Coil-to-Flower Transition of a Polymer Chain Pinned near a Stepwise External Potential: Finite Size Effects

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ABSTRACT: We study the behavior of a polymer chain near a stepwise external potential u. The exact partition function of the chain tethered at a distance z_0 away from this interface is analyzed in a Landau framework. In this model, there exists a conformational coil-to-flower transition. Here the flower has a strongly stretched stem from the grafting point toward the interface and, on top of it, a crown composed of the remaining segments in a (perturbed) coil conformation. The classical behavior of binodal and spinodal states of the system is identified. A phase diagram in the z_0 vs u coordinates is presented with a line of first-order phase transitions ending at a critical point at $z_0 = 0$. In this last point, the transition is referred to as the rolling transition. Particular attention is payed to small systems, i.e., to systems near the critical point. This region is relevant for relatively short polymer chains and small values of the external field.

Introduction

The topic of polymers at interfaces has a rich history, and much is known about its characteristics. Typically, the aim is to manipulate interfaces and to obtain systems with well-controlled interfacial properties. The problem is studied both from a theoretical point of view and an experimental point of view, and the insights obtained from these studies seem to converge, especially for the well-defined aspects such as the equilibrium behavior of, e.g., long homopolymers at the solid−liquid interface.[1]

The Gaussian chain is a convenient model for a polymer system. Its behavior can be mapped on the problem of a diffusing particle, and mathematically there is a strong link with the probability theory.[2] A Gaussian chain with one of its end-segments fixed to a solid substrate is a system with particular significance. It is one of the only systems, in the field of polymers at interfaces, for which an exact partition function is available.[3,4] The adsorption parameter c is a central characteristic in the system. For example, a chain strongly adsorbs at the flat solid boundary when this c-parameter assumes a value larger than the inverse of the radius of gyration of the chain, i.e., $c > 1/R_g$. It then forms an adsorbed layer with thickness $1/c$. If, however, $c < 0$, the chain avoids the surface. The adsorption energy per segment is then too small to overcome the entropy loss that occurs upon adsorption. The adsorption transition at $c = 0$ is a phase transition of the second-order type and the transition point is a bicritical point. It has been shown that a first-order transition can be invoked in this system when a force is applied to the free end of the chain.[5]

Polymers at liquid−liquid interfaces are much less studied. Perhaps this will change because recently a new solvable model was proposed.[6] Again, it involves a Gaussian chain for which one end is at a known fixed position in space. In this case the end-point is positioned exactly at an interface (e.g. between two media). The model includes the simplification that the solvents are represented by an external potential which has a finite value in one-half of the space (region) and is zero (reference side) in the other. The model features a phase transition which has been analyzed in some detail from a polymer perspective in ref.[7] As soon as $|u| > 1/N$, the chain rolls its segments into the low potential region, where the grafting point is the pivoting point. The transition takes place upon shifting the high potential side from one-half-space to the other. The classification of the rolling transition has its problems. Initially, it was thought that the transition was a genuine first-order phase transition, because the derivative of the free energy with respect to the external field is discontinuous at the transition point. However, it was shown that the metastable states are absent. Moreover, the entropy at the transition point remains completely analytical. This points toward critical behavior.[6] In this paper, we will elaborate further on this issue.

When there is a first-order phase transition in the system, one usually should be able to find two coexisting phases near or at least at the point of transition, i.e., at the binodal. When the thermodynamic system is comprised of a single molecule, the two phases are identified as two sets of conformations. For example, in the rolling transition the two populations of conformations are as follows: (1) conformations that have most of their segments in one region $z < 0$; (2) conformations that are predominantly in the other region $z > 0$. At the transition point the two populations are equally large.

There are general methods to analyze phase transitions. One can analysis the free energy and its derivatives. This may be called the Ehrenfest route. A second route to analyze phase transitions that can be followed when the exact partition function is available is the analysis of the complex zeros of the partition function as suggested by Lee, Yang,[8] and Fisher.[9] For the rolling transition both routes have been elaborated on before.[6,7] A third option, which is placed centrally in the present paper, is the use of the Landau function.[10]

