



## Depletion-induced phase separation in colloid– polymer mixtures

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### Abstract

Phase separation can be induced in a colloidal dispersion by adding non-adsorbing polymers. Depletion of polymer around the colloidal particles induces an effective attraction, leading to demixing at sufficient polymer concentration. This communication reviews theoretical and experimental work carried out on the polymer-mediated attraction between spherical colloids and the resulting phase separation of the polymer–colloid mixture. Theoretical studies have mainly focused on the limits where polymers are small or large as compared to the colloidal size. Recently, however, theories are being developed that cover a wider colloid–polymer size ratio range. In practical systems, size polydispersity and polyelectrolytes (instead of neutral polymers) and/or charges on the colloidal surfaces play a role in polymer–colloid mixtures. The limited amount of theoretical work performed on this is also discussed. Finally, an overview is given on experimental investigations with respect to phase behavior and results obtained with techniques enabling measurement of the depletion-induced interaction potential, the structure factor, the depletion layer thickness and the interfacial tension between the demixed phases of a colloid–polymer mixture.

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*Keywords:* Depletion; Polymers; Colloids; Phase behavior; Polydispersity; Charges

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## 1. Introduction

Depletion interaction between colloidal spherical particles due to non-adsorbing polymers is a subject that has gained a gradually increasing amount of attention since the 1980s. Understanding depletion phenomena is relevant in many ways. It first helps to understand when and why phase separation occurs in mixtures of polymers and colloids, which are often jointly present in applications. Furthermore, depletion-induced phase separation is a way of concentrating colloidal dispersions in a convenient way. If the colloids and/or polymers are polydisperse, depletion-induced phase separation can be used for (large-scale) size fractionation in industrial applications. Besides these practical reasons, depletion studies provide an accessible way of changing the range of the interaction potential between the colloidal particles by varying the size ratio. This is helpful for studying the properties of liquids, as well as crystallization and gelation phenomena, using colloid systems instead of low-molar-mass substances.

This communication aims at qualitatively describing the achievements reached in understanding depletion in polymer–(spherical) colloid mixtures. The focus is on the description of the physical properties of mixtures of polymers and colloids in a common solvent, in which the polymers do not adsorb onto the colloids. We restrict

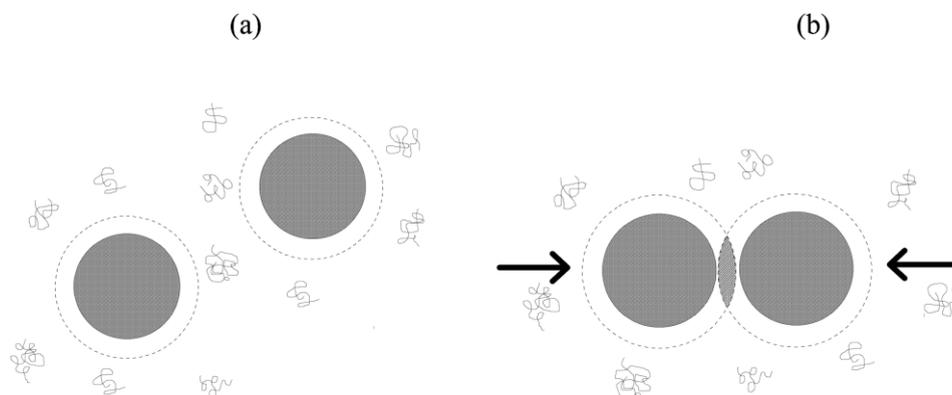


Fig. 1. Schematic picture of two colloidal spheres in a polymer solution with non-adsorbing polymers. The depletion layers are indicated by short dashes. When there is no overlap (a) the osmotic pressure on the spheres due to the polymer solution is isotropic. For overlapping depletion layers (b) the osmotic pressure on the spheres is unbalanced; the excess pressure is indicated by the arrows.

ourselves to the case of spherical colloids, while noting that the colloidal shape (spherical, rod-like, platelet-like) strongly affects the properties of a polymer–colloid dispersion. Attention is given to the interaction and the resulting phase separation. Phase separation kinetics are omitted here; the interested reader is referred to a review by Poon and Haw [1] on the structure formation and phase separation kinetics.

The mechanism that is responsible for depletion interaction can be explained on the level of a pair of spherical colloids in a solution of non-adsorbing polymers, as depicted in Fig. 1. There is a concentration gradient in the average equilibrium polymer-segment concentration profile when going from the bulk (the maximum segment concentration) to the sphere surface (where the concentration is zero).

A popular simplification of the concentration profile is to replace it with a step function (a Heaviside function). One part of the step function now consists of a layer in which the polymer segment concentration equals zero, denoted as the depletion layer, as indicated by the (*dashed*) layers around the spheres in Fig. 1. Outside this layer the polymer segment concentration equals the bulk polymer segment concentration. The depletion layer results in an osmotic pressure gradient. For a single sphere this pressure is isotropic (Fig. 1a). However, if the depletion layers overlap, the osmotic pressure becomes anisotropic and there is a net osmotic force, as indicated by the arrows (Fig. 1b). In this case, for ideal (the polymer segments do not ‘feel’ other segments) polymers, the effective free energy of interaction equals the overlap volume (indicated by the hatched region) multiplied by the osmotic pressure. If the sphere is big enough, it induces a phase transition in a macroscopic dispersion upon exceeding a certain concentration of colloidal spheres and polymers. A colloid-enriched phase is then in equilibrium with a polymer-enriched phase.

The outline of this review is as follows. After an explanation of the mechanism itself, we discuss its effect on mixtures of monodisperse hard spheres and neutral polymers in Section 2. The relevant theoretical approaches are explained on a qualitative level and the effect of the polymer/colloid size ratio on the interaction potential and the phase diagram is discussed. Theoretical studies on the effect of polydispersity on depletion-induced attraction and phase separation, often encountered in experimental systems, are discussed in Section 3. In Fig. 4 attention is given to the effect of charges on the colloidal sphere surface and polyelectrolytes on the effective depletion interaction. This brings the study closer to practice, where the particles often have a net charge and experience a Van der Waals attraction. Experimental work is discussed in Section 5 with a focus on the relation with theoretical predictions, followed by the main conclusions and outlook in Section 6.

## 2. Depletion interaction in monodisperse and neutral polymer–colloid mixtures: theory

### 2.1. An exact result: the interaction between parallel plates due to ideal polymer chains

In 1954, Asakura and Oosawa showed that two plates immersed in a solution of ideal non-adsorbing polymers attract one another [2]. This was the first theory on depletion interaction. Using statistical mechanics they derived an expression for the partition coefficient: the polymer concentration between the plates divided by the concentration outside the plates, by solving the Edwards diffusion equation for polymers. The term diffusion is used, as there is an analogy with a diffusion process; the random walk conformation of a polymer chain can be described as a diffusion process. Consequently, the concentration difference leads to an expression for the pressure difference outside and between the plates. The partition function thus allows calculation of the osmotic pressure difference between the plates as a function of the distance between the plates,  $h$ . Integration of this force then yields the interaction potential  $W(h)$ . The result is plotted as a function of  $h/R_g$  as the full curve in Fig. 2, where  $R_g$  is the radius of gyration of the polymer.

### 2.2. Penetrable hard sphere (PHS) approach

In a following paper, Asakura and Oosawa [3] indicated along what lines depletion theories could be extended. In order to describe the interaction between two spheres in a solution with ideal non-adsorbing polymers, they proposed simplification of an ideal polymer chain by replacing it with a penetrable hard sphere (PHS), also denoted as a non-additive hard sphere. A PHS is a sphere that is hard for a colloidal particle, but which can freely permeate through another PHS. This leads to a simple depletion potential between two spheres:

$$\frac{W(h)}{kT} = -\frac{2}{3}\pi n_p a_{\text{PHS}}^3 \left(1 - \frac{h}{2a_{\text{PHS}}}\right)^2 \left(2 + \frac{3R}{a_{\text{PHS}}} + \frac{h}{2a_{\text{PHS}}}\right) \quad (1)$$

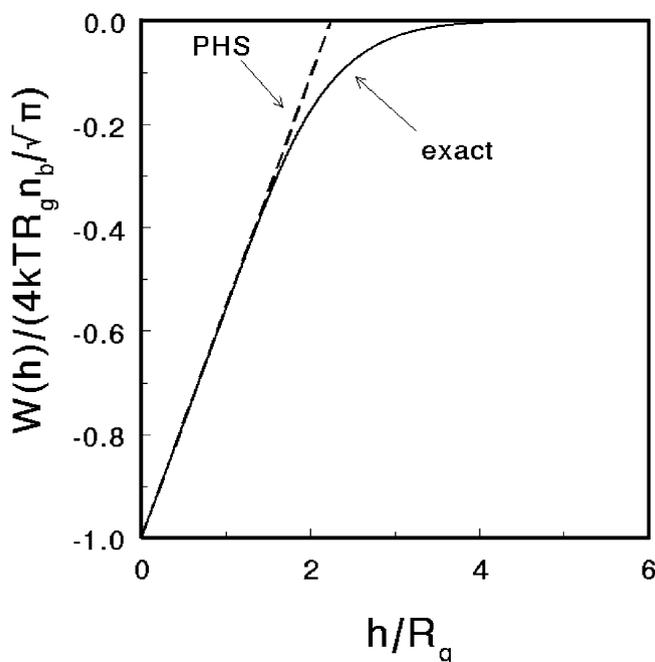


Fig. 2. Interaction potential  $W(h)$  between two plates. The full curve is the exact result [2] and the dashed line is the PHS result.

where  $n_p$  is the bulk concentration of polymers,  $a_{\text{PHS}}$  is the radius of a PHS, and  $R$  is the radius of the colloidal particle. The PHS concept was independently developed and extended by Vrij [4]. It can be shown that the radius of a PHS ( $a_{\text{PHS}}$ ) that enables the minimum of the PHS-induced interaction potential [the plate contact value  $W(h=0)$ ] to match with the minimum of the ‘exact’ potential, plotted in Fig. 2, equals  $2R_g/\sqrt{\pi}$ , which is of the order of magnitude of the radius of gyration of the polymer.

