

Depletion potential between two attractive plates mediated by polymers

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Abstract

Depletion interactions in polymer-colloid mixtures in the presence of the attraction between polymers and particle surfaces are computed from the simulation data on polymer partitioning. The gap between two large colloid particles is approximated by the slit plates immersed in a dilute polymer solution. The difference between the intra-slit and bulk pressures of polymers Δp (net pressure) and the effective pair potential of plates W is calculated as a function of the plate separation D and the attraction strength ε of plates to polymer segments. Weak attraction strengths ε are considered, including the region around the compensation point ε_c (the depletion/adsorption threshold) where the partition coefficient of polymers $K=1$. A fit of the simulation data for the free energy confinement $\Delta A = -k_B T \ln K$ served as a base of computations of the above depletion characteristics. The analytical functions deduced for $\Delta p(D, \varepsilon)$ and $W(D, \varepsilon)$ predict a reduction of the range and depth of depletion interaction by an increase in the attraction strength $|\varepsilon|$. Variation of the thickness δ of depletion layers near the plates with attraction ε was also determined. Consequences of reduced depletion interaction for the effective second virial coefficient B_2 and for the stability of colloidal suspensions were discussed. At the compensation point ε_c the depletion effect disappears and the stability of polymer-colloid mixtures in dilute solution is not affected by the polymer concentration.

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1. Introduction

The depletion forces in polymer-colloid systems are of continuing interest in last few decades. Depletion interaction arises from the presence in solution of species intermediate in size between colloidal particles and solvent molecules. The most common case occurs when colloidal dispersion contains dissolved nonadsorbing polymer molecules. The depletion mechanism was first described by Asakura and Oosawa (AO) [1] in the ‘colloid limit’, where the particle radius R_p greatly exceeds the size of a polymer coil expressed by the radius of gyration R_g . In the AO concept the polymer molecules are excluded from the depletion zones near to particle surfaces. As the particles approach, the depletion zones overlap and the coils are expelled from the gap between the surfaces. The difference in the pressure Δp between the depletion zones and the bulk solution leads to a force pushing the particles together. Depletion attraction (of entropic origin) of ideal noninteracting chains is described by the AO potential $W(D)$ (an integral of

the net pressure Δp). This polymer-mediated depletion attraction may lead to demixing of a dispersion into the polymer- and colloid-enriched phases at sufficient polymer concentration [2,3].

In the colloid limit ($R_p \gg R_g$) a colloidal particle resembles a hard planar wall on a relevant length scale. Thus depletion interaction is associated with the partitioning equilibrium in a slit formed by two walls immersed in a dilute polymer solution [1,4,5]. The partition coefficient K , the polymer concentration between the plates divided by the bulk concentration, can be calculated by the rigorous theory for ideal polymers [6]. An ideal chain partitioning was considered in original calculations of the net pressure Δp [1] and is still used today as a point of reference in numerous improvements of the AO model. For example, these developments [7–10] focused on influences of the concentration and/or solvent quality on depletion interactions in dilute and semidilute solutions in a case of a repulsive slit and the hard-wall type of interaction between polymers and plates.

Molecular simulations represent a versatile tool to compute the partition coefficient K in diverse situations. Using this approach various aspects of nonideality of polymer partitioning such as the chain excluded volume, solvent quality, solute concentration were explored [11–14]. In these computations full equilibrium conditions of a free exchange of polymer

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molecules between solutions in a slit and in bulk were assumed. The dependence of the partition coefficient K on the ratio of the coil diameter to the plate separation, $2R_g/D$, found from simulations of non-ideal partitioning may appreciably differ from the prediction for the ideal chains, signifying important consequences for a variety of separation methods based on partitioning such as liquid chromatography. Furthermore, the simulations provided the input parameters to calculations of the net pressure Δp due to depletion interactions in dilute and semidilute polymer solutions in a repulsive slit [15].