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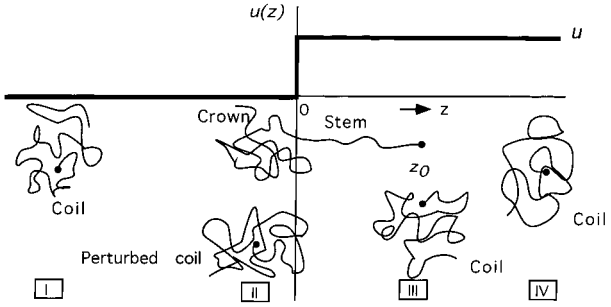

Figure 1. Illustration of the system of interest. A liquid−liquid interface is modeled as an Heaviside step function of the external potential: it assumes a value u for positive z and 0 otherwise. An isolated Gaussian chain is fixed with one of its ends at a position z_0 as indicated by the black dots. When the grafting point is either at very negative [I] or very positive [IV] coordinates, the chain is in an unperturbed Gaussian conformation. When the chain is near the interface but on the negative site [II] the coil is perturbed. More interestingly, when the grafting point is within the high-potential region [III], there can be a phase transition where, at the transition point, the coil and flower (stem + crown) conformations coexist.

In this paper, we will be primarily interested in first-order phase transitions. In this case the Landau function should have two minima. Each minimum represents one phase the system can be in. In the thermodynamic limit, the only relevant points in the Landau function are these minima, and the fluctuations outside these points have died out. In this case the binodal condition is characterized by the requirement that both minima are equally deep. For finite chains, the shape of the whole Landau function, or at least that near the minimum, is relevant. Without being mentioned otherwise we will ignore these fluctuations (also for short chains) and concentrate on the analysis of the minima in the Landau function as a function of a control parameter.

Analytical Investigation of the Coil-to-Flower Transition in the Gaussian Limit. In Figure 1, we present schematically what might be expected for chains grafted with one end near a penetrable interface. Far away from the interface, the coils do not know of the presence of the interface, and the chains are in a random coil conformation. When the chain is with the grafting point near the interface, one of the two things may occur. If the chain is at the favorable side, it will keep all its segments in that phase, and only when the endpoint is near the interface the chain will be somewhat perturbed. On the other hand, when the chain is grafted near the interface but on the unfavorable side, it will form a flower. To understand the structure of such flowers it is not too important to bother about the molecular features that generate the interface. In the following we will replace the effect of the molecules by a fixed external potential u felt by the polymer segments. Then it is not necessary any more to specify the origin of the external potential. It may have an entropic origin, i.e., when the two phases are polymer gels which differ only in polymer density, or have an enthalpic nature, i.e., when two strongly segregating liquids are considered.

The external potential changes its value at $z = 0$. The chain, with degree of polymerization N, is restricted with one of its ends at $z = z_0$ (see Figure 1). When $z_0 = 0$, we arrive at the most symmetrical case, which has been analyzed for the Gaussian chain in some depth before.[6] For this special case, the model is exactly solvable and we will return to this system in the discussion.

In passing we note that there is already some literature on inhomogeneously stretched chains. Such chains have been analyzed for the case that a chain is pinned in the middle under a large cylinder. Upon confinement of the chain by a disk with radius much larger than the radius of gyration of the chains, a so-called escape transition occurs.[11−14] It is shown that the transition has first-order characteristics and several of the predictions, based upon Gaussian chain models and scaling arguments have been tested by simulations.[15,16] So upon compression, the chain first remains as a (compressed) coil under the disk and then stepwise changes its conformation into a flower: it forms a tether from the grafting point toward the edge of the cylinder and then puts the remainder of the segments as a crown outside the compression region. It was shown by Sevick and Williams[17] that the disk is not necessary, that one can replace the disk by a region of unfavorable potential, and that in the Gaussian limit accurate partition functions can be found. One of the significant results is that the chain will escape from a region with unfavorable interactions in such a way that half its segments are "liberated".

In a Gaussian chain problem, the dimensionallity is not very important. Sevick and Williams consider the case that the chain "lives" in 2D and experiences stripes in the x-direction. In the problem discussed in this paper, the chain "lives" in 3D and finds a region of unfavorable interactions in the z-direction. The escape transition has not been examined in the context of a Landau function, and therefore, we can suggest that many of the results presented below can readily be transferred to and are relevant for the escape transition. We will use the language of the coil-to-flower transition in order to remain consistent with respect to ref 18, where an adsorption-to-flower transition has been discussed for a long minority chain admixed into a brush. As one of the primary applications of the present analysis will be the development of an improved model for the adsorption-to-flower transition in a polymer brush, we feel that it is appropriate to use the similar language of coil-to-flower transition rather than an escape transition. All this will then also remain consistent with ref 19.

