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Entropic interactions in mixtures of colloids and non-ionic polymers

Abstract In binary colloidal mixtures, depletion forces of purely entropic origin play an important role besides interaction like Coulomb or van der Waals interactions. We have measured the potential energy between a single, negatively charged polystyrene sphere ($R = 1.5\ \mu$m) close to an equally charged wall in the presence of uncharged polymer coils ($r = 150$ nm) by means of total internal reflection microscopy. Our results show a strong dependence on the polymer concentration n and can be explained by the occurrence of depletion forces. Comparison of our data with a theory which is only correct in first-order n shows good agreement. We also present first observations in a system with an increased particle/polymer size ratio ($R = 5\ \mu$m, $r = 0.15\ \mu$m) where higher-order terms in the depletion potential become important.

Key words Depletion forces – Binary mixtures – Polymers – Evanescent waves – Total internal reflection microscopy

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Introduction

When colloidal particles are suspended in a fluid also containing smaller particles, e.g. other colloids, micelles, or polymer coils, their mutual interaction may be considerably altered owing to the occurrence of depletion forces. The principle of these purely entropic forces is easily understood when, for example, a hard sphere of radius R suspended in a fluid containing smaller spheres of radius r (the latter are referred to as macromolecules in the following) in front of a wall at distance z is considered (see Fig. 1). For z smaller than the diameter of the macromolecules they are expelled from the region between the sphere and the wall, which depletes the concentration of macromolecules in this region compared to that of the bulk and gives rise to an effective osmotic pressure, causing a net attraction between the sphere and the wall. This effect remains when the wall is replaced by another hard sphere. The first quantitative theoretical explanation was given by Asakura and Oosawa [1]. The depletion force is predicted to be always attractive, non-zero only for distances $z < 2r$, and proportional to the overlapping excess volume ΔV (see Fig. 1). The depletion potential between a sphere of radius R at distance z above a flat surface in the presence of macromolecules of radius r and particle density n is predicted to be

$$\frac{\Phi(z)}{k_B T} = n \cdot \pi \cdot \left[4Rr^2 + \frac{4}{3}r^3 + \frac{1}{3}z^3 + (R-r)z^2 - 4Rrz\right] \times \Theta(2r - z) \equiv \Phi_{\mathrm{depl}} \qquad (1)$$

where Θ is the Heaviside step function. According to this theory, which dates back to 1954 and treats the macromolecules as particles with no mutual interaction, depletion forces should be always attractive. This, however, is only valid for very small n. Considerable deviations are predicted if higher-order terms in the density (or equivalently more realistic density profiles) of the macromolecules at contact with the sphere and the wall are considered [2, 3]. As a result, in addition to the repulsive parts, attractive parts in the depletion forces are also predicted which are most pronounced for high n and large R/r ratios, respectively.

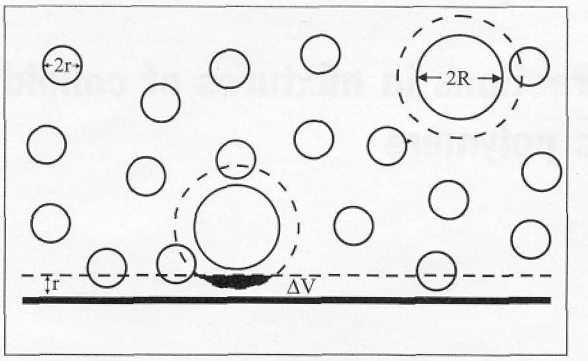

Fig. 1 Illustration of the depletion interaction in a binary sphere mixture. The *dashed region* corresponds to the area not accessible to the centers of smaller spheres

While there are a lot of experimental results which demonstrate the existence of depletion effects, e.g. by measuring phase diagrams, flocculation rates, or phase separation phenomena [4], only a few direct measurements of depletion forces have been reported. This may be largely due to the necessity to measure very small forces which are typically on the order of nano- or even pico-Newtons. Accordingly, it was the invention of the surface force apparatus and the atomic force microscope which made direct measurements of depletion forces possible within recent years [5, 6]. It is not clear, however, to what amount those measurements are intrusive to the investigated systems.

The first non-intrusive distance-dependent depletion force measurements between a free suspended colloidal particle and a flat surface were performed by total internal reflection microscopy (TIRM). With this technique, which will be discussed in more detail below, measurements on both, systems of highly charged [7–9] and (very recently) uncharged macromolecules [10] were successful.