In the mentioned and many other calculations it is assumed that there is no attraction between the polymer and slit walls. However, such an attraction is encountered in many experimental situations involving equilibria in polymer and colloidal systems. An analytical theory was developed to account for dependence of the partition coefficient K of ideal chains on the attraction between polymers and plate walls [16]. Partitioning of the excluded-volume chains in a presence of polymer/wall energetic interactions was examined in simulation studies [13,14,17–19], particularly in the context of liquid chromatography of polymers. Some effort to include polymer/wall attraction into the framework of the AO model was also reported. The analytical results were derived for the net pressure Δp on two attractive surfaces immersed in a solution of ideal block copolymers [20]. Furthermore, the simulations of excluded-volume polymers in attractive slits were used [21] to compute depletion interactions manifested in the net pressure profiles $\Delta p(D)$ and in the polymer segment concentration profiles $\phi(x)$.

As an extension of the mentioned endeavour we examine in the present paper how polymer/wall energetic interaction shapes the depletion potential in polymer-colloid mixtures. The presented computations of the effective pair potential of two plates immersed in dilute polymer solution $W(D, \varepsilon)$ rely on a fit of simulation data of the partition coefficient K . The analytical functions $\Delta p(D, \varepsilon)$ and $W(D, \varepsilon)$ resulting from the fit predict a reduction of the range and depth of depletion interaction by an increase in the attraction strength $|\varepsilon|$. A unique behaviour of depletion characteristics in the region near to the depletion/adsorption threshold is analyzed.

2. Theory

The depletion interaction in a dilute solution in the limit $R_p \gg R_g$ is now quantitatively understood in case of hard-body type of interaction between polymers and surfaces. The principle of depletion of nonadsorbing polymers is illustrated in Fig. 1. There are depletion zones on the segment concentration profiles near the two plates. The polymer

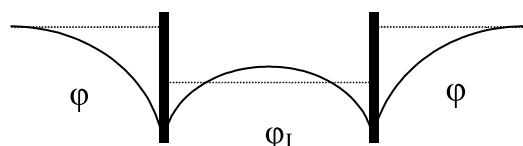


Fig. 1. Schematic of the depletion concentration profiles and the average volume fractions ϕ_I and ϕ (dotted lines) in solutions inside the gap and in bulk.

solution between plates is taken to be in equilibrium with a much larger reservoir of a bulk solution. Addition of nonadsorbing polymers to a stable solution of colloidal particles results in effective (polymer-mediated) attraction arising from unbalanced pressures on the plates within the particle gap and from surrounding bulk solution. The pressure p_I exerted by the polymers confined inside a slit-like gap is given as the product of the osmotic pressure π_I inside the slit and the confinement term [1,4,5]

$$p_I = \pi_I(1 + D\beta f) \quad (1)$$

where $\beta = (1/k_B T)$ and D is the separation of slit plates. The confinement force f is defined as a derivative $f = -d\Delta A/dD$ [15]. The Helmholtz energy of confinement ΔA represents the free energy of transfer of a macromolecule from a bulk solution of the average volume fraction ϕ to a solution in a slit of the average volume fraction ϕ_I . The partition coefficient $K = \phi_I/\phi$ is related to the free energy as $\beta\Delta A = -\ln K$.

The intra-slit pressure p_I in Eq. (1) is a function of the plate separation through the dependence of the both osmotic pressure π^{id} and the confinement force f on D . The confinement force term $D\beta f$ can formally be regarded as an increase in the effective number of molecules in the slit that produce the pressure p_I . In the narrow slits $D\beta f \gg 1$ and this term is the leading term in parenthesis in Eq. (1). In contrast, in wide slits and nondilute solutions the contribution of the term $D\beta f$ to the pressure p_I becomes smaller.

The plates also experience the osmotic pressure π from the surrounding bulk solution. As plates approach at full equilibrium, the polymer molecules move out of the particle gap into bulk solution. In the low concentration limit the net pressure $\Delta p = p_I - \pi$ exerted on plates can be expressed by the ideal osmotic pressure π^{id} in a bulk [1,4,5,15]

$$\begin{aligned} \Delta p(D) &= -\left(\frac{k_B T \phi}{N}\right) [1 - K(1 + D\beta f)] \\ &= -\pi^{id} \left(1 - K - \frac{DdK}{dD}\right) \end{aligned} \quad (2)$$

where N is the number of segments in a chain. At depletion, p_I is smaller than π and the negative sign of the net pressure Δp implies the attractive force between colloidal particles. The term $(1 - K)$ in the above equation represents an attraction due to the osmotic effect whereas the second term gives the repulsion due to confinement of chains between plates.