A Scaling Analysis. Let us thus consider a Gaussian chain grafted to a general position z_0. One can easily construct a scaling picture of the coil-to-flower transition as is discussed in more detail in ref 19. The flower (cf. Figure 1) consists of a stem of m segments crossing the unfavorable region from the grafting point to the interface and the crown of $N - m$ segments residing in the favorable region. The free energy of this state has two contributions. The first one is due to the stretching of the stem, which is given in the Gaussian approximation by $3z_0^2/2m$. The second contribution is due to the interactions with the external field. This amounts to mu, where it is assumed that the crown avoids the unfavorable phase completely. Here and below we will use the convention that $k_BT = 1$. Minimization the free energy with respect to m gives

$$m = z_0\sqrt{3/(2u)} \tag{1}$$

This leads to the free energy of the flower state $F_{fl} =$

$z_0\sqrt{6u}$. In a 1 k_BT per blob ansatz, it follows that the flower contains blobs of size $\xi = 1/\sqrt{6u}$. Equating the free energy of the flower state to that of the coil, $F_c = uN$, one obtains the transition point for the coil-to-flower transition:

$$\frac{z_0^*}{N} = \sqrt{\frac{u}{6}} \tag{2}$$

Combination of eqs 1 and 2 leads to the result that, at the transition point, the stem contains $m = N/2$ number of segments and the crown contains the remaining half. This result is also obtained for the escape transition.[17]

In conclusion, for $z > z_0$ the chain prefers to be in the coil state in the unfavorable region. When $z < z_0$ the chain becomes inhomogeneous by putting half its segments in a stem and the other half in the crown. The fraction of segments in the crown increases upon decreasing distance of the grafting point to the step in the potential and remains unity when the chain is grafted on the favorable side of the interface.

Unfortunately a scaling analysis cannot give a much more detailed picture of the coil-to-flower transition. Therefore it is of interest to develop an analytical model for this phenomenon. For Gaussian chains, this is possible. The analysis of a Gaussian model, concentrating in particular to the scaling dependencies for large external fields are worked out in another publication.[19] Below we will invest the Gaussian model in more detail by keeping track of logarithmic corrections. In other words, we will also pay attention to the features of the system that occur for weak external fields and relatively short chains.

An Exact Analytical Approach. It is necessary to realize that we distinguish basically three cases (cf. Figure 1). The first two cases are that the chain has no intersections with the interface and then it can be that the chain is in the favorable side of the system (case I, Figure 1) or the chain is in the unfavorable side of the system (case IV, Figure 1). More interesting, the chain crosses the interface at least once (cases II and III, Figure 1). Let us first consider a chain which does not pass the interface. Let us introduce $Q(z_0|m)$ as the partition function for the chain starting at coordinate z_0 and which makes m contacts with the negative half space. When the grafting coordinate is in the negative half-space, we must have $m = N$ and of course $m = 0$ otherwise. The partition function for a chain which does not cross the interface can be found by the so-called mirror reflection method. When the chain starts at positive coordinates (case IV, Figure 1), we have to realize that all segments feel the external potential:

$$Q(z_0|0) = \frac{1}{\sqrt{2\pi R_g}}\int_0^\infty e^{-((z-z_0)/2R_g)^2} - e^{-((z+z_0)/2R_g)^2}\,dz\; e^{-U} = \mathrm{erf(a)}\; e^{-U} \quad z_0 > 0 \tag{3}$$

where $a = z_0/(2R_g)$ and $U = uN$. When the grafting distance is not further out than the chain diameter, $a \ll 1$, we can approximate the erf(a) with erf(a) $\approx 2a/\sqrt{\pi}$ and when $a > 1$, erf(a) ≈ 1. When the chain starts at negative coordinates (case I, Figure 1), none of the segments feel the external field and we simply have

