

## Depletion potentials in colloidal mixtures of spheres and rods

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2003 J. Phys.: Condens. Matter 15 S277

(<http://iopscience.iop.org/0953-8984/15/1/337>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.97

The article was downloaded on 18/05/2010 at 19:25

Please note that [terms and conditions apply](#).

# Depletion potentials in colloidal mixtures of spheres and rods

**R Roth**<sup>1,2</sup>

<sup>1</sup> Max-Planck Institut für Metallforschung, Heisenbergstraße 1, D-70689 Stuttgart, Germany

<sup>2</sup> Institut für Theoretische und Angewandte Physik, Universität Stuttgart, Pfaffenwaldring 57, D-70569 Stuttgart, Germany

E-mail: Roland.Roth@mf.mpg.de

Received 16 October 2002

Published 16 December 2002

Online at [stacks.iop.org/JPhysCM/15/S277](http://stacks.iop.org/JPhysCM/15/S277)

## Abstract

We calculate the depletion potential between two hard spheres of radii  $R_s$  and that between one hard sphere and a planar hard wall in a sea of hard rigid spherocylindrical rods of length  $L$  and radius  $R_r$ . Unlike earlier studies our approach takes into account the true geometry of the problem and gives, to first order in the rod density, the exact depletion potential for *all* values of  $R_s$ ,  $L$ , and  $R_r$ .

## 1. Introduction

Recently progress was made in understanding colloidal mixtures by mapping the mixture onto an effective one-component system described by an effective Hamiltonian that is then tractable for conventional liquid state approaches [1]. In order to make this mapping, the degrees of freedom of one component, usually that of the smaller colloids, must be integrated out, resulting in effective particle–particle and where appropriate particle–wall interactions of the remaining (big) species. If the bare pair interactions in the mixture are solely hard-core repulsions, the effective interactions are purely entropic in origin and are usually referred to as *depletion interactions*.

Depletion potentials were first studied theoretically by Asakura and Oosawa for a simple model mixture of hard colloidal spheres and non-interacting spherical polymer [2]. They found that in this system the depletion forces are purely attractive and if enough polymer is present in the system the potential at contact can be of the order of several  $k_B T$ . Later [3] they showed that if long thin rods are used as the depletion agent instead of spherical polymer, strongly attractive depletion potentials can be found for much lower number densities of the depletant. Despite these early studies and the potential importance of mixtures of spherical and rod-like colloids for understanding biological systems, relatively little is known about the depletion effects in these systems. The depletion potential between two colloidal spheres in a sea of long and thin rods was studied using the so-called Derjaguin approximation [4, 5], which is

restricted in its application to the regime of large colloidal spheres in a sea of short needles, and numerical integration [6] for a mixture of spheres and infinitely thin needles of arbitrary aspect ratio  $L/R_s$ .

In this paper we present a theory for depletion potentials between two spheres or between one sphere and a planar wall that is exact to first order in  $\rho_r$ , the density of the rods, and that is valid for arbitrary values of  $R_s$ ,  $L$ , and  $R_r$ , where  $R_s$  is the radius of the sphere,  $L$  and  $R_r$  the length and the radius of the rods, respectively. This theory was recently applied successfully to interpret the first direct measurement of the wall–sphere depletion potential induced by rigid rods [7].

## 2. Theory

A very effective and general approach for calculating depletion potentials within the framework of density functional theory (DFT) was presented in [8, 9]. In a recent application of this approach a quantitative prediction of an *entropic torque* acting on non-spherical object was made [10]. The approach requires  $\mathcal{F}_{ex}[\rho_s, \rho_r]$ , the intrinsic excess (over ideal gas) Helmholtz free energy functional for the mixture of spheres and rods. Here  $\rho_s(\mathbf{r})$  and  $\rho_r(\mathbf{r}, \vec{\omega})$  are the density profiles of spheres and rods, respectively. Using this functional in the limit of vanishing sphere density  $\rho_s \equiv 0$ , we first calculate the density profile of rods  $\rho_r(\mathbf{r}, \vec{\omega})$  in an external potential  $V_{ext}(\mathbf{r}, \vec{\omega})$ , that is either the potential of a planar hard wall or that of one fixed hard sphere of radius  $R_s$ .