In this work we present a systematic study of distance-dependent depletion potentials between a single sphere and a flat surface in the presence of uncharged macromolecules. While for the size ratio $R/r = 10$ used in these experiments the depletion force is found to be always attractive, we further present a first result for a system with $R/r = 33$ which also demonstrates repulsive interactions.

Experimental

We used TIRM [11, 12] to measure the potential of a colloidal sphere immersed in a fluid of coiled, non-ionic polymer chains close to a glass surface. The method of TIRM and our setup is described only in brief; for details we refer to the literature [11, 13, 14].

When light is reflected at a solid/fluid interface at an angle $\theta > \theta_C$ (where θ_C is the critical angle of total internal reflection) (Fig. 2), an evanescent wave is formed whose intensity decays exponentially perpendicular to the interface with a decay length β^{-1} which depends on the incident angle θ, the wavelength of the light beam, and the refractive indices at the interface. When an object which scatters light, e.g. a colloidal sphere, approaches the surface close enough to enter the evanescent field, frustrated total reflection will occur. The scattering intensity I of the colloidal sphere is then proportional to that of the evanescent wave and can be written as $I = I_0 e^{-\beta z}$ [15]. Measuring I (which fluctuates owing to Brownian motion of the sphere) as a function of time thus provides a sensitive and non-intrusive method to determine z. In thermal equilibrium the sphere-wall-interaction potential $\Phi(z)$ can be calculated as a function of z from the probability distribution $p(z)$ by using the Boltzmann distribution. To obtain the potential energy as a function of absolute distance it is necessary to determine I_0. This is done by measuring the intensity of a particle at contact with the glass surface. This can be achieved by increasing the salt concentration above 2 mM, which leads to an irreversible sticking of the sphere to the surface owing to van der Waals forces.

Figure 2 shows a schematic representation of our TIRM setup. A cell was composed of two fused silica glass plates separated by a spacer ($d = 1$ mm, not shown). After assembling the cell, a BK7 prism was optically matched to one of the glass plates. Then the cell was connected to a closed circuit which contained the colloidal suspension. We used monodisperse polystyrene (PS) spheres with radius $R = 1.5\ \mu$m (PS1.5) and 5 μm (PS5), respectively, which are suspended in water. The particles are charge stabilized with sulfate surface groups. Only highly diluted suspensions with a particle density less than 0.5 mm^{-3} were used to guarantee that only a single particle was in the field of view and contributed to the scattering signal. The suspension was pumped through the circuit, which contained an ion exchange resin and an electrical conductivity probe to control the ionic strength of the suspension. After adjusting the desired ionic strength, a given amount of poly(ethylene oxide) (PEO) with a molecular weight $M_w = 2 \times 10^6$ was added. The maximum polymer concentration used in our experiments was 25.5 $\mu\mathrm{m}^{-3}$, which is smaller by a factor of 2.4 than a critical concentration n^*. Only below n^* (corresponding to the diluted case) can the polymer molecules be regarded as hard spheres [16].

The evanescent wave was obtained by reflecting a HeNe laser ($\lambda = 632.8$ nm, 10 mW) from the glass/fluid interface at an angle θ which corresponded to a penetration depth of $\beta^{-1} = 0.845\ \mu$m. It should be mentioned that special care has to be taken in the determination of the penetration depth, which is calculated from the incident angle and the refractive indices of the prism, respectively. Deviations of less than 1% in the refractive indices or in the incident angle can give rise to changes of more than 100% in the penetration depth and explains previous differences between experimentally and theoretically determined Debye lengths [17]. This experimental uncertainty, however, is eliminated in our present TIRM setup by an improved resolution of the angle of incidence.

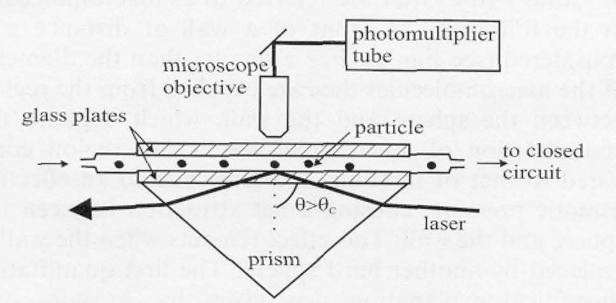

Fig. 2 Schematic total internal reflection microscopy setup used in our experiment

No detectable change in the penetration depth and the electrical conductivity was observed after PEO was added to the suspension. The scattered intensity was collected by a microscope objective lens (Plan L50×, Leitz) and focused onto a photomultiplier tube. To obtain sufficient data and to minimize statistical errors, the scattering intensity of a particle was sampled over at least 1000 s at a sampling rate of 50 Hz.