$$Q(z_0|N) = \mathrm{erf}(a) \quad z_0 < 0 \tag{4}$$

When in this case the grafting distance is far from the surface we have an unperturbed coil in the low potential region and $Q(z_0|N) = 1$. In other words, this is the reference state for the free energy of the coils. For the set of conformations that cross the interface at least once, the strategy is to split the chain up into two parts. The first one is from the grafting point toward the interface and the second one starts from the interface, distributing its segments over the two phases just as it is possible in the rolling transition.[6] To find an expression for the first part, we realize that there is an exact result for the case that one chain-end ($s = N$) is fixed at a solid boundary at $z = 0$ and the other end ($s = 1$) at a distance z_0 from the interface, $Q(1,z_0|N,0)[c]$, for an arbitrary interaction of the segments with this surface.[7] Here we are interested in the partition function of a chain with length N which starts in $z = z_0$ and arrives at $z = 0$ without making any other contact, i.e., it has exactly 1 contact: $Q_N(z_0|1)$. This means that we select strongly repulsive interactions; $c \ll 0$. In this limit the exact result for $\tilde{Q}(1,z_0|N,0)[c]$ simplifies to

$$Q_N(z_0|1) = \tilde{Q}(1,z_0|N,0)[c \ll 0] \approx \frac{3}{-c\sqrt{\pi}}\frac{a}{N}e^{-a^2} \tag{5}$$

The next step is to replace the wall with a penetrable interface and consider the walks start at $z = 0$. The partition function for a chain of length N having m segments in the region $z < 0$ is known as well.[7]

$$Q_N(0|m) = \frac{1}{\pi\sqrt{m(N-m)}}e^{-u(N-m)} \tag{6}$$

Let us combine the results of eqs 5 and 6 in such a way that the full chain of length N is split up in a chain fragment with length n necessary to travel from a positive $z = z_0$ to $z = 0$ and the remainder $N - n$ segments that can be used to generate m contact with the region z < 0. The partition function for case II in Figure 1 is given by:

$$Q(z_0|m) = \int_{n=0}^{N-m} Q_n(z_0|1)Q_{N-n}(0|m)\,dn = \frac{6\sqrt{\pi}}{-c}\frac{1}{\pi\sqrt{m(N-m)}}e^{-a^2/(1-m/N)-U(1-m/N)} \quad z_0 > 0 \tag{7}$$

provided $m > 0$. Alternatively, when the chain starts at negative coordinates (case III in Figure 1), a similar reasoning leads to

$$Q(z_0|m) = \frac{6\sqrt{\pi}}{-c}\frac{1}{\pi\sqrt{m(N-m)}}e^{-a^2/m/N-U(1-m/N)} \quad z_0 < 0,\ m < \mathrm{N} \tag{8}$$

It is necessary that when $z_0 = 0$, we should arrive at the result of eq 6, and therefore we chose $c = -6\sqrt{\pi}$. Indeed this value is sufficiently negative such that the limit used in eq 5 is very good and the result (eq 8) is exact. We show elsewhere[19] that there are alternative routes leading to eq 8 indicating that this result is exact in the Gaussian model. The overall partition function $Q(z_0)$ is found after intergration over all m values, i.e., $Q(z_0) = \int Q(z_0|m)dm$. We will not evaluate the overall partition function and keep m as a variable.

We may move forward to formulate the Landau function for this situation. Let us introduce the order

parameter as the difference between the fraction t of segments on the negative side $t = m/N$ and that of the positive side: $\varphi = t - (1 - t) = 2t - 1$. This means that when all the $m = N$ segments are on the negative side $\varphi = 1$ and when all the segments are on the positive side we have $\varphi = -1$. Introducing the Landau function $\Phi[\varphi] = -(1/N)\ln[Q(z_0|\varphi)]$,we find when the grafting point is outside the region of the external potential:

$$N\Phi[\varphi] = \begin{cases} -\ln \operatorname{erf}(-a) & \varphi = 1 \\ \ln(N\pi/2) + \frac{1}{2}\ln(1-\varphi^2) + \frac{2a^2}{1+\varphi} + U\frac{1-\varphi}{2} & \varphi < 1 \end{cases} \qquad a < 0 \quad (9)$$

Alternatively, for the case that the grafting point is in the region of the (unfavorable) external potential

$$N\Phi[\varphi] = \begin{cases} -\ln \operatorname{erf}(a) + U & \varphi = -1 \\ \ln(N\pi/2) + \frac{1}{2}\ln(1-\varphi^2) + \frac{2a^2}{1-\varphi} + U\frac{1-\varphi}{2} & \varphi > -1 \end{cases} \qquad a > 0 \quad (10)$$

