordinates so that $0 \leq \theta \leq \pi/2$; the number density of rods in the reservior with orientation in the range $(\Omega, \Omega + d\Omega)$ is then $n_{\text{res}}\, d\Omega/2\pi$.) The presence of our proposed rod at r is permitted only if the volume $v_{\text{exc}}(\Omega_2)$ is empty for all orientations Ω_2; the probability of this is given, to first order, as

$$P_b = 1 - \frac{n_{\text{res}}}{2\pi} \int v_{\text{exc}}(\Omega_2)\, d\Omega_2 = 1 - n_b \frac{\pi}{2} DL^2. \tag{5}$$

To find the density n_b of rod centers at the arbitrary point r in the bulk, we argue that if a rod is allowed there (probability P_b) the density is n_{res}; otherwise it is zero. Hence $n_b = n_{\text{res}} P_b = n_{\text{res}}[1 - (\pi/2)c_b]$ where $c_b = n_b DL^2$ is the reduced density. Inverting this relation gives $n_{\text{res}} = n_b[1 + (\pi/2)c_b + \mathcal{O}(n_b^2)]$.

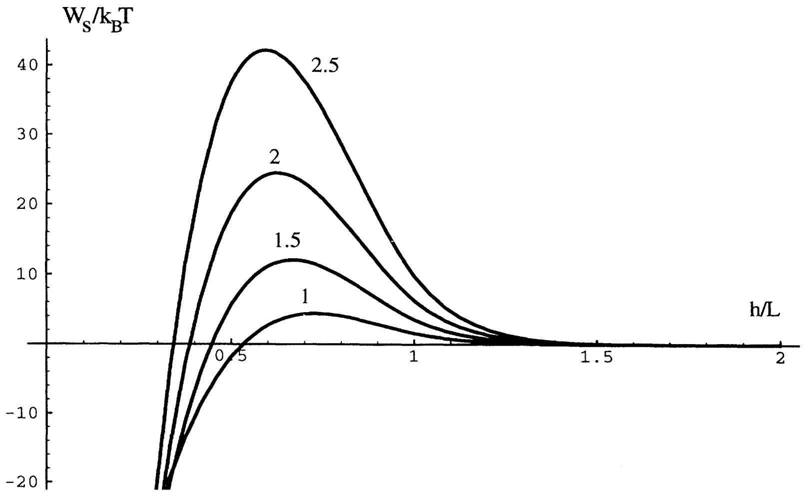

FIG. 2. A plot of a typical second-order depletion potential; $R/L = 10$, $L/D = 20$, $c_b = 1.0, 1.5, 2.0, 2.5$ (bottom to top). For $c_b = 2$ there is a repulsive barrier of $25k_BT$.

The next step is to calculate $n_e(h)$, the end density contacting a confining plate separated by h from another, in terms of $n_{\rm res}$. Consider a rod touching the plate with orientation Ω_1 and a second rod touching this rod with relative orientation Ω_2. (See Fig. 4). The height from the wall of the two ends of the first rod are respectively 0 and z_0; those of the second rod, z_1 and z_2; S_1 and S_2 locate the position of the contact point of the rods as shown. The z variables can be expressed in terms of the others using elementary geometry [17]. The volume excluded by the first rod to the (midpoint of the) second rod at fixed (Ω_1, Ω_2) is then found by integrating over the contact point:

$$v_{\rm exc}(h, \Omega_1, \Omega_2) = 2D \int_0^L \int_0^L \Xi |\sin\theta_2| \, dS_1 \, dS_2 \,, \quad (6)$$

with $\Xi = H(h - z_1)H(h - z_2)H(z_1)H(z_2)$ where the H's, the Heaviside unit step functions, are needed to eliminate all configurations forbidden by the interaction with the confining walls. We may now write $n_e(h) = \int n_c(h, \Omega) \, d\Omega$, where n_c, the density of rods with orientation Ω_1 at contact with the wall, obeys

$$n_c(h, \Omega_1) = \frac{n_{\rm res}}{2\pi} P(h, \Omega_1) H(h - z_0) \quad (7)$$

in which the step function accounts for the constraint on Ω_1 arising from the presence of a second plate, and $P(h, \Omega_1)$ is the prior probability that the volume excluded by such a rod, in contact with the wall, contains no other rods. To first order in $n_{\rm res}$ (or in n_b) we have

$$P(h, \Omega_1) = 1 - \frac{n_{\rm res}}{2\pi} \int d\Omega_2 v_{\rm exc}(h, \Omega_1, \Omega_2) \quad (8)$$

