Depletion forces between two spheres in a rod solution

K. Yaman[1], C. Jeppesen[2] and C. M. Marques[3]

[1] *Department of Physics, UCSB - California - 93106 9530, USA*
[2] *Materials Research Laboratory - UCSB, California, 93106, USA*
[3] *RP-CNRS, Complex Fluid Laboratory UMR166 - Cranbury, NJ 08512–7500, USA*

Abstract. – We study the depletion interaction between spherical particles of radius R immersed in a dilute solution of rigid rods of length L. The computed interaction potential is, within numerical accuracy, exact for any value of L/R. In particular we find that for $L \sim R$, the depth of the depletion well is *smaller* than the prediction of the Derjaguin approximation. Our results bring new light into the discussion on the lack of phase separation in colloidal mixtures of spheres and rods.

Mixtures of colloids are abundant in industry as paints, glues, lubricants and other materials [1]. They are also present in the preparation of foods and drugs, and in the biological realm: many living organisms or components of living organisms are colloidal suspensions of a variety of sizes and shapes. A pervasive issue in the colloidal domain is the stability of colloidal suspensions. Stability is often necessary for practical purposes as in paint formulation for instance, but certain applications like water treatment or mineral recovery might instead require aggregation or flocculation to occur. The determination of the stability criteria or the study of the flocculation kinetics can be achieved with reasonably good accuracy once the interparticle interaction potentials are known [2]. In a system of a *pure* colloidal species the two main interactions are the van der Waals attraction and the hard-core repulsion. Such a system is intrinsically unstable, the van der Waals attractive component of the potential always leading to flocculation. In practice the stabilization of the suspension is enforced by using the screened electrostatic repulsion in aqueous solutions or steric polymer layers in organic solvents. To a good approximation the stabilized suspension can then be regarded as hard-core particles with no attractive potential component. One way of treating the stability issue in a colloidal *mixture* of two components is by considering the effective potential that the second species induces between two particles of the first species.

A well-studied case [3], [4] is the attractive potential that a solution of hard-core spheres of radius r_0 induce between two spheres of radius R (see fig. 1). To first order in concentra-
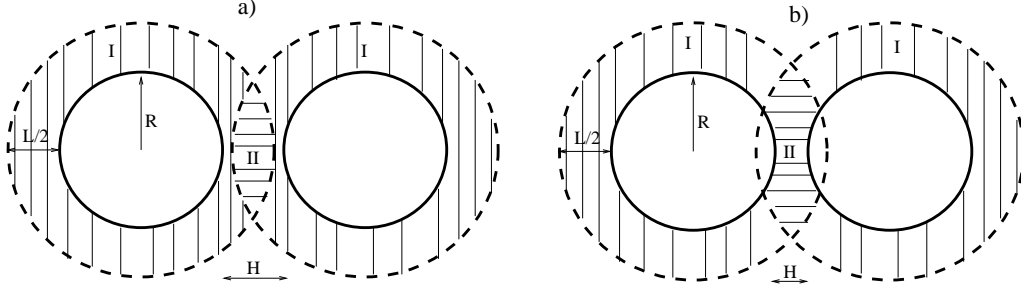
Fig. 1. – The depletion region: a) for $H > L/2$, b) for $H < L/2$.

tion [5], [6] this potential reads

$$U_{\mathrm{s}}(H) = -k_{\mathrm{B}}T\frac{3}{8}\,\phi\,\frac{R}{r_0}\left(2 - \frac{H}{r_0}\right)^2\left(1 + \frac{2}{3}\frac{r_0}{R} + \frac{1}{6}\frac{H}{R}\right), \text{ for } H \leq 2r_0, \tag{1}$$

where H is the distance between the two large spheres and ϕ the volume fraction of the small spheres. Of course, U_{s} is zero if $H \geq 2r_0$; by definition of the depletion potential the depletion at $H = 2r_0$ is the zero point. We will only give the potential in the regions where it is nonzero from now on. The depletion attraction has been known since the pioneering work [7] of Asakura and Oosawa who calculated the interaction energy between two flat plates immersed in a hard-sphere solution:

$$u_{\mathrm{f}}(H) = -\frac{k_{\mathrm{B}}T}{r_0^2}\frac{3}{4\pi}\phi\left(2 - \frac{H}{r_0}\right). \tag{2}$$