Vrij [4] used the PHS concept (in the literature this is often referred to as the AO model) to calculate the interaction between two spheres. The stability limit of a dispersion containing colloidal spheres mixed with ideal non-adsorbing polymer chains that can be described using the second osmotic virial coefficient  $B_2$ , which is related to the interaction potential via:

$$B_2 = 2\pi \int_0^\infty dr \left( 1 - \exp\left(-\frac{W(r)}{kT}\right) \right) \quad (2)$$

where  $r$  is the center-to-center distance between the spheres. De Hek and Vrij [5] used a simple argument to estimate the spinodal [the line in parameter space polymer vs. colloid concentration where demixing into two phases (colloid-rich and polymer-rich) occurs spontaneously]. An expansion of the osmotic compressibility

at the spinodal in the limit of very low colloid volume-fractions leads to the relation:  $0 = 1 + 2B_2\phi_{sp}$ , which relates the polymer concentration (which determines  $B_2$ ) to the volume fraction of colloids at the spinodal,  $\phi_{sp}$ .

In the early 1980s, Gast et al. [6] proposed a pair-wise perturbation theory for the free energy of a mixture of colloids and PHSs. Using the hard-sphere system as a reference, they could calculate the phase behavior from the free energy. This extension of the PHS theory made it possible to assign the nature (i.e. colloidal gaseous, liquid or solid state<sup>1</sup>) of the coexisting phases. For small values of  $a_{PHS}/R$ , increasing the PHS concentration broadens the hard sphere fluid–solid coexistence region. The work of Gast et al. [6] thus revealed that the PHS model predicts a gas–solid coexistence if the PHSs are much smaller than the colloidal spheres ( $a_{PHS} \ll R$ ), with a gas–liquid branch lying inside the unstable regions. Upon increasing the  $a_{PHS}/R$  ratio the gas–liquid coexistence curve crosses the gas–solid curve, i.e. for large  $a_{PHS}/R$  ratios a gas–liquid coexistence is expected.

A semi-grand canonical treatment was proposed by Lekkerkerker [7], who developed an osmotic equilibrium model for a PHS and colloid mixture, taking into account the effective accessible volume for the PHSs. In this theory polymer partitioning between the phases is taken into account. A polymer plus colloid mixture is in equilibrium with a polymer solution, separated by a semi-permeable membrane through which polymers can permeate but colloids cannot. The resulting phase diagrams calculated by Lekkerkerker et al. [8] showed that for  $a_{PHS}/R < 0.3$  coexisting gas–solid phases are predicted, whereas at low colloid volume fractions a gas–liquid coexistence is found for  $a_{PHS}/R > 0.3$ . In Fig. 3 the phase diagram for  $a_{PHS}/R = 0.2$  (a) and  $a_{PHS}/R = 0.5$  (b) are plotted as illustrations. The colloid volume fraction is denoted as  $\phi_c$  and the polymer concentration as  $c_p$ . The asterisk refers to the overlap concentration of polymers, i.e. the concentration at which the coils have a volume fraction unity. Furthermore, for a ratio of  $a_{PHS}/R$  near 0.4 a triple gas–liquid–solid phase region is predicted. This was also confirmed for instance by the data of Poon et al. [9], reproduced in Fig. 4.

Using the theory of Lekkerkerker et al. [8], it is also possible to calculate the tie-lines along which the system demixes. This makes it very suitable to compare the theory with experimental phase boundaries. Recently, Dijkstra et al. [10] derived an expression for the effective two-body Hamiltonian, which makes it possible to determine the phase diagrams for PHSs more precisely. The results of Dijkstra et al. [10] showed that the free volume theory is quantitatively very accurate for  $a_{PHS}/R < 0.5$ . Above that ratio the osmotic equilibrium theory overestimates the phase boundary as compared to PHS simulation results [10].

The osmotic equilibrium theory for colloidal spheres mixed with PHSs was tested with computer simulations on a dispersion of spheres immersed in a solution of ideal lattice polymer chains by Meijer and Fenkel [11]. Their simulation results showed that for small values of  $a_{PHS}/R$  the agreement with the free volume PHS theory of Lekkerkerker et al. [8] is very good. Deviations appear for larger values

<sup>1</sup> This terminology refers to the distance correlation function for the colloidal particles, which is compared to the respective function in classical statistical thermodynamics of atomic systems [46].

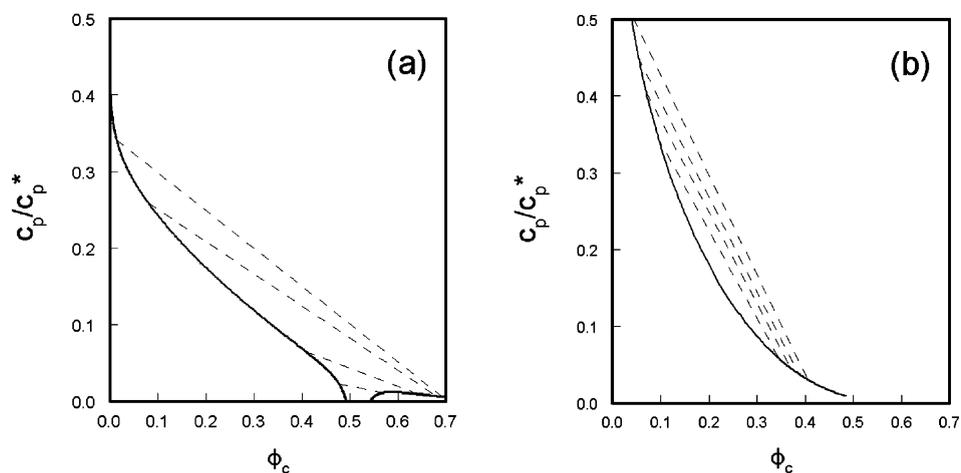


Fig. 3. Phase diagram of a polymer–colloid mixture with the polymers modeled as PHSs for a size ratio  $a_{\text{PHS}}/R=0.2$  (a) and 0.5 (b). Illustrative tie-lines are inserted as dashes.

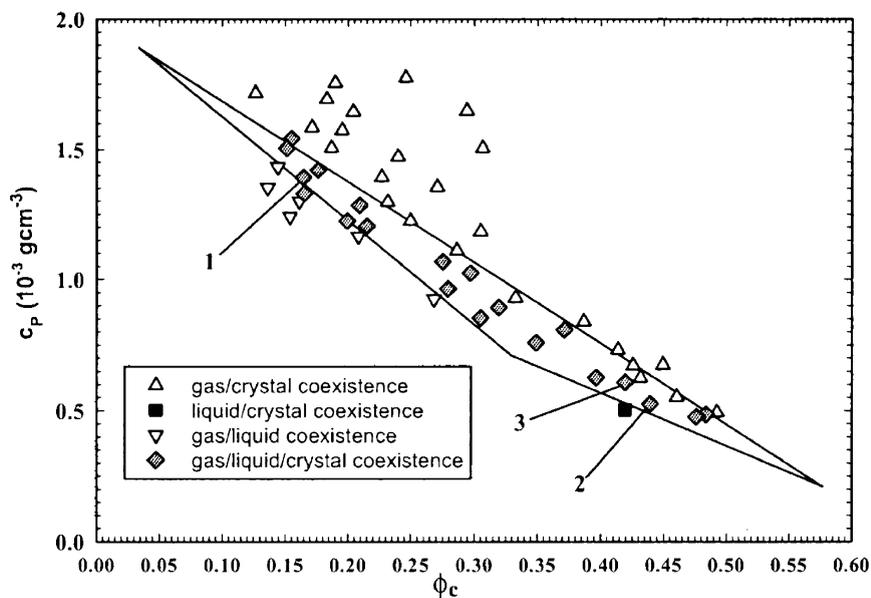


Fig. 4. Experimental phase diagram for a size ratio  $R_g/R=0.37$  from Poon et al. [9] in which a three-phase coexistence was found. Reprinted from Poon, W.C.K., Renth, F., Evans, R.M.L., Fairhurst, D.J., Cates, M.E., Pusey, P.N., Phys. Rev. Lett. 83 (1999) 1239. Copyright (1999) of the American Physical Society. Reprinted with permission.

of  $a_{\text{PHS}}/R$ . It is clear that the properties of polymers are oversimplified when they are regarded as PHSs. Besides that, in the PHS model it is customary to take the effective excluded volume of a polymer near a plate. Thus, for  $a_{\text{PHS}}$  a value of  $2R_g/\sqrt{\pi}$  (or, as is often found in the literature,  $R_g$ ) is usually taken, in agreement with the theory of Asakura and Oosawa [2].