In the present work we consider the fluid of rods at low densities, so the exact low-density excess free energy functional

$$\beta\mathcal{F}_{ex}[\{\rho_i\}] = -\frac{1}{2} \sum_{i,j} \int d\mathbf{q} \rho_i(\mathbf{q}) \int d\mathbf{q}' \rho_j(\mathbf{q}') f_{ij}(\mathbf{q}, \mathbf{q}'), \quad (1)$$

with  $\beta = 1/k_B T$ , can be employed. In equation (1) the variables  $\mathbf{q}$  denote either coordinates of the centres of spheres  $\mathbf{r}$  or of the centres and orientations of rods  $(\mathbf{r}, \vec{\omega})$ .  $f_{ij}(\mathbf{q}, \mathbf{q}') = \exp[-\beta V_{ij}(\mathbf{q}, \mathbf{q}')] - 1$  is the Mayer  $f$ -function of the interaction potential  $V_{ij}$  between particles of species  $i$  and  $j$ .

Since long thin rods were found to generate deep depletion potentials at relatively low number densities [3–6] for which correlation effects are rather unimportant, we will neglect interactions between rods and set  $f_{rr} \equiv 0$  in the following. This assumption simplifies the calculations dramatically because the density profile of the rods reduces to that of an ideal gas, i.e.

$$\rho_r(\mathbf{r}, \vec{\omega}) \equiv \rho_r(\mathbf{q}) = \frac{\rho_r}{4\pi} \exp[-\beta V_{ext}(\mathbf{r}, \vec{\omega})] = \frac{\rho_r}{4\pi} \exp[-\beta V_{ext}(\mathbf{q})], \quad (2)$$

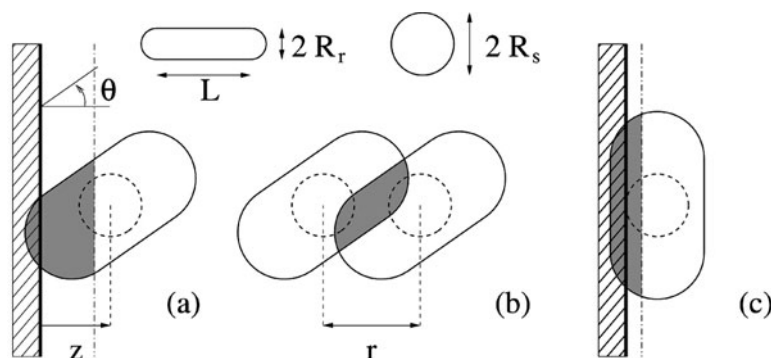
where  $\rho_r$  is the density of rods in the bulk fluid. If one were to include interactions among the rods, the density profile would follow from the numerical minimization of the appropriate density functional [9].

Using the density profile (2) we can calculate the direct one-body correlation function of spheres in the limit  $\rho_s \rightarrow 0$  [11]:

$$c_s^{(1)}(\mathbf{r}) \equiv -\frac{\delta\beta\mathcal{F}_{ex}[\rho_s, \rho_r]}{\delta\rho_s(\mathbf{r})} = \frac{\rho_r}{4\pi} \int d\mathbf{q}' \exp[-\beta V_{ext}(\mathbf{q}')] f_{rs}(\mathbf{r}, \mathbf{q}'), \quad (3)$$

and finally the depletion potential  $\beta W(\mathbf{r}) = c_s^{(1)}(\infty) - c_s^{(1)}(\mathbf{r})$  [9]. Since we will focus on the sphere–wall and sphere–sphere geometries we can simplify the expression for the depletion potential by performing one angular integration to obtain

$$\beta W(\mathbf{r}) = -\rho_r \int_0^{\pi/2} d\theta \sin\theta \int d\mathbf{r}' (\exp[-\beta V_{ext}(\mathbf{r}', \theta)] - 1) f_{rs}(\mathbf{r}, \mathbf{r}', \theta). \quad (4)$$