The depletion potential has a purely entropic origin: the exclusion of the small particles from the gap creates a pressure deficit and hence an effective attraction between the plates. When the exact analytical form of the interaction is only known for flat plates, one can still compute the interaction potential between spheres much larger than the range of the potential by employing the so-called Derjaguin approximation [8]. For instance, the asymptotic behaviour (as $R/(2r_0) \gg 1$) of eq. (1) can be obtained from eq. (2):

$$U_{\mathrm{Der}}(H) = -\pi R\int_H^\infty \mathrm{d}H'u_{\mathrm{f}}(H') = -k_{\mathrm{B}}T\frac{3}{8}\,\phi\,\frac{R}{r_0}\left(2 - \frac{H}{r_0}\right)^2. \tag{3}$$

Note that the Derjaguin approximation underestimates the attraction in this case. Indirect experimental evidence for the depletion effect was since long ago provided by the flocculation observed in colloids and emulsions, but more direct observations of the attraction have been only recently performed by force measurements [9] with surface force apparatus or microscopy techniques [10].

A much less studied case is the depletion induced by hard-core rods, a surprising fact considering that rod-shaped particles in the colloidal range are present in a large variety of mineral and organic systems [11]; they also exist in the biological realm where examples range from TMV-like virus to fibrils of amyloid β-protein, the molecular agent at the origin of the Alzheimer disease. The depletion interaction between two flat surfaces immersed in a dilute rod solution was studied in [7]:

$$u_{\mathrm{f}}(H) = -\frac{k_{\mathrm{B}}T}{LD}\,4.2\,\frac{\phi}{\phi^*}\frac{1}{2}\left(1 - \frac{H}{L}\right)^2, \tag{4}$$

with D the diameter of the rod, and ϕ^* the Onsager volume fraction, below which the solution is isotropic. For spheres in a rod solution the potential can be written to first order in concentration as

$$U_{\mathrm{s}}(H) = k_{\mathrm{B}}T \, 4.2 \, \frac{\phi}{\phi^*} \, \frac{R}{D} \, K_1(H/L) \qquad (5)$$

but no explicit form of K_1 is available except in the Derjaguin approximation: $K_1^{\mathrm{Der}}(x) = -(\pi/6)\,(1-x)^3$, which is expected to apply only for $L/R \ll 1$. Since this potential has quite a large contact value compared to $k_{\mathrm{B}}T$, one would expect on this basis to observe flocculation also in rod/sphere mixtures. Surprisingly, such a phase separation has not yet been clearly identified experimentally. A possible explanation for this lack of experimental evidence has recently been proposed [12], based on repulsive contributions from the surface modification of the rod-rod excluded-volume interactions. However, such contributions are second order in the rod concentration, and thus small below the Onsager concentration [13], $\rho_{\mathrm{b}}^* = 4.2/(L^2 D)$. The authors of reference [12] also note that most systems of interest involve rods that are of comparable size to the spherical particles; in particular the experiments [14] cited in [12] have $1.16 < L/R < 4.34$, a range where the use of the Derjaguin approximation to compute the depletion potential in questionable.

In this letter we present *exact* results for the depletion potential to first order in rod density. Our results are numerical in nature, but exact, *i.e.* the inaccuracy of our calculation is only limited by the numerical nature of the integration performed. It is for our case reducible to levels at which the error bars on the figures given below are not visible. The method of our calculation is based on the work on surface tension of objects immersed in rigid rod solutions that we published elsewhere [15], [16]. We now briefly discuss this method and present our results.

We consider two spheres of radius R in a solution of rods of length L, and thickness D, with $L/D \gg 1$. We work to first order in the density of the rods, hence we really consider one rod
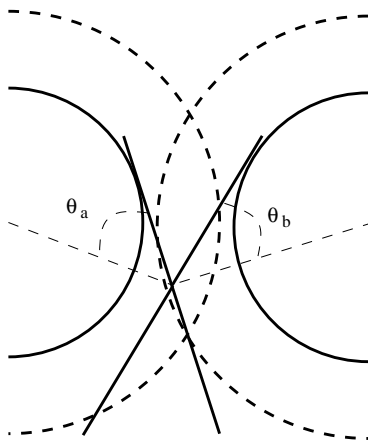

Fig. 2. – The basic construction of the numerical integration method. For a given position of the center of mass we compute two angles, θ_a and θ_b. Conditions for deciding the functional form of the free-energy density at a given position of the center of mass can be written as a function of these angles. Using the functionals determined in our previous work [16], we reduce the problem to a tractable two-dimensional numerical integration from a four-dimensional one.

and two spheres. *A priori* this is only valid when the rod-rod interactions can be ignored: for rod concentrations below the threshold ρ_b^*.