Thermodynamically, the proper choice for  $a_{\text{PHS}}$  is the depletion layer thickness  $\Delta$ . The depletion layer thickness is defined such that the negative adsorption around a sphere immersed in a polymer solution is identical to that of a sphere in a dispersion with PHSs [12]. The quantity  $\Delta$  can thus be calculated from the negative adsorption of polymer segments around the colloidal particle or from the free energy of immersion of a colloidal particle in a polymer solution [13]. In order to do so, the polymer density profile is required. The polymer density of ideal polymer segments near a single plate was calculated by Eisenriegler [14] and yields  $\Delta = 2R_g/\sqrt{\pi}$ . Taniguchi et al. [15] and Eisenriegler et al. [16] calculated the ideal polymer concentration profile around a single sphere, leading to the following expression for the depletion layer thickness  $\Delta$  as a function of  $q = R_g/R$ :

$$\frac{\Delta}{R_g} = \frac{1}{q} \left[ \left( 1 + \frac{6q}{\sqrt{\pi}} + 3q^2 \right)^{1/3} - 1 \right] \quad (3)$$

and the result is plotted in Fig. 5. Eq. (3) was recently derived by Louis et al. [13] from the free energy of immersing a sphere into an ideal polymer solution. For  $R_g/R < 0.3$ ,  $\Delta$  still is of the order of  $R_g$ , while it strongly decreases for  $R_g/R > 0.3$ . This clearly illustrates the limitations of the ‘classical’ PHS approach. It may thus be concluded that replacing the ideal polymers by PHSs with a radius of the order of  $R_g$  is only valid in the so-called ‘colloid limit’, where  $R_g \ll R$ .

An interesting application of the PHS model is a recent computation of the properties of the interface in a phase-separated colloid–PHS dispersion by Brader and Evans [17]. They used a density functional approach to compute the density profiles of the interface and the surface tension  $\gamma$ . When scaled properly, the magnitude of the surface tension can be compared with that of a simple liquid, showing that the generally accepted scaling relation  $\gamma \approx kT/\xi_i^2$ , with  $\xi_i$  the interfacial width, which is related to the size of the relevant particles, also holds for demixed polymer–colloid mixtures.

### 2.3. Mean-field approaches

In the previous section the validity of the PHS model for polymers was discussed. It has been shown in the past that the PHS model works well in the limit  $R_g \ll R$ , but becomes worse as the radius of gyration has the same order of magnitude as the colloid radius. For  $R_g \geq O(R)$  the details of polymer physics should be described in a better way to quantify the depletion interaction. Furthermore, the polymers were assumed to be ideal in Sections 2.1 and 2.2. In practice, polymers interact due to mutually excluded volumes of the polymer segments, which affects the thermo-

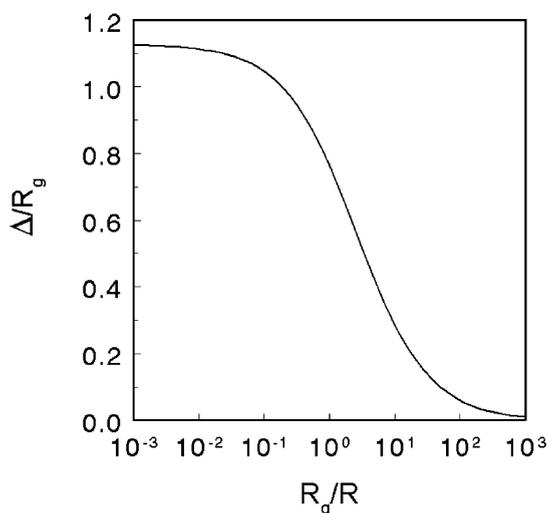


Fig. 5. Depletion layer thickness  $\Delta$ , normalized with  $R_g$ , as a function of the ratio  $R_g/R$ .

dynamic properties of the polymer solution significantly as compared to ideal polymer solutions. Classically, the insights into polymer physics have increased tremendously through the development of mean-field theories, which allow both inclusion of excluded volume interactions and give insights into details in the configurations of polymers. Mean-field treatments for depletion interaction were first proposed by De Gennes [18] and Joanny et al. [19].

The pioneering work of De Gennes [18] has made clear how useful scaling results can be in order to understand the properties of polymers near interfaces. With respect to depletion-type interactions, he considered the contact potential between two colloidal spheres in a semi-dilute polymer solution in a good solvent for two limiting cases. For very large spheres, where the only relevant length scales are the sphere radius and the correlation length  $\xi$ , the Derjaguin approximation should be valid, leading to the following scaling relation for the minimum of the interaction potential [20]:

$$\frac{W(0)}{kT} \simeq -\frac{R}{\xi} \quad (4)$$

with an unknown prefactor  $O(1)$  (it was recently shown to be close to unity [12]). Since for this situation  $R \gg \xi$ , the attraction between the two spheres is predicted to be very substantial.

In the second case where  $R \ll \xi$ , De Gennes [20] considered the immersion free energy  $F$  to insert a small sphere into a polymer solution, which is proportional to the number of segments in a volume of  $\sim R^3$ . In that case  $F/kT \approx n_b R^3$  or, using  $\xi \approx n_b^{-3/4}$ ,  $F/kT \approx (R/\xi)^{4/3}$ . For very small spheres  $F \approx -W(0)$  (see also [21]), so

the final result for the contact potential is [20]:

$$\frac{W(0)}{kT} \approx -\left(\frac{R}{\xi}\right)^{4/3} \quad (5)$$

Since  $R \ll \xi$ , a very weak attractive potential is expected.

Joanny et al. [19] calculated the polymer segment concentration profile between two plates using the Edwards equation with a mean-field expression for the potential the monomers exert on each other. They showed that the range of the interaction potential between two colloidal particles scales with the polymer correlation length, and thus decreases with increasing polymer concentration in the semi-dilute regime.

Using a Flory–Huggins-like mean-field model, Feigin and Napper [22] calculated the free energy of interaction between two flat plates and noted that a repulsive barrier is introduced due to depletion for high polymer concentrations. The potential at plate contact, however, is negative. Feigin and Napper [22] suggested that if the repulsive barrier is large enough, this might lead to so-called depletion stabilization; a colloidal dispersion is restabilized at high polymer concentrations. A conceivable intuitive explanation is that at high polymer concentrations it is hard to push polymer chains out of the gap between two particles, since the bulk osmotic pressure is very high in a concentrated polymer solution to which remaining chains have to be transported. Scheutjens and Fleer [23] developed a numerical self-consistent field (SCF) method that enables calculation of the equilibrium SCF concentration profiles near interfaces. This SCF method was applied to depletion interaction in [24], showing that the depletion layer thickness is close to  $R_g$  at low polymer concentrations, but decreases with increasing polymer concentration in the semi-dilute regime. In the concentrated regime, very close to the melt concentration, the polymer concentration between the plates is at some positions at certain plate separations slightly higher than the bulk polymer concentration. This finding is supported by Monte Carlo computer simulations by Broukhno et al. [25]. The interaction potential between the plates was also calculated by Scheutjens and Fleer [24]. For dilute polymer solutions the range of the potential is close to  $2R_g$  and the depth of the potential increases with increasing solvent quality. For approximately 10% polymer segments in the system (a very high polymer concentration in practice) a weak repulsive part in the interaction potential appears. This repulsion appears at lower concentrations for better solvent quality [24,26].

Wijmans et al. [27] used the SCF method to calculate the interaction between two parallel plates with grafted polymer layers in the presence of non-adsorbing polymer. For small chain lengths of the non-adsorbing polymer ('free' polymer) as compared to the height of the grafted polymers, the main effect of 'free' polymer is to compress the grafted layers, thereby increasing the repulsion between two plates with grafted layers. For 'free' polymers that are larger than the brush height, a depletion-induced attraction appears between the grafted plates. From this work we can conclude that depletion interaction still leads to attraction between particles that also contain a (relatively short) grafted stabilization layer. Spheres with a

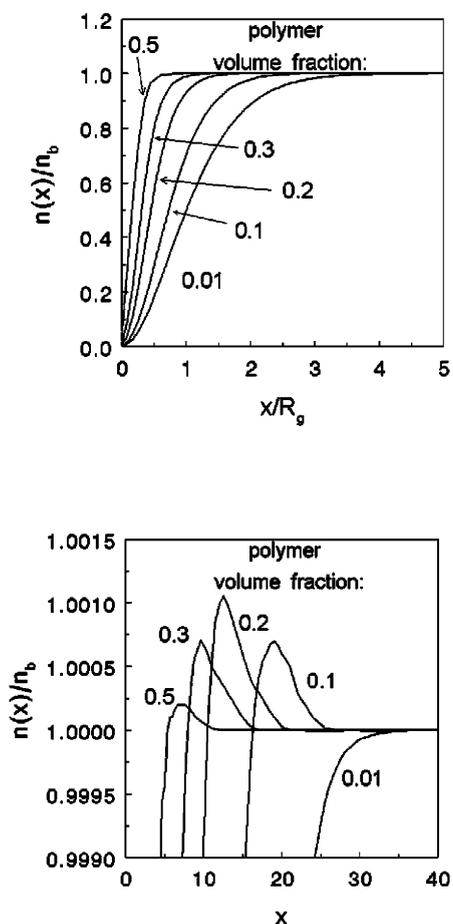


Fig. 6. (a) Results from Van der Gucht et al. [25] for the profile of an ideal polymer solution near a wall for various polymer volume fractions as indicated as a function of the number of layers from the wall  $x$ -normalized with  $R_g$  ( $=9.13$  layers). (b) Details of the repulsions from (a) of results from Van der Gucht et al. [25].

grafted layer are also denoted as ‘soft’ spheres. The work of Wijmans et al. [27] thus opens the route for studies on depletion interaction between ‘soft’ spheres.