Results and discussion

Without depletion forces the potential of a negatively charged PS sphere above a glass plate is composed of two parts: at larger distances z the potential increases linearly because for these z gravity is the dominant force. Towards smaller z the potential increases exponentially owing to the electrostatic interaction between the negatively charged PS sphere and the fused silica surface, which is also negatively charged when in contact with water [18]. In this case the potential acting on the sphere can be written as

$$\frac{\Phi(z)}{k_B T} = B \cdot e^{-\kappa z} + G \cdot z \equiv \Phi_0 \qquad (2)$$

where B is a constant including the surface charge of the particle and the wall, respectively, $G = (\rho_p - \rho_w)Vg$ is the weight of the particle with ρ_p and ρ_w being the density of the particle and water, V the volume of the sphere, and g the acceleration due to gravity [11, 13]. This potential is shown in the inset of Fig. 3 (symbols). The solid line is the fit curve according to Eq. (2) with the two fit parameters found to be $B = 16.5$ and $\kappa^{-1} = 33$ nm, the latter being in agreement with the value expected from the electrical conductivity measurement. The particle weight G was calculated by inserting the radius of the PS sphere obtained by electron microscopy ($R = 1.5$ μm), the density of the PD sphere and water, respectively. This good agreement between theory and experimental data is found by all groups using TIRM [10, 12, 13, 19].

If polymer is added to the system the potential is modified. Figure 3 shows the potentials for $n = 0$ (squares), $n = 10.2$ μm^{-3} (circles), $n = 12.7$ μm^{-3} (triangles), and $n = 25.5$ μm^{-3} (diamonds). With increasing polymer concentration an additional attractive part in the interaction potential develops which finally forms a pronounced potential well close to the surface. Since the depth of this potential well for the measurements at polymer density $n = 12.7$ μm^{-3} (triangles) and $n = 25.5$ μm^{-3} (diamonds) is about 3–5 times $k_B T$, the particle does not leave the well during our measuring time and therefore no data outside the well were collected. To demonstrate that these potentials can be explained with depletion forces, we compare them with the theory of Asakura and Oosawa. Accordingly, we assume the total interaction to be

$$\Phi_{total}(z) = \Phi_0(z) + \Phi_{dept}(z). \qquad (3)$$

Since no change in the electrical conductivity and the effective particle weight G was observed by adding PEO to the system, $\Phi_0(z)$ is assumed to be independent of the polymer concentration n, which was determined by weighing the amount of polymer added to the system before each measurement. Thus the only free parameter in Eq. (3) is the polymer radius r. Best agreement for all

