

Coil size oscillatory packing in polymer solutions near a surface

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The theory developed by Scheutjens and Fleer to describe polymer adsorption and depletion is used to calculate the density profile of nonadsorbing polymers near a surface. The theory predicts damped oscillations in the segment density profile with a wavelength of about the coil size. As a consequence, the interaction energy between two surfaces immersed in a solution of nonadsorbing polymers is an oscillatory function of the separation distance, too. The decay length of the oscillations is proportional to the coil size and independent of the polymer concentration. The oscillations are associated with a liquid-like layering of polymer coils near the surface. An increase in concentration or chain length causes a decrease in the amplitude of the oscillations, because the stronger interpenetration of the coils suppresses inhomogeneities. In dilute solutions no oscillations are observed, because the decay length of the oscillations is smaller than the depletion correlation length, in analogy with the Fisher–Widom criterion in simple fluids. For polymer solutions it is found that the Fisher–Widom condition coincides with the overlap concentration. Our results show that the blob size is not the only relevant length scale above the overlap concentration. The size of the individual coils plays a role, too. © 2000 American Institute of Physics.

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I. INTRODUCTION

The behavior of polymers at interfaces is of considerable interest, both from a theoretical point of view and because of their practical relevance. An important application is their use in colloidal systems, where they can enhance or diminish the colloidal stability.^{1–4}

Most investigations have focused on adsorbing polymers. Polymer adsorption can cause both flocculation through the formation of bridges and stabilization by steric repulsion.^{3–7} The interest in nonadsorbing polymers is more recent. They generally have a destabilizing effect on dispersions at relatively low polymer concentrations.^{3,8–10} The origin of this effect, termed depletion flocculation, is the decrease in conformational entropy of a polymer molecule if it approaches an impenetrable surface. For nonadsorbing polymers this entropy loss is not compensated by an adsorption energy, so that a region exists near the surface with a lower polymer concentration than the bulk of the solution. This region is called the depletion layer. If two particles approach each other so that their depletion layers overlap, the polymer concentration between the particles is lower than the bulk concentration. The higher osmotic pressure in the bulk then pushes the particles together and if this effect is strong enough, flocculation or phase separation is observed. In some cases restabilization occurs at high polymer concentrations.^{3,8–10}

Several theoretical models have been proposed to describe the behavior of nonadsorbing polymers at an interface and the effect on the interaction between surfaces. The first

satisfactory theoretical treatment of the depletion effect was performed by Asakura and Oosawa.^{11,12} These authors showed that a volume exclusion mechanism leads to the existence of a depletion zone next to a surface in contact with a solution of nonadsorbing macromolecules. Attraction between two such surfaces is predicted at all polymer concentrations. Feigin and Napper¹³ calculated the free energy of interaction between two surfaces immersed in a solution of nonadsorbing polymers, accounting for the segment density profile in the depletion layer. Their model predicts destabilization at low polymer concentrations and restabilization at high polymer concentrations. According to Feigin and Napper, the latter phenomenon is associated with a maximum in the free energy curve at intermediate particle separation, which forms a kinetic barrier. Scheutjens and Fleer^{4,5,14,15} developed a self-consistent field theory, which proved to be successful in describing polymer adsorption and depletion. The density profile is evaluated and the interaction free energy between two surfaces is calculated as a function of the separation distance. For surfaces in the presence of nonadsorbing polymers a free energy minimum is predicted at zero separation. This minimum becomes less deep with increasing polymer concentration, so that the depletion attraction decreases. This model also predicts a maximum in the free energy curve at intermediate separation,^{7,16,17} but this maximum is much smaller than the one predicted by Feigin and Napper and insufficient to cause stabilization. Scheutjens and Fleer therefore argued that the stabilization observed at high concentration is not a kinetic effect, but a thermodynamic effect due to the weakness of the attraction. An explanation for the presence of the maximum was not given.

De Gennes used an analytical mean field model to calculate the concentration profile of nonadsorbing polymers

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near a surface. This approach is similar to the one by Scheutjens and Fler, but contains some additional approximations. He showed that the volume fraction profile of segments in a good solvent ($\chi \ll \frac{1}{2}$) can be approximated as^{4,18}

$$\varphi_1(z) = \varphi_1^b \tanh^2\left(\frac{z}{2\xi_d}\right), \quad (1)$$

where $\varphi_1(z)$ is the segmental volume fraction at a distance z from the surface, φ_1^b is the bulk volume fraction of polymer and ξ_d is the depletion correlation length, a measure for the depletion layer thickness. In the Appendix we will show that Eq. (1) is also a reasonable approximation for the depletion profile in a theta solvent ($\chi = \frac{1}{2}$). The depletion correlation length is related to the correlation length ξ in a bulk polymer solution. In dilute polymer solutions the depletion correlation length corresponds to the radius of gyration R_g of the polymer coils, which scales with the chain length N as $R_g \propto N^{1/2}$ in a theta solvent.^{4,18} At concentrations higher than the overlap concentration the size of the individual coils is generally believed to become irrelevant and the polymer solution is best described as a closely packed array of blobs. The relevant length scale in this regime is the typical mesh size (blob size). The blob size scales with $(\varphi_1^b)^{-1}$ in a theta solvent and is independent of the chain length.^{4,18} These results are in qualitative agreement with the results obtained by Scheutjens and Fler.^{7,16,17} These authors also predict a depletion layer thickness that is independent of φ_1^b in the dilute regime and decreases as $(\varphi_1^b)^{-1}$ in the concentrated regime. For a diagram of regimes see Ref. 4.

