CCA-1742

Effect of Adsorbing and Nonadsorbing Polymer on the Interaction Between Colloidal Particles*

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In this paper it is described how a recent theoretical model can be applied to a system of two colloidal particles in the presence of adsorbing and nonadsorbing polymer. It turns out that in the case of adsorption the most suitable boundary condition is restricted equilibrium, in which a constant amount of polymer is in local equilibrium inside the gap between two particles. At a low polymer dose the formation of bridges gives rise to bridging flocculation, at higher amounts of polymer steric stabilization occurs due to the mutual repulsion of two extended polymer layers. If the polymer does not adsorb on the particles, full equilibrium applies in which the chemical potentials of solvent and polymer in the gap are the same as in the equilibrium bulk solution. The depletion of polymer near the surface may lead to depletion flocculation in not too concentrated polymer solutions. In very concentrated systems the thickness of the depletion zone is relatively small, and the attraction between the particles becomes too weak to overcome the particle entropy. Then the system is restabilized.

INTRODUCTION

Polymers are widely used to modify the stability of hydrophobic colloids. In many cases the polymer adsorbs on the surface of the particles. At a (very) low dose of polymer, destabilization of the colloidal system may occur whereby long tails protruding from one particle attach to another particle and form bridges. By progressive adsorption of polymer segments the free energy of interaction between the particles may become lower with decreasing particle separation, leading to aggregation. This so called *bridging flocculation* is very important in, e. g., the mining industry and in waste water treatment. Destabilization by bridging takes usually place at polymer concentrations in or below the ppm-range.

At higher polymer dosages, at concentrations of the order of 1⁰/o, all the particles are covered by a relatively extended polymer layer. Upon approach of two covered particles, the protruding loops and tails hinder

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* Based on an invited lecture presented at the *7th »Ruđer Bošković« Institute's International Summer Conference on the Chemistry of Solid/Liquid Interfaces*, Red Island — Rovinj, Croatia, Yugoslavia, June 25—July 3, 1986.

each other by osmotic forces and entropic restrictions occur due to the confinement of the available space. This situation is generally known as *steric stabilization* and finds many applications in the stabilization of paints, of magnetic suspensions, of food emulsions, etc. Now the protective polymer coatings prevent particle aggregation.

In the past, several attempts have been made to describe these phenomena theoretically. A recent monograph by Napper gives a good overview.[1] Most theories concentrate on the steric stabilization issue, and cannot cope with the general observation that stabilization and flocculation occur for the same combination of colloid and polymer, albeit in quite different polymer concentration regimes.

Not always do polymers adsorb on particle surfaces. Nevertheless, it is now generally accepted that also nonadsorbing polymers can affect the stability of colloidal systems when the other interparticle forces are relatively weak.[1-8] The physical background is that nonadsorbing polymer will try to avoid the surface region because of a lower conformational entropy close to the surface. If two particles approach each other to a distance which is, in a dilute polymer solution, smaller than twice the radius of gyration of the polymer coils, there is only solvent between the particle surfaces, and the osmotic pressure of the polymer in the outside solution pushes the particles together. The resulting attraction between the particles may become high enough to destabilize the colloidal system. Usually, the effect is only strong enough in the concentration regime where coil overlap occurs. This phenomenon has been named *depletion flocculation*[1] because the reason of the attraction is the depletion of polymer near a wall.

At still higher concentrations of nonadsorbing polymer (of the order of 10% or more) the free polymer does not give rise to flocculation any longer: the system is restabilized. Napper and Feigin have ascribed this to a free energy barrier occurring at intermediate particle separations, which would stabilize the colloids kinetically.[7] On the basis of this concept they introduced the term depletion stabilization.[1,7] Recently, we have questioned this terminology because in many cases the barrier turned out to be insignificantly small with respect to the kinetic energy of the particles.[8] However, it has been shown that the attraction between the colloids decreases with increasing polymer concentration in concentrated systems, mainly because the thickness of the depletion zone (which is about the radius of gyration in dilute systems) becomes smaller as the osmotic pressure goes up.[6,8] Therefore, if any the term *depletion restabilization* would be more appropriate.

It turns out that the model of Scheutjens and Fleer[9-10] for chain molecules in a concentration gradient can handle all possible interactions between colloids and polymers, both adsorbing and nonadsorbing, in a straightforward way. In this paper we highlight the main points. We shall also pay attention to the important issue whether there is full thermodynamic equilibrium at any point during particle approach or whether some restrictions apply. It is shown that *full equilibrium* is relevant for depletion interaction, whereas for adsorbing polymer *restricted equilibrium* applies. In the former case all the chemical potentials are the same in the gap between the particles and in the equilibrium solution. In restricted equilibrium there is no time for polymer desorption and transport during the time of, say, a Brownian

collision, and a constant amount of polymer is present, which is only in local equilibrium inside the gap.

INTERACTION AT FULL EQUILIBRIUM

The qualitative features of the interaction between flat surfaces in the presence of adsorbing and nonadsorbing polymer are depicted in Figure 1. Concentration profiles are given for large plate separation (top) and for a situation where the plates are relatively close (middle). The expected dependence of the excess amount Θ_{ex} of polymer between the plates as a function of the plate separation M is sketched in the bottom diagrams.
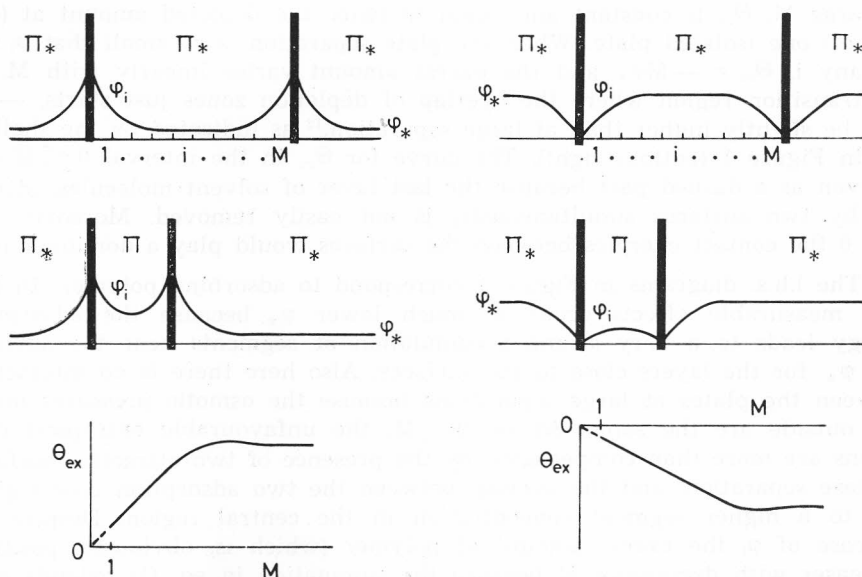

Figure 1. Adsorption (left) and depletion (right) of polymer between two plates. At large plate separation the osmotic pressure inside and outside the gap is the same and no interaction occurs (top). When the plates approach each other (middle) the segment density halfway between the plates becomes higher (adsorption) or lower (depletion) than the solution concentration and an attractive force develops, mainly because of a decrease in the (absolute value of the) adsorbed amount (bottom).

Let us first consider the situation for nonadsorbing polymer (right in Figure 1). At large M the volume fraction of segments halfway between the plates equals that of the bulk solution outside the plates. We denote the bulk solution concentration as φ_* ; in the case of depletion it is relatively high. Near the surfaces the volume fraction is lower than φ_* because the segments have no affinity for the plates and entropical conditions are unfavourable. When the coils in the solution do not overlap, the depletion zone extends over a distance comparable to the radius of gyration. At high φ_* the depletion thickness is smaller because the osmotic pressure Π_* pushes the chains closer to the plates. At large M the same Π_* is found inside the gap and the free energy of interaction is zero. At separations smaller than twice the depletion thickness the entropical restrictions become high enough to

prevent the polymer to reach the same concentration in the gap as in the outside solution. Now the average inside osmotic pressure Π is smaller than Π_* and the plates attract each other.

The excess amount Θ_{ex} is negative for nonadsorbing polymer. If we consider a semicrystalline lattice and number the lattice layers between the plates $i = 1, 2, \ldots, M$ the excess amount is found in equivalent monolayers by virtue of the definition:

$$\Theta_{ex} = \sum_{i=1}^{M} (\varphi_i - \varphi_*) \tag{1}$$

At large M, Θ_{ex} is constant and equal to twice the depleted amount at (one side of) one isolated plate. When the plate separation is so small that $\varphi_i = 0$ for any i, $\Theta_{ex} = -M\varphi_*$ and the excess amount varies linearly with M. In the transition region where the overlap of depletion zones just starts, $-\Theta_{ex}$ may be slightly higher than at large separation,[12] as indicated by the shallow dip in Figure 1 (bottom right). The curve for Θ_{ex} in the interval $0 < M < 1$ is given as a dashed part because the last layer of solvent molecules, attracted by two surfaces simultaneously, is not easily removed. Moreover, for M = 0 the contact energies between the surfaces would play a dominant role.

The l.h.s. diagrams in Figure 1 correspond to adsorbing polymer. In this case measurable effects occur at much lower φ_* because the adsorption energy leads to a very strong accumulation of segments near the surface: $\varphi_i \gg \varphi_*$ for the layers close to the surfaces. Also here there is no interaction between the plates at large separations because the osmotic pressures inside and outside are the same. At smaller M, the unfavourable entropical conditions are more than compensated by the presence of two attractive surfaces at close separation, and the overlap between the two adsorption layers gives rise to a higher segment concentration in the central region. Despite the increase of φ_i the excess amount of polymer (which is, obviously, positive) decreases with decreasing M because the summation in eq. (1) extends over a smaller number of layers. Some polymer has to desorb and diffuse away into the bulk solution in order to maintain full equilibrium (constant chemical potentials).

The dependence of Θ_{ex} on M is illustrated in the bottom left diagram in Figure 1. Again a hump in the transition region, corresponding to Θ_{ex} exceeding slightly twice the excess amount near an isolated surface, may occur[10,11] but its effect is relatively minor. The decrease of Θ_{ex} at small M is more important. It continues down to M = 1 (one layer between the plates) but the surfaces cannot come into contact. For $0 < M < 1$ the same effects play a role as for nonadsorbing polymer. In addition, the last layer of polymer segments experiences a double adsorption energy, leading to a volume fraction that is higher than in the layer adjoining an isolated surface.

The question as to the free energy of interaction for adsorbing polymer is not easily answered without detailed computations. The higher osmotic pressure inside the gap would suggest a repulsion; however, Θ_{ex} decreases and less polymer is involved. Therefore, the interaction could very well be attractive. As a matter of fact, we shall show below that in full equilibrium always attraction is found, also for adsorbing polymer.

The above qualitative arguments can be made more quantitative by considering the dependence of Π on segment concentration, taking into account the concentration gradient inside the gap and, hence, the variation of Π_i with layer number i. According to the Flory-Huggins theory, the osmotic pressure in the homogeneous bulk solution is given by:[13]

$$\Pi_* v^\circ / kT = - (1 - 1/r)\, \varphi_* - \ln (1 - \varphi_*) - \chi \varphi^2_* \tag{2}$$

where v° is the solvent molecular volume, kT the thermal energy, r the ratio of molar volumes of polymer and solvent (or the number of segments per chain) and χ the polymer-solvent interaction parameter. This expression could also be written in terms of the solvent chemical potential in the solution with respect to pure solvent, which according to standard thermodynamics equals $-\Pi_* v^\circ$. Analogously to eq. (2), we may define the osmotic pressure Π_i in layer i with respect to pure solvent:

$$\Pi_i v^\circ / kT = - (1 - 1/r)\, \varphi_i - \ln (1 - \varphi_i) - \chi \varphi_i \langle \varphi_i \rangle \tag{3}$$

The only difference between eq. (3) and eq. (2) is the site volume fraction $\langle \varphi_i \rangle$ accounting for the number of contacts of a site in layer i with its neighbours in a concentration gradient. For example, in a cubic lattice (6 neighbours) 4 contacts are in layer i and 1 contact exists with each of the neighbouring layers $i - 1$ and $i + 1$: $\langle \varphi_i \rangle = \varphi_{i-1}/6 + 4\varphi_i/6 + \varphi_{i+1}/6$. Note that Π_* and Π_i are positive quantities, as can be seen immediately by expanding the logarithm: $\Pi_* v^\circ / kT = \varphi_* / r + (1/2 - \chi)\, \varphi^2_* + \varphi^3_* /3 + \ldots$

Previously, we have derived an expression for the excess free energy $f(M)$ per surface site in terms of the concentration profile $\{\varphi_i\}$.[10,11] This may be rewritten in terms of Π_i and Π_* in a very simple way:

$$f^{FE}(M) = 2\gamma^\circ a - \sum_{i=1}^{M} (\Pi_i - \Pi_*)\, v^\circ \tag{4}$$

where γ° is the surface tension of pure solvent in contact with the surface and a the area per site. The superscript FE denotes full equilibrium. At large separations ($M \to \infty$), the surfaces do not interact and $f^{FE}(\infty) = 2\gamma a$. In the latter expression, γ is the surface tension of a single plate with the equilibrium amount of polymer adsorbed on it. For adsorbing polymer on a single plate, $\Pi_i > \Pi_*$ and $\gamma < \gamma^\circ$ according to eq. (4), in agreement with Gibb's adsorption law for positive adsorption. Similarly, in the case of depletion $\Pi_i < \Pi_*$ and $\gamma > \gamma^\circ$ as expected for negative adsorption.

The free energy of interaction per surface site $\Delta f^{FE}(M)$ is defined as $f^{FE}(M) - f^{FE}(\infty)$. Hence,

$$\Delta f^{FE}(M) = 2(\gamma^\circ - \gamma)\, a - \sum_{i=1}^{M} (\Pi_i - \Pi_*)\, v^\circ \tag{5}$$

The difference $\gamma^\circ - \gamma$ can also be written as a sum over all layers for isolated plates. Since $\Delta f^{FE}(\infty) = 0$, $(\gamma^\circ - \gamma) a = \sum_{i=1}^{\infty} (\Pi_i - \Pi_*)\, v^\circ$ for a single plate. Note that all Π_i's are a function of the plate distance M.

The crucial point is the dependence of $\Delta f^{FE}(M)$ on the plate separation. For nonadsorbing polymer, the trends can be easily predicted. If M is small

enough, only solvent remains between the plates and $\Pi_i = 0$. In that case we have

$$\Delta f^{FE} (M) = 2 (\gamma^o - \gamma) a + \Pi_* v^o M \tag{6}$$

According to eq. (6), the extrapolated value of the free energy $\Delta f^{FE} (0) = 2 (\gamma^o - \gamma) a$ is negative, corresponding to attraction. With increasing plate separation, $\Delta f^{FE} (M)$ increases linearly with M.

In the case of adsorbing polymer, the situation is more complicated. Extrapolation to $M = 0$ is not easy because Δf is not linear in M. We consider the free energy at $M = 1$. From eq. (5) we have:

$$\Delta f^{FE} (1) = 2 (\gamma^o - \gamma) a - (\Pi_1 - \Pi_*) v^o \tag{7}$$

where Π_1 is the osmotic pressure due to the sandwich structure of one layer of concentrated polymer segments between two plates. The term $-\Pi_1 v^o$ in eq. (7) is attractive, the others are repulsive. The net effect depends on the relative magnitude of $2 (\gamma^o - \gamma) a$ and $-\Pi_1 v^o$ (in dilute solutions Π_* is negligible with respect to Π_1). Both terms depend on the details of the concentration profiles and cannot easily be estimated on the basis of general considerations. However, in all numerical computations $\Delta f^{FE} (M)$ was found to be attractive, in agreement with other theories.[14,15] Apparently, $\Pi_1 v^o$ is always the largest term in eq. (7).

Hence, it may be concluded that colloidal systems cannot be sterically stabilized by homopolymers in full equilibrium. If steric stabilization occurs, for which there is much experimental evidence, there is apparently no time for the polymer to desorb and diffuse away. We must then consider restricted equilibrium, which is treated in the next section.

We may observe that in the equations given above no distinction is made between, e. g., osmotic effects and volume restriction, as was done in older theories.[1,16,17] These contributions are automatically and fully accounted for by the use of the correct segment concentration profiles in eqs. (4) and (5) which are the result of all energetic and entropical effects.

INTERACTION AT RESTRICTED EQUILIBRIUM

In practical situations it is likely that the polymer chains cannot escape from the gap between two particles when this gap is narrow. In this case a reasonable assumption is full equilibrium at large M (where the interaction is weak) until at a given separation M' the polymer is trapped. Upon closer approach of the surfaces the total amount Θ_t of polymer remains now constant. Analogously to eq. (1), Θ_t is defined as

$$\Theta_t = \sum_{i=1}^{M'} \varphi_i = \Theta_{ex} (M') + M' \varphi_* \tag{8}$$

The principle of restricted equilibrium is sketched in Figure 2. On the right, two full equilibrium curves $\Theta_t (M)$ are given at two bulk solution concentrations, φ_* and φ'_*. In this example, φ_* and φ'_* are 10^{-6} and 10^{-2}, respectively, and the transition between full and restricted equilibrium is assumed to occur at $M' = 20$. The left hand side diagram of Figure 2 gives
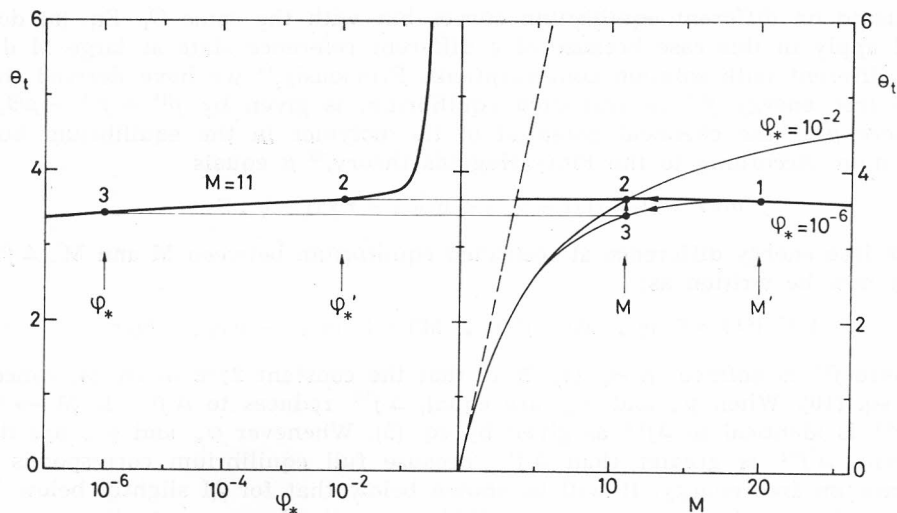
Figure 2. The adsorption between two plates at $M = 11$ as a function of the equilibrium solution concentration φ_* (left) and as a function of plate separation M (right). The dashed line, $\Theta_t = M$, represents the maximum possible amount of polymer between the plates at given M. Point 1 corresponds to the transition between full equilibrium at $M > M'$ and restricted equilibrium at $M < M'$ (horizontal line). At point 2 ($M = 11$) the polymer would be in equilibrium with a solution concentration $\varphi'_* = 10^{-2}$. The path $1 \rightarrow 3$ would apply if full equilibrium with a solution concentration of $\varphi_* = 10^{-6}$ were to be maintained down to $M = 11$. Hexagonal lattice, $r = 1000$, $\chi = 0.5$, $\chi_s = 1$.

an "adsorption" isotherm $\Theta_t(\varphi_*)$ at a given plate separation (in this case $M = 11$).

Beyond M' full equilibrium exists, and the free energy of interaction is given by eq. (5). Below M' restricted equlibrium applies in which the constant amount of polymer Θ_t distributed itself over loops, trains, tails, and bridges in local equilibrium. However, the chemical potential of the chains is no longer the same as in the bulk solution. At any $M < M'$, a situation is obtained in which this Θ_t (corresponding to full equilibrium at M' and φ_*, point 1 in Figure 2) would be in full equilibrium with a higher bulk solution concentration φ'_* at separation M (point 2 in Figure 2). We denote φ'_* as the pseudo-equilibrium concentration. Obviously, φ'_* is a function of M; its magnitude follows from the adsorption isotherm (left in Figure 2) as the concentration at the intersection point of the isotherm at plate distance M and the horizontal line corresponding to the constant value Θ_t. If full equilibrium were to be maintained at separation M and bulk solution concentration φ_*, point 3 in Figure 2. with lower Θ_t would be reached.

The minimum possible distance in restricted equilibrium is $M = \Theta_t$, indicated as the dashed line in Figure 2. At this minimum distance, the pseudo-equilibrium volume fraction is equal to unity.

The free energy difference between points 3 and 1, both belonging to the full equilibrium curve $\Theta_t(\varphi_*)$ can be found directly from eq. (5). However, we are now interested in the difference between points 2 and 1,

situated on different equilibrium curves but with the same Θ_t. Eq. (5) does not apply in this case because of a different reference state at large M due to different bulk solution concentrations. Previously,[10] we have derived that the free energy f^{RE} in restricted equilibrium is given by $f^{RE} = f^{FE} + \mu\Theta_t/r$, where μ is the chemical potential of the polymer in the equilibrium bulk solution. According to the Flory-Huggins theory,[13] μ equals

$$\mu/kT = (1-r)(1-\varphi_*) + \ln\varphi_* + r\chi(1-\varphi_*)^2 \qquad (9)$$

The free energy difference at restricted equilibrium between M and M′, $\Delta'f^{RE}$, can now be written as:

$$\Delta'f^{RE}(\Theta_t) = f^{FE}(\varphi'_*, M) - f^{FE}(\varphi_*, M') + \{\mu(\varphi'_*) - \mu(\varphi_*)\}\Theta_t/r \qquad (10)$$

where f^{FE} is defined in eq. (4). Note that the constant $2\gamma°a$ in eq. (4) cancels in eq. (10). When φ_* and φ'_* are equal, $\Delta'f^{RE}$ reduces to $\Delta'f^{FE}$. If M′ $\to \infty$, $\Delta'f^{FE}$ is identical to Δf^{FE} as given by eq. (5). Whenever φ_* and φ'_* are different, $\Delta'f^{RE}$ is greater than $\Delta'f^{FE}$ because full equilibrium corresponds to minimum free energy. It will be shown below that for M slightly below M′ the difference between $\Delta'f^{RE}$ and $\Delta'f^{FE}$ is small. However, at close particle approach $\Delta'f^{RE}$ becomes repulsive, which may lead to steric stabilization.

In the foregoing, we have chosen the transition between full and restricted equilibrium to occur at an arbitrary distance M′. In practical situations, M′ depends on the dynamics of the experimental system. In most cases M′ will be situated somewhere in the plateau of $\Theta_{ex}(M)$. Then the precise choice of M′ is immaterial for the final result, especially in not too concentrated solutions, where M′φ_* is small with respect to $\Theta_{ex}(M')$.

Above, we have addressed only the question of how to compute interaction free energies, assuming that the segment concentration profiles between the surfaces are known. The latter are obtained by taking into account all possible chain conformations and the appropriate contact energies between segments, solvent molecules and surface sites. The M unknown segment concentrations can be solved from a rather complicated set of implicit equations. For the details of this procedure we refer to the literature.[9-12]

The parameters used in the model are the number r of segments per chain and the interaction parameters χ and χ_s. The former has been used above (eqs. (2) and (3)), the latter is the dimensionless adsorption energy difference between a segment and a solvent molecule on the surface. For adsorbing polymer χ_s is positive, in the case of depletion it is taken as zero. Moreover, the lattice type has to be specified. In the examples discussed below a hexagonal lattice is chosen.

RESULTS FOR ADSORBING POLYMER

Figure 3. shows two examples of concentration profiles for chains of 1000 segments with $\chi_s = 1$ in a gap of 10 lattice layers in equilibrium with a bulk solution concentration $\varphi_* = 10^{-4}$. The full curve is for a Θ-solvent ($\chi = 0.5$), the dashed curve for athermal conditions ($\chi = 0$). In the former case the segments experience a net attraction, so that the concentration in the gap is much higher at $\chi = 0.5$ than at $\chi = 0$, leading to a concentration halfway between the plates that is 2000 times that in the bulk of the solution. For $\chi = 0$ this concentration is much lower.
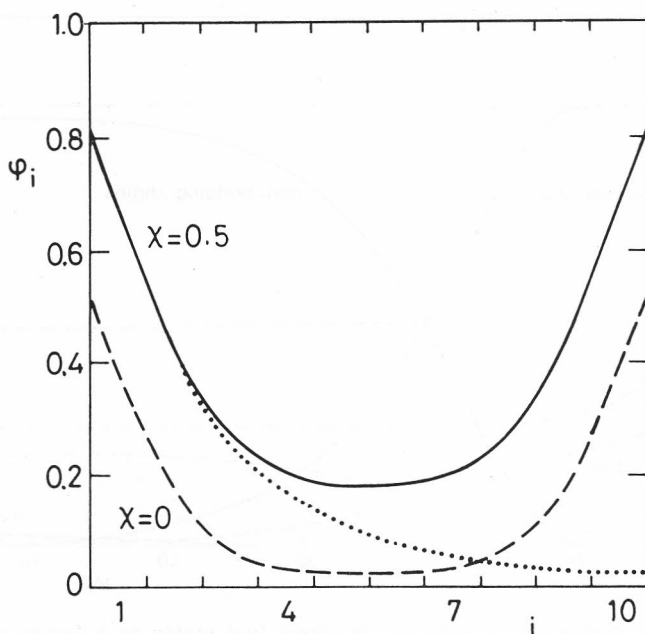
Figure 3. Segment density profiles of adsorbing polymer between two plates, 10 lattice layers apart, for a theta solvent (full curve, $\chi = 0.5$) and for a good solvent (dashed curve, $\chi = 0$). The dotted curve gives the profile near the left surface for $\chi = 0.5$ when the plates are far apart. $r = 1000$, $\varphi_* = 10^{-4}$, $\chi_s = 1$.

The dotted curve in Figure 3 is the profile for an isolated plate at $\chi = 0.5$ in equilibrium with $\varphi_* = 10^{-4}$. It can be seen that in the layers close to the surface there is hardly any difference in φ_i (at this plate separation), whereas in the middle region the full curve is approximately given by adding two dotted curves. Consequently, Θ_t is at $M = 10$ still in the plateau region of $\Theta_t(M)$ (see Figures 1 and 2) and about equal to twice the amount adsorbed per isolated plate. Only at smaller M desorption of polymer (in full equilibrium) sets in.

In Figure 4 some structural information is collected as a function of the plate separation, for $r = 1000$, $\chi = 0.5$, $\chi_s = 1$, and $\Theta_t = 5$ (restricted equilibrium). For $M \to \infty$, this value of Θ_t corresponds to $\varphi_* = 5 \cdot 10^{-3}$. A similar plot for full equilibrium would be virtually the same. We can distinguish adsorbed and free chains. The contribution of the free chains is very small, even at large separations. The adsorbed fraction may be subdivided into chains that are in contact with one surface only (non-bridging) and those that have at least one segment on each surface (bridging). For $M > 50$, hardly any bridges occur. With decreasing M the number of bridging chains increases, until below $M = 10$ all the polymer molecules contain at least one bridge. Analogously, the contribution of non-bridging chains decreases from about 95% at large M to zero for $M < 10$. Note that for $\Theta_t = 5$ the minimum plate separation in restricted equilibrium is 5 layers.
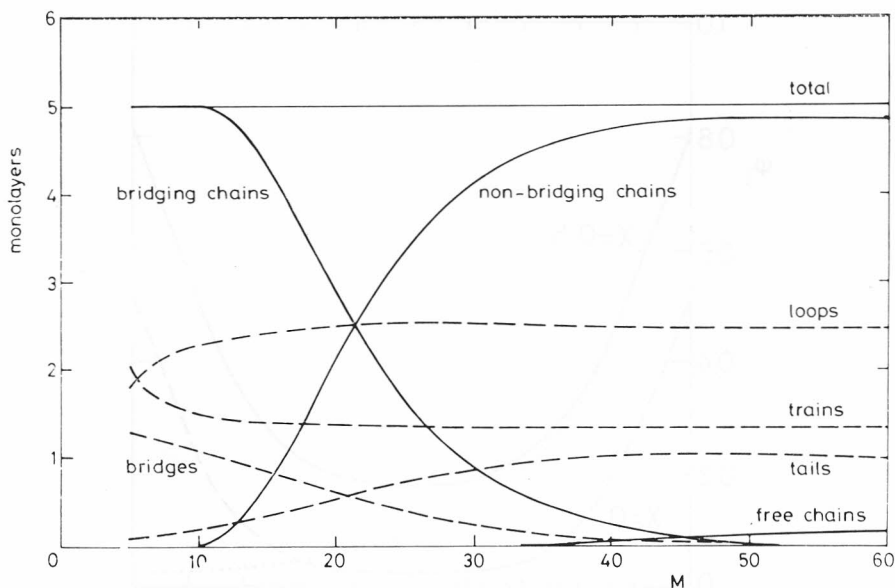
Figure 4. The composition of polymer between two plates as a function of the plate separation. The polymer is subdivided into bridging, nonbridging, and free (non-adsorbing) chains. The dashed curves give the amounts of segments in trains, loops, tails, and bridges. $r = 1000$, $\chi = 0.5$, $\chi_s = 1$, $\Theta_t = 5$ (corresponding to $\varphi_* = 5 \cdot 10^{-3}$ for large M).

The segments of adsorbing chains are in trains, loops, tails, and (for bridging chains) in bridges. The amounts of segments in these sequences are given in Figure 4 as dashed curves. For loops, trains, and tails no distinction was made between bridging and non-bridging chains. The contribution of loops and trains is nearly constant over a large range of plate separations. Only at very small interparticle distances the number of loop segments decreases slightly and that of train segments increases somewhat, in such a way that the combined contribution of loops and trains remains approximately constant. For tails the situation is quite different, the fraction of tail segments decreasing already around $M = 40$, at the same separation where the first bridges appear. With decreasing M the bridge fraction increases at the expense of tails, showing clearly that tails and bridges play a very important role in particle interactions.

Figure 5 gives an example of interaction free energies in restricted (full curves) and full equilibrium (dashed curve), for $r = 1000$ and $\chi = 0.5$. The restricted equilibrium curves apply to $\Theta_t = 3$, 3.5, and 5, respectively, corresponding to bulk volume fractions at large separation of 10^{-12}, 10^{-6}, and 10^{-2}. The full equilibrium curve is only shown for $\varphi_* = 10^{-6}$.

In full equilibrium, attraction is found under all conditions. As discussed above, this is a general feature in all theories. Comparison of Δf^{RE} and Δf^{FE} shows that for large M there is hardly any difference between the two. However, at smaller separations both curves diverge strongly, Δf^{RE}
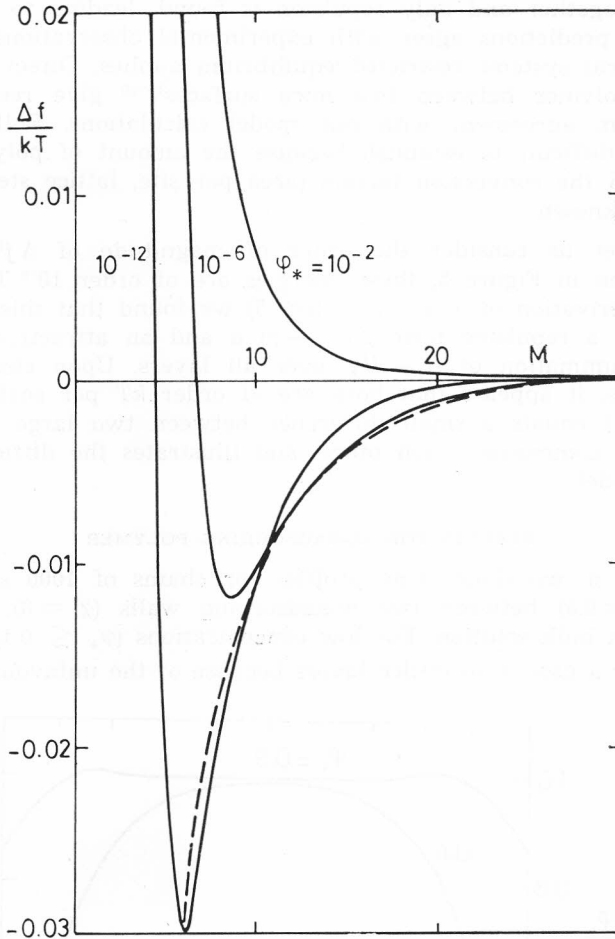
Figure 5. Interaction free energy per surface site between two plates with adsorbing polymer. The dashed curve is for full equilibrium and $\varphi_* = 10^{-6}$. The full curves apply for restricted equilibrium where after equilibration at large plate separation in a solution of $\varphi_* = 10^{-12}$, 10^{-6}, or 10^{-2} the amount of polymer between the plates remains constant ($\Theta_t = 3$, 3.5, or 5, respectively). $r = 1000$, $\chi = 0.5$, $\chi_s = 1$.

becoming repulsive when the particles approach each other relatively close. At intermediate separations, an attractive well appears, which could lead to bridging flocculation if it is, per pair of particles, deeper than kT. The numbers in Figure 5. refer to the free energy per surface site, and must be multiplied by the number of interacting sites in order to obtain the particle pair potential due to the polymer. For particles in the colloidal size range, Δf^{RE} should probably be multiplied by a factor of order one thousand or more.

The attractive well in Δf^{RE} becomes deeper and shifts to shorter separations if the bulk solution concentration is decreased to 10^{-12}. On the other hand, for relatively concentrated systems ($\varphi^* = 10^{-2}$) the attractive part

disappears altogether and only repulsion is found, leading to steric stabilization. These predictions agree with experimental observations and suggest that in practical systems restricted equilibrium applies. Direct force measurements of polymer between two mica surfaces[18-20] give results that are qualitatively in agreement with our model calculations. Full quantitative agreement is difficult to establish because the amount of polymer between the plates and the conversion factors (area per site, lattice step length) are insufficiently known.

Finally, let us consider the order of magnitude of Δf^{RE} and Δf^{FE}. As can be seen in Figure 5, these energies are of order 10^{-2} kT per lattice site. In the derivation of, e. g., Δf^{FE} (eq. 5) we found that this quantity can be written as a repulsive term $2(\gamma^0 - \gamma)$ a and an attractive term representing the summation of $\Pi_i - \Pi_*$ over all layers. Upon closer inspection of these terms, it appears that both are of order kT per surface site. This shows that Δf equals a small difference between two large numbers that approximately compensate each other, and illustrates the difficulties of any theoretical model.

<div align="center">RESULTS FOR NONADSORBING POLYMER</div>

In Figure 6. we show some profiles for chains of 1000 segments in a Θ-solvent ($\chi = 0.5$) between two nonadsorbing walls ($\chi_s = 0$), in full equilibrium with a bulk solution. For low concentrations ($\varphi_* \lesssim 0.1$) the polymer does not enter a gap of 10 lattice layers because of the unfavourable entropic
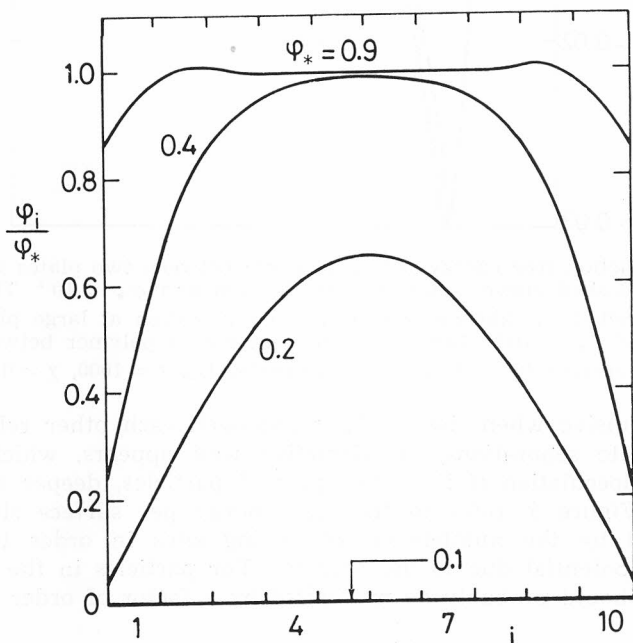

Figure 6. Segment density profiles of nonadsorbing polymer between two plates at four different solution concentrations. $r = 1000$, $\chi = 0.5$, $\chi_s = 0$.

conditions. With increasing φ_* the higher osmotic pressure in the solution forces some polymer between the plates, leading to concentrations in the middle region that are about 60% of the bulk concentration at $\varphi_* = 0.2$ and about 99% at $\varphi_* = 0.4$. For very concentrated solutions ($\varphi_* = 0.9$) the profile becomes rather homogeneous, with regions where φ_i is even slightly higher than φ_*. We have no simple physical explanation for the latter effect but note that Feigin and Napper[7] found the same trend in a similar model as ours.

In Figure 7 the free energy of interaction is plotted as a function of the particle separation for two values of φ_*. The curves are linear in the region where there is no polymer between the plates, and this region is wider for lower polymer concentrations. As soon as the polymer enters the gap a deviation from this linearity occurs. Comparison with Figure 6 shows that $M = 10$ is in the linear range for $\varphi_* = 0.1$ and in the transition region for $\varphi_* = 0.2$.
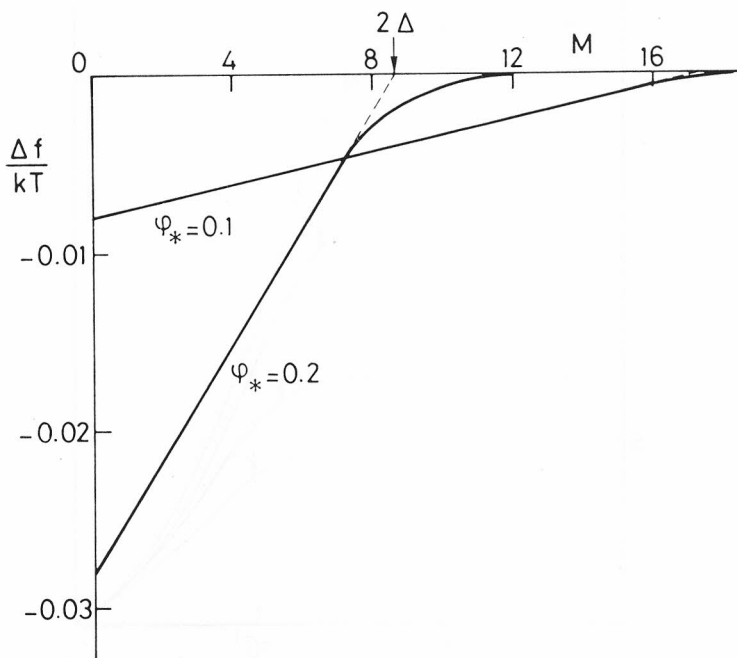

Figure 7. Interaction free energy per surface site between two plates with non-adsorbing polymer for two different solution concentrations φ_*. The depletion thickness Δ can be obtained by extrapolation to $\Delta f = 0$ (dashed line). $r = 1000$, $\chi = 0.5$, $\chi_s = 0$.

In the theoretical section we derived an equation for the linear range (eq. 6): the intercept equals $2(\gamma^0 - \gamma)a$ (where $\gamma > \gamma^0$ for negative adsorption) and the slope is $\Pi_* v^0$. Extrapolation of the linear section towards the abscissa gives the depletion thickness 2Δ, which is a measure for the gap width where, upon decrease of M, the polymer is squeezed out completely. Another essentially equivalent definition of Δ can be given. At distance 2Δ

the excess amount of polymer in the gap is $-2\Delta\varphi_*$ so that the depletion thickness follows from the numerical data as $2\Delta = -\Theta_{ex}/\varphi_*$

In terms of Δ, the free energy of interaction can also be written as

$$M \leq 2\Delta \qquad \Delta f(M) = \Pi_* v^o (M - 2\Delta)$$

$$M \geq 2\Delta \qquad \Delta f(M) = 0$$

(11)

In this equation, the nonlinear »tail« in the $\Delta f(M)$ curves of Figure 7 is neglected.
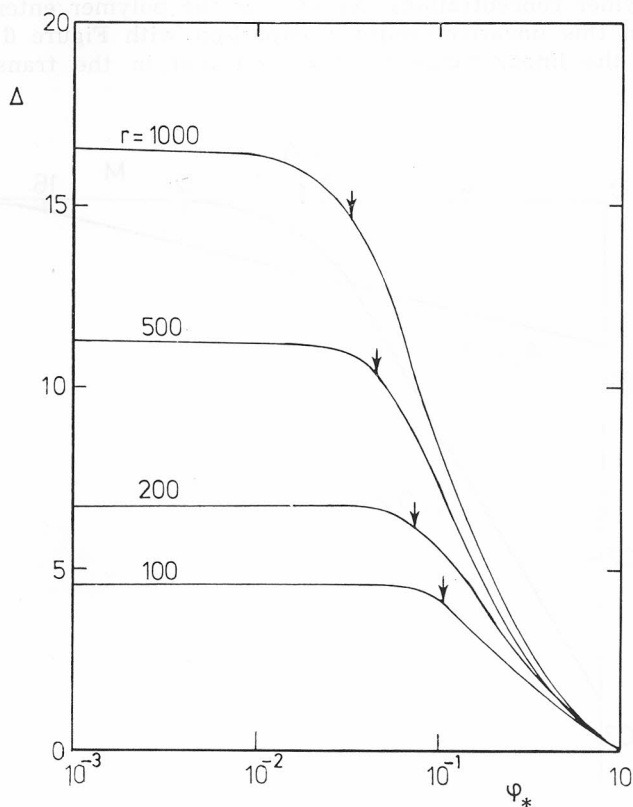

Figure 8. The depletion thickness Δ as a function of the polymer concentration for four chain lengths. Arrows indicate the concentration where the polymer coils in solution begin to overlap. $\chi = 0.5$, $\chi_s = 0$.

Figure 8 gives the results for Δ as a function of φ_* for various chain lengths. In dilute solutions, Δ is independent of φ_* and proportional to the square root of the chain length r. As a matter of fact, in this region Δ is approximately equal to the radius of gyration R_g of the coils in solution. This is a very reasonable result, implying that polymer coils below the overlap concentration are excluded from a gap width equal to twice the coil radius.

With increasing solution concentration, the individual coils in solution begin to overlap. A measure for the overlap concentration is the volume fraction of polymer at which close-packed spheres of radius R_g just touch. This concentration is indicated in Figure 8 by the arrows. It is clearly seen that, as soon as the polymer coils in solution begin to interpenetrate, also the depletion thickness decreases and narrower gaps can be entered. In very concentrated solutions Δ drops gradually, reaching zero for $\varphi_* = 1$ (corresponding to the polymer melt), while at the same time the molecular weight dependence becomes weaker. From polymer solution properties it is well known that the osmotic pressure depends on molecular weight in dilute solutions, whereas in concentrated systems the effect of chain length becomes relatively much less. These trends are closely related.

From eq. (11) we see that $\Delta f(0)$ for flat surfaces is proportional to the product $\Pi_* \Delta$, where both Π_* and Δ depend on φ_*. With increasing φ_*, Π_* increases and Δ decreases. It can be shown that in concentrated solutions the increase of Π_* with φ_* is stronger than the decrease of Δ, leading to a depletion attraction that increases with increasing φ_*, at least for flat geometries.

For spherical particles the situation is different. Numerical data for the interaction energy between spheres are not available as yet. However, we may approximate the interaction between spherical particles, Δf_p, by using the Deryagin approximation $\Delta f_p(M) = \pi R \int_M^\infty \Delta f(M) \, dM$.[21] In this expression R is the dimensionless sphere radius (expressed as the number of lattice steps), and $\Delta f(M)$ is given by eq. (11). For spheres, M is the shortest distance between two spherical particles. With this equation we obtain:

$$M \leq 2\Delta \qquad \Delta f_p(M) = \pi R \Pi_* v^\circ (M - 2\Delta)(\Delta - {}^1/_2 M)$$
$$M \geq 2\Delta \qquad \Delta f_p(M) = 0 \tag{12}$$

We see that the linear region of $\Delta f(M)$ disappears in $\Delta f_p(M)$: eq. (12) is quadratic in M. The physical background, obviously, is the spherical geometry of two overlapping depletion shells, where the overlap volume increases more than linearly with decreasing M. More important for our present purpose is the fact that $\Delta f_p(0)$ is not proportional to $\Pi_* \Delta$ (as for plates) but to $\Pi_* \Delta^2$. Whereas for plates the depletion interaction becomes stronger in concentrated solutions (above coil overlap), it decreases for spheres because of the quadratic dependence on Δ. Therefore, $-\Delta f_p$ increases with φ_* in dilute solutions (where Δ is constant), then passes through a maximum, and becomes smaller at still higher concentrations.

These trends are illustrated in Figure 9. In this diagram we have plotted the depletion interaction free energy Δf_d per particle, when this particle is transferred from a dilute dispersion to a floc phase where each particle is in contact with z neighbouring particles. Hence, $\Delta f_d = (z/2) \Delta f_p(0) = -\pi z R \Pi_* v^\circ \Delta^2$. In figure 9, $\pi z R$ was chosen as 500, corresponding to a particle diameter of order 40 nm (assuming a lattice step length of 1 nm). Plots are given for two chain lengths, $r = 100$ and $r = 1000$. The osmotic pressure Π_* was calculated from eq. (2), the depletion thickness from the numerical data for flat plates through $2\Delta = -\Theta_{ex}/\varphi_*$.
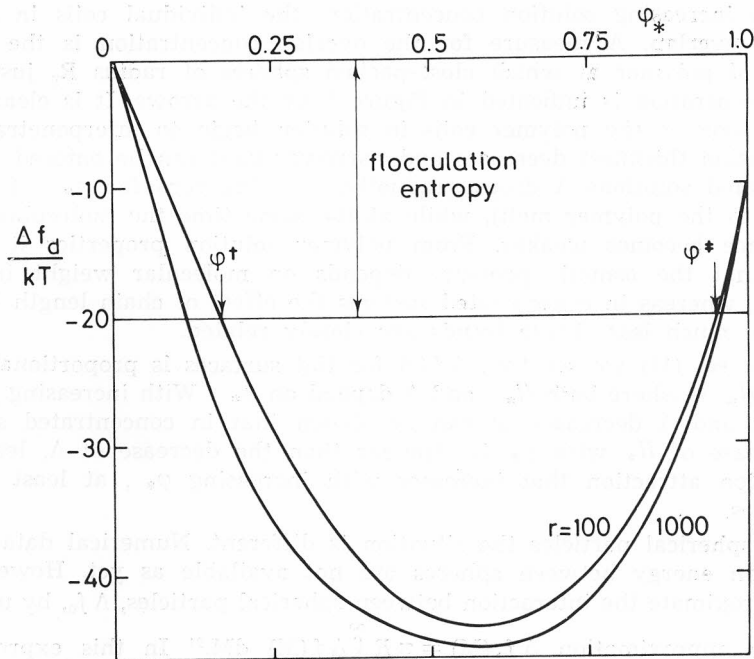
Figure 9. The change in free energy per flocculating particle due to depletion, for two chain lengths, as a function of the polymer concentration. Between φ^+ and $\varphi^\ddagger$ this free energy gain overcompensates the entropy loss of the particles, so that flocculation occurs. $\chi = 0.5$, $\chi_s = 0$, $\pi z R = 500$.

It follows from Figure 9 that indeed the depletion attraction is weak for low and for very high polymer concentrations, and is strongest in the region $\varphi_* \simeq 0.3 — 0.7$. For $\varphi_* \to 1$, Δf_d is nonzero (even if $\Delta \to 0$) because the polymer in a melt looses entropy when it is forced to enter a narrow slit. However, the accuracy for Δf_d at very high φ_* as given in Figure 9 is limited, due to the approximation involved in eq. (11) and (12): in concentrated solutions the »tail« in $\Delta f(M)$ around $M = 2\Delta$ (see Figure 7) is not negligible.

In order to derive the implications of the dependence $\Delta f_d(\varphi_*)$ on dispersion stability, we have to compare the magnitude of Δf_d with other interparticle interactions, such as Van der Waals forces and entropy effects when particles from a dilute dispersion are transferred to a floc. These interactions are difficult to calculate accurately without detailed statistical mechanical models, but they may be assumed to be independent of the polymer concentration.

In Figure 9 a horizontal line is drawn, corresponding to a free energy of particle transfer of 20 kT. Let us assume that the particle translational entropy difference between floc phase and dilute dispersion is the major contribution to this free energy of transfer. For ideally dilute phases differing a factor of, say, 10^4 in particle concentration, this free energy difference is $kT \ln 10^4 \simeq 10\, kT$. However, the floc phase is very concentrated with a very low translational entropy for the particles, and the free energy difference is

much higher. Therefore we choose more or less arbitrarily 20 kT in our example, probably representative for a dispersion with a particle volume fraction of order 10^{-4}. A different choice would not affect the qualitative picture.

Now we may deduce from Figure 9 how the stability of a dilute dispersion of spheres depends, at given particle concentration, on the concentration of nonadsorbing polymer. Below a treshold concentration φ^+ the depletion attraction is too weak to overcome the particle entropy loss and the dispersion is stable. In the range $\varphi^+ < \varphi_* < \varphi^\ddagger$ depletion flocculation occurs, and above $\varphi^\ddagger$ the depletion attraction is again too small to induce flocculation. One could denote φ^+ as the depletion flocculation concentration; similarly $\varphi^\ddagger$ is the restabilization concentration. It may be noted that the restabilization is not caused by a repulsive barrier as suggested by Feigin and Napper[7], but is simply a consequence of too weak an attraction due to the smaller depletion thickness in concentrated solutions.

From the above discussion it is clear that φ^+ and $\varphi^\ddagger$ depend on the particle concentration, on the polymer molecular weight, on the solvent quality, and on the presence of other interparticle forces. A full analysis of these effects has not been made so far. In a previous paper[8] we have shown how experimental data of De Hek and Vrij[4] for hard spheres can be interpreted satisfactorily with the present simple model.

Many experiments[2,3,22] have been reported for a system of »soft« spheres consisting of particles covered by a layer of grafted polymer. Such a system is expected to behave differently from hard spheres since the magnitude of the depletion thickness and its dependence on φ_* will be effected by the hairy layer. Experimental evidence suggests that both φ^+ and $\varphi^\ddagger$ are lower for soft spheres as compared to hard particles. A simplified model for soft spheres has been given by Vincent et al.[22]; further progress can be made by performing numerical computations on the basis of the Scheutjens-Fleer model for hairy surfaces in the presence of free polymer.

CONCLUSIONS

Our lattice theory for chain molecules in a concentration gradient has been succesfully applied to interaction between two particles in the presence of polymer, both adsorbing and nonadsorbing. In the case of adsorbing polymer, conditions of restricted equilibrium must be defined (constant amount of polymer). On the other hand, depletion effects can be described in a theory for full equilibrium (constant chemical potentials).

In dilute solutions of adsorbing polymer an attractive well is present in the interaction free energy. This gives rise to bridging flocculation. With increasing polymer concentration the depth of this minimum decreases until it disappears altogether and only repulsion is found (steric stabilization).

In the case of nonadsorbing polymer, a depletion thickness can be defined as half the slit width below which no polymer enters the gap between two particles. As a consequence, the particles attract each other by osmotic forces. In dilute polymer solutions the attraction is too weak to overcome the particle flocculation entropy, in more concentrated system depletion flocculation occurs. At very high polymer concentrations the thickness of the depletion zone decreases, resulting in restabilization.

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SAŽETAK

Efekt adsorbirajućeg i neadsorbirajućeg polimera na interakciju među koloidnim česticama

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Opisana je primjena teorijskog modela na sustav koji se sastoji od dvije koloidne čestice u prisutnosti adsorbirajućeg i neadsorbirajućeg polimera. U slučaju adsorpcije model predviđa da je najpovoljniji granični uvjet ograničena ravnoteža pri kojoj je konstantna količina polimera koja se nalazi u prostoru između dvije čestice u lokalnoj ravnoteži. Kod malih količina polimera stvaranje mostova dovodi do flokulacije premoštavanjem (»bridging flocculation«) dok kod većih količina polimera dolazi do steričke stabilizacije zbog uzajamnog odbijanja dva proširena polimerna sloja. Ako se polimer ne adsorbira na čestice može se pretpostaviti potpuna ravnoteža, u kojoj su kemijski potencijali otopine i polimera u prostoru između dviju čestica jednaki onima u ravnotežnoj otopini. Smanjenje količine polimera blizu površine može dovesti do flokulacije putem smanjenja količine (»depletion flocculation«) u otopinama polimera koje nisu odviše koncentrirane. Kod vrlo koncentriranih sistema zona smanjene količine polimera uz površinu čestice razmjerno je malena, i privlačenje među česticama postaje preslabo da prevlada entropiju čestice. Sistem tada biva ponovno stabiliziran.