Van der Gucht et al. [28] used the SCF theory to specifically investigate oscillations in the polymer concentration profile near a single wall. This effect is expected to lead to repulsion between the plates. For a polymer solution with 500 segments per polymer and  $\chi = 1/2$  (so-called theta conditions), the result is plotted in Fig. 6a,b. From these calculations it follows that mean-field theory predicts very weak, damped oscillations in the polymer segment concentration. Hardly any effective repulsion can be expected based on these results for realistic polymer concentrations. Maassen et al. [29] developed a continuum mean-field theory, taking

into account the excluded volume effect, and reproduced the non-monotonic behavior. The most significant repulsion was found just above the overlap concentration, which is in agreement with the data in Fig. 6b. Furthermore, Maassen et al. [29] derived an analytical mean-field expression in the semi-dilute regime for the polymer segment concentration profile in the small curvature limit. This expression shows that upon increasing the curvature, the thickness of the depletion layer is reduced.

Although SCF approaches provide very useful insights into the physics of depletion phenomena, it should be realized that neglecting fluctuations often leads to wrong scaling exponents. Self-consistent field approaches make it possible, however, to investigate trends in more complicated systems.

#### 2.4. Theoretical models for the ‘protein limit’

During the last decade, increased attention has been focused on the development of depletion interaction in the protein limit where  $R_g \gg R$ . It was De Gennes [20] who, using scaling arguments derived from Eq. (5), showed that it would be hard to induce phase separation in a mixture of very small colloids and relatively large polymer chains. This work is very useful, since it is relevant for description of the stability of mixtures of polysaccharides and proteins, of which many food products and other biological systems consist. In certain cases the proteins are not very small compared to the polysaccharides [30] and the depletion force leads to phase separation in biological systems. In cells for instance, biopolymer mixtures are held responsible for the macromolecular crowding [31]. For an overview of the phase behavior of polysaccharide–protein mixtures we refer to the recent review by Doublier et al. [32].

The concept of De Gennes [20] was further elaborated by Odijk [33,34], who published an interesting series of papers devoted to spheres immersed in a polymer solution of which the characteristic length scale ( $\xi$  or  $R_g$ , depending on the polymer concentration regime) is much larger than that of the spheres. Odijk [33] derived a very simple shape of the profile of the polymer segment concentration in a semi-dilute polymer solution around a very small sphere, which agrees with the expression of Taniguchi et al. [15] in the limit  $R_g/R \rightarrow \infty$ . Odijk [33] also calculated the second osmotic virial coefficient between polymer and colloid for the  $R_g \gg R$  case and concluded that no phase separation is expected on mixing very long chains with very small spheres.

Subsequently, Odijk [34] investigated many-body effects. Odijk [34] showed that in many cases the Edwards (diffusion) equation for polymers around a small sphere could be simplified, allowing a calculation of the depletion-induced attraction using void-correlation functions. Here statistical geometrical approaches are required to compute the correlations [35]. The result from Odijk’s analysis [34] is that the depletion-induced attraction levels off to a maximum value as a function of the colloid concentration near a volume fraction of 30%.

Odijk [36] extended his approach for depletion interaction between small colloids in solutions with long polymer chains to colloids with an ellipsoidal shape, to mimic

proteins. Eisenriegler [37] calculated the density profile around and the interaction between two infinitely small colloids in an ideal polymer solution using field-theoretical methods. Next, progress was made by computing depletion effects due to ‘real’ chains on the colloidal stability of two very small spheres by introducing the lowest-order effects of the excluded volume interaction between the polymer segments [38]. In order to take into account the full excluded-volume effects, Eisenriegler [21] used renormalization group theory of polymers, from which accurate expressions for the relevant thermodynamic quantities are available [39]. The resulting calculations showed that the second osmotic virial coefficient between two infinitely small spheres decreases weakly with increasing polymer concentration until the overlap concentration, above which it *increases*.

Although most of the focus is on the interaction between colloids and many methods try to integrate out the polymers, it is also possible to focus on how the stability of a polymer solution changes by adding small colloids. Van der Schoot [40] derived an expression for the Hamiltonian of a polymer solution in the presence of small colloidal spheres and showed that adding colloids leads to a distortion of the conformational entropy of a polymer chain. Effectively, adding spheres thus decreases the solvent quality and a polymer is expected to collapse above a certain colloid concentration. This effect originates from the mutual exclusion of polymer segments and colloidal spheres. The concept of Van der Schoot [40] is also supported by computer simulations of large polymer chains in a system with random small obstacles by Wu et al. [41], who found that the size of the polymers decreases when small particles are added.

Schaink and Smit [42] proposed a cell model to describe a dispersion of small colloidal spheres and polymers. The system is divided into a number of cells that equals the number of colloidal hard spheres. Each sphere is placed in the center of a cell. Using a minimization of the free energy using the Edwards (diffusion) equation for polymers, the polymer concentration profile in the cell is computed. Excluded volume interactions are taken into account in a mean-field fashion. For mutual overlap of the cells, corrections are made. It is, however, not certain to what degree the cell model is valid, and a comparison with computer simulations could therefore be very interesting.

### 2.5. *Liquid-state theory approaches*

From the foregoing it can be concluded that in descriptions of depletion interaction the focus is either on the colloids or on the polymers. If the focus is on the colloids, the polymers are usually simplified (as in the PHS approach), or vice versa the colloids are simplified to either extremely small spheres or plates if the focus is on the polymers (field-theoretical approaches or mean-field lattice approaches). Over the last decade liquid-state theories have been developed for polymers [43–45], which, with respect to for instance the osmotic pressure, agree with accurate renormalization group theory results. These liquid-state types of theories for polymers are referred to as PRISM theories (polymer reference interaction site model). Since liquid-state theory is well developed (see for instance [46]) and can

be applied very well to colloidal dispersions [47,48], it is a promising tool to investigate mixtures of colloids and (both ideal and interacting) polymers. A liquid-state theory for colloid–polymer mixtures [49–51] could be a candidate for properly incorporating the polymer correlation length dependence as a function of polymer concentration and the flexibility of polymers that allows them to adjust their configuration in voids between the colloidal spheres. Early investigations by Haronska and Vilgis [49] showed that within a single integral equation theory the colloid limit and protein limit regimes could both be identified; if the chains are smaller than the colloids, depletion around the colloids leads to instability, whereas the polymer chains collapsed in the presence of small colloids. The problem in liquid-state approaches is, however, that they require appropriate closure relations for the colloid–polymer interaction (for the polymer–polymer and colloid–colloid correlations, reasonable closures exist). Recently, Fuchs and Schweizer [52] have proposed a closure relation for the hard sphere–Gaussian coil direct correlation function. It includes an unknown length scale, which can be determined by imposing thermodynamic consistency for the polymer insertion chemical potential [52,53]. The advantage of this approach is that it applies to any colloid/polymer size ratio. Comparisons with computer simulations still should test the accuracy of the closure relations. A comparison with experimental data shows that the predictions of the spinodal are in reasonable agreement with the phase lines observed [54], and that the second osmotic virial coefficient measured for proteins with added polymers is qualitatively well described [55,56].