The alleged irrelevance of the individual coil size above the overlap concentration is caused by the interpenetration of the polymer coils. In simple fluids on the other hand, where overlap of the molecules is not possible, the diameter of the molecules is a relevant length scale at all densities. It is well known that short ranged repulsions in hard sphere or Lennard-Jones fluids can result in an oscillatory density profile near a surface.^{19,20} These density oscillations can be associated with the radial distribution function of the bulk fluid. Density correlations result in layering of the fluid molecules near a surface. The period of the oscillations corresponds to the diameter of the fluid molecules. Fisher and Widom pointed out that the density profile can be described as a superposition of monotonic and damped oscillatory contributions.²¹ The asymptotic behavior can be described by^{19,22}

$$\rho(z) - \rho^b = A \exp(-\alpha_0 z) + B \exp(-\alpha_0^{\text{osc}} z) \cos\left\{2\pi \left(\frac{z - z_0^{\text{osc}}}{\sigma}\right)\right\} \quad (2)$$

where $\rho(z)$ and ρ^b are the densities at a distance z from the surface and in the bulk of the solution, respectively. The pure exponential decay in Eq. (2) is the solution of a van der Waals type square gradient mean-field theory with α_0^{-1} as correlation length. The damped oscillatory term is associated with the layered ordering of the molecules near the surface. The amplitudes of the monotonous contribution, A , and of the oscillations, B , depend on the fluid density, the temperature, and the nature of the surface, whereas the inverse decay

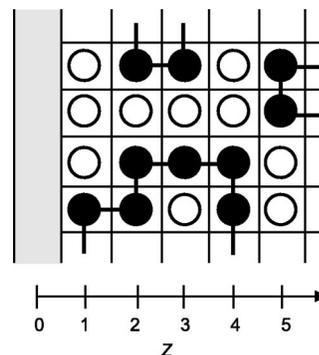


FIG. 1. A two-dimensional depiction of our model (NB in our calculations we used a three-dimensional cubic lattice). Left of layer 1 there is an inert solid surface. Layers 1 to M contain polymer chains (filled circles) and solvent (open circles). The distance of closest approach to the surface is at $z=1$.

lengths α_0 and α_0^{osc} are determined solely by the fluid density and the temperature. The wavelength of the oscillations σ is approximately equal to the diameter of the fluid molecules and hardly varies with varying density or temperature. The phase of the oscillations is given by z_0^{osc} . Fisher and Widom investigated the conditions under which the asymptotic decay of the density correlation function in fluids is monotonic or oscillatory.^{21,22} The crossover between these two regimes is exactly where $\alpha_0 = \alpha_0^{\text{osc}}$. This boundary defines a line in the (ρ, T) plane [referred to as the Fisher–Widom (FW) line]. Below this line, at low density and temperature, the asymptotic decay is monotonic and above this line, at high density and temperature, the asymptotic decay is oscillatory. The nature of the asymptotic decay of the density profile is believed to play a crucial role for wetting phenomena in liquid mixtures. On the oscillatory side of the FW line, complete wetting is replaced by partial wetting.^{19,20,22,23}

In this article we will present theoretical results that show that even for solutions of flexible linear polymer chains, oscillations of the segment density can be observed. The density oscillations suggest the presence of an ordered structure in the solution adjoining the surface. The length scale of this ordering is proportional to the size of the individual coils, which indicates that the individual coil properties are not completely irrelevant in the concentrated regime. The calculations are done with the Scheutjens–Fler (SF) theory. Our results can explain the maximum in the free energy reported by Scheutjens and Fler.^{7,16,17}

II. SELF CONSISTENT FIELD THEORY

A full description of the theory can be found elsewhere in literature.^{4,6,7,14,15} Only the main features are outlined here. In the Scheutjens–Fler theory the polymer chains are described as walks upon a lattice. The space adjoining a solid surface is divided into a number of parallel lattice layers, numbered $z=1, 2, 3, \dots, M$. The surface layer is at $z=0$ (Fig. 1). The lattice geometry is defined by the fraction λ_0 of neighboring sites that a lattice site has in the same layer. The fraction λ_1 of neighbors in an adjacent layer is then fixed by $\lambda_0 + 2\lambda_1 = 1$. In this article we will use a cubic lattice, in which the lattice coordination number is 6, $\lambda_0 = \frac{4}{6}$ and λ_1

$=\frac{1}{6}$. All lattice sites are occupied by either a polymer segment (component 1) or a solvent molecule (component 0). The whole system is in equilibrium with a bulk solution of polymers.

Polymer chains can adopt many different conformations. The conformation of a chain is specified by the sequence of layers in which the successive segments of the chain are situated. The equilibrium situation corresponds to the most probable set of conformations.

