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Depletion force in colloidal systems

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Abstract

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 large spheres (of radius R) in a dilute solution of mutually avoiding small spheres (of diameter $\sigma \ll R$ and volume fraction ϕ), to third order in ϕ. In addition to the well-known attractive force for $0 < h < \sigma$, we find a repulsive barrier at larger separations, and beyond that a secondary minimum. Except for unusually large size ratios (perhaps abetted by relatively high density ϕ), these features of the interaction potential are too small, compared to k_BT, for kinetic stabilization (arising from the barrier) or flocculation into the secondary minimum, to be widespread, although such effects are possible in principle. For feasible size ratios, the same features should have observable consequences for the radial distribution function of the large spheres. Such effects can be viewed as precursors, at low density, of liquidlike structuring (solvation forces) expected at higher ϕ. Our third order calculation gives satisfactory agreement with a recent computer simulation at moderate density and size ratio ($2R/\sigma = 10$; $\phi = \pi/15$).

1. Introduction

The depletion force [1] is central to issues of colloidal stability [2, 3, 4]; it arises between large spheres suspended in a dilute solution of nonadsorbing polymers, micelles, or smaller hard spheres. The last case is amenable to detailed analysis (at least at low densities) [1, 5, 6], and serves as a model for the others. The basic effect is quite simple: for separations $h < \sigma$, small particles of diameter σ are excluded from the gap between the larger ones. For flat plates, this leads to an attractive force equal to the osmotic pressure Π of the small spheres outside the plates. The force f_s between

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large spheres of radius $R \gg \sigma/2$ then follows by the Derjaguin approximation [2]:

$$f_s(h) = -\pi R \int_{\infty}^{h} \Pi(h')\,\mathrm{d}h' \tag{1}$$

This *attractive* force can give rise to depletion flocculation and phase transition [2, 3, 4].

Napper and coworkers [7, 8] argued some time ago that depletion could, in addition, lead to a *repulsive* interaction at larger distances and higher depletant concentration. The resulting free energy barrier might be enough to kinetically stabilize the large colloidal spheres against flocculation. This claim, though partially supported by experiment [8, 9], was not considered theoretically convincing, and has since been disregarded by many experts. Indeed, recent monographs on colloids [2] and polymers at surfaces [3] describe in detail the depletion attraction, but do not discuss depletion stabilization. Very recently however [10], results have been given for the depletion interaction arising from small mutually avoiding spheres at volume fraction ϕ, calculated in a virial expansion to order ϕ^2. These results show a *repulsive barrier* (discussed further below) which could in principle be large compared to k_BT for large size ratios. It seems clear, therefore, that the widespread consensus that the depletion force is purely attractive, now needs revision.

In fact, the publication of [10] occurred after we had ourselves obtained the same result by a different method. In this paper we now take the calculation one stage further, to order ϕ^3. At this order a *secondary minimum* appears in the interaction potential between large particles. This means that in principle a rich range of colloidal kinetics (reversible flocculation into the secondary minimum; slow barrier crossing to irreversible contact, etc.) could arise *purely* from depletion forces. In practice however this scenario would require exceedingly large values of the size ratio $2R/\sigma$. On the other hand, the depletion potential between two large spheres $W_s(h)$ found below (at centre-to-centre separation $r = R + h$) is related by the Boltzmann distribution to the radial distribution function $g(r)$ of the (dilute) large spheres:

$$g(r) = \text{const.} \times \exp[-W_s(r-R)/k_BT]\,, \tag{2}$$

which can be probed in principle by scattering experiments [11, 12]. Even when the new features of the depletion potential are too small to lead to large kinetic effects, they will lead to oscillations in $g(r)$ with a characteristic period associated with the radius of the *small* spheres. The depletion barrier and the secondary minimum, which arises already at order ϕ^2 and ϕ^3 respectively, can thus be viewed as a limiting case of the layering-induced solvation repulsion predicted at *liquid-like densities* of the small spheres [13]. In fact, it can be shown that for hard sphere fluids the long-range depletion force is damped oscillatory regardless of density with the same wavelength and decay length as those of hard sphere radial distribution function [14].

It is plausible to conjecture that each new maximum or minimum in the depletion potential requires a calculation to one higher order in ϕ than the previous minimum or maximum. If this is true, then almost all the qualitative physics of solvation forces is already present *in principle* in the virial expansion, a fact that has perhaps not been widely appreciated. In practice, however, the analytical calculation to third order presented below already involves serious difficulties, and the possibility of calculating higher terms appears remote. In any case, in the concentration range where these become important, an approach based on any of the many approximate liquid state theories [15] might be more appropriate; for example some results based on Percus–Yevick approximation can be found in Ref. [16].

In what follows (Sections 3) we calculate the force between plates (and hence, by the Derjaguin approximation, large hard spheres) arising from depletion by small, mutually avoiding hard spheres. As discussed above, our calculation is exact to order ϕ^3; two checks in special cases to this order are contained in Appendix A. In Section 4 we give a simple explanation for the maximum of the repulsive force between plates, and make a comparison of our perturbative results with a calculation of the depletion interaction by computer simulation, recently performed by Bladon and Biben [17]. We also discuss how the results might differ for other depletants, such as polymers, for which mutually-avoiding small hard spheres might or might not provide a good model.