Another recent liquid-state theory-like approach is to map the polymer chains onto a fluid of particles, which interact via an effective interaction potential, that agrees with the mutual interactions between self-avoiding random walk (SAW) polymers so as to describe interacting polymer chains. Louis et al. [57] launched such a concept by proposing a Gaussian core (GC) model for the polymer coils. These GC particles become increasingly mutually repulsive as the degree of overlap increases. They put the GC spheres into a liquid-state theory [58] and could reasonably well reproduce RG theory results, as well as SAW simulations they performed. Next, they investigated the properties of the GC particles near a single wall and between two walls. Near a single wall the GC profiles correspond to a hyperbolic tangent profile, with the relevant length scale being the correlation length, which for the GC particles corresponds to that of SAW polymers. From the results between two walls, the interaction potentials were determined both with Monte Carlo simulation of SAW polymers and by simulations for the GC model. The potential at contact, as well as the initial slope of the potential for the GC model, matches very well with the simulation results. For polymer concentrations close to overlap, the GC model predicts a significant repulsion in the range  $1 < h/R_g < 2$ , where  $h$  is the distance between the plates. The repulsion is hardly present in the SAW simulation results. Repulsion is also found when hard spheres are the depleting agents [59], and using a density functional approach it has recently been shown [60–62] that the strength of that repulsion depends on the degree of additivity of the hard spheres. From the SAW simulations it follows that the degree of

additivity of the excluded volume polymers is very small, and that the GC model thus exhibits somewhat too much colloid behavior. Nevertheless, the GC methodology predicts many features quite well and its extension towards the interaction with a hard sphere is promising [13]. An interesting approach to describe mixtures of long ideal polymers and colloids for arbitrary size ratio was proposed by Sear [63] by treating a polymer as consisting of a chain of blobs, each of which behaves as a penetrable hard sphere. The number of blobs can be adjusted to match the size ratio. To calculate the properties of the blob of PHSs, Sear used the integral theory of Wertheim [64]. The critical density in the resulting phase diagram shifts to smaller colloid concentration as the chains become longer. A comparison with simulation or other theory has not been made.

## 2.6. Negative adsorption method

Interaction between colloidal particles can be calculated in a convenient way using the negative adsorption method. The Gibbs adsorption equation leads to the following expression for the interaction potential between two hard macrobodies [65,66]:

$$W(h) = \int_{-\infty}^{\mu} d\mu' [\Gamma(h, \mu') - \Gamma(\infty, \mu')] \quad (6)$$

where  $\Gamma(h, \mu)$  is the amount of adsorbed particles in the system [67] when the closest distance between the particle surfaces is  $h$  at the relevant chemical potential  $\mu$  of the particles involved. For depletion interaction due to ideal polymers, the chemical potential of the polymer chains is simply proportional to  $\ln(n_p)$ , where  $n_p$  is the bulk polymer concentration, and Eq. (6) becomes:  $W(h)/kT = \Gamma(\infty) - \Gamma(h)$ . The excess amount of particles or the adsorption is the integral over the polymer segment concentration profile. Using field-theoretical approaches it is quite hard to calculate the profile between particles. Tuinier et al. [67] proposed to take the product of the individual profiles, which are known for a single plate [14] and a single sphere [15] for ideal chains, as the total profile. This approach follows from considering the single concentration profiles as probability functions. Introducing a second particle then leads to a probability that a segment can be at a certain position if the product of the probabilities is taken. By a comparison with ideal-chain computer simulations, it was shown that the product function is very accurate [67]. Calculations of the second osmotic virial coefficient showed that for polymer chains larger than the colloids, the depletion interaction becomes very ineffective, which agrees with the work presented in the protein limit section above. The advantage of the adsorption method combined with the product function is that it applies for any polymer/colloid size ratio. Progress is ongoing in extending this method towards polymer depletion with excluded volume interaction. The product function approximation was recently incorporated into the adsorption method as applied to excluded volume interactions [68], yielding reasonable agreement with SAW simulation

results for the interaction between two plates. Recently, a field-theory method was used to compute the interaction potential between two walls, as induced by excluded volume polymers [69]. The results agree with Monte Carlo simulation data [70] and with the recently measured force between a sphere and a plate in a polymer solution [71,72]. Thus, although field theories on this level require quite sophisticated mathematical treatment, progress is still possible.

### 3. Polydispersity effects on depletion interaction

The number of studies on polydispersity effects on depletion interaction due to non-adsorbing polymers is still rather limited. Upon using (penetrable) hard spheres as depletants, considerable progress has been made nevertheless. The system considered in these studies consists of a dispersion of two large, hard spheres in a bath with relatively small, hard spheres. Walz and Sharma [73] proposed a force balance theory including second-order concentration effects to calculate the interaction between the large spheres in a bath of small, hard spheres and showed that these effects lead to repulsion. Soon after, Mao et al. [59] developed an analytical exact theory for the potential between the large, hard spheres up to lowest orders in colloid concentration. At contact the interaction potential is attractive, as expected. At larger separations, however, the interaction potential oscillates around a zero potential, being damped with increasing separation distance between the large spheres. This was later confirmed with density functional theory [60]. Subsequently, Mao [74] extended the approach towards size polydispersity of the small, hard spheres, showing that the oscillations become much less pronounced with increasing polydispersity. Thus, although it is already known that non-adsorbing polymers contribute to rather weak repulsion at high polymer concentration, it is expected that this weak repulsion is even dampened due to polydispersity, as is the case for hard spheres. Using integral theory, Chu et al. [75] also calculated the interaction between two large spheres as modified by small ones, and also found that the repulsive part of the potential is strongly reduced due to polydispersity.

The theory of Lekkerkerker et al. [8] was extended to a PHS mixture to model polydispersity by Warren [76]. Warren found that polydispersity enhances the tendency to phase separate when a bidisperse polymer mixture is compared to a monodisperse mixture having identical number-averaged molar masses. Warren also found that the phase threshold of the colloid–bidisperse polymer mixture is almost identical to that of a colloid–monodisperse polymer mixture when the weight-averaged molar mass of the bidisperse mixture is taken as the monodisperse molar mass [76]. Sear and Frenkel [77] investigated a colloid–PHS mixture using a full distribution of polydisperse PHSs. Their calculations demonstrated that phase separation leads to size fractionation of the PHSs. Piech and Walz [78,79] recently extended the force balance method of Walz and Sharma [73] towards small colloid size polydispersity. For constant particle concentration, the minimum of the interaction potential decreases with increasing polydispersity. The effect of polydispersity is small, however; for a relative standard deviation of 60% the minimum of the

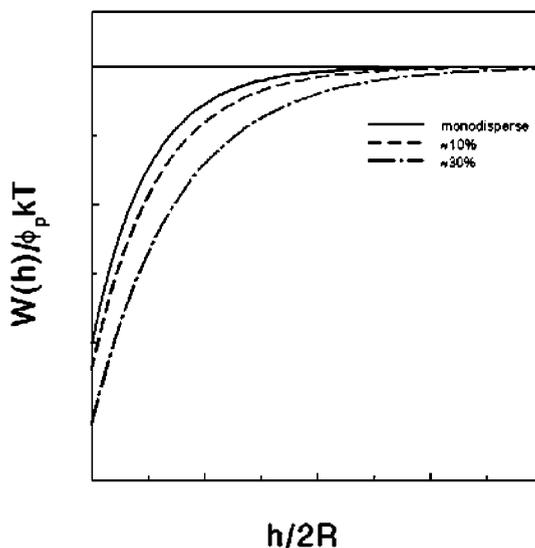


Fig. 7. Schematic representation of the interaction potential between two spheres immersed in a polymer solution and the effect of polydispersity of the polymers. The qualitative curves drawn correspond to monodisperse polymers, polymers with size distributions with standard deviations of approximately 10% and 30%.

potential is less than 1.4-fold as large as the minimum of the potential in the monodisperse case.

Goulding and Hansen [80] computed the interaction potential between two spheres in a polydisperse bath of penetrable hard spheres (polydisperse PHS model), which obey a Schulz size distribution. Up to a polydispersity characterized by a standard deviation of 30%, there is hardly any effect on the slightly increased range and slightly deeper potential between the hard spheres. Above 30% polydispersity, the effects become more significant. Goulding and Hansen [80] also used DFT theory to investigate the case of depletion due to small, hard spheres. Their findings correlate with Mao's analytical results, but also show that Mao's Derjaguin approximation already deviates from the DFT result for a size ratio of 5.

As an illustration of the effect of polymer polydispersity, a qualitative picture can be drawn on the basis of the theoretical studies [73,80] that have been performed; see Fig. 7. In this figure the interaction potential (normalized with the polymer coil volume fraction) between two spheres in a polymer solution is sketched for a monodisperse polymer (*full curve*), a slightly polydisperse polymer (*dashed curve*) and for a very polydisperse polymer (*dot-dashed curve*). As an indication, the polydispersity corresponds to, say 10 and 30% in standard deviation. Both the range and the contact potential thus increase when making the polymers more polydisperse but keeping the volume fraction of polymer coils fixed.

It would be interesting to investigate the phase behavior of a mixture of colloids and polymers that are both polydisperse, which is a computationally time-consuming case. The degree of size fractionation due to phase separation of polydisperse polymer–colloid mixtures is still unknown. Fractionation is already quite significant for the case of a bidisperse mixture of polymers mixed with monodisperse, hard colloidal spheres [76].

Of significant relevance also is the size polydispersity of the colloidal spheres. Polydispersity in size of the hard spheres leads to a change in the fluid–solid transition. In the absence of polymer the fluid–solid transition takes place at a volume fraction of 0.49 and 0.54. Polydispersity tends to shift these volume fractions to above 60% [81]. This demonstrates that the use of polymers to concentrate dispersions as far as possible should be very useful, especially in very polydisperse colloidal systems. In general it seems that there are still unknown factors related to polydispersity effects.