The segmental weighting factor $G_{0/1}(z)$ gives the relative preference of a solvent molecule or a free segment to be in layer z rather than in the bulk solution:

$$G_{0/1}(z) = \exp[-(u'(z) + \chi(\langle\varphi_{1/0}(z)\rangle - \varphi_{1/0}^b) + u_{0/1}\delta_{z-1})], \quad (3)$$

where χ is the Flory–Huggins polymer–solvent interaction parameter,²⁴ $\varphi_{1/0}^b$ is the bulk concentration of polymer or solvent and

$$\langle\varphi_{0/1}(z)\rangle = \lambda_1\varphi_{0/1}(z-1) + \lambda_0\varphi_{0/1}(z) + \lambda_1\varphi_{0/1}(z+1). \quad (4)$$

This term denotes a weighted average of the volume fractions of polymer or solvent in layer z and its two adjacent layers. Variations within one lattice layer are ignored, according to a mean field approximation. The term $u'(z)$ in Eq. (3) is a potential that accounts for the hard core interaction in layer z relative to the bulk solution. The last term in Eq. (3) accounts for the interaction of segments or solvent molecules with the surface. The adsorption energy of a solvent molecule or a segment is $u_{0/1}$ and the Kronecker delta δ_{z-1} is unity for $z=1$ and zero elsewhere. It follows from Eq. (3), with $\langle\varphi_0(z)\rangle + \langle\varphi_1(z)\rangle = 1 - \lambda_1\delta_{z-1}$, that

$$\ln\left(\frac{G_1(z)}{G_0(z)}\right) = 2\chi(\langle\varphi_1(z)\rangle - \varphi_1^b) + (\chi_s + \lambda_1\chi)\delta_{z-1}, \quad (5)$$

where $\chi_s = -(u_1 - u_0)$. This gives the relative preference of a lattice site in the first layer to be occupied by a free segment rather than by a solvent molecule. In this article we choose $\chi_s = -\lambda_1\chi$, so that the last term in (5) vanishes. For this condition depletion of polymers at the surface occurs. Note that $\ln(G_1(1)/G_0(1)) \neq 0$ for $\chi \neq 0$, so that there is still an energetic contribution to the occupation of the first layer, which depends on the volume fraction of segments in the bulk. See the Appendix for more details.

For each segment s of a polymer molecule of N segments we can write an end point distribution function $G_1(z, s|1)$. It gives the statistical weight of all possible walks starting from segment 1 in an arbitrary layer in the lattice and ending at segment s in layer z . The end point distribution functions can be calculated from the segmental weighting factors $G_1(z)$ through the recurrence relation:

$$G_1(z, s|1) = G_1(z)\langle G_1(z, s-1|1)\rangle, \quad (6)$$

where the angular brackets denote averaging over adjacent layers, similar to the averaging in Eq. (4). The distribution function of segment s can be found by considering that segment s joins the two chain parts $1, 2, \dots, s$ and $s, s+1, \dots, N$. If segment s is in layer z , the first chain part has a statistical weight $G_1(z, s|1)$ and the other $G_1(z, s|N)$.

The statistical weight of all chains with segment s in layer z is therefore $G_1(z, s|1)G_1(z, s|N)/G_1(z)$, where the factor $G_1(z)$ corrects for double counting of the weighting factor of segment s . The volume fraction of segments s in layer z is proportional to this. The total polymer volume fraction in layer z is found by summation over all segments s :

$$\varphi_1(z) = \frac{\varphi_1^b}{N} \sum_{s=1}^N \frac{G_1(z, s|1)G_1(z, s|N)}{G_1(z)}, \quad (7)$$

where φ_1^b/N is a normalization factor. Equations (3) and (7) with the M boundary conditions $\varphi_0(z) + \varphi_1(z) = 1$ constitute a set of M implicit equations which can be solved numerically, giving the concentration profile $\{\varphi_1(z)\}$.

If we want to study a polymer solution confined between two surfaces, an extra surface is introduced at layer $z=M+1$. The concentration profile is calculated in the same manner as for one surface. The free energy of interaction per unit area Δf between the two surfaces at a separation of M layers can be calculated as^{5,6}

$$\Delta f(M) = 2(\gamma(M) - \gamma(\infty)), \quad (8)$$

where $\gamma(M)$ and $\gamma(\infty)$ are the interfacial tensions at a surface separation of M lattice layers and at infinite separation, respectively. The interfacial tension can be calculated from the concentration profile:^{5,6}

$$\frac{(\gamma(M) - \gamma_0)a}{kT} = \left(1 - \frac{1}{N}\right)\theta_1^{\text{ex}} + \sum_{z=1}^M \ln \frac{\varphi_0(z)}{\varphi_0^b} + \chi \sum_{z=1}^M (\varphi_1(z)\langle\varphi_1(z)\rangle - (\varphi_1^b)^2), \quad (9)$$

where γ_0 is the interfacial tension of a surface in contact with pure solvent, a is the area per lattice site and θ_1^{ex} is the excess amount of polymer between the plates:

$$\theta_1^{\text{ex}} = \sum_{z=1}^M (\varphi_1(z) - \varphi_1^b). \quad (10)$$

In the SF theory it is assumed that the segments are distributed randomly in the lateral direction. Hence intra- and intermolecular segment–segment interactions are accounted for on a mean field level. As a consequence, coil swelling in a dilute and semi-dilute polymer solution in a good solvent is not accounted for in this approach. For $\chi = \frac{1}{2}$ (theta conditions) it is actually true that polymer chains behave according to ideal-chain statistics ($R_g \propto N^{1/2}$). So the present theory is expected to be very accurate for $\chi = \frac{1}{2}$ and somewhat more approximate for other solvency conditions. Therefore in this article we will examine only systems with $\chi = \frac{1}{2}$ and thus $\chi_s = -\lambda_1/2 = -\frac{1}{12}$.