2. Depletion Force Between Plates

It was shown by Henderson [18], in the context of solvation forces, that the net force per unit area on a hard plate immersed in a solution of spheres is given by the differential contact density of the solute particles:

$$f = k_B T(n_+ - n_-) , \tag{3}$$

where $n_{+,-}$ are the contact densities of particle on either side of the plate. (The contact density of hard spheres of diameter σ is defined as the limit $n(\sigma/2)$, *as* $\varepsilon \to 0$, of the number per unit volume n of particle centres, evaluated at a distance $\sigma/2 + \varepsilon$ from the plate.)

This result can be explained as follows. The particle velocities are separable degrees of freedom and therefore *always* obey the Maxwell–Boltzmann distribution. The force per unit area on a confining hard plate is therefore given rigorously of elementary kinetic theory as $f = k_B T n$, where n is the number density of particle centres at a distance from the surface corresponding to the point of impact. This is, of course, the contact density. This argument applies whenever the interaction between the particles and the plate is of hard wall type. Ref. [19].

The Henderson formula reduces our problem of the depletion force to simply finding $n_{in}(h)$, the surface contact density *inside* a pair of parallel plates at separation h. For we already know that the pressure *outside* the plates is $k_B T n_{out}$, with:

$$n_{out} = n_b + B_2 n_b^2 + B_3 n_b^3 + \cdots , \tag{4}$$

where the Bs' are hard sphere virial coefficients for pressure: $B_2 = 2\pi\sigma^3/3$, $B_3 = 5\pi^2\sigma^6/18$. The depletion force per unit area on a plate is therefore simply:

$$f_p = k_B T(n_{in} - n_{out}) \tag{5}$$

This offers a fundamental simplification over more direct approaches based, for example, on calculating the partition function of particles confined between the plates. We have pursued the latter to second order in ϕ (with results that agree with those given below) but a third order calculation is probably not feasible by this method: it would involve integrating over particles with centres at three different positions. Using the Henderson formula, we may hold one of the three particles in contact with a plate- a substantial reduction in the integrals required.

If the plate separation obeys $h < \sigma$ then no particle can enter, and the surface contact density n_{in} between two plates is simply $n_{in} = 0$. In this range of h, the depletion force is, to all orders in ϕ, simply the unbalanced osmotic pressure on the exterior of the plates. To find $n_{in}(h)$ with $h \geqslant \sigma$, is more subtle, however, and we introduce the following argument. Suppose we put our system of particles and parallel plates in contact with a hypothetical reservoir, in which particles are exempt from mutual hard sphere interactions. Then the particle density n_{res} in the reservoir must be such that the chemical potential μ is the same everywhere:

$$\ln n_{res} = \frac{\mu}{k_B T} = \ln n_b + 2B_2 n_b + \tfrac{3}{2} B_3 n_b^2 + \cdots \tag{6}$$

This condition gives n_{res} in terms of the bulk density n_b in our system, as

$$n_{res} = n_b[1 + 2B_2 n_b + 2B_2^2 n_b^2 + 3B_3 n_b^2/2 + O(n_b^3)]\,. \tag{7}$$

Now consider an infinitesimal volume δv, situated between the two plates, centred at a height $z \geqslant \sigma/2$ from one of them (see Fig. 1). Due to the hard sphere interaction between particles, there will be no particle in δv unless the sphere S_z of radius σ, centered on δv, but excluding the infinitesimal volume δv itself, is vacant. (By "vacant", we mean it does not contain the *centres* of other particles). If the sphere S_z is vacant, the density in δv is the same as n_{res}. In other words, the density at height z may be written

$$n(z) = n_{res} P(z), \qquad z \geqslant \sigma/2\,, \tag{8}$$

where $P(z)$ is the probability of the sphere S_z being vacant. The contact density is then just $n(\sigma/2)$. Eq. (8) can be viewed as an example of the application of the potential distribution theorem due to Widom [20, 21].

Dividing S_z into small pieces, we may now write:

$$P(z) = \prod_{r \in S_z} [1 - n(\boldsymbol{r})\,\mathrm{d}^3\boldsymbol{r}] \tag{9}$$

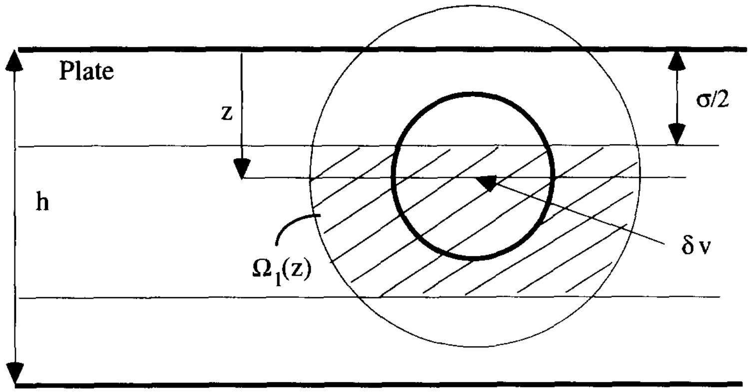

Fig. 1. The geometric interpretation of $\Omega_1(z)$.