These Landau functions eqs 9,10 reduce to the Landau function for the rolling transition,[6] for $a = 0$: $N\Phi_{a=0}[\varphi] = \ln(N\pi/2) + 1/2\ln(1 - \varphi^2) + U(1 - \varphi)/2$. There are some new features. (i) By way of construction, the Landau functions shown in eqs 9 and 10 are nonanalytical at the extremes $\varphi = 1$ when $a < 0$ and $\varphi = -1$ when $a > 0$. (ii) Although expansion of $1/2\ln(1 - \varphi^2)$ leads to even powers of the order parameter, series expansion of the new terms $2a^2/(1 + \varphi)$ and $2a^2/(1 - \varphi)$ gives contributions in the order parameter both with odd and even terms. Therefore, this new Landau function will have contributions in all powers of the order parameter. The reason for the appearance of the odd powers in the order parameter is the symmetry breaking due to the position of the grafting point. When choosing the grafting condition on one side of the system, it will be natural that results for positive order parameters will differ from that of negative ones. The new term is proportional to a^2. Because of this, it is, in the absence of an external field, of no consequence when the sign of the order parameter is reversed.

We note that in the case of the present model we have a complete expression for the Landau function, and we do not need a series expansion as typically done in this context.

In Figure 2, the Landau function is potted for very small displacements of the grafting point for the interface as well as for grafting points well above the radius of gyration (in this case $R_g \approx 12.91$). It is clearly seen that for very small z_0 values the Landau function has a maximum near $\varphi_{max} = 0$ and two minima, $\varphi_{min} = \pm 1$. For slightly larger distances of the grafting point from the step in the potential, the Landau function changes as expected in such a way that there remains just one minimum at $\varphi_{min} = 1$.

The effect of an external potential on the Landau functions is shown in Figure 3. Here two examples are given for the case that $N = 1000$ and the chain is grafted with one of its ends exactly at $a = -1/2$ and at $a = 1/2$, or equivalently at $z_0 = -R_g$ and $z_0 = R_g$, respectively. In both cases there is, in the absence of an external field, a smoothly decreasing function with its lowest point at $\varphi = 1$. Because the function is minimal to this point we refer to it as the minimum (although it is clear that the Landau function has no zero slope at this point). For symmetry reasons, these two curves in Figure 3 parts a and b are mirror images. As a function of the external potential, nothing special is found in Figure 3a; the functions remain continuously decreasing. However in Figure 3b, the situation is fundamentally different. Now a new minimum appears. This new minimum is separated by a maximum from the minimum at $\varphi = -1$. This is the signature of a first-order phase transition. For the binodal of this transition the two minima are equally deep. The two chain conformations that coexist can be deduced from Figure 3 as well. One of the minima, i.e., at $\varphi = -1$ corresponds to the unperturbed coil in the unfavorable region. The other one with $\varphi^* > 0$ is a conformation for which the majority of its segments are in the favorable half-space. This suggests a flower conformation with the property that the chain has a stem composed of a stretched chain fragment crossing the unfavorable region from the grafting point to the interface, and a crown with coillike behavior in the favorable half-space. The exact binodal is not easily extracted from the figure because one cannot see how deep the minimum is at $\varphi = -1$, but numerical inspection shows that it occurs near $U = 9$. The order parameters corresponding with the binodal conditions are $\varphi^* = -1$ for the first minimum and $\varphi^* > 0$ for the other minimum. We may in addition identify spinodal points. The spinodal is defined as the point where one of the minima disappears. In this particular case it is seen from Figure 3b that a spinodal point is found exactly at $U = 1$. This spinodal point corresponds to the loss of metastable flower states. There exists also a spinodal point where the metastable coil state is lost. This point will receive some atttention in the discussion. Obviously, our main interest will be in positive values of the grafting distance.

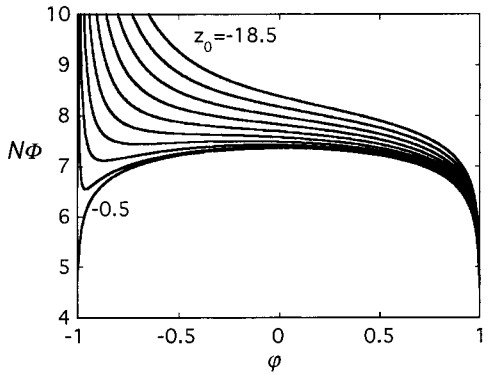

Figure 2. Graphical representation of N times the Landau function as a function of the order parameter for the Gaussian chain for various values of the grafting point, as indicated (steps in Δz_0 between lines are 2). There is no external field, $u = 0$, and the chain length is $N = 1000$.