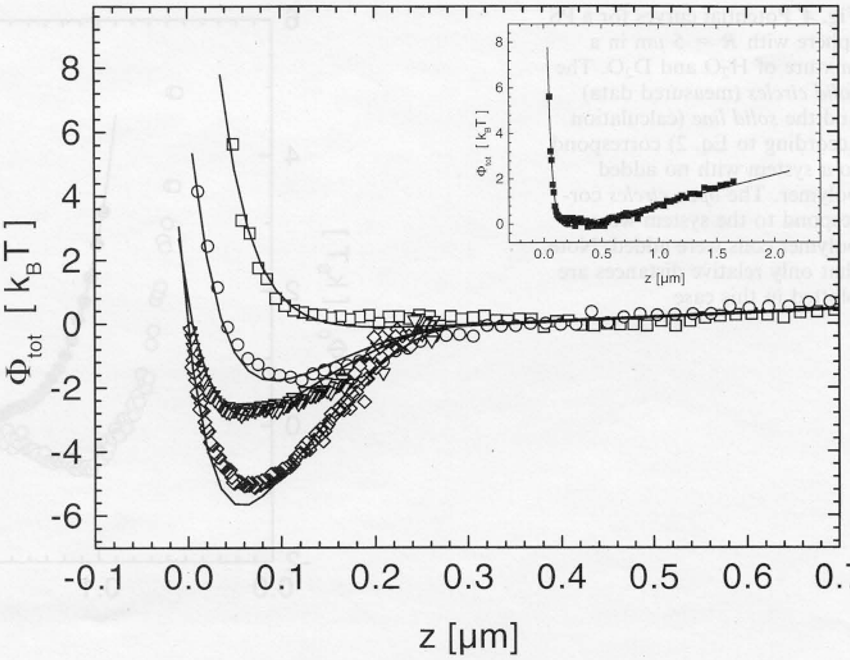

Fig. 3 Potential curves (symbols) of a PS sphere with $R = 1.5$ μm as a function of its distance z from a flat surface for polymer concentration $n = 0$ (*squares*), 10.2 μm^{-3} (*circles*), 12.7 μm^{-3} (*triangles*), and 25.5 μm^{-3} (*diamonds*). The *solid lines* are calculations according to Eq. (3)

data sets between theory and experiment was achieved for $r = 150$ nm, as demonstrated by the solid lines in Fig. 3. As can be seen, our data are in good agreement with what is predicted by Eq. (3).

The characteristic length scale of the PEO polymer is its radius of gyration, which is determined for the molecular weight used in this experiments to be $r_G = 101$ nm [16]. The value of r_G is of the same order of magnitude yet distinctly smaller than the radius r. However, it is not clear whether r used in Eq. (1) has to be identical to r_G because Eq. (1) is based on the assumption of rigid spheres. If the interaction of the polymer is not perfectly hard-sphere-like, r is expected to be larger than r_G. This idea is also supported by the results of Ohshima et al. [20], who used the same polymer in their experiments. Their experimental values for the maximum depletion force are larger than expected if one assumes $r = r_G$. If we replot their results with $r = 150$ nm, however, almost perfect agreement between theory and their data is obtained.

As has been mentioned already, depletion forces do not always have to be attractive but may also contain repulsive parts. From a virial expansion analysis, Mao et al. [3] obtained an expression for a repulsive barrier in the depletion potential. For the R/r ratio used so far, however, this barrier is below the resolution limit of TIRM an justifies a posteriori the validity of the Asakura-Oosawa approximation in our experiments. In contrast, if the size ratio of the particles is sufficiently large, this barrier increases above our detection threshold and should become visible.

Therefore we repeated the experiments described above, but with PS spheres of $R = 5$ μm in radius. Owing to the increased weight of those particles (which is about 37 times larger than before), it was necessary to increase their buoyancy to allow the PS spheres to have large enough thermally driven vertical excursions from the surface. By suspending the particles in a mixture of deuterated water and normal water, a reduction of the weight by a factor of 8.5 was achieved. Figure 4 shows a first result for this system. Only relative distances were plotted because the scattering intensity I_0 at particle-wall contact was not known in this case. The solid symbols correspond to the potential without added polymers, i.e. without depletion forces. The solid line is the expected potential according to Eq. (2) with κ obtained from the electrical conductivity measurement and G calculated from particle size, density of the solvent and the sphere.

After adding some amount of PEO polymer the potential is considerably changed, as indicated by the open symbols. Similar to the case with the smaller PS spheres, the potential minimum in the presence of PEO is shifted to smaller z values owing to attractive depletion forces. Unlike in Fig. 3, however, where all the curves for increasing z approximate the same linear part of the potential from below, this is not true in Fig. 4. The slope of the potential at larger separation distances is increased compared to that with no PEO until it approaches the linear part from above. This feature, which has never been observed by us in the case of smaller PS spheres, gives rise to a small repulsive