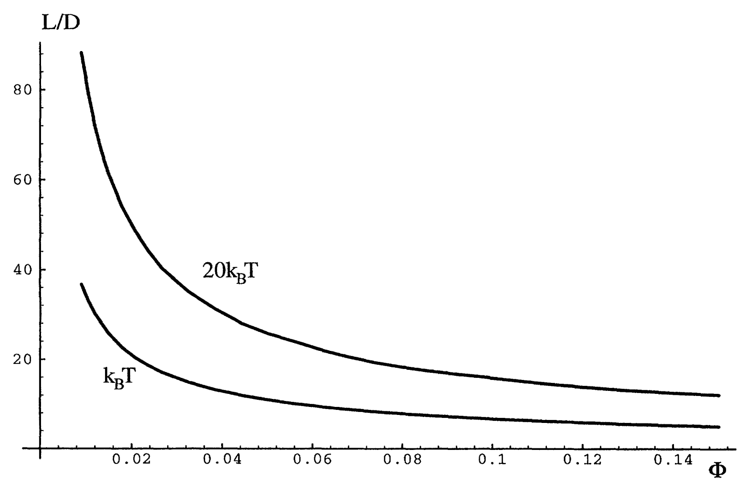

FIG. 3. Volume fraction of rods required to attain a barrier of $20k_BT$ (upper curve) and k_BT (lower curve) as a function of the aspect ratio R/D. Here $R/L = 10$ is held fixed.

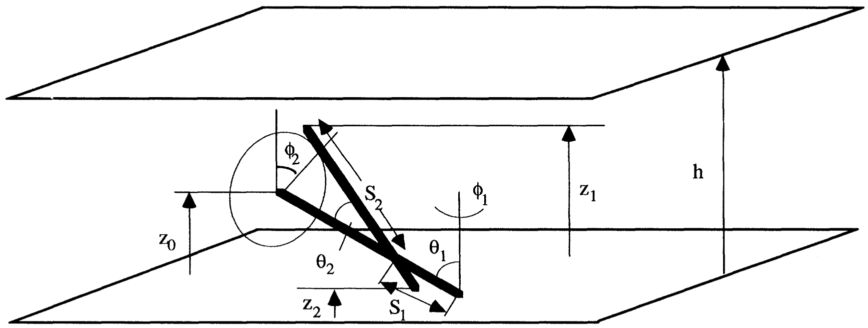

FIG. 4. Geometry of the two-rod excluded volume calculation.

Combining this result with Eqs. (6) and (7), we obtain, as promised, Eq. (3), with $E_1(h/L) = \min[h/L, 1]$ and

$$E_2(h/L) = \frac{1}{\pi} \int_0^{D_1} d\cos\theta_1 \int_0^1 d\cos\theta_2 \times \int_0^{2\pi} d\phi_2 \int_0^1 d\tilde{S}_1 \int_0^1 d\tilde{S}_2\, \Xi |\sin\theta_2| , \quad (9)$$

where $\tilde{S}_{1,2} = S_{1,2}/L$. This completes the specification of the two dimensionless functions $E_{1,2}(h/L)$, from which $K_{1,2}(h/L)$ follow by straightforward analytic (K_1) or numerical (K_2) integrations.

As emphasized previously, the calculations given above furnish the depletion interaction to second order in density and are quantitatively accurate only for small c_b. In fact, following the work of Ref. [14] for a single wall, one can formulate a self-consistent integral equation for the rod density between plates that is, for large aspect ratios L/D, formally valid to all orders in c_b [18]. Its solution, which poses formidably numerical problems, should allow a quantitative confirmation of the scenario we have outlined; we leave this to future work [18].

In summary, we have shown that a relatively small concentration of long thin rods should serve as an effective stabilizer of colloidal suspensions of larger particles by providing a large barrier to flocculation into the primary minimum of the depletion potential. The barrier arises purely by steric (depletion) effects. This kinetic stabilization, though quite unanticipated in previous theories of depletion by rods [3,4], is essentially thermodynamic in origin (and quite separate from any effects arising from the high viscosity of the intervening rod solution). It is tempting to attribute the anomalous phase stability of sphere-rod mixtures to the stabilization barrier that we predict. However, the condition of the Derjaguin approximation ($R \gg L$) is not met in the sphere-rod systems studied so far [5,6], and our results therefore not directly applicable. Further experimental investigations of suitable systems are highly desirable.

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