III. RESULTS AND DISCUSSION

The depletion of polymer at a single surface is illustrated in Fig. 2(a), giving the segment volume fraction as a function of the distance to the surface for a nonadsorbing polymer chain of 200 segments at several bulk concentrations. The volume fractions in Fig. 2 have been divided by the bulk volume fraction φ_1^b in order to show more detail. At large

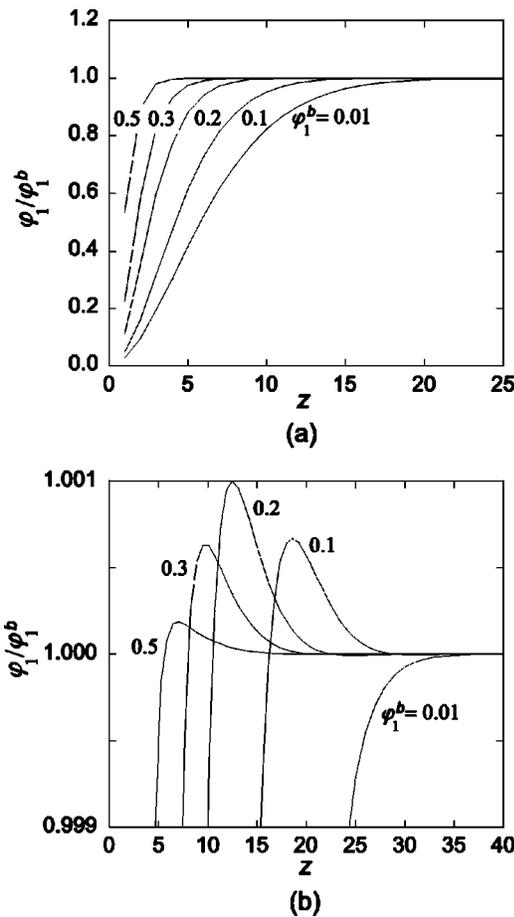


FIG. 2. (a) Segment volume fraction for a nonadsorbing polymer of 200 segments in a theta solvent versus the distance to the surface for several bulk polymer concentrations. The volume fractions have been divided by the bulk volume fraction ϕ_1^b . (b) The same density profiles as in (a), but magnified 2000 times.

distance from the surface, the volume fraction of segments equals ϕ_1^b . Near the surface the volume fraction is lower than ϕ_1^b because of conformational restrictions. The region where the deviation from the bulk concentration starts is enlarged in Fig. 2(b). It can be seen that the volume fraction exhibits a maximum. This maximum is too small to be visible on the scale of Fig. 2(a). A closer look at the density profile learns that in fact the volume fraction goes through several oscillations. The amplitude of the oscillations decays quickly with increasing distance from the surface. Such an oscillatory profile is not observed in very dilute polymer solutions.

The segment density profile of Fig. 2 is well described by

$$\phi_1(z) - \phi_1^b = \phi_1^b \left\{ \tanh^2 \left(\frac{z - z_0}{2\xi_d} \right) - 1 \right\} + B \exp(-\alpha_0^{\text{osc}} z) \cos \left\{ 2\pi \left(\frac{z - z_0^{\text{osc}}}{\sigma} \right) \right\}. \quad (11)$$

The first (monotonic) term in (11) is the solution obtained by de Gennes [Eq. (1)], which also applies in a theta solvent (see the Appendix). As mentioned in the Introduction, ξ_d is related to the depletion layer thickness. The parameter z_0 is

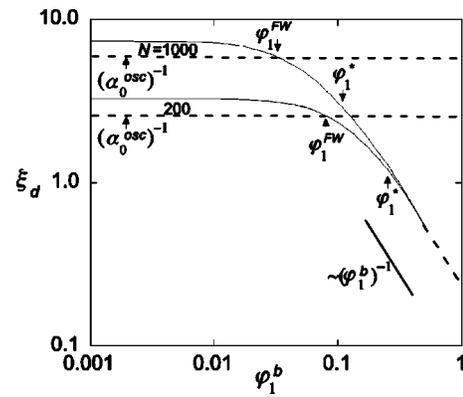


FIG. 3. The depletion correlation length versus the bulk volume fraction for two different chain lengths. The dotted lines give the value of $(\alpha_0^{\text{osc}})^{-1}$ for these two chain lengths. The overlap concentrations ϕ_1^* are indicated and the volume fractions ϕ_1^{FW} at which $\xi_d = (\alpha_0^{\text{osc}})^{-1}$.

related to the small energetical contribution to the occupation of the first layer [Eq. (5)] and depends on ϕ_1^b . Its value varies between -0.3 and 0.3 . See the Appendix for more details. The second term in (11) represents the damped oscillations in the profile. The parameter B is related to the extent of ordering in the polymer solution caused by the surface, α_0^{osc} is a measure for the range of the ordering and σ is the periodicity of the oscillations. In the asymptotic region, for $z \gg \xi_d$, the first term in Eq. (11) can be approximated as $A \exp(-z/\xi_d)$. Hence the asymptotic behavior of the segment density profiles in polymer solutions is as given in Eq. (2).