#### 4. The role of charges in depletion interaction

In many practical polymer–colloid mixtures, charges on the particles are present. In cases where, besides depletion interaction, several other types of interaction are present in a system, the total potential can be calculated via the superposition approximation [82–84]:

$$W_{\text{tot}}(h) = W_{\text{dep}}(h) + W_{\text{vdw}}(h) + W_{\text{er}}(h) + W_{\text{c/pe}}(h) \quad (7)$$

where  $W_{\text{tot}}(h)$  is the total interaction potential,  $W_{\text{dep}}(h)$  the depletion interaction potential,  $W_{\text{vdw}}(h)$  the Van der Waals attraction and  $W_{\text{er}}(h)$  the electrostatic repulsion. In addition, the polymer may be a charged polyelectrolyte. Therefore, a contribution  $W_{\text{c/pe}}(h)$  should be added, which is the contribution to the total potential due to polyelectrolyte–(charged) colloidal interaction. In cases where charges are involved, the ionic strength strongly influences the properties, such as the colloidal stability of such dispersions.

An early theoretical depletion interaction study with polyelectrolytes as depleting agents was carried out by Böhmer et al. [85], who used the self-consistent field method of Scheutjens and Fleer [23,26]. The electrostatic interactions were inserted into the lattice model via a multi-Stern-layer model. All mean-field interaction parameters were chosen such that all interactions were isothermal [ $\chi_{(s)} = 0$ ]. The investigations of Böhmer et al. [85] were performed with polymers having a chain length of 500 segments. For neutral polymers the depletion layer thickness is close to the radius of gyration in the dilute regime, whereas it equals the correlation length in the semi-dilute regime. For polyelectrolytes the polymer overlap concentration depends on the extent of repulsion between the charged segments, which in turn is determined by the salt concentration. For high salt concentrations the polymer concentration dependence of the depletion layer thickness matches that of an uncharged polymer in solution. Below a salt concentration of 1 M, the depletion layer thickness starts to decrease with increasing polyelectrolyte concentration at

lower polymer concentration. This is due to the swelling of a polyelectrolyte upon lowering the salt concentration; the Debye length is increased and the charged monomers repel each other. Therefore, the overlap concentration, above which the depletion layer thickness starts to decrease, is lowered as the salt concentration is lowered. At low salt concentrations the results of the calculations by Böhmer et al. [85] showed a significant repulsive barrier in the potential between two uncharged, parallel flat plates. Due to depletion of polyelectrolyte in the gap between two flat plates, a potential is built up between the plates in order to maintain electroneutrality. The contact potential is, however, much larger compared to the high-salt-concentration case. Due to swelling of the polyelectrolytes, the depletion layer thickness increases (it is of the order of the radius of gyration near a wall), thereby increasing the depletion overlap volume at contact.

A force balance theory on the Derjaguin approximation level for the interaction between two spheres in dispersion with macromolecules (regarded as hard spheres), with (like) charges on them was developed by Walz and Sharma [73]. For low concentrations of the ‘macromolecules’, the interaction potential curve is attractive for any salt concentration. The value of the potential at contact is increased as the Debye length increases, or if the charge density on the large colloidal spheres (same sign as the ‘macromolecules’) increases. The range of the potential increases as the Debye length increases. At higher concentrations of the small particles, a repulsive barrier in the interaction potential curve appears for sufficiently large size ratio of small and large colloid and sufficient Debye lengths. This might lead to depletion stabilization. The trends that follow from the work of Walz and Sharma [73] from the interaction potential between two charged spheres due to like-charged macromolecules are schematically drawn in Fig. 8. Curve 1 (*full curve*) refers to the interaction potential between two charged spheres immersed in a solution with charged macromolecules mixed with a considerable amount of salt ions with a small Debye length,  $\kappa_1^{-1}$ . Upon increasing the Debye length to  $\kappa_2^{-1}$ , the value of the contact potential as well as the range of the potential increases; see the dot-dashed curve 2 in Fig. 8. In addition, increasing the concentration of charged macromolecules leads to the interaction potential given by the dashed curve (curve 3). In that case the value of the contact potential increases and a repulsive part in the potential appears. In the model of Walz and Sharma [73] the polymers are modeled, however, as hard spheres. It is therefore questionable whether this method applies to colloid-polymer mixtures in which the polymer-colloid repulsion is very soft. Piech and Walz [79] extended the method to incorporate charge heterogeneity by taking a distribution in the surface potential of the small colloidal particles. The result of charge heterogeneity appeared to be weak.

Ferreira et al. [86] carried out an integral equation study using PRISM (see Section 2.5) on mixtures of charged polyelectrolytes and charged colloids. The electrostatic interactions were taken into account via a screened Coulombic potential. The colloid radius was always taken to be much larger than the monomer size. For neutral polymers and colloids they found that the depth of the minimum of the interaction potential between the colloids scales linearly with the polymer concen-

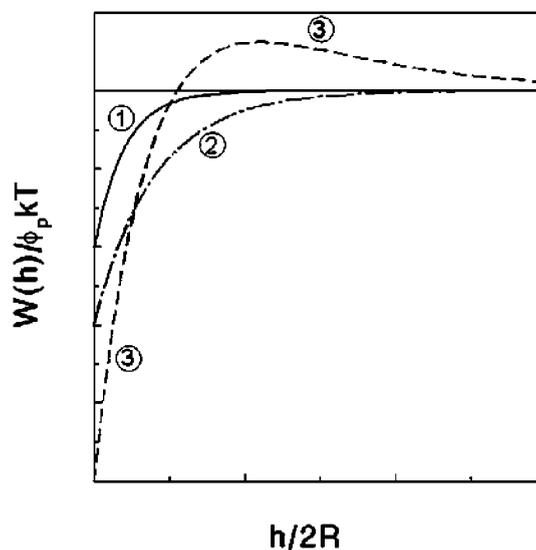


Fig. 8. Qualitative sketch of the effects of the salt concentration (Debye length) and charged macromolecule concentration on the interaction potential between two charged spheres immersed in a salt solution with charged macromolecules. Curves: (1) low Debye length and low concentration of charged macromolecules; (2) larger Debye length compared to (1); and (3) as for (2), but with higher concentration of charged macromolecules.

tration. The range of the potential scales with the polymer radius of gyration in the dilute regime and is related to the correlation length in the semi-dilute regime. For charged polymers mixed with charged colloids, the interaction potential exhibits a very ‘rich’ behavior and is highly dependent on the parameters chosen. For low Debye lengths (high salt concentration) the potential at contact is highly repulsive due to strong repulsion between the colloids, as in the DLVO theory [87]. The repulsion is stronger if the polymer is neutral. At further separation there is an attractive part of the potential. The attraction is stronger for charged compared to neutral polymers. For low Debye lengths there is stronger repulsion between charged colloids immersed in a solution with neutral polymer. However, in the presence of highly charged polymer the contact potential becomes attractive. At further interparticle distance the potential is repulsive and tends to zero potential for large particle separation.

Odijk [88] incorporated the effect of (like) charges on polymer (polysaccharide) and colloid (protein) in his theory [33] for two small colloidal spheres immersed in a polyelectrolyte solution. He related the effective depletion radius for small charged spheres, immersed in a solution with oppositely charged polyelectrolytes, to the Debye length, the effective number of charges on the protein, the hard sphere radius and the Kuhn length. If the effective depletion radius becomes larger than  $\xi$ , a phase separation due to depletion is expected. In summary it seems that at high salt concentrations, like charges on polymers and colloids do not seem to affect the

depletion-induced attraction between colloids due to polymers. At low ionic strength, however, the situation becomes quite complicated and detailed theories still have to be developed that enable computation of the stability of such systems.

## 5. Depletion interaction in polymer–colloid mixtures: experiments

### 5.1. Early experimental findings of depletion interaction

Experimental work dealing with depletion interaction was already reported a long time before Asakura and Oosawa [2] first gave a theoretical background for the phenomenon. It has been known for a long time (for over two centuries according to [89]) that red blood cells tend to cluster at high concentrations of the blood serum proteins; for a review on this matter see Fåhræus [89]. By now it is well recognized that physicochemical mechanisms such as depletion can be used to explain erythrocyte aggregation and precipitation [90].

The microbiologist Beijerinck [91] tried to mix gelatin and starch and reported that these biopolymers could not be mixed since ‘emulsion droplets’ appeared. With current knowledge this can now be regarded as very early detection of depletion-induced demixing. In the beginning of the last century Traube [92] showed that adding certain polysaccharides derived from plants and seaweed to aqueous latex dispersions led to a concentration of latex. Vester [93] published a review on ways to optimize the creaming speed of lattices.

Cockbain [94] reported the enhanced creaming of oil droplets in a stabilized oil-in-water emulsion when the surfactant concentration exceeded the critical micelle concentration. This phenomenon was left unexplained at the time, until Fairhurst et al. [95] made a connection with depletion interaction theories and suggested that the micelles play an identical role to non-adsorbing polymers.

### 5.2. Depletion-induced phase transitions

Soon after the establishment by Asakura and Oosawa that non-adsorbing polymers lead to an effective attraction, Sieglaff [96] demonstrated that a depletion-induced phase transition may occur upon adding polystyrene to a microgel (colloidal spheres) dispersion (in toluene). Sieglaff [96] also theoretically demonstrated that the concept of Asakura and Oosawa could be extended such that the attractive depletion force is sufficiently strong to induce a phase separation.