Phase Diagrams. From graphs such as Figure 3, it is possible to extract the relevant data to construct the phase diagrams. The result for the binodal and the spinodal line corresponding to the loss of metastable flowers, can be found from numerical evaluation of the roots of the derivative of eq 10. It is illustrative to give the full result before analyzing the asymptotes.

In Figure 4a an example is shown for the binodal for $N = 100$ and a spinodal line. Again, the binodal line is found from the condition that the two minima are equally deep. The spinodal line gives the limiting

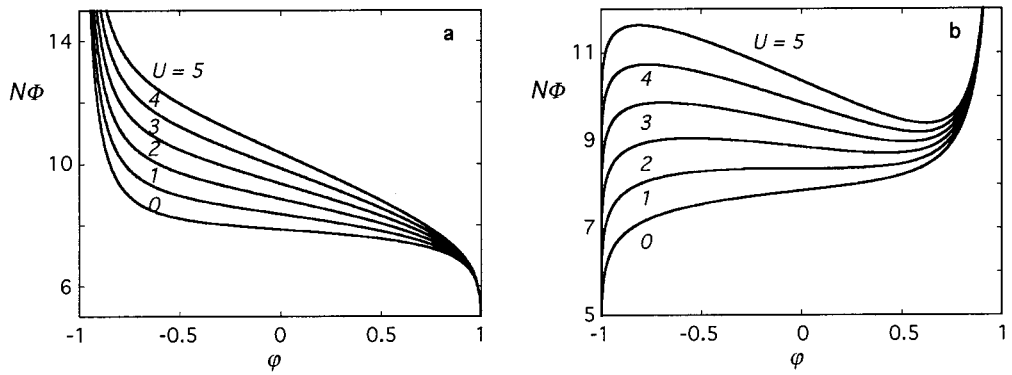

Figure 3. Landau function multiplied by the chain length ($N = 1000$) as a function of the order parameter in the system for various values of the external potential $U = uN$ as indicated: (a) $a = -1/2$; (b) $a = 1/2$.

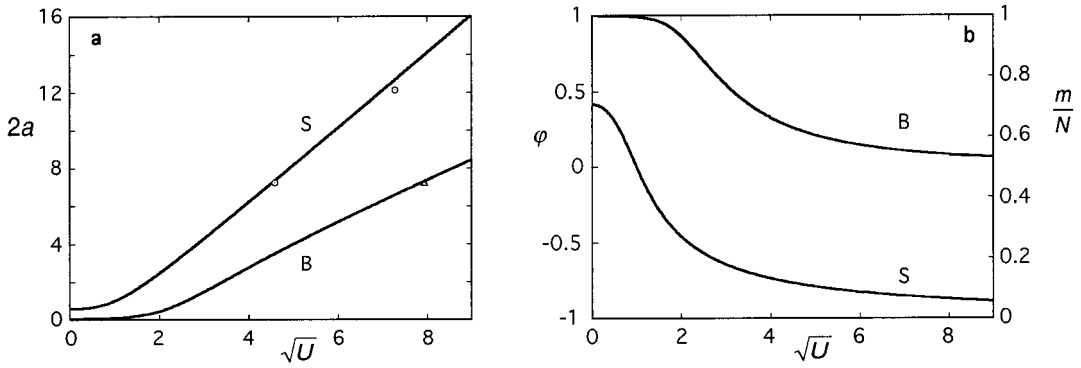

Figure 4. (a) Phase diagram for the Gaussian chain model for $N = 100$ in the coordinates $2a = z_0/R_g$ vs $\sqrt{U} = \sqrt{uN}$. The binodal line is indicated by the letter "B" and the spinodal, connected to the disappearance of metastable flowers, with the letter "S". The second spinodal line which is connected to the disappearance of metastable coils is close to $a = 0$ axis (not indicated). The symbols are numerical freely jointed lattice chain results (for details see ref 19). (b) Order parameter or, equivalently, the fraction of segments in the low potential region m/N, presented vs the $\sqrt{U} = \sqrt{uN}$ for both the binodal "B" and spinodal "S" line.