Expanding to second order in local density gives:

$$P(z) = 1 - \int_{S_z} n(\boldsymbol{r})\,\mathrm{d}^3\boldsymbol{r} + \frac{1}{2}\int_{S_z}\int_{S_z} n(\boldsymbol{r}_1)n(\boldsymbol{r}_2\,|\,\boldsymbol{r}_1)\,\mathrm{d}^3\boldsymbol{r}_1\, d^3\boldsymbol{r}_2\,, \tag{10}$$

with $n(\boldsymbol{r}_2\,|\,\boldsymbol{r}_1)$ the conditional density that a particle is at $\boldsymbol{r}_2$ given that one is already present at $\boldsymbol{r}_1$. This is simply $n(\boldsymbol{r}_2)$ if $\boldsymbol{r}_1$ and $\boldsymbol{r}_2$ do not exclude each other, and zero if they do. [Note that the truncation of (10) at second order in the density will be sufficient to calculate n_{in} to third order, because of the extra factor n_{res} on the right hand side in (8).]

We now define expansion coefficients $\Omega_1(z)$, $\Omega_{2.1}(z)$, $\Omega_{2.2}(z)$ in terms of the integrals appearing in P:

$$\int_{S_z} n(\boldsymbol{r})\,\mathrm{d}^3\boldsymbol{r} \equiv \Omega_1(z)n_b + \Omega_{2.1}(z)n_b^2 + \mathrm{O}(n_b^3)\,, \tag{11}$$

$$\frac{1}{2}\int_{S_z}\int_{S_z} n(\boldsymbol{r}_1)n(\boldsymbol{r}_2\,|\,\boldsymbol{r}_1)\,\mathrm{d}^3\boldsymbol{r}_1\,\mathrm{d}^3\boldsymbol{r}_2 \equiv \Omega_{2.2}(z)n_b^2 + \mathrm{O}(n_b^3)\,, \tag{12}$$

so that the probability P that the sphere S_z is vacant has the expansion:

$$P(z) = 1 - \Omega_1(z)n_b + \Omega_2(z)n_b^2 + \mathrm{O}(n_b^3)\,, \tag{13}$$

where $\Omega_2 = -\Omega_{2.1} + \Omega_{2.2}$. According to (8) the surface contact density between the two plates obeys:

$$n_{\text{in}} = n_{\text{res}}P(\sigma/2), \quad \text{for } h \geqslant \sigma; \qquad n_{\text{in}} = 0, \quad \text{for } h < \sigma\,. \tag{14}$$

This equation combined with (4), (7), (13), determines in principle the depletion force $f = k_\mathrm{B}T(n_{\text{in}} - n_{\text{out}})$ to third order in bulk concentration n_b.

3. Results

3.1. First order

The first order calculation is simple, $n_{\text{out}} = n_b$ (unperturbed to this order by virial effects) and $n_{\text{in}} = 0$ or n_b according to whether the plate separation h, is larger or less than the diameter σ of our small spheres. The depletion force per unit area is 0 for $h > \sigma$, and $-n_b k_B T$ otherwise. So the potential due to this force is linear for flat plates, and quadratic for spheres after the Derjaguin approximation, which involves a further integration. Writing $\lambda = (h - \sigma)/\sigma$, the depletion potential W_s between large spheres of radius R, caused by small spheres of volume fraction ϕ, is then given as:

$$W_s(\lambda)/k_B T = 0, \qquad h \geqslant \sigma, \tag{15}$$

$$W_s(\lambda)/k_B T = -(3R\phi/\sigma)\lambda^2, \qquad h < \sigma, \tag{16}$$

where $\phi = n_b \pi \sigma^3/6$ is the volume fraction of the small particles. These are the classical results first derived by Asakura and Oosawa just over 40 years ago [1], and in most circumstances provide a simple and effective description of the depletion force between spheres. But for large enough size ratios, at even moderate concentrations, this is no longer satisfactory, as we discuss in what follows.

3.2. Second order

To find the depletion force to second order in ϕ, we have $n_{\text{out}} = n_b(1 + B_2 n_b)$, and require the leading correction to $n_{\text{in}} = n_{\text{res}} P(\sigma/2)$. Here n_{res} can be found to order n_b^2 using (7), but we also need to find $P(\sigma/2)$ to order n_b, i.e., we want to compute the leading correction $\Omega_1(\sigma/2)$ as defined in Eq. (13). In evaluating Ω_1, we can take $n(\boldsymbol{r})$ to be either n_b, if the position $\boldsymbol{r}$ is accessible to a particle (i.e., not excluded by either plate), or zero if inaccessible. So the situation is till rather simple as shown in Fig. 1; we have $P(\sigma/2) = 1 - \Omega_1(\sigma/2) n_b$ where $\Omega_1(\sigma/2)$ is just the effective volume excluded by a particle at contact:

$$\Omega_1(\sigma/2) = \tfrac{2}{3}\pi\sigma^3, \qquad h \geqslant 2\sigma, \tag{17}$$

$$\Omega_1(\sigma/2) = \tfrac{1}{3}\pi\sigma^3\lambda(3 - \lambda^2), \qquad 2\sigma > h > \sigma. \tag{18}$$