The net pressure can be integrated to obtain the effective pair potential (per plate unit area) between two flat plates immersed in a dilute polymer solution

$$W(D) = -\int_D^\infty \Delta p(D') dD' \quad (3)$$

As seen from above relations the evaluation of the depletion characteristics requires the knowledge of the dependence of the partition coefficient K on D [22]. For ideal (Gaussian) macromolecules in a repulsive slit the analytical relation K_{id}

vs $2R_g/D$ was derived by Casassa [6] in the form of infinite series

$$K_{id} = \left(\frac{8}{\pi^2}\right) \Sigma(2m+1)^{-2} \exp\left\{-\left((2m+1)\left(\frac{\pi}{2}\right)\frac{2R_g}{D}\right)^2\right\} \quad (4)$$

(where $m=0,1,\dots$). Clearly, the ideal chain partitioning is governed solely by the coil-to-slit size ratio $2R_g/D$ and not by these terms taken individually. The simpler relations follow from Eq. (4) for K_{id} in the limits of wide ($2R_g \ll D$) and narrow ($2R_g \gg D$) slits. However, the depletion phenomena are occurring mainly in the middle region, around $2R_g/D \approx 1$ and below.

The Casassa approach was later extended to the partitioning of ideal chains in the presence of an attraction between polymers and plate walls [20] but the mathematical relations derived are rather unwieldy and mostly their limits in wide and narrow slits are used. Alternatively, the nonideal partitioning of self-avoiding chains in attractive slits was quantified by the lattice Monte Carlo simulations in good solvents [13,14]. The simulation data of the Helmholtz energy of confinement of chains of the length of $N=100$ segments were fitted [14] by the power-law function

$$\beta\Delta A = p\left(\frac{2R_g}{D}\right)^q \quad (5)$$

where the parameters p and q depends on the polymer/wall attraction strength ε

$$p = 2.04 + 2.01\varepsilon - 22.01\varepsilon^2 \quad q = 1.57 + 2.17\varepsilon \quad (6)$$

The radius of gyration of chains of the length $N=100$ was $R_g/a=6.45$, where a is the lattice unit. In lattice models the attraction strength ε is defined as the difference between the polymer-surface interaction energy and the solvent-surface interaction energy in units of $k_B T$. The approximation of the Helmholtz energy changes by Eqs (5) and (6) is valid in the region of weak attractions between the limits $\varepsilon=0$ (purely steric repulsion) and about $\varepsilon=-0.3$. The corresponding three-dimensional plot of the function $\beta\Delta A(2R_g/D, \varepsilon)$ is shown in Fig. 2. The net pressure $\Delta p(D, \varepsilon)$ and the effective depletion potential between attractive plates $W(D, \varepsilon)$ in dilute solutions of nonideal chains are hereafter computed from these data.

3. Results and discussion

3.1. Partitioning in attractive slits

Lattice simulations of excluded-volume chains present universal properties of flexible macromolecules regardless of atomistic details. The correspondence between the lattice models and real polymers is usually sought through the notion of chains stiffness, by equating the lattice modulus a to the length of so-called Kuhn segment l_k of real polymers. For example, in atactic polystyrene (PS) in a good solvent the Kuhn segment length is about 1.8 nm and each lattice unit represents 6.9 styrene monomers. Hence, the chains of 100 segments

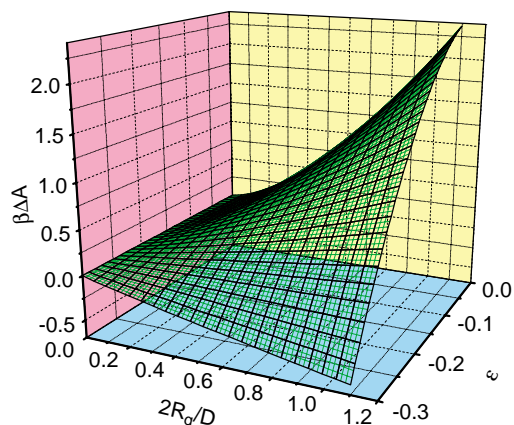


Fig. 2. Helmholtz energy of confinement $\beta\Delta A$ of a excluded volume chains of 100 segments in an attractive slit of the width D in dilute solutions calculated from Eq. (5) as a function of the confinement ratio $2R_g/D$ and the polymer/wall attraction strength ε .

examined in simulations should correspond to PS of molar mass about $M=72,000$. As the plot in Fig. 2 should represent the partitioning of any flexible polymer in a good solvent, similar link can be made to other types of macromolecules.