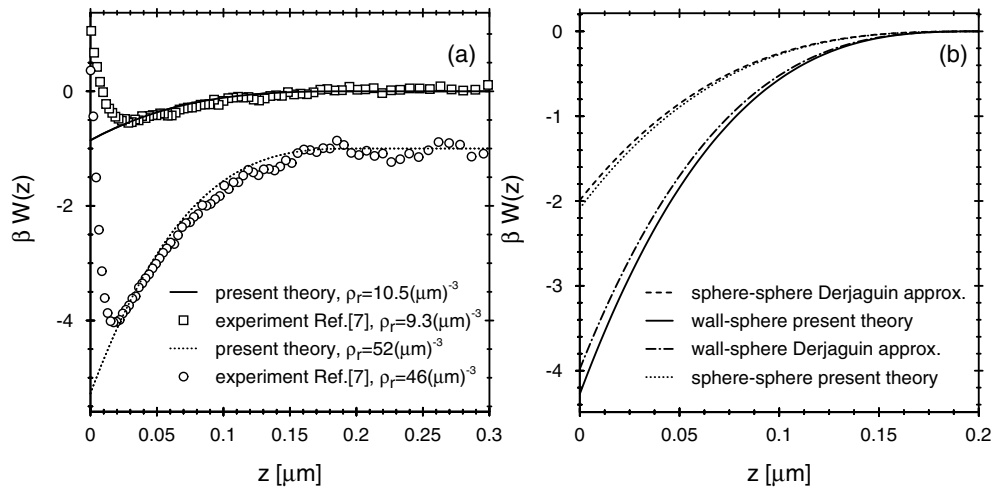
**Figure 1.** The geometry of the overlap (grey shaded) of volumes excluded to the centres of rods of length  $L$ , radius  $R_r$ , and orientation  $\theta$  in the sphere–wall (a) and sphere–sphere (b) geometries. From (c) it becomes clear that rods of non-zero radius and orientation  $\theta = \pi/2$  in contact with the wall contribute to the depletion potential, while in the needle limit  $R_r \equiv 0$  this contribution vanishes.

This formula can be regarded as the generalization to non-spherical depletion agents of equation (11) in [9]. In the case of hard wall–rod and sphere–rod interactions, the integral in equation (4) has a purely geometrical meaning and calculates the overlap of volumes excluded to the centres of rods of a given orientation. For spherocylindrical rods of length  $L$ , radius  $R_r$ , and orientation  $\theta$ , the geometry of the overlap of the excluded volumes is shown in figure 1. In the case of the wall–sphere geometry the overlap (grey-shaded area) of the depletion layer at the wall, that is formed because the centres of rods cannot approach the planar hard wall located at  $z = 0$  closer than  $z_{min} = R_r + L|\cos(\theta)|/2$  (dashed–dotted curve), and around the hard sphere, a spherocylinder of length  $L$  and radius  $R_r + R_s$  (solid curve)—see figure 1(a)—must be calculated. For the sphere–sphere geometry the overlap of two parallel spherocylinders (grey-shaded area), both of length  $L$  and radius  $R_r + R_s$ —see figure 1(b)—must be calculated. In order to obtain the depletion potential, the overlaps of excluded volumes for all orientations  $\theta$  must be added. Both integrations in (4) are computed numerically.

It is important to realize that since the present approach is exact to first order in the density of the rods for *all* values of  $R_s$ ,  $L$ , and  $R_r$ , in the limit  $L \rightarrow 0$  and  $R_r > 0$  the well-known Asakura–Oosawa [2] result for the mixture of colloids and ideal (spherical) polymer is recovered by (4). Furthermore, the present approach reproduces the exact results for the sphere–sphere depletion potential in the limit of infinitely thin needles  $R_r/L \rightarrow 0$ , but with arbitrary  $L/R_s$ , presented in [6].

### 3. Results

In figure 2(a) we present a comparison of the calculated depletion potential (curves) between a planar hard wall and a colloidal sphere with radius  $R_s = 1.85 \mu\text{m}$  immersed in sea of rods of length  $L = 203 \text{ nm}$  and radius  $R_r = 9 \text{ nm}$  and direct measurements (symbols) made using total internal reflection microscopy (TIRM) [7] for two different rod densities. The experimental system was prepared such that interactions were suppressed apart from the hard-core repulsion. The measured depletion potentials are in excellent agreement with those predicted using the present theory for the model system consisting of hard rods and a single hard sphere close to a planar hard wall. Only at very small distances from the wall are there small deviations of the measured depletion potentials from the theoretical ones, reflecting a small degree of softness



**Figure 2.** (a) Comparison between experiment (symbols) [7] and theory (curves) for the depletion potential between a planar wall and a colloidal sphere of radius  $1.85 \mu\text{m}$  in a sea of rods of length  $L = 203 \text{ nm}$  and radius  $R_r = 9 \text{ nm}$  for rod densities of  $\rho_r \approx 10$  and  $50 \mu\text{m}^{-3}$ . For clarity, the curve for the second density is shifted by  $-1$ . (b) We show for the same values of  $R_s$ ,  $L$ , and  $R_r$  and  $\rho_r = 52 \mu\text{m}^{-3}$  the depletion potential between a sphere and a hard wall (full curve). This is about double the potential between two spheres (dotted curve).