Having by this procedure obtained $n_{\text{in}} = n_{\text{res}} P(\sigma/2)$ to second order in n_b, we can proceed to write down the depletion force. Again writing $\lambda = (h - \sigma)/\sigma$, we obtain for the total force per unit area f_p between flat parallel plates:

$$f_p(\lambda)/k_B T = 0, \qquad h \geqslant 2\sigma, \tag{19}$$

$$f_p(\lambda)/k_B T = 2n_b\phi(2 - 3\lambda + \lambda^3), \qquad 2\sigma > h \geqslant \sigma, \tag{20}$$

$$f_p(\lambda)/k_B T = -n_b(1 + 4\phi), \qquad \sigma > h. \tag{21}$$

This depletion force to second order in ϕ has recently been derived by Walz and Sharma by a somewhat different method [10]. Note that the force is repulsive, and of order n_b^2 (since $\phi = n_b \pi \sigma^3/6$), at intermediate distances. Its maximum value is $f_{p,\max} = 4 n_b \phi k_B T$, arising at $h = \sigma^+$ (just as the particles become fully excluded from between the plates). We give a simple explanation of this value in Section 4 below.

Integrating the force leads to the depletion potential, W_p, between flat parallel plates[1]:

$$W_p(\lambda)/k_B T = 0, \qquad h > 2\sigma\,, \tag{22}$$

$$W_p(\lambda)/k_B T = \tfrac{1}{2} n_b \sigma \phi (3 - 8\lambda + 6\lambda^2 - \lambda^4), \qquad 2\sigma > h \geqslant \sigma\,, \tag{23}$$

$$W_p(\lambda)/k_B T = \tfrac{1}{2} n_b \sigma (2\lambda + 3\phi + 8\lambda\phi), \qquad h < \sigma\,. \tag{24}$$

The depletion force between spheres is given by the Derjaguin approximation as $f_s = \pi R W_p$, and one further integration gives us the potential between spheres:

$$W_s(\lambda)/k_B T = 0, \qquad h > 2\sigma\,, \tag{25}$$

$$\frac{W_s(\lambda)}{k_B T} = \frac{R\phi^2}{5\sigma}(12 - 45\lambda + 60\lambda^2 - 30\lambda^3 + 3\lambda^5), \quad \text{for } 2\sigma > h \geqslant \sigma \tag{26}$$

$$\frac{W_s(\lambda)}{k_B T} = -\frac{3R\phi}{\sigma}\lambda^2 + \frac{R\phi^2}{5\sigma}(12 - 45\lambda - 60\lambda^2), \quad \text{for } h < \sigma\,, \tag{27}$$

which has a positive maximum value of:

$$W_{s,\max}/k_B T = 12 R\phi^2/5\sigma, \quad \text{at } h = \sigma(1 - \tfrac{3}{2}\phi)\,, \tag{28}$$

and a minimum value at contact:

$$W_{s,\min}/k_B T = -3\phi R/\sigma - 3\phi^2 R/5\sigma\,. \tag{29}$$

These formulae for $W_{s,\max/\min}$ are accurate to order ϕ^2.

The most notable feature is obviously the barrier $W_{s,\max}$. To take a somewhat extreme example, spherical micelles of radius 5 nm, used as a depletant [22] for large (10 μm) particles, gives a barrier of 24 $k_B T$ at $\phi \simeq 0.1$, see Fig. 2. (The third order correction, calculated below, is also shown in the figure.) This would lead to a very strong kinetic stabilization of the colloid. For less extreme size ratios, the effect will be much weaker but there could still be a strong influence on the radial distribution function of the large spheres.

3.3. Third order

To this order, $n_{\text{out}} = n_b(1 + B_2 n_b + B_3 n_b^2)$. For n_{in}, we need all terms in Eq. (13). The evaluation of the linear term $\Omega_1(\sigma/2)$ is just as before, but $\Omega_2(\sigma/2)$ is more tricky.

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[1] It is appropriate, at this point, to correct a (printing) error in Ref. [10], where the last term on line 2 of Eq. (24) should read $-3v\rho_\infty$.