The interaction potential is given [16] by the differences in the grand potentials of the spheres at infinite separation and inside the range of the potential, L. These grand potentials are integrals over the phase space available to a rigid rod: If the rod's center of mass is at a perpendicular distance z greater than $L/2$ to the surface of a sphere, then the rod is free to rotate, otherwise its rotational degrees of freedom are limited. The "depletion region" of the rod is shown in fig. 1. This region can be further broken into two: In the first one (I) the rod interacts only with one sphere, whereas in the second one (II) interactions with both spheres are possible. Our previous work [16] provides exact expressions for the contribution of region I to the free energy for all values of (L/R). Region II needs to be further broken down to three sub-regions where the functional form of the phase space allowed to the rod is different. The character of each of these regions depends on whether the rod touches each of the surfaces with one end or along its length [16]. The integration over the angular degrees of freedom can still be performed analytically, but integration over the possible center of mass positions is complicated by the lack of analytical expressions for the boundaries between the sub-regions where different functional forms apply. We therefore use the following procedure: once the position of the center of mass is given, we compute two angles, θ_a and θ_b (see fig. 2), from its coordinates, and then numerically decide what functional form to use. Since we have exact expressions for the allowed phase spaces, this procedure reduces the problem to a two-dimensional numerical integration from a four-dimensional one, which can be performed rapidly on a personal computer.

One can, of course, do the calculation using Monte Carlo integration, and we have checked our results using this technique. When region II is not too small as compared to the total depletion region, Monte Carlo yields reasonable accuracy, moderately fast. The results for these small H values are in perfect agreement (see fig. 3) with the exact method, for values of (L/R) anywhere from 0.1 to 15.0. When H gets larger, though, Monte Carlo results fluctuate considerably; longer machine time is needed to reduce these fluctuations.

Representative results for the function $K_1(x)$ defined in eq. (5) are shown in fig. 4. The Derjaguin function, $K_1^{\mathrm{Der}}(x)$, is also shown for comparison. As can be seen from this plot,

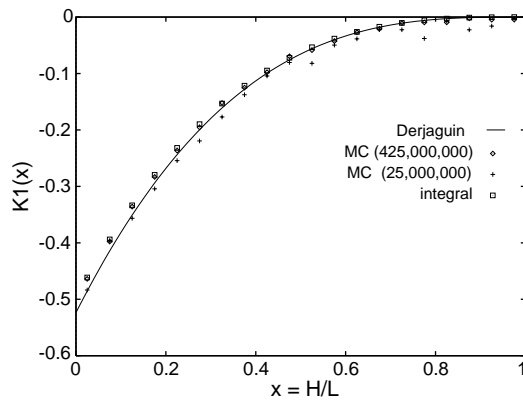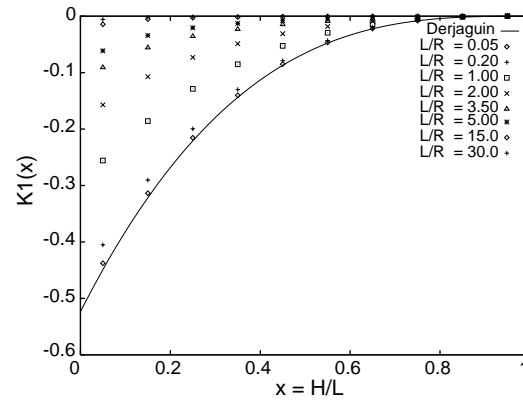Fig. 3

Fig. 4

Fig. 3. – Monte Carlo compared to the numerical integral for $L/R = 0.1$.