It took several years before subsequent work was carried out. Kose and Hachisu [97] added sodium polyacrylate to polystyrene latex particles (both components are negatively charged), which leads to crystallization of the colloidal spheres. Since polymers and particles repel each other, the crystallization is probably induced by depletion interaction, although the authors themselves did not mention depletion as such. Vincent and co-workers [98–100] reported on the reversible flocculation of a dispersion of sterically stabilized latex spheres with added non-adsorbing polyethylene oxide. The reversibility of the flocculation demonstrates that the mechanism is depletion interaction, since bridging flocculation is irreversible [26].

A direct link between theoretical and experimental work on depletion-induced phase separation of a colloidal dispersion due to non-adsorbing polymers was made by De Hek and Vrij [5,101]. They mixed sterically stabilized silica dispersions with polystyrene in cyclohexane and could quantitatively explain the ‘limiting polymer concentration’ (phase separation threshold) using Vrij’s PHS model [4]. By mixing aqueous hydroxyethylcellulose (HEC) with latex, Sperry [102,103] and co-workers [104] observed phase separation and made a study of the effect of the structure of the colloid-rich phase as a function of the colloid/polymer size ratio. They found that a fluid–solid equilibrium is found when the polymers are relatively small and a gas–liquid equilibrium for relatively large polymers. This inspired Gast et al. [6] to develop their theory, which explains these phenomena. Following this work a series of publications appeared [105–108] semi-quantitatively confirming the work of Gast et al. [6] and Sperry [102].

To oil-in-water emulsions polymers are often added in order to impose a certain emulsion viscosity. This may, however, lead to instability problems, as is known in food emulsions. Bibette and co-workers [109–111] were the first to relate quantitatively phase transitions in emulsions due to non-adsorbing polymers to depletion-induced forces. They also showed that it is possible to size-fractionate an emulsion with a depletion-induced phase transition [111].

An interesting aspect of (micro-)emulsion droplets is that they are not hard spheres. Both Snowden et al. [112] and Xia et al. [113] studied the phase behavior of a micro-emulsion mixed with non-adsorbing polymers and could explain the phase behavior by adding a hard plus sticky sphere attraction, which is required to describe the micro-emulsion itself, to the depletion attraction to take into account the effect of non-adsorbing polymer. Often the polymer is larger or has the same order of magnitude as the ‘spheres’ in polymer/micro-emulsion mixtures. Therefore, for a proper description of the phase behavior, the effect of the decreasing depletion layer thickness due to closer packing of polymer around a small sphere must be taken into account.

### 5.3. *Studies on the depletion layer thickness*

In the PHS concept the depletion layer thickness is an essential item. Therefore, work evolved that focused on measuring the depletion layer thickness. Allain et al. [114] used the evanescent wave (EW) technique to measure the depletion layer thickness near a glass prism in contact with a solution of fluorescence-labeled non-adsorbing polystyrene. The depletion layer thickness measured was of the order of magnitude of the polymer radius of gyration. Again using the EW technique, Ausserré et al. [115] measured the depletion layer thickness as a function of polymer concentration below and above overlap near a quartz wall in contact with a labeled xanthan solution. Below the overlap concentration, the depletion layer thickness equals the radius of gyration, whereas in the semi-dilute regime the depletion layer thickness decreases as  $\Delta \approx n_p^{-0.8}$ , which corroborates the work of de Gennes [20] and Joanny et al. [19], in which it was established that the depletion layer thickness equals the correlation length  $\xi$ , which scales as  $\xi \approx n_p^{-3/4}$ . Cosgrove et al. [116]

measured the spin–spin nuclear resonance time of a dispersion of silica with added sodium polystyrene sulfonate (NaPSS). The resonance time could be related to the depletion layer and they found that the depletion layer thickness decreased with increasing concentration of NaPSS, which is in agreement with the scaling theory of Joanny et al. [19].

#### 5.4. Detailed studies on phase behavior

Rather than generally showing that non-adsorbing polymers lead to a depletion-induced phase transition, several studies have been performed on mapping out the details of the phase behavior of polymer–colloid mixtures. Gast et al. [104] verified their theory experimentally. Their results agreed semi-quantitatively with the theoretical predictions from their theory [6]. A fluid–fluid phase transition is found for  $R_g/R > 0.3$  and a gas–solid transition for  $R_g/R < 0.3$ , in agreement with their perturbation theory. After publication of the theory of Lekkerkerker et al. [8], who predicted a coexisting gas–liquid–solid three-phase system for  $R_g/R \approx 0.4$ , it became interesting to investigate whether this three-phase system could be identified experimentally as well. The work of both Pusey et al. [117] and Leal-Calderon et al. [118] demonstrated that this three-phase region existed. Subsequently, Ilett et al. [119] carried out a series of experiments to determine the phase diagrams of colloid–polymer mixtures with size ratios  $R_g/R$  of 0.08, 0.24 and 0.57. The phase diagrams were quantitatively compared with the result from the theory of Lekkerkerker et al. [8]. The topology of the phase diagrams corresponded well for size ratios of 0.08 (gas–solid coexistence) and 0.57 (gas–liquid coexistence). The crossover between the two topologies was found at a size ratio of 0.24, whereas theory predicts that this occurs at a size ratio of approximately 0.32. Quantitatively, the predictions for the binodal are rather accurate for a size ratio of 0.08, but the agreement becomes less satisfying with increasing polymer/colloid size ratio. The polymers that Ilett et al. [119] use are still significantly polydisperse, while the recently reported phase diagrams of Ramakrishnan et al. [54] were prepared with almost monodisperse polymers. For large size ratios where gas–liquid coexistence dominates, the theoretical predictions can be compared with for instance results from colloid–polymer mixtures having a size ratio close to  $2R_g = R$  (see Bodnár et al. [120]) or close to unity (De Hoog and Lekkerkerker [121]), for which the coexisting binodals have been fully determined [120,121]. Comparing these results with theoretical predictions using the free volume theory [8] leads to the conclusion that the latter significantly underpredicts the binodal. Ramakrishnan et al. [54] claimed that their result agrees better with PRISM theory, although their phase diagrams were compared with calculations of the spinodal.

Fears and Luckham [122] studied the effect of the amount of polymer grafted onto colloid surfaces on the phase behavior of polymer–colloid mixtures. They showed that decreasing the amount of grafted polymer increased the phase separation concentration of polymers at similar colloid concentration, demonstrating that it is worthwhile to investigate the effect of the presence of brushes in combination with non-adsorbing polymers. For emulsions mixed with polymers the theory of Lekker-

kerker et al. [8] was found to agree qualitatively as regards the phase behavior, as studied by Meller and Stavans [123]. Tuinier and de Kruif [124] found that phase separation took place in a mixture of an emulsion with whey proteins as stabilizers if non-adsorbing polysaccharides were added. The phase separation threshold could be described semi-quantitatively using the theory of Vrij [4,5]. Quenching too deep into the unstable regions leads to gelation [1], as was found by Tuinier and de Kruif [124].

### 5.5. Modern techniques measuring the depletion-induced attraction

#### 5.5.1. Scattering

Ye et al. [125,126] presented a neutron scattering study on the structure of  $\text{CaCO}_3$  spherical particles (with a radius of 2.0 nm) with an adsorbed monolayer (also of 2.0 nm) of alkylbenzene sulfonate surfactant mixed with a narrow-size-distribution polyethylene propylene copolymer (PEP) with a radius of gyration of 8.3 nm. The effective radius of the sphere equals 4.0 nm, which means that  $R_g/R = 2.1$ . The PEP polymers were made invisible using an appropriate solvent. In that case the colloid–colloid structure factor could be measured directly. Upon increasing the polymer concentration, the colloid–colloid structure factor measured increased in the wave vector regime for  $a_c Q < 1/2$ , where  $Q$  is the scattering wave vector. These experiments clearly illustrate that non-adsorbing polymers lead to an effective attraction between the hard colloidal spheres. The authors theoretically described the structure factor by inserting the depletion potential for PHSs [Eq. (1)] into integral theory for hard spheres plus an attraction using the mean spherical approximation, which is a perturbative treatment of the Percus Yevick equation [46]. Tuinier et al. [127] used the integral theory to calculate the structure factor of hard spheres plus depletion interaction. The main trends are identical: depletion attraction leads to an increase in the structure factor in the long-wavelength limit. In the same paper Tuinier et al. [127] also demonstrated how simple light transmission measurements, as well as dynamic light scattering measurements, enable measurement of the attraction between colloidal particles due to non-adsorbing polymer.

Bodnár et al. [120] used both static and dynamic light scattering to determine the spinodal of a polymer–colloid mixture with  $R_g/R \approx 0.5$ . Near the critical point the polymer-induced attraction between the colloidal spheres can be described via an effective correlation length. It is assumed that this description generally holds at the spinodal. The authors demonstrated how this correlation length increases when the concentration of polymer and colloid is increased towards the stability threshold [120]. At the spinodal the correlation length tends to infinity, which is used to determine experimentally the spinodal with both scattering techniques.