The depletion correlation length ξ_d can be obtained from a fit of the numerical data to Eq. (11). Only the data in the surface region, where the oscillatory term is negligible compared to the monotonic term, is used to determine ξ_d . Figure 3 shows the dependence of ξ_d on the concentration for two chain lengths. When the coils in the solution do not overlap, ξ_d is comparable to the radius of gyration and is independent of the concentration. At high concentrations ξ_d corresponds to the blob size, which is smaller than the radius of gyration. It scales as $(\phi_1^b)^{-1}$ and becomes independent of the chain length, as predicted by the scaling law of de Gennes.¹⁸ The transition between these two regimes is at the overlap concentration, which can be estimated as the concentration where spheres with a radius of R_g start to overlap:

$$\phi_1^* \approx \frac{N}{\frac{4}{3}\pi R_g^3} \approx 3.5N^{-1/2} \quad (12)$$

in a theta solvent. The overlap concentrations for chains of 200 segments and 1000 segments are indicated in Fig. 3. It can be seen that Eq. (12) gives a rather high estimation of the overlap concentration. The deviation of ξ_d from R_g starts at volume fractions much lower than ϕ_1^* . Summarizing,

$$\text{for } \phi_1^b \ll \phi_1^*: \quad \xi_d \approx 0.24(\phi_1^b)^0 N^{1/2}$$

and

$$\text{for } \phi_1^b \gg \phi_1^*: \quad \xi_d \approx 0.26(\phi_1^b)^{-1} N^0.$$

The period of the oscillations σ is obtained from the numerical data as the average distance between successive

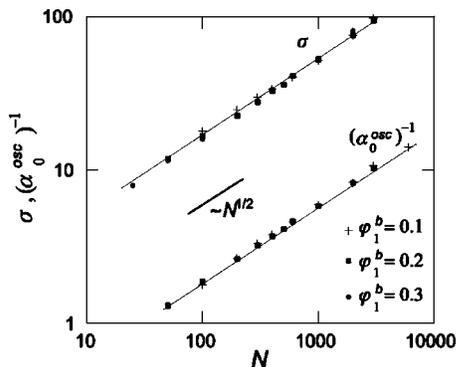


FIG. 4. The period σ and the decay length $(\alpha_0^{\text{osc}})^{-1}$ of the oscillations in the density profile versus the chain length for several bulk concentrations.

maxima or minima. The effect of the polymer concentration and the chain length on σ is shown in Fig. 4. The period of the oscillations is independent of the concentration and it is proportional to $N^{1/2}$:

$$\sigma \approx 1.5(\varphi_1^b)^0 N^{1/2}.$$

It can be concluded that the characteristic length scale determining the oscillations in a concentrated polymer solution is not the blob size, but the size of the individual coils (which is proportional to $N^{1/2}$ in a theta solvent). The relevant measure for the coil radius ($\approx 0.75N^{1/2}$) is somewhat larger than the radius of gyration [$R_g \approx (N/6)^{1/2}$].

The nature of the density oscillations can be explained in terms of liquid-like ordering of individual coils. Oscillatory density profiles are well known in hard sphere and Lennard-Jones liquids near surfaces.^{19,20} They are the result of ordering of molecules in layers near the surface. The ordering in polymer solutions is expected to be much weaker than in hard sphere liquids, because the polymer coils are able to interpenetrate to some extent. This coil overlap suppresses density inhomogeneities. Our calculations show that the ordering does not vanish completely. Density oscillations are still observed, although the amplitude is very small. Larger oscillations have been observed in polyelectrolyte solutions,^{25–27} but these oscillations have a different origin. It was shown that the oscillations in polyelectrolyte solutions cannot be attributed to the ordering of individual coils, but that they are due to a balance between the segment–segment electrostatic interactions and the translation entropy of the chains.²⁵ To our knowledge oscillations with a wavelength of the coil size have never been reported before for polymer solutions. In this article we investigate the nature of these density oscillations.