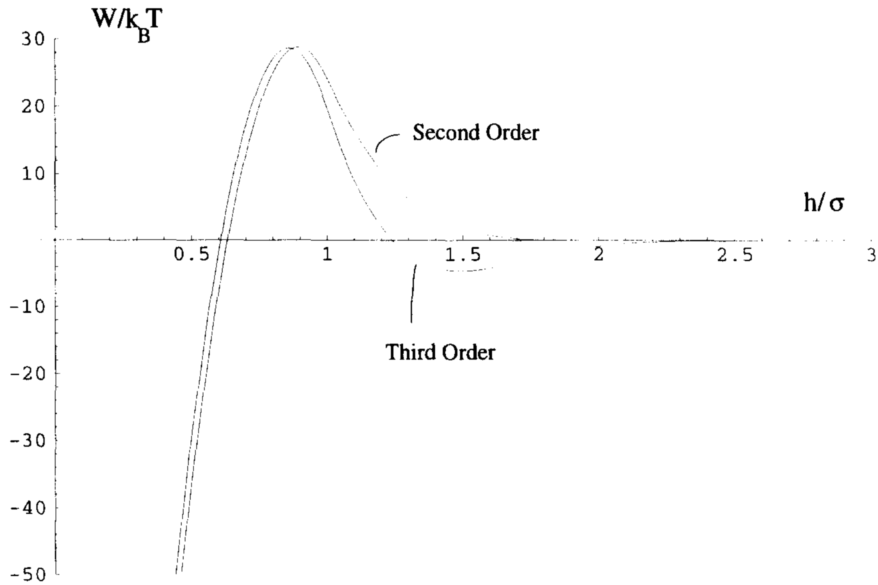

Fig. 2. The calculated second and third order interaction energy $W(h)/k_BT$ against reduced separation h/σ between large spheres suspended in small spheres at volume fraction $\phi = 0.1$. The size ratio $2R/\sigma = 2000$.

Firstly we need to find $\Omega_{2.1}(\sigma/2)$ as defined in Eq. (11), which involves knowing $n(\boldsymbol{r})$ to order n_b^2 for a general position $\boldsymbol{r}$ within the plates. Clearly $n(\boldsymbol{r})$ depends on z only, and can as before be written as [see Eq. 8)]: $n(\boldsymbol{r}) = n_{\text{res}}P(z)$ for $h \geqslant \sigma$ and 0 for $h < \sigma$. To find $\Omega_{2.1}(\sigma/2)$ here, we need to know $P(z)$ for all z (not just $z = \sigma/2$) though only to first order in the bulk density n_b.

From Eq. (13), $P(z)$ can be found in terms of $\Omega_1(z)$ which is simply the volume of the truncated sphere shown in Fig. 1. The result may be written:

$$\Omega_{2.1}(\sigma/2) = \int\limits_{S_{\sigma/2}} [2B_2 - \Omega_1(z)]\, \mathrm{d}^3\boldsymbol{r}\,, \tag{30}$$

which can be evaluated to give:

$$\Omega_{2.1} = \tfrac{2}{9}\pi^2\sigma^6, \qquad h \geqslant 3\sigma\,, \tag{31}$$

$$\Omega_{2.1} = \tfrac{1}{180}\pi^2\sigma^6(200 - 192\lambda + 80\lambda^3 - 30\lambda^4 + \lambda^6), \qquad 3\sigma > h \geqslant 2\sigma\,, \tag{32}$$

$$\Omega_{2.1} = \tfrac{1}{180}\pi^2\sigma^6(240\lambda - 180\lambda^2 - 80\lambda^3 + 90\lambda^4 - 11\lambda^6), \qquad 2\sigma > h \geqslant \sigma\,. \tag{33}$$

To complete the third-order calculation, we need to find $\Omega_{2.2}(\sigma/2)$ as defined by (12):

$$n_b^2\Omega_{2.2} = \frac{1}{2}\int\limits_{S_{\sigma/2}}\int\limits_{S_{\sigma/2}} n(\boldsymbol{r}_1)n(\boldsymbol{r}_2\,|\,\boldsymbol{r}_1)\,\mathrm{d}^3\boldsymbol{r}_1\,\mathrm{d}^3\boldsymbol{r}_2\,. \tag{34}$$

Here, we can set $n(\boldsymbol{r}) = n_b$ since the integral is already of order n_b^2. Also, as discussed previously, $n(\boldsymbol{r}_2 \,|\, \boldsymbol{r}_1)$ is also n_b unless $\boldsymbol{r}_2$ and $\boldsymbol{r}_1$ are mutually excluding, in which case it is zero. Thus:

$$\Omega_{2.2}(\sigma/2) = \int_{\tilde{S}} \mathrm{d}^3\boldsymbol{r}_1 \int_{\tilde{S}'} \mathrm{d}^3\boldsymbol{r}_2 \,, \tag{35}$$

which is the (6-dimensional) volume available to two mutually excluding spheres within the excluded volume $\tilde{S}$ of a hypothetical particle contacting the plate. For $h \geqslant 2\sigma$ the volume $\tilde{S}$ is a hemisphere, and for $2\sigma > h > \sigma$, $\tilde{S}$ is a truncated hemisphere. In both cases, $\tilde{S}'$ is the incomplete hemisphere available to a second particle; the algebra involved is accordingly rather complicated.