Three regions of the Helmholtz energy of confinement are discernible in Fig. 2. In the depletion region the penalty of entering a slit, ΔA , is positive and reduces gradually by increasing the polymer/wall attraction ε ; the partition coefficient K is within the range $0 < K < 1$. The crossover between depletion and adsorption occurs at $\Delta A = 0$ or $K = 1$ [13,14]. At this condition, termed the compensation point, ε_c , the attraction energy compensates the conformational entropy loss. Simulations of excluded volume chains of 100 segments gave $\varepsilon_c = -0.2625$ [13,14] and this value is used further in computations. Below $|\varepsilon|$ the negative adsorption (depletion) of a polymer on a surface takes place, whereas above $|\varepsilon|$ the accumulation of polymers (positive adsorption) occurs and ΔA attains the negative value. Alternatively, the reduced variable $\varepsilon_{rel} = (\varepsilon - \varepsilon_c)/\varepsilon_c$ can be used to measure the strength of polymer/wall attraction. This relative expression gives the distance from the compensation point where $\varepsilon_{rel} = 0$. The repulsive slits ($\varepsilon = 0$) of maximum of depletion interaction corresponds to $\varepsilon_{rel} = -1$, whereas the positive adsorption is characterized by $\varepsilon_{rel} > 1$.

The compensation point $\varepsilon_c = -0.18$ in ideal polymers on a cubic lattice is independent of the chain length [16,23]. Notably, its value for ideal polymers is identical to the critical point of adsorption of a polymer near a single wall $(\varepsilon_{crit})_{wall}$ [16,24] and to the analogous value in a slit $(\varepsilon_{crit})_{slit}$. However, this identities seems not to be fulfilled in excluded volume chains and the difference between the above three quantities and their variations with system parameters is matter of current investigations [13,17–19]. For example, in excluded-volume chains minor shifts of the compensation point with the chain length N and the polymer concentration were observed [13,17]. Moreover, in contrast to repulsive slits, the partition coefficient K in attractive slits may depend on the sizes of a coil and a slit taken separately, and not on their ratio $2R_g/D$ only [19,21]. The prediction of the partition coefficient K in attractive slits is of

particularly importance in liquid chromatography of polymers. Here the changes of a solvent or temperature for a given column may control the balance of separation modes according to the size-exclusion or the adsorption. In the cross-over region around the depletion/adsorption threshold the so called ‘critical chromatography’ is being developed as a valuable analytical tool for the complex polymers [25].

3.2. Net pressure

By expanding the AO concept to attractive slits we have calculated the net pressure $\Delta p(D, \varepsilon)$ exerted by excluded-volume chains on the plate walls as a function of the plate separation and the attraction strength. Substitution of Eq. (5) into Eq. (2) yields the relative net pressure of dilute polymer solutions

$$\frac{\Delta p}{\pi^{\text{id}}} = \exp(-\beta\Delta A)(1 + q\beta\Delta A) - 1 \quad (7)$$

The relative net pressure calculated by Eq. (7) is plotted for some values of ε_{rel} in Fig. 3. As a reference a corresponding function for ideal chains, computed by substituting Eq. (4) into Eq. (2), is also shown. It is seen that in a purely repulsive slit ($\varepsilon_{\text{rel}} = -1$) the intra-slit pressure p_I drops significantly below the bulk pressure at the wall separations less than about $3R_g$ due to expulsion of molecules from the slit. This manifestation of the depletion effect is slightly weaker in excluded-volume chains than in ideal chains. The positive net pressure computed for $\varepsilon_{\text{rel}} = -1$ at plate distances around $4R_g$ is most probably an artifact ensuing from an approximate nature of the fitting functions Eqs. (5) and (6). The depletion effect is substantially weakened by an increase in attraction ε_{rel} : the onset of depletion moves to the left, the steepness of pressure profiles raises and the depletion gap area is diminishing with ε_{rel} .