A plot of the magnitude of successive extrema versus the distance to the surface on a semi-logarithmic scale gives a straight line. An exponential fit yields values for the inverse decay length α_0^{osc} and the amplitude B . The effect of concentration and chain length on the decay length of the oscillations $(\alpha_0^{\text{osc}})^{-1}$ is shown in Fig. 4. It can be seen that the decay length is independent of the concentration and proportional to the coil size, just like the period of the oscillations:

$$(\alpha_0^{\text{osc}})^{-1} \approx 0.19(\varphi_1^b)^0 N^{1/2}.$$

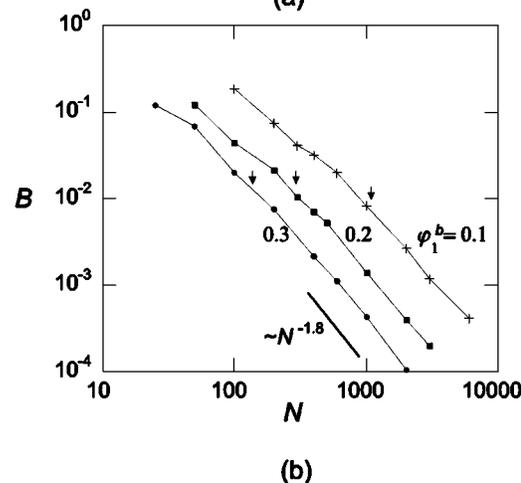
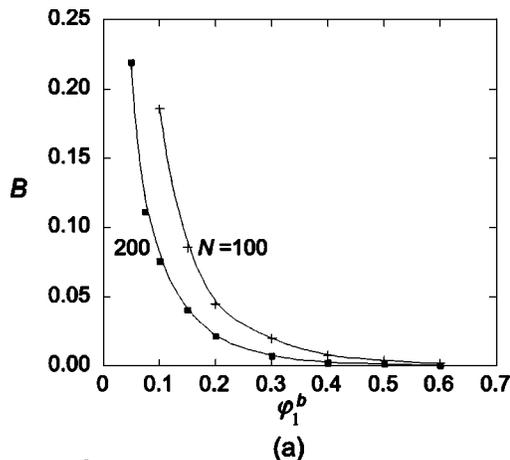


FIG. 5. (a) The amplitude of the oscillations in the density profile versus the bulk volume fraction for two different chain lengths. (b) The amplitude of the oscillations in the density profile versus the chain length for three different bulk concentrations. The arrows indicate the chain length above which there is overlap of coils, according to Eq. (12).

The proportionality constant is about 0.19, so that the magnitude of the oscillations decreases roughly with a factor $\exp(1.5/0.19) = 3000$ over each period at all concentrations and for all chain lengths.

In Fig. 5, the effect of φ_1^b and N on the amplitude of the oscillations B is shown. The amplitude decreases strongly with increasing concentration and chain length. This is in agreement with expectations, because the increasing overlap of the coils with increasing concentration or chain length suppresses inhomogeneities in the concentration profile. The curves in Fig. 5(b) suggest that we can distinguish two regimes. For long chains B appears to be proportional to $N^{-1.8}$, whereas for short chains B decreases less strongly with increasing N . The transition between these two regimes occurs in the region where the chains start to overlap [marked with the arrows in Fig. 5(b)]. Further investigations are needed to explain this behavior. In Fig. 2(b), B appears to go through a maximum with varying concentration, but this is caused by the different positions of the first maximum at different concentrations [z_0^{osc} in Eq. (11) is different]. With decreasing concentration, the position of the first maximum shifts away from the surface, which causes the magnitude to decrease exponentially. Similarly, the first maximum shifts away from

the surface with increasing chain length (not shown). The physical background behind the different positions of the first maximum is not yet fully understood, but our observations suggest that it is related to the thickness of the depletion layer.

No oscillations are observed in dilute polymer solutions, even though the amplitude B increases with decreasing concentration [Fig. 5(a)]. This can be explained in terms of the Fisher–Widom (FW) line. It was discussed in the Introduction that the asymptotic decay of the density profile is oscillatory if the decay length of the damped oscillatory contribution $(\alpha_0^{\text{osc}})^{-1}$ is larger than the decay length of the monotonic contribution ξ_d . The volume fractions where $\xi_d = (\alpha_0^{\text{osc}})^{-1}$ are indicated in Fig. 3 as φ_1^{FW} . At volume fractions lower than φ_1^{FW} , ξ_d is larger than $(\alpha_0^{\text{osc}})^{-1}$ and the density profile is monotonic. At volume fractions higher than φ_1^{FW} , ξ_d is smaller than $(\alpha_0^{\text{osc}})^{-1}$ and the density profile is oscillatory. A plot of φ_1^{FW} versus the chain length N (not shown) shows that φ_1^{FW} has the same power law dependence on N as the overlap concentration φ_1^* [defined by Eq. (12)]:

$$\varphi_1^{\text{FW}} \approx 1.2N^{-1/2}.$$

Therefore φ_1^{FW} can be seen as an alternative (and lower) choice for the overlap concentration. It is noteworthy that the critical volume fraction φ_1^{cr} scales in the same way:^{4,18,24} $\varphi_1^{\text{cr}} \approx N^{-1/2}$. The position of the Fisher–Widom line in a polymer solution remains therefore fixed with respect to φ_1^{cr} .