The integral is, however, similar to that treated by Fischer [23, 24], who studied the particle density near an *isolated* wall as a power series in the bulk density. For our problem, the integration limits have to be changed, and the calculations are very involved. We therefore only quote the answer:

$$\Omega_{2.2} = \tfrac{1}{12}\pi^2\sigma^6, \qquad h > 2\sigma \,, \tag{36}$$

$$\Omega_{2.2} = \tfrac{1}{60}\pi^2\sigma^6(-10 + 38\lambda - 30\lambda^2 + 10\lambda^4 - 3\lambda^6), \qquad 2\sigma \geqslant h \geqslant (\sqrt{3}/2 + 1)\sigma \,, \tag{37}$$

$$\begin{aligned}
\frac{\Omega_{2.2}}{\pi\sigma^6} &= \sqrt{3 - 4\lambda^2}\left(\frac{\lambda^2}{8} - \frac{\lambda^4}{20}\right) - \left(\frac{1}{6} - \frac{\lambda^2}{2} + \frac{\lambda^4}{3} - \frac{\lambda^6}{18}\right)\pi \\
&\quad + \frac{\lambda^2}{180}\left[(-180 + 90\lambda^2 - 11\lambda^4)\arccos\left(\frac{1}{2\sqrt{1-\lambda^2}}\right)\right. \\
&\quad \left. - 10(3 - \lambda^2)^2 \arccos\left(\frac{-1 + 2\lambda^2}{-2 + 2\lambda^2}\right)\right] + \frac{19\lambda}{15}\arctan\left(\frac{\lambda}{\sqrt{3 - 4\lambda^2}}\right) \\
&\quad + \frac{1}{4}\left[\arctan\left(\frac{3 - 4\lambda}{\sqrt{3 - 4\lambda^2}}\right) + \arctan\left(\frac{3 + 4\lambda}{\sqrt{3 - 4\lambda^2}}\right)\right] \\
&\quad + \lambda\,\frac{16 + 30\lambda - 10\lambda^3 + 3\lambda^5}{120}\left[\arctan\left(\frac{3 - 2\lambda - 4\lambda^2}{(1 + 2\lambda)\sqrt{3 - 4\lambda^2}}\right)\right. \\
&\quad \left. - \arctan\left(\frac{3 + 2\lambda - 2\lambda^2}{(1 + 2\lambda)\sqrt{3 - 4\lambda^2}}\right)\right] \\
&\quad - \lambda\,\frac{16 - 30\lambda + 10\lambda^3 - 3\lambda^5}{120}\left[\arctan\left(\frac{-3 + 2\lambda + 2\lambda^2}{(1 - 2\lambda)\sqrt{3 - 4\lambda^2}}\right)\right. \\
&\quad \left. - \arctan\left(\frac{-3 - 2\lambda + 4\lambda^2}{(1 - 2\lambda)\sqrt{3 - 4\lambda^2}}\right)\right], \quad \sigma < h < (\sqrt{3}/2 + 1)\sigma \,.
\end{aligned} \tag{38}$$

Combined with the previous results, we obtain finally the depletion force between flat plates as:

$$f_p/k_B T = n_{res}[1 - \Omega_1(\sigma/2)n_b - [\Omega_{2.1}(\sigma/2) - \Omega_{2.2}(\sigma/2)]n_b^2] - n_b(1 + B_2 n_b + B_3 n_b^2)\,, \quad (39)$$

with n_{res} as given in Eq. (7), and Ω_1, $\Omega_{2.1}$, $\Omega_{2.2}$ from (17, 18), (31)–(33) and (36)–(38) respectively. The maximum of the repulsive force remains at $h = \sigma^+$ (as in the second order calculation) but the value is shifted to $f_{p,\max} = n_b k_B T(4\phi + 37\phi^2)$. In addition, this force changes from repulsion to attraction as separation increases from σ to 2σ, and it is purely attractive at separations between 2σ and 3σ, with a maximum attraction in this region of $\frac{19}{5} n_b \phi^2 k_B T$. This gives a secondary minimum in the interaction potential between flat plates.

The above completes our calculation of the depletion force between plates to third order in n_b. Two further integrations are then performed numerically to give $W_s(h)$, the interaction potential between large spheres or radius R in a sea of small ones of diameter σ and bulk density n_b. The results may be written:

$$\frac{W_s(h)}{k_B T} = \frac{2R}{\sigma}[A_1(h)(n_b\sigma^3) + A_2(h)(n_b\sigma^3)^2 + A_3(h)(n_b\sigma^3)^3 + O((n_b\sigma^3)^4)]\,, \quad (40)$$

where $n_b\sigma^3$ is the dimensionless density, and the functions $A_1(h)$, $A_2(h)$, $A_3(h)$ are plotted in Fig. 3. (This data allows the third order prediction for the interaction potential to be reconstructed for any chosen ϕ.)