conditions for which it is possible to have metastable states. In this context, a metastable state is one where the chain has more segments in the unfavorable region as would be thermodynamically preferable. This condition may exist as a result of a maximum in the free energy landscape which prevents the smooth transfer of the segments of the chain to these lower energy states. As can be seen, both lines become approximately straight lines in the coordinates when the grafting distance is scaled with the radius of gyration and the square root of the field is used. Above the indicated spinodal line the chains are all in the coil conformation. For systems between the binodal and the indicated spinodal line the coil state is stable, but there may exist metastable flower states. To the right of the binodal the flower conformation is stable, but the coil becomes metastable. The second spinodal line below which only flowers can "grow" is not indicated. We note that the first spinodal line goes through the point $(a^{**},U^{**},\varphi^{**}) = (^1/_2,1,0)$, which means that when the end point is exactly one radius of gyration away from the interface and when the field has a value $U = 1$, the chain can distribute exactly half its segments in each phase, but this state is exactly on the edge of being locally stable.

Of course the results for the Gaussian chains must deviate from that of the freely jointed-chains[19] for very large values of the grafting distance. Inspection of Figure 4a shows that for $N = 100$ the freely jointed-chain results do not deviate from the Gaussian ones until approximately $z_0 \gtrsim 10R_g$ where the Gaussian chain slightly underestimates the potential needed for a given extension. The finite extensibility of the freely jointed chain results in a higher opposition against extension than the Gaussian chain. A more detailed analysis of the finite extensibility effects can be found elsewhere.[19]

In Figure 4b, the corresponding information is given on the value of the order parameter at the binodal and spinodal lines. For convenience, it is also indicated what the corresponding fraction of segments in the low potential region is. Interestingly, for very high fields, the binodal condition approaches the value $\varphi = 0$ or $m/N = 0.5$. The value of the spinodal approaches a value which is not far from $\varphi \approx -1$ or $m/N \approx 0$.

Some more insight in the physics of the system is obtained from the analytical analysis of the asymptotic behavior. From Figure 4, it will be clear that the two limits are the strong external field, $U > 1$, and the weak (positive) external field, $U < 1$, cases. We will investigate these two limits in order.

Binodal Strong Field. The binodal properties at strong fields can be found by considering the thermodynamic limit. From differentiation of eq 10, the minimum in the Landau function is located at

$$\varphi_{\min} \approx 1 - 2\frac{a}{\sqrt{U}}\left(1 - \frac{1}{4a\sqrt{U}} + \frac{1}{32a^2U}\right) \qquad (11)$$

The value of the Landau function at this point equals

$$N\Phi[\varphi_{\min}] \approx \ln(N\pi/2) + \frac{1}{2}\ln\left(\frac{4a}{\sqrt{U}}\right) + \frac{1}{2}\ln\left(1 - \frac{a}{\sqrt{U}}\right) + 2a\sqrt{U} \qquad (12)$$

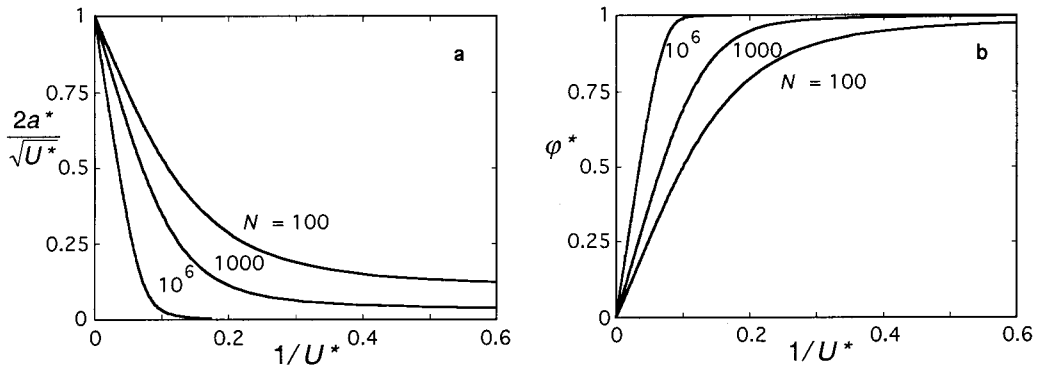

Figure 5. (a) Ratio between twice the grafting distance and $\sqrt{U}$ at the binodal plotted against the inverse of the external field for three degrees of polymerization as indicated. (b) Value of the order parameter of the second minimum at the binodal as a function of the inverse of the external field for the corresponding lengths of the polymer chains. The other minimum is at $\varphi^* = -1$.

Of course the second minimum remains at $\varphi = -