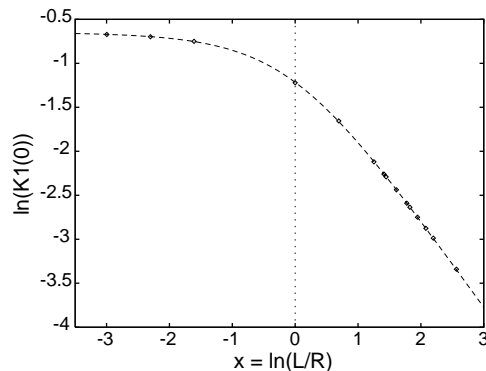Fig. 4. – The function $K_1(x)$ for several values of L/R.

Fig. 5. – Contact values. The function plotted here is the one given in the text. Notice the drastic change in the functional form of the data when L crosses $2R$.

Derjaguin is indeed an excellent approximation to the depletion potential when $(L/R) \ll 1$. What is noteworthy is the *large* and systematic deviation from this approximation when (L/R) grows. This deviation is about 50% when $(L/R) = 1$, and becomes more pronounced as (L/R) increases. This can be understood in the light of general results we presented [16] recently. These results relate the second derivative of the free energy of a rod system to the measure of configurations where the rod can wedge between two points on the surface. Clearly, in our case for a fixed H, this measure goes to zero as the rod gets longer. This implies that the free energy becomes a linear function of (L/R), and the function K_1, being related to the free energy by a factor of $(L/R)^2$, vanishes as R/L. Figure 5 shows the behaviour of the contact value, $K_1(0)$, as a function of the rod/sphere ratio. We fitted the data of fifteen points to a function with three parameters. The resulting fit is

$$K_1(0) = -\frac{\pi}{6} \frac{1 + 0.8762\,(L/R)}{1 + 1.33198\,(L/R) + 0.98225\,(L/R)^2}\,; \tag{6}$$

as can be seen in fig. 5 the fit is very good indeed for the range $0.05 < L/R < 13$.

The lack of phase separation in the experiments [14] is less surprising in the light of our results. Previous expectations based on Derjaguin approximation estimate the value of the attraction minimum at 10–$20\,k_{\mathrm{B}}T$. Our results show that the real value is much lower. This reduction amounts to a factor of three to five for these experiments and reduces the depth of the depletion potential to a few $k_{\mathrm{B}}T$. Note also that other factors like chain flexibility are likely to reduce the strength of the attraction further.

$$***$$

REFERENCES

[1] RUSSEL W. B., SAVILLE D. A. and SCHOWALTER W. R., *Colloidal Dispersions* (Cambridge University Press, Cambridge) 1989.

[2] *Proceedings of the First Meeting of the European Network on Colloid Physics*, *Physica A*, **235** (1997).

[3] ASAKURA S. and OOSAWA F., *J. Polymer Sci.*, **33** (1958) 183.

[4] VRIJ A. and OVERBEEK J. TH. G., *J. Colloid Interface Sci.*, **17** (1962) 570.

[5] MAO Y., CATES M. E. and LEKKERKERKER H. N. W., *Physica A*, **222** (1995) 10.

[6] WALZ J. Y. and SHARMA A., *J. Colloid Interface Sci.*, **168** (1994) 485.

[7] ASAKURA S. and OOSAWA F., *J. Chem. Phys.*, **22** (1954) 1255.

[8] ISRAELACHVILI J. N., *Intermolecular and Surface Forces* (Academic Press, London) 1985.

[9] RICHETTI P. and KEKICHEFF P., *Phys. Rev. Lett.*, **68** (1992) 1951.

[10] DINSMORE A. D., YODH A. G. and PINE D. J., *Nature*, **383** (1996) 239.

[11] BUINING P. A., *J. Phys. Chem.*, **97** (1993) 11510.

[12] MAO Y., CATES M. E. and LEKKERKERKER H. N. W., *Phys. Rev. Lett.*, **75** (1995) 4548.

[13] ONSAGER L., *Ann. N.Y. Acad. Sci.*, **51** (1949) 627.

[14] TRACY M. A., GARCIA J. L. and PECORA R., *Macromolecules*, **26** (1993) 1862.

[15] YAMAN K., PINCUS P. and MARQUES C. M., *Phys. Rev. Lett.*, **78** (1997) 4514.

[16] YAMAN K., JENG M., JEPPESEN C., PINCUS P. and MARQUES C. M., *Physica A*, **247** (1997) 159.