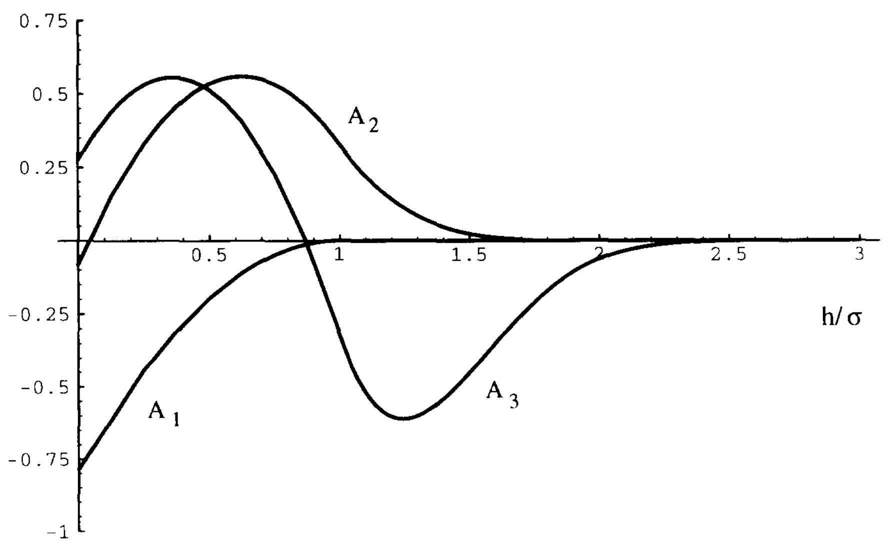

Fig. 3. The coefficients in the expansion of the depletion force, Eq. (40).

4. Discussion

We give first a direct physical argument for the origin of the repulsive part of depletion force, and explain its maximum magnitude (between plates), $f_{p,\max} = n_b k_B T(4\phi + 37\phi^2)$, which arises for $\lambda = h - \sigma \to 0^+$. The key idea is that, for small λ, the mutual repulsion of spheres within the gap is substantially reduced. Such spheres are very rarely close to each other: to first order in concentration their *voluminal* number density within the allowed region for particle centres (which is of thickness λ) is simply n_b, the same as outside the plates. However the *areal* density is $n_b\lambda$, which vanishes as $\lambda \to 0$. In this limit the spheres between the plates become *noninteracting*: their density must therefore approach n_{res} as defined in Eq. (7). To cubic order in n_b, this yields an enhanced ideal-gas [18] osmotic pressure within the gap of

$$\Pi_{in} = k_B T n_{res} = k_B T n_b(1 + 2B_2 n_b + (2B_2^2 + 3B_3/2)n_b^2)\,. \tag{41}$$

The osmotic pressure outside is also enhanced (by interactions), but as usual obeys

$$\Pi_{out} = k_B T n_b(1 + B_2 n_b + B_3 n_b^2)\,. \tag{42}$$

The difference between these two pressures gives for $\lambda \to 0^+$ a repulsive depletion force

$$f_{p,\max} = k_B T[B_2 n_b^2 + (2B_2^2 + B_3/2)n_b^3]\,, \tag{43}$$

precisely as found in Section 3.2 and [10] (to second order in ϕ), and in Section 3.3 (to third order).

We have shown already in Fig. 2 the interaction curves at second and third order for a (rather extreme) size ratio and volume fraction that might correspond to depletion by micelles of large colloidal particles. For less extreme size ratios, the flocculation barrier will be weak, at least in the range where the theory is reliable, and the main effect of higher order corrections may then be to alter the depth and, to some extent the width, of the primary attractive minimum. However, there may still arise a significant barrier at higher ϕ. This prospect is implicit in the prediction of Attard [13], of a pronounced minimum in the radial distribution function $g(h) \propto \exp[-W_s(h)/k_B T]$ of two large spheres in a dense fluid of small ones, which, in that work, was intended as a model of a molecular solvent. Indeed, the depletion repulsion can be viewed, in this light, as simply the repulsive part of a solvation interaction mediated by the small spheres. This is usually interpreted as a layering effect arising from crowding [13], but the results here show that a repulsion arises, in principle, even at very low ϕ. In fact, at order ϕ^2, a sort of layering is already present: the density of small particles near a large one has an 'enhancement zone' (at distances r obeying $\sigma/2 < r < 3\sigma/2$). Here particles are more likely to be found since they are then adjacent to the usual "depletion zone" ($0 < r < \sigma/2$), and are thus partially relieved of their excluded volume interaction with other small spheres [23, 25].