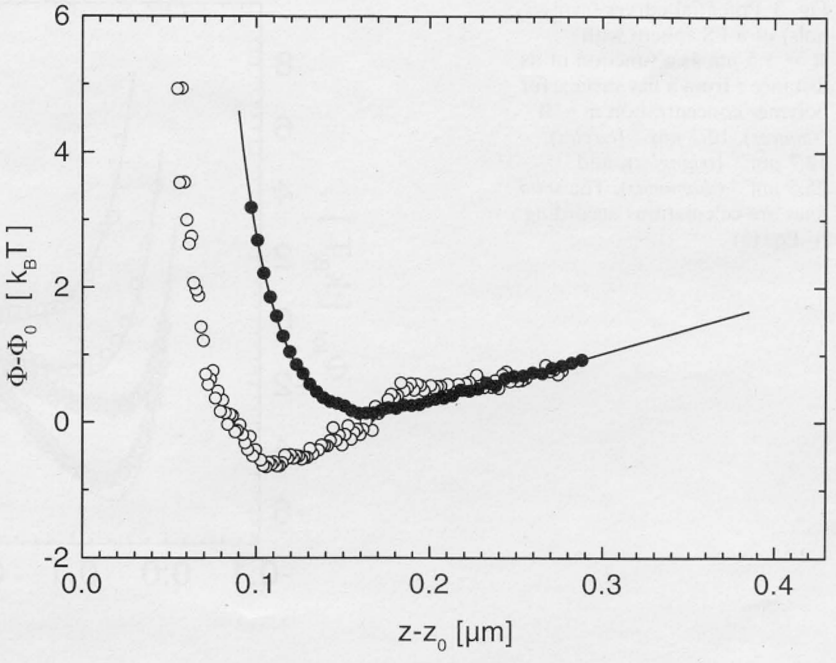

Fig. 4 Potential curves for a PS sphere with $R = 5$ μm in a mixture of H_2O and D_2O. The *solid circles* (measured data) and the *solid line* (calculation according to Eq. 2) correspond to a system with no added polymer. The *open circles* correspond to the system were polymer coils were added. Note that only relative distances are plotted in this case

barrier of about 1 k_BT and is a first indication of the influence of higher-order terms.

Systematic investigations are in progress to clearly demonstrate the occurrence of repulsive depletion effects in purely entropic driven systems and to compare those results with existing theories.

Conclusion

We have measured the potential energy of a 1.5 μm PS sphere close to a surface in the presence of smaller macromolecules. We presented systematic measurements as a function of polymer density and found a strong dependence of the potentials from that parameter. We found that our results can be explained completely in terms of the theory of Asakura and Oosawa, which predicts a purely attractive depletion interaction. The polymer radius determined for the description of depletion interactions is larger than the radius of gyration r_G and agrees with the results of other authors. Finally, we presented a first result with 5 μm PS spheres which indicates the presence of repulsive depletion forces.

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References

1. Asakura S, Oosawa F (1954) J Chem Phys 22:1255
2. Götzelmann B, Evans R, Dietrich S (1998) Phys Rev E 57:6785
3. Mao Y, Cates ME, Lekkerkerker HNW (1995) Physica A 222:10
4. Russel WB, Saville DA, Schowalter WR (1989) In: Batchelor GK (ed) Colloidal dispersions. Cambridge University Press, Cambridge, pp 349
5. Richetti P, Kekicheff P (1992) Phys Rev Lett 68:1951
6. Milling A, Biggs S (1995) J Colloid Interface Sci 170:604
7. Sharma A, Walz JY (1996) J Chem Soc Faraday Trans 92:4997
8. Sharma A, Tan SN, Walz JY (1997) J Colloid Interface Sci 191:236
9. Sharma A, Tan SN, Walz JY (1997) J Colloid Interface Sci 190:392
10. Rudhardt D, Bechinger C, Leiderer P (1998) Phys Rev Lett 81:1330
11. Prieve DC, Luo F, Lanni F (1987) Faraday Discuss Chem Soc 83:297
12. Walz JY (1997) Curr Opin Colloidal Interfaces Sci 2:600
13. Prieve DC, Bike SG, Frej NA (1990) Faraday Discuss Chem Soc 90:209
14. Haughey D, Earnshaw JC (1998) Colloids Surf A 136:217
15. Prieve DC, Walz JY (1993) Appl Opt 32:1629
16. Devanand K, Selser JC (1991) Macromolecules 24:5943
17. Rudhardt D, Bechinger C, Leiderer P (1998) Prog Colloid Polym Sci 110:37
18. Hunter RJ (1988) The zeta potential in colloid sciences. Academic Press, London
19. Haughey D, Earnshaw JC (1996) Colloids Surf A 106:237
20. Ohshima YN, Sakagami H, Okumoto K, Tokoyoda A, Igarashi T, Shintaku KB, Toride S, Sekino H, Kabuto K, Nishio I (1997) Phys Rev Lett 78:3963