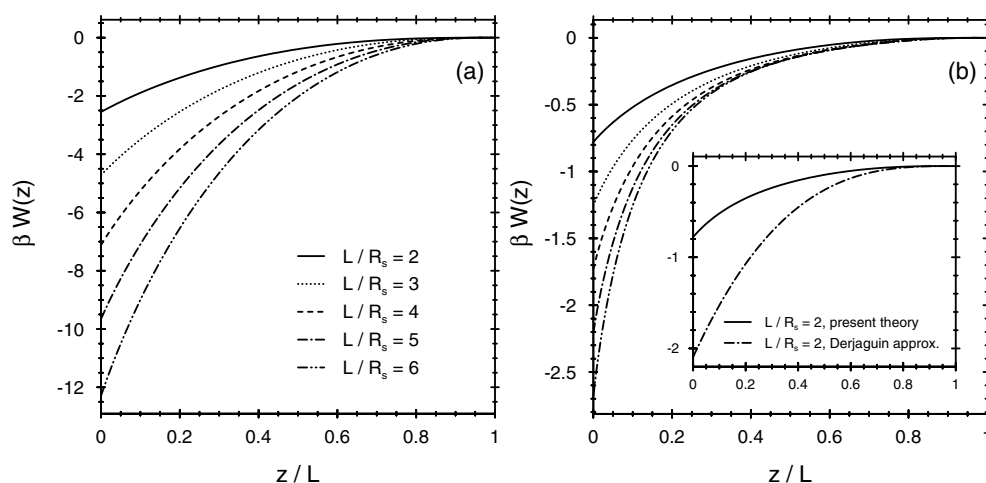
of the wall. Details of the experiment and a more detailed comparison between theory and experiment can be found in [7].

In figure 2(b) we compare for the same system as in (a) at the higher rod density  $\rho_r = 52 \mu\text{m}^{-3}$  the wall-sphere (full curve) and the sphere-sphere (dotted curve) depletion potentials. It is interesting to note that for these values of  $R_s$ ,  $L$ , and  $R_r$  the wall-sphere potential is to a very good approximation twice the sphere-sphere potential. As already noted in [6], the Derjaguin approximation (dashed and dashed-dotted curves) employed in [4, 5] provides a good account of the exact depletion potentials in the regime  $R_r \ll L \ll R_s$ . In the Derjaguin approximation the wall-sphere potential (dashed-dotted curve) is simply twice the sphere-sphere (dashed curve) potential.

Although the scaling demonstrated in figure 2(b) is valid for the Asakura-Oosawa model of a model colloid-polymer mixture at large size asymmetries [2], it is not generic for the mixture of spheres and rods. Rather, it is specific to the choice of parameters  $R_r \ll L \ll R_s$ . In this range the geometry of the excluded volumes is similar to that of the Asakura-Oosawa model and hence the scaling is to be expected. If, however, the length of the rods becomes large compared to the radius of the spheres  $L \gg R_s$ , the difference between the sphere-wall and sphere-sphere geometries becomes more pronounced—see figure 1.

As an example of this effect we compare in figure 3 the wall-sphere and sphere-sphere depletion potentials at a fixed number density  $\rho_r R_s^3 = 1$  of needles ( $R_r = 0$ ) for various aspect ratios  $L/R_s$ . As the aspect ratio  $L/R_s$  becomes larger the shape of the sphere-sphere potential changes significantly: the overlap of two long thin parallel spherocylinders (see figure 1(b)) is large only if the spheres are close together. For larger separations only rods with orientations  $\theta \approx 0$  contribute to the depletion potential.