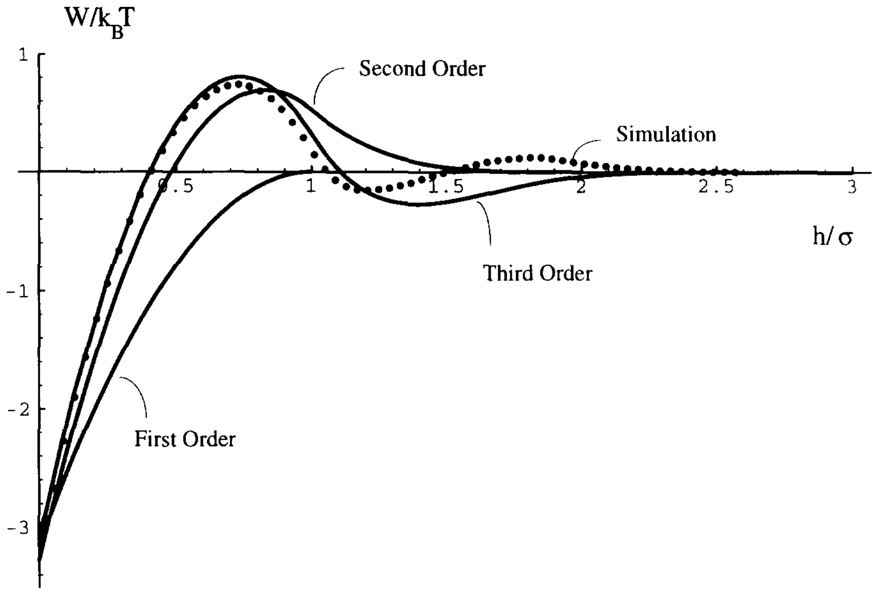

Fig. 4. A comparison of our calculations with computer simulation results. The small sphere volume fraction is $\phi = \pi/15$ and the size ratio $2R/\sigma = 10$. Simulation data courtesy of P. Bladon and T. Biben (Ref. [17]).

A secondary depletion zone, brought about by the exclusion interaction with particles in the enhancement zone, first appears in the ϕ^3 calculation.

The density profile of particles between confining plates is given by Antonchenko et al. [26] using Monte-Carlo method, and also analytically by Glandt [27]. Glandt gave the density between plates in a virial expansion to third order, but not for the crucially important region of $\sigma < h < 2\sigma$. Otherwise the results in Ref. [27] agrees with that found in Section 3 for the contact density.

The oscillatory nature of the depletion interaction has been measured directly with a surface force apparatus [28]. The experimental results can not be directly compared to our theoretical predictions because of the presence of charged double layers in the experimental system. Our results can, however, be directly compared with recent computer simulations [17] in which the interaction potential was itself calculated. For a particular size ratio of $2R/\sigma = 10$, and volume fraction $\phi = \pi/15$ the predictions to various orders in ϕ are plotted in Fig. 4 and compared with the simulation data. Clearly the shape of the primary attraction, and also the depletion barrier, are qualitatively described by the second order calculation and reproduced very well at third order. (This is despite use of the Derjaguin approximation[2].) The third-order

[2] We have made a numerical estimate of the depletion force to second order in density without the Derjaguin approximation which shows the error to be of order a few percent for this size ratio.

calculation also predicts the secondary minimum, though this is at too large separations and somewhat too deep. The simulation shows also a second maximum, which, as mentioned in Section 1, one would expect in principle to recover at fourth order in ϕ. Considering the magnitude of ϕ in this example, the perturbative results are probably better than one could reasonably have anticipated. As mentioned above, it does seem that much of the physics of solvation forces [18], as well as the depletion force, is already contained in the perturbation expansion to the first few orders in ϕ.

Finally, it is important to consider to what extent our hard-sphere results could be applicable to other depletants, such as charged spheres or polymers. The nature of the depletion for interacting spheres confined between symmetric walls was considered by Henderson [29]. For polymers in a good solvent, there might arise a repulsive depletion barrier at volume fractions below but close to the overlap threshold: such polymers have a strong tendency to mutual avoidance. However, the presence of the barrier (and the subsequent secondary minimum) arises for spheres in part because the *attractive* interaction for short distances cuts off abruptly at $h = \sigma$. For polymers this contribution would fall off more slowly because of fluctuations in coil shape. This smearing of the (order ϕ) attraction could easily wipe out the rather delicate higher order features of the interaction curve. Analytic calculations for mutually avoiding chains seem extremely formidable. Work in progress is instead addressed to the case of depletion by rigid rods, where similar considerations apply, with the smearing in this case arising from the orientational distribution of the particles [30]. Polydispersity, which has not been addressed so far, is also the subject of ongoing research.

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Appendix A

Here we present two checks on our results, including equation (39), by comparing with limiting cases.

A.1. Check with surface tension

As we bring two plates close together to a distance σ, two particle-wall interfaces disappear. Therefore $W_{\text{plates}}(\sigma) = -2\gamma$, where γ is the surface tension. The virial expansion for this quantity was given by Bellemans [31, 32] more than 30 years ago,

$$\frac{\gamma\sigma^2}{k_B T} = -\frac{9}{2\pi}\phi^2 - \frac{1341}{70\pi}\phi^3 . \tag{44}$$

Combining the above two equations we find

$$W_{\text{plates}}(\sigma) = \frac{2k_B T}{\sigma^2}\left(\frac{9}{2\pi}\phi^2 + \frac{1341}{70\pi}\phi^3\right). \tag{45}$$

We have checked numerically to high precision that this result agrees with that given by Eq. (39).

A.2. Check with small λ limit

It follows from the work of Henderson – Ref. [18], Eqs. (10), (21) – that for the limit of $0 < \lambda \ll 1$, we have

$$n_{\text{in}}(\lambda) = n_b[1 + (8 - 6\lambda)\phi + (47 - 96\lambda)\phi^2] , \tag{46}$$

This expression for surface contact density in between plates has been verified as a special case of Eqs. (13), (14) with:

$$\Omega_1 = \pi\sigma^3\lambda + O(\lambda^2) , \tag{47}$$

$$\Omega_2 = -\tfrac{4}{3}\pi^2\sigma^6\lambda + O(\lambda^2) . \tag{48}$$

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