#### 5.5.2. Force methods

The surface force apparatus [128,129] is a tool that enables direct measurement of the interaction potential between two surfaces. Luckham and Klein [130,131] aimed at measuring the force between two mica plates as induced by polystyrene in toluene, but the detection limit exceeded the depletion force for the system under

investigation. In order to measure the depletion potential between two mica surfaces, as induced by CTAB micelles, Pashley and Ninham [132] successfully used the surface force apparatus. Under different conditions Richetti and Kékicheff [133] could not find depletion-induced attraction and concluded that electrostatic double-layer interactions dominated. Later, Mondain-Monval et al. [134] measured the force in a system in which depletion, as well as double layer repulsion, affects the final result. They described their data with a model that includes both DLVO and depletion effects (see Section 4).

Ohshima et al. [135] used radiation pressure to measure directly the depletion force. They measured the force between a latex sphere, with a diameter of 1.0  $\mu\text{m}$ , and a glass plate in a solution of polyethylene oxide polymers with a radius of gyration of 101 nm. The values for the force they measured are of the same order of magnitude as theoretical estimates.

Milling and Biggs [136] measured depletion force using atomic force microscopy (AFM). A silica sphere with a radius of 3.8  $\mu\text{m}$  was immersed in a cyclohexane solution with polydisperse PDMS polymers and brought to a planar silica surface. Using a mean-field model they could describe the force measured between the sphere and the plate. From their data Milling and Biggs [136] estimated a depletion layer thickness of 10 nm, which is close to the average size of the PDMS polymers. Biggs et al. [137] made direct measurements with AFM of the force between two silica surfaces in a solution with sodium polystyrene sulfonate. They found a secondary minimum in the interaction potential. This minimum became deeper on either increasing the polymer concentration or molar mass. The effects are not completely understood. The repulsive forces due to charges on polymer and colloid obviously play a role. Burns et al. [138] used AFM to investigate the structure of depletion-induced flocculated polystyrene latex dispersion by adding non-adsorbing polyacrylic acid. The flocculated particles had a higher fractal dimension if the molar mass of polyacrylic acid was smaller, and this was used to explain the differences the authors found between the force curves measured when varying the molar mass of the non-adsorbing polymer.

### 5.5.3. Total internal reflection microscopy (TIRM)

A new tool to study the interaction between colloidal sphere and a planar surface is total internal reflection microscopy (TIRM). Use is made of the total reflection of a light beam at an optical interface such that an evanescent wave is formed in the fluid. A sphere close to the interface scatters the reflected light, from which the distance between the sphere and the wall can be derived. From the position probability profile the potential can be derived. For a review on TIRM see [139]. Walz and co-workers [140–143] measured the depletion interaction between a latex sphere and a glass wall in the presence of various non-adsorbing particles. The measurements partly agreed with theoretical predictions.

Rudhardt et al. [71,72] made TIRM measurements on the interaction between a charged glass plate and a polystyrene sphere with a radius of 5  $\mu\text{m}$  in a polyethylene oxide (PEO) solution, the PEO polymers having a reported radius of gyration of 68 nm. The data correlate with theoretical predictions following the AO model [3,4].

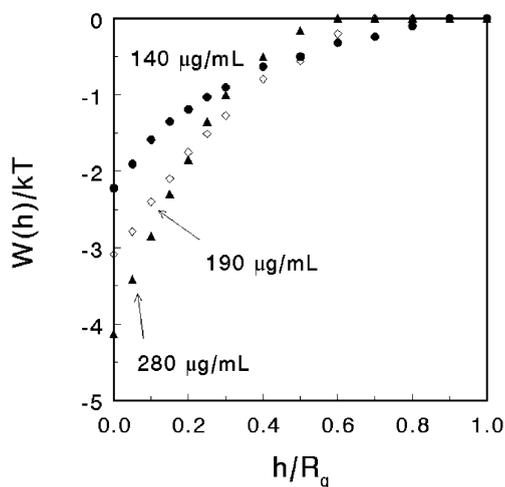


Fig. 9. Interaction potential between two silica spheres in a DNA solution as a function of the distance  $h$  between the sphere surfaces as measured with scanning optical tweezers [145,146]. DNA concentrations as indicated.

For high concentrations of the polymers, electrostatic interactions (the charged glass plate induces a dipole moment in the neutral polymers) have to be taken into account to describe the effective potentials measured [144].

#### 5.5.4. Optical tweezer measurements

For the past few years it has been possible to measure directly the potential of mean force between two colloidal spheres, as long as the spheres are sufficiently large, using scanning optical tweezer measurements. Verma et al. [145,146] measured the force between two silica spheres immersed in a solution with DNA molecules. Some examples of the interaction potential curves measured in the semi-dilute regime are reproduced in Fig. 9. It is shown that the range of the potential decreases with increasing polymer concentration, which is at variance with the early predictions of Joanny et al. [19]. Furthermore, the minimum of the interaction potential is slightly less than proportional with increasing polymer concentration, which agrees with recent theoretical predictions [12]. The polymer–colloid size ratio  $R/R_g$  was 1.25 in this study. This type of measurement yields the possibility in the future of testing depletion theories on the pair potential level.

#### 5.5.5. Interfacial properties

When a colloid–polymer mixture phase separates into a colloid-rich and polymer-rich phase, an interface appears between the phases. It is interesting to study the magnitude of the interfacial tension between the phases, since it is related to phase separation kinetics. Scaling theory suggests that the interfacial tension has a value close to  $kT/\delta^2$ , where  $\delta^2$  is the interfacial width, the length scale over which the

concentrations of polymer and colloid significantly deviate from their bulk concentrations. The surface tension of molecular liquids therefore has a typical value of 10 mN/m. It is assumed that  $\delta$  is associated with the sizes of polymer and colloid. Besides that,  $\delta$  diverges at the critical point. In recent years the spinning drop method was successfully used to determine the interfacial tension in demixed colloid–polymer mixtures [147], yielding tension values of a few  $\mu\text{N}/\text{m}$  [121,147], corroborating the relation between the interfacial tension and  $kT/\delta\delta$ . The order of magnitude of the data of De Hoog and Lekkerkerker [121] was comparable with the theoretical results of Van der Schoot [148] and of Brader and Evans [17]. From the results of Chen et al. [149], it follows that the interfacial tension increases as a function of distance from the critical point, at variance with scaling theories. De Hoog et al. [150,151] demonstrated with ellipsometry and breaking up an elongated droplet in a centrifugal field (spinning drop method) that the order of magnitude of the interfacial tension was independent of the method used. An interesting following step would be to study the relation between phase separation kinetics and the interfacial tension.

## 6. Conclusions and outlook

The depletion-induced interaction between colloidal spheres has attracted significant attention, especially over the last decade. Theoretically, the situation of ideal chains mixed with relatively large spheres is now well understood when describing the polymers as penetrable hard spheres. The penetrable hard-sphere approach leads to a simple description of depletion interaction between spheres in a polymer solution, but applies only if the polymers are sufficiently large and in the dilute regime. The effect of polymer flexibility around a sphere also has to be taken into account to describe the phase behavior when the polymers have a size of the order of the spheres or larger. For larger values of  $R_g/R$  the phase threshold shifts into the semi-dilute polymer concentration regime, and taking into account the non-ideality effects becomes essential. Towards the overlap concentration and above it, the correlation length rather than the radius of gyration becomes the relevant polymer characteristic, and the thermodynamic properties deviate strongly from ideal behavior. These regimes are still less well understood, although hopeful developments are in progress. Liquid state-like theories, such as PRISM or DFT, enable tackling of complex cases, but they are computationally involved to such a degree that it is not easy to recognize the trends in the effects in terms of the parameters involved. In the ‘protein limit’ where the small sphere is at least an order of magnitude smaller than the characteristic polymer size, various workers have gained useful results, which show that the depletion mechanism then becomes inefficient. Recent theories aim at describing depletion interaction for arbitrary size ratio, enabling a prediction of the interactions in practical systems. The effects of size polydispersity and charges on colloid and polymer are not yet completely understood, and require further investigation. For these and other complex cases, self-consistent mean-field methods allow insight into the trends. Experimental data match modern theoretical insights, although experiments have not revealed repulsive

depletion effects in neutral systems, which have been reported in the theoretical area. Nowadays, direct force measurements enable test of new theories on the pair potential level. The interfacial tension between demixed colloid–polymer dispersions is an item that has both experimentally and theoretically interesting aspects, since its magnitude still requires interpretation and relates to phase separation kinetics.

*Note added in proof:* Just before this review was published two papers appeared that consider the phase behavior of a dispersion of colloidal spheres mixed with excluded volume interacting polymers [152,153]. Bolhuis et al. [152] could perform Monte Carlo simulations using a many-body version of their GC model. Aarts et al. [153] extended the free volume theory of Lekkerkerker et al. [8] by incorporating excluded volume interaction between the polymer segments. The trends in both papers are similar.

### Acknowledgments

RT thanks H.N.W. Lekkerkerker, E. Eisenriegler, M. Fuchs, P. Van der Schoot, G.A. Vliegthart, P.G. Bolhuis, E.J. Meijer, R. Evans, A.A. Louis, D.G.A.L. Aarts and J. Groenewold for valuable discussions on depletion interactions. J. Van der Gucht is thanked for providing Fig. 6.

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