The excess amount of polymer between two plates immersed in a solution of nonadsorbing polymers can be calculated from the density profile using Eq. (10). The free energy of interaction between the plates is calculated from Eqs. (8) and (9). Figure 6 depicts θ_1^{ex} and Δf as a function of the separation distance M for $N=200$ and several values of φ_1^b . At large M , θ_1^{ex} is constant and equal to twice the depleted amount at a single surface. The polymer concentration in the middle of the gap equals φ_1^b and the osmotic pressure inside and outside the gap are equal, so that $\Delta f=0$. At very small M , it becomes very unfavorable for the polymer coils to be inside the gap between the plates and $\varphi_1(z)=0$ for any z . It follows from Eq. (10) that $\theta_1^{\text{ex}} = -M\varphi_1^b$ in this region, so that the excess amount varies linearly with M . The interaction curves are linear in this region, too, and it can be shown that the slope of the curves in the linear region is equal to the bulk osmotic pressure.⁷ In the transition region, where the overlap of the depletion zones just starts, oscillations are observed in θ_1^{ex} and Δf at sufficiently high concentration. The period of the oscillations in θ_1^{ex} and Δf is the same as for the oscillations in the density profile at an isolated surface. On the scale of Fig. 6, only the first minimum in θ_1^{ex} and the first maximum in Δf are visible. These first extrema were also reported by Scheutjens and Fleer,^{7,16} but an explanation was not given by them. From our calculations it is clear that the origin of the oscillations is the layered ordering of the individual coils. If the separation between the plates is such that an integer number of coil diameters can be fitted inside the gap, Δf is at a minimum. At these distances the maxima in the density profiles of the individual plates coincide and there is a constructive interference of the ordering ensuing from each of the two surfaces. For surface separations for

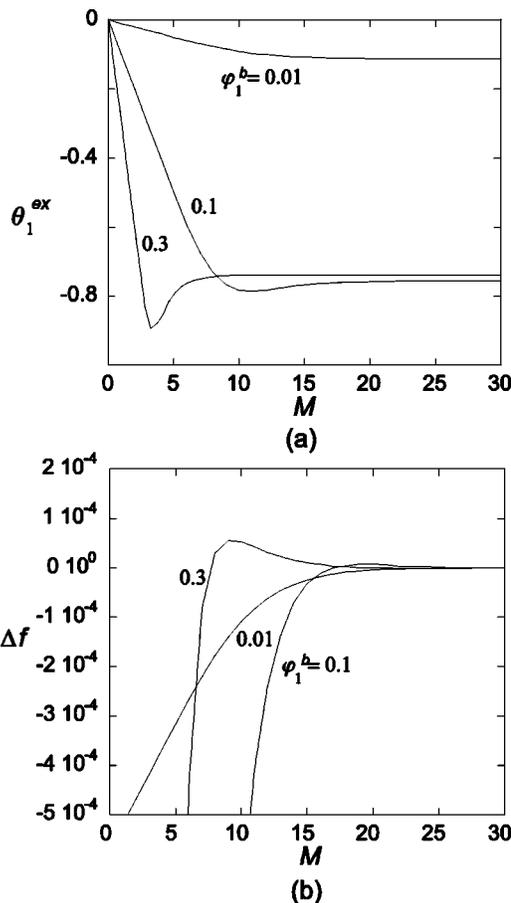


FIG. 6. (a) The excess amount of polymer between two plates immersed in a solution of nonadsorbing polymers ($N=200$) versus their separation distance for several φ_1^b . (b) The free energy of interaction for the same two plates.

which the segment density maxima ensuing from one surface would coincide with the segment density minima of the other surface there will be a destructive interference of the layered ordering and Δf will be at a maximum.

One may question the practical relevance of the oscillations described in this article. Because of their small amplitude they will be extremely difficult to detect experimentally. We are convinced, however, that the results presented here are of considerable interest from a theoretical point of view and will improve our understanding of the behavior of polymers near a surface. For fluids it was shown that even very small oscillations in the asymptotic density profile can have a large effect on the wetting behavior^{19,20,22,23} and the same can be expected for polymer solutions. One can also imagine systems where the oscillations become more pronounced. In solutions of highly branched polymers, such as dendrimers, for example, the oscillations are expected to be larger, because the interpenetration of branched polymer coils is much more difficult. Inhomogeneities are therefore not as strongly suppressed as for linear polymers. By systematical variation of the degree of branching, one can cover the complete range from flexible linear chains to hard spheres. Further research is needed to find out whether an ordered structure can be observed experimentally in such systems. The solvent quality may play a role, too. Some preliminary calculations (not

shown) suggest that the oscillations are larger in good solvents ($\chi \ll \frac{1}{2}$). This is probably due to the larger excluded volume interactions. Furthermore, in this article we chose a small negative value for χ_s , for which depletion of polymers occurs. If χ_s is taken close to the critical adsorption energy χ_{sc} , however, the monotonic term in Eq. (11) vanishes^{4,18} and only the oscillatory contribution remains. The oscillations may play a larger role in this case.