Moreover, we find that there is no longer a simple scaling between the wall-sphere and the sphere-sphere depletion potentials. The contact values in those two cases differs by more than a factor of three for  $L/R_s = 2$  and by more than a factor of 4.5 for  $L/R_s = 6$ , the largest



**Figure 3.** Comparison between the wall–sphere (a) and the sphere–sphere (b) depletion potentials in a sea of needles ( $R_r = 0$ ) at a constant number density of needles  $\rho_r R_s^3 = 1$  for various aspect ratios  $L/R_s$ . In (a) and (b) the same curves correspond to the same parameters.

aspect ratio used in figure 3. In the inset of figure 3(b) a comparison of the sphere–sphere depletion potential for  $L/R_s = 2$  between the present theory (full curve) and the Derjaguin approximation employed in [4, 5] (dashed–dotted curve) is shown. The large deviation between results demonstrates clearly the breakdown of the Derjaguin approximation outside the regime  $R_r \ll L \ll R_s$ .

Within the framework of effective Hamiltonians for colloidal mixtures [1], the sphere–sphere depletion potentials shown in figure 3 can enable us to understand the fluid–fluid phase separation into a sphere-rich fluid and a sphere-poor fluid phase that was found by simulations [12], by DFT [13, 14], and by the free volume theory [12, 13, 15], and the fluid–solid phase separation and the wall crystallization found experimentally [16, 17].

In the case of long thin rods, an approximation that retains only the sphere–sphere depletion potential, i.e. the effective pair interaction, is expected to be sufficient to give an accurate description of the bulk phase behaviour. Many-body effective interaction potentials should be small compared to the pair potential and hence should not significantly influence the phase boundaries calculated from the effective pair potential alone.

Since the sphere–sphere potentials shown in figure 3(b) are much less attractive than the wall–sphere potentials, shown in 3(a), the adsorption of spheres at a planar hard wall at a state point in the sphere-poor phase lying close to phase separation should be very large indeed and should lead to complete wetting by the sphere-rich phase.

In summary, we have presented results of calculations of depletion potentials in a colloidal mixture of spheres and rods that are exact to first order in the rod density. These potentials can be input into an effective Hamiltonian in order to study the thermodynamic behaviour and correlation functions of the spheres in a mixture for both homogeneous and inhomogeneous situations. This procedure provides an alternative to the DFT (full mixture) route described in [13, 14].

### Acknowledgments

It is a pleasure to thank Joe Brader, Bob Evans and Markus Rauscher for stimulating and helpful discussions.

## References

- [1] Dijkstra M, van Roij R and Evans R 1998 *Phys. Rev. Lett.* **81** 2268  
Dijkstra M, van Roij R and Evans R 1999 *Phys. Rev. Lett.* **82** 117  
Dijkstra M, van Roij R and Evans R 1999 *Phys. Rev. E* **59** 5744
- [2] Asakura S and Oosawa F 1954 *J. Chem. Phys.* **22** 1255
- [3] Asakura S and Oosawa F 1958 *J. Polym. Sci.* **32** 183
- [4] Mao Y, Cates M E and Lekkerkerker H N W 1995 *Phys. Rev. Lett.* **75** 4548
- [5] Mao Y, Cates M E and Lekkerkerker H N W 1997 *J. Chem. Phys.* **106** 3721
- [6] Yaman K, Jeppesen C and Marques C M 1998 *Europhys. Lett.* **42** 221
- [7] Helden L, Roth R, Koenderink G H, Leiderer P and Bechinger C 2002 submitted
- [8] Götzelmann B, Roth R, Dietrich S, Dijkstra M and Evans R 1999 *Europhys. Lett.* **47** 398
- [9] Roth R, Evans R and Dietrich S 2000 *Phys. Rev. E* **62** 5360
- [10] Roth R, van Roij R, Mecke K R, Andrienko D and Dietrich S 2002 *Phys. Rev. Lett.* **89** 088301
- [11] Evans R 1979 *Adv. Phys.* **28** 143
- [12] Bolhuis P and Frenkel D 1994 *J. Chem. Phys.* **101** 9869
- [13] Schmidt M 2001 *Phys. Rev. B* **63** 050201
- [14] Brader J M, Esztermann and Schmidt M 2002 *Phys. Rev. E* **66** 031401
- [15] Vliegthart G A and Lekkerkerker H N W 1999 *J. Chem. Phys.* **111** 4153
- [16] Vliegthart G A, van Blaaderen A and Lekkerkerker H N W 1999 *Faraday Discuss.* **112** 173
- [17] Koenderink G H, Vliegthart G A, Kluijtmans S G J M, van Blaaderen A, Philipse A P and Lekkerkerker H N W 1999 *Langmuir* **15** 4693