The depletion layer thickness δ is a useful measure of depletion interactions [8,24]. The δ values can be approximated by the inflection points in the pressure profiles in Fig. 3.

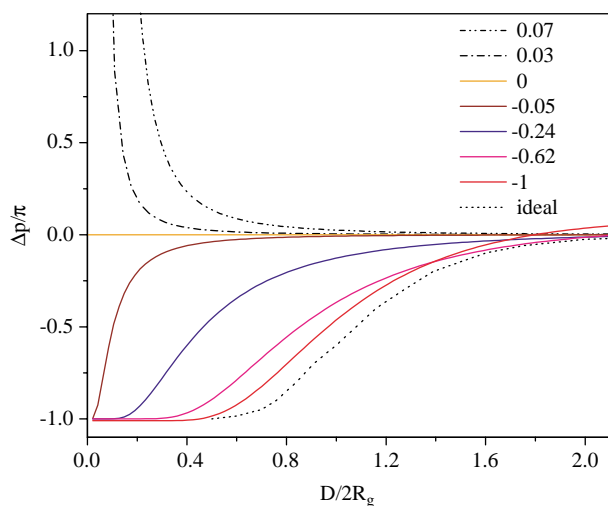


Fig. 3. The dependence of the reduced net pressure $\Delta p/\pi$ of macromolecules on the normalized plate separation in an attractive slit. The reduced attraction strength ε_{rel} corresponding to curves from top to bottom is given in the legend.

As expected, the depletion thickness δ is reduced with increasing polymer/wall attraction ε_{rel} . The rate of these changes become striking in the vicinity of ε_c . At the compensation point the intra-slit pressure p_I is equal to the bulk pressure π and depletion layer vanishes ($\delta=0$). The reduction of the depletion thickness δ with ε_{rel} is readily discernible in the concentration profiles across the slit $\phi_I(x)$ reported earlier [13,17]. At the compensation point an essentially flat segment concentration profile $\phi_I(x)$ was observed [13,17], equivalent in Fig. 1 to a horizontal line inside the gap and in bulk solution. In other words, the polymer at this condition does not ‘feel’ the plates (colloid particles). However, one should remember that a correct estimation of occupation of the first one or two layers is notoriously difficult in the lattice models with finite segment size.

Above $\varepsilon_{\text{rel}}=0$ the intra-slit pressure p_I exceeds the bulk pressure π and positive sign appears in the Eq. (2) to reflect ensuing repulsive forces. In fact, the pressure profiles in Fig. 3 at polymer/wall attraction slightly above the compensation point show a significant repulsion at short separations due to accumulation of segments near the slit walls. The repulsion rapidly diminishes with D and the net pressure levels off to zero. Similar changes from the attractive to repulsive pressure profiles were noted in simulations of short (decamer) oligomers using the isotensional ensemble [26].

3.3. Depletion potentials

The depletion potential between two plates induced by a polymer solution is defined by Eq. (3) as the work (Helmholtz energy difference) of bringing two plates infinitely far apart to the distance D . The Helmholtz energy at infinite distance of plates is given by the cost of making two depletion layers.

An evaluation of integral in Eq. (3) with the net pressure Δp expressed by Eq. (2) furnishes the effective polymer-mediated potential of mean force $W(D, \varepsilon)$ per unit area of a plate in the dilute solution limit [8,24]

$$W(D, \varepsilon) = W(0) + \pi^{\text{id}}D(1 - K) = -\pi^{\text{id}}[2\delta - D(1 - K)] \quad (8)$$

The contact potential is negative, $W(0) = -2\pi\delta$, since two depletion layers are destroyed at contact of plates.

The reduction of the depletion potential by the bulk osmotic pressure eliminates an additional variable, polymer concentration. An explicit relation akin to Eq. (7) (not shown) for the normalized depletion potential W/π^{id} as a function of separation D and attraction ε can be written down by substituting in Eq. (8) the coefficient $K = \exp(-\beta\Delta A)$ and utilizing the fitting functions Eqs. (5) and (6). The normalized depletion potential calculated by such formula is shown in Fig. 4 for the representative values of ε_{rel} . The slopes of the normalized potentials seem to be unaffected by ε_{rel} . On the other hand, the depth and the range of the potential are reduced by the increasing attraction strength ε_{rel} . These variations of the normalized potential W/π^{id} induced by polymer/wall interaction resemble the changes of the depletion potential $W(D)$ in repulsive slits by of polymer concentration [7–9,27].

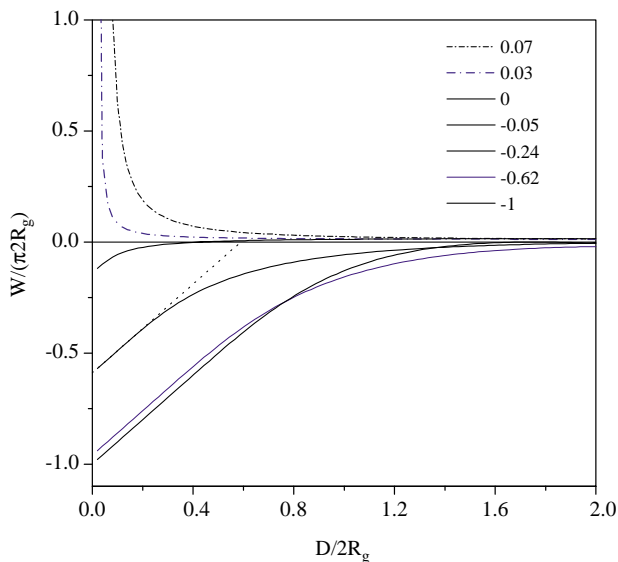


Fig. 4. The reduced depletion potential between attractive plates separated by the distance $D/2R_g$ at the normalized attraction strength ε_{rel} given in the legend (for curves from top to bottom). The dotted line for $\varepsilon_{\text{rel}} = -0.24$ illustrates the prediction of the step-function model.

The concentration effect on depletion potential in dilute solutions can be introduced into data in Fig. 4 by removing the normalization by π^{id} . In dilute solutions the depth of the depletion potential $W(0)$ for given ε_{rel} increases in a linear fashion with volume fraction ϕ , however, this linearity should be lost at elevated concentrations. Moreover, the changes in variables ϕ and ε may be interrelated at elevated concentrations; for example, it was found, that the polymer concentration have an effect on the polymer/wall energy ε_c at the compensation point [17].

Often a simplified step-function model is applied to estimate the depletion potential [8,10]. According to this notion virtually no polymer is expected to penetrate between plates at small separations and curves in Fig. 3 can be approximated by the step functions at the corresponding depletion layer thickness δ . Accordingly, at small separations $K=0$ in Eq. (2) and the plates are pressed together by the bulk osmotic pressure. This approximation leads to a linear increase of the depletion potential with D . The step-function model, illustrated in Fig. 4 just for a single case of $\varepsilon_{\text{rel}} = -0.24$, emulates at small separations the depletion potentials but neglects the fine effects in the curved region of potentials on approaching their saturation limit.

The depletion potential vanishes around the compensation point $\varepsilon_{\text{rel}}=0$ for all plate separations. At this threshold the polymer-mediated depletion attraction is balanced by steric repulsion of quasi-adsorbed chains. Repulsion of plates coated with adsorbed chains prevails above the threshold. The signs on the right side of Eq. (8) are reversed, the depletion potential W changes to the adsorption potential and the contact potential $W(0)$ become positive (Fig. 4). Furthermore, increasing adsorption strength at $\varepsilon_{\text{rel}}>0$ may give rise to formation of polymer bridges between the plates. The bridging force is attractive and may compete with steric repulsion [26].

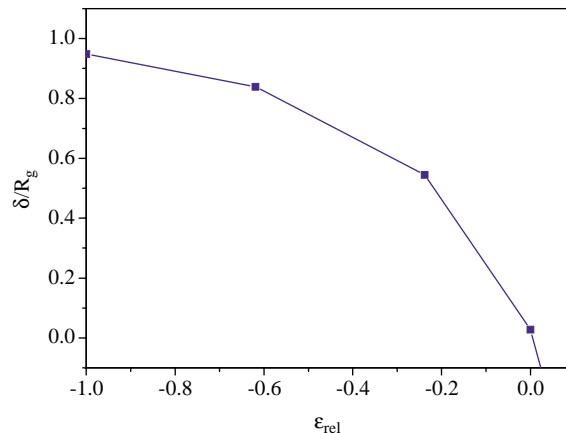


Fig. 5. Variation of the normalized depletion layer thickness with relative attraction ε_{rel} calculated from the contact potentials $W/\pi^{\text{id}}(0)$ in Fig. 4.

Furthermore, in strongly adsorbed polymers ($\varepsilon_{\text{rel}} \gg 0$) none-equilibrium conditions may prevail even at a time scale of hours. In such a case the condition of the restricted equilibrium, i.e. of the fixed amount of polymer inside a slit at variations of the plate separation, may be a more suitable stipulation than the full equilibrium [20,24].

The depletion thickness δ as a function of polymer/wall attraction ε_{rel} can be determined from the contact values of the normalized potential $W/\pi^{\text{id}}(0) = -2\delta$ shown in Fig. 4. The depletion thickness δ diminishes with increasing attraction ε_{rel} , in particular in the vicinity of the compensation point $\varepsilon_{\text{rel}}=0$ (Fig. 5). The negative values of the thickness δ at $\varepsilon_{\text{rel}}>0$ in Fig. 5 are a sign of the change of a depletion layer into an enrichment (adsorption) layer. The depletion thickness of ideal chains near a repulsive plate ($\varepsilon_{\text{rel}} = -1$) is $\delta_{\text{id}} = (2/\sqrt{\pi})R_g = 1.13R_g$ [6,8,16]. Excluded-volume chains near repulsive plates in a slit give in Fig. 5 a slightly smaller value $\delta/R_g = 0.96$.

Alternatively, the depletion thickness δ as a function of ε_{rel} can be determined from the partition coefficients K in wide slits. Recently it was demonstrated [28] that the ideal chain partition relation, Eq. (4), in the limit of wide slits reduces to the form

$$K_{\text{id}} = 1 - \left(\frac{2}{\sqrt{\pi}} \right) R_g = 1 - 2 \left(\frac{\delta}{D} \right) \quad (9)$$

where $\delta = \delta_{\text{id}}$ in this case. This simple expression was also used in an adaptation of the Casassa approach [6] to higher concentrations [8]. In analogy, one can assume that Eq. (9) can as well be applied to non-ideal chains in attractive slits. Hence, the depletion thickness δ was evaluated from the slope of plots of the partition coefficient K vs $2R_g/D$ shown in Fig. 6, using the simulation data in wide attractive slits reported earlier [21]. The changes in the depletion thickness δ with relative attraction ε_{rel} deduced from slopes of lines in Fig. 6 are consistent with the function plotted in Fig. 5.

Recent developments in experimental techniques make possible the direct measurement of depletion interaction between a wall and a single colloidal particle [29,30]. The magnitude of depletion forces at small concentrations is

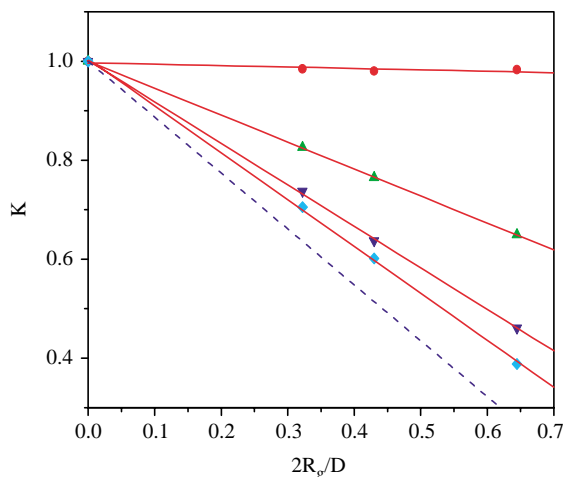


Fig. 6. Variation of the partition coefficient K with $2R_g/D$ in wide attractive slitlike pores for $\varepsilon_{\text{rel}}=0, -0.24, -0.62, -1$ (full lines, from top to bottom) and for ideal chains (dashed line) compiled from simulation data for $N=100$ from Ref. [21].

typically of the order of piconewtons. In recent atomic force microscopy experiments with stearylated silica surfaces in cyclohexane it was established [30] that the measured depth of the depletion potential $W(0)$ was only about 16% of the depth predicted by the lattice SCF theory [24] for purely repulsive plates. The smaller magnitude of the measured Helmholtz depletion energy was explained [30] by the presence of the polymer-surface attraction. The reduced value $\varepsilon_{\text{rel}} = -0.41$ was assigned from the comparison of measured data of the contact potential $W(0)$ with SCF calculations, assuming the marginal solvent quality parameter $\chi=0.4$, not far from the theta limit ($\chi=0.5$). Besides, the SCF method predict the positive sign of $W(0)$ in the adsorption region. These findings are in full qualitative accord with our calculations of the dependence of the contact potential $W(0)$ on ε_{rel} shown in Fig. 4.

The effective pair potential of plates $W(D, \varepsilon)$ can be useful in assessment of the stability of suspensions of large colloidal particles. The potential is related to the effective second virial coefficient B_2 of colloidal spheres of the radius R_p in polymer solution. The coefficient B_2 is given by the sum of the hard-sphere interaction and the polymer-mediated interaction [8]

$$B_2 = \left(\frac{16}{3}\right)\pi R_p^3 + 2\pi \int_0^{\infty} (D + 2R_p)^2 \{1 - \exp[-\beta W(D, \varepsilon)]\} dD \quad (10)$$

For very large spherical particles the curvature effects in the annular slit can be neglected and the plate potential $W(D, \varepsilon)$ can be used in the second term. The positive B_2 indicates the effective colloid–colloid two-body repulsion and thus a stability of a dispersion, while $B_2 < 0$ indicates a particle attraction. The previous calculations [8] for the purely repulsive spheres ascertained that the hard-core repulsive term in Eq. (10) prevailed in dilute solutions and thus $B_2 > 0$.

As concentration increased the depletion interaction term in Eq. (10) shifted B_2 in the negative direction [8].

Since, the depletion interactions become weaker on increase in ε_{rel} , one can infer from above information that the tendency to attain the negative value of the coefficient B_2 will be shifted to higher concentrations by an increase in $\varepsilon_{\text{rel}} > 0$. Hence, the range of concentration over which the dispersion of spheres is stable should expand with increasing ε_{rel} . The behaviour at the compensation point, when $W(D, \varepsilon)$ is about zero, is of a particular interest. At this condition B_2 is determined solely by the first term in Eq. (10), the excluded volume of colloidal particles; i.e. although the polymer is present in solution, its interaction with particles is annulled. In a way, this situation bears a resemblance to the definition of the theta point in polymer solutions. Since, the polymer becomes effectively invisible at the depletion/adsorption threshold, its concentration should not affect the coefficient B_2 and the stability of a polymer–colloid solution.

On the whole, these results suggest that an adjustment of the parameter ε_{rel} by a solvent or temperature, especially near to $\varepsilon_{\text{rel}}=0$, may represent an effective way of fine-tuning of depletion forces and thus of the phase behaviour of colloid–polymer mixtures. It is hoped that liquid–chromatography measurements, particularly near the cross-over region around ε_c (critical chromatography), could be instrumental in providing an estimation of the polymer–surface attraction strength ε_{rel} for a specific colloid–polymer–solvent systems.

4. Concluding remarks

The entropy-based AO concept of depletion interaction between two flat plates immersed in dilute polymer solution was extended to include energetic interactions between polymers and plates (colloidal particles). The net pressure $\Delta p(D, \varepsilon)$ exerted on the plate walls and the effective pair potential of plates $W(D, \varepsilon)$ were calculated as a function of the plate separation D and the attraction strength ε . The computations rest on a fit of the lattice simulation data for the partition coefficient K of excluded-volume chains in an attractive slit. The deduced relations for $\Delta p(D, \varepsilon)$ and $W(D, \varepsilon)$ predict a reduction of the range and depth of depletion interaction by an increase in the attraction strength $|\varepsilon|$. Variation of the depletion layer thickness δ near the plate walls with the attractive strength ε was established. The outcome of reduction in depletion interaction for the effective second virial coefficient B_2 and for the stability of colloid–polymer mixtures were discussed. A unique behaviour of depletion characteristics in the region near to the depletion/adsorption threshold is pointed out. The analytical functions suggested provide an estimation of the depletion characteristics of non-ideal neutral macromolecules in situations where polymer–particle attraction cannot be neglected and theoretical relations for ideal chains and repulsive slits are not applicable.

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