APPENDIX: ANALYTICAL APPROXIMATION FOR THE MONOTONIC COMPONENT OF THE DENSITY PROFILE IN A THETA SOLVENT

De Gennes used a continuum description to derive the polymer density profile near a surface in a good solvent [Eq. (1)]. The recurrence relation, Eq. (6), is transformed into a differential equation and the end-point distribution function is expanded in a series of eigenfunctions. The eigenfunctions are given by the following differential equations:^{4,18}

$$\lambda_1 \frac{d^2 g_1(z)}{dz^2} - u(z)g_1(z) = \varepsilon g_1(z), \quad (\text{A1})$$

where z is expressed in units of the segment length and $u(z)$ is the potential at position z in units kT . It is assumed that the eigenfunction with the largest eigenvalue ε dominates the expansion. This is referred to as the ground state approximation (GSA).^{4,18,28,29} In this approximation ε equals zero. The volume fraction of polymers is given by

$$\varphi_1(z) = \varphi_1^b g_1^2(z). \quad (\text{A2})$$

Clearly, for $z \rightarrow \infty$, $g_1(z) = 1$ and all derivatives $g_1^{(n)}(z)$ are equal to zero. We use a Flory–Huggins expression for the potential $u(z)$:^{4,24}

$$u(z) = -\ln \frac{1 - \varphi_1(z)}{1 - \varphi_1^b} - 2\chi(\langle \varphi_1(z) \rangle - \varphi_1^b) - (\chi_s + \lambda_1 \chi) \delta_{z-1}, \quad (\text{A3})$$

where $\langle \varphi_1(z) \rangle$, defined in Eq. (4), may be approximated as $\varphi_1(z) + \lambda_1 \varphi_1''(z)$. The last term in (A3) vanishes in our case, since $\chi_s = -\lambda_1 \chi$. The logarithm in (A3) is expanded and third order and higher terms are neglected. Substitution in (A1) for $\chi = \frac{1}{2}$ leads to

$$\lambda_1 \frac{d^2 g_1(z)}{dz^2} = \frac{1}{2} (\varphi_1^b)^2 (g_1^5(z) - g_1(z)) - \lambda_1 \varphi_1^b \frac{d^2 (g_1^2(z))}{dz^2} g_1(z). \quad (\text{A4})$$

After multiplying with $g_1'(z)$ and integrating, using $g_1'(z) = 0$ and $g_1(z) = 1$ for $z \rightarrow \infty$, this can be written as

$$\frac{dg_1(z)}{dz} = \frac{\varphi_1^b}{\sqrt{6\lambda_1}} \sqrt{g_1^6(z) - 3g_1^2(z) + 2}. \quad (\text{A5})$$

This can be solved for $2\varphi_1^b g_1^2(z) \ll 1$, which is equivalent to neglecting the nonlocal contribution $\varphi_1''(z)$ to $\langle \varphi_1(z) \rangle$. We find the following expression for $g_1(z)$:

$$\sqrt{\frac{2}{\lambda_1}} \varphi_1^b(z - z_0) = \operatorname{arctanh} \left(\frac{\sqrt{3} g_1(z) \sqrt{g_1^2(z) + 2}}{2g_1^2(z) + 1} \right), \quad (\text{A6})$$

where z_0 is an integration constant, which can be found from the boundary condition at the surface.²⁸ This boundary condition follows from the recurrence relation (A1):

$$\lambda_0 g_1(1) + \lambda_1 g_1(2) - u(1)g_1(1) = 0$$

with

$$u(1) = -\ln \left(\frac{1 - \varphi_1^b g_1^2(1)}{1 - \varphi_1^b} \right) - \varphi_1^b (\lambda_0 g_1^2(1) + \lambda_1 g_1^2(2) - 1). \quad (\text{A7})$$

This gives a relation between $g_1(1)$ and $g_1(2)$. From an expansion of the right-hand side of (A6) it follows that within a reasonable approximation this term can be reduced to $\sqrt{6} \operatorname{arctanh}(g_1(z))$, so that

$$g_1(z) = \tanh \left(\frac{\varphi_1^b(z - z_0)}{\sqrt{3\lambda_1}} \right), \quad (\text{A8})$$

or, with (A2),

$$\varphi_1(z) = \varphi_1^b \tanh^2 \left(\frac{z - z_0}{2\xi_d} \right), \quad (\text{A9})$$

so that Eq. (1) is found again. The value of z_0 can be found by solving Eq. (A7) with (A8) numerically. The depletion correlation length ξ_d in a theta solvent is given by

$$\xi_d = \frac{\sqrt{3\lambda_1}}{2\varphi_1^b} \approx 0.35(\varphi_1^b)^{-1}. \quad (\text{A10})$$

The curves in Fig. 2 are excellently fitted by Eq. (11), which indicates that the assumptions made in the derivation of (A9) are justified. The $(\varphi_1^b)^{-1}$ scaling of ξ_d is in good agreement with Fig. 3, but extrapolation in this figure to $\varphi_1^b = 1$ leads to a prefactor that is slightly lower than 0.35 (about 0.26). This is probably due to the ground state and other approximations made in the derivation of (A9). Below the overlap concentration the GSA is inapplicable. Therefore (A9) does not predict the $\xi_d \propto N^{1/2}$ scaling in the dilute regime. To find this scaling, it is necessary to take into account all eigenfunctions. Nevertheless, it was found that Eq. (A9) fits the data in the dilute regime, too, with a depletion correlation length proportional to the coil size. Note that taking into account all eigenfunctions is completely analogous to the Scheutjens–Fleer theory. Therefore, if an analytical solution could be found for the complete set of eigenfunction equations, this solution should contain the damped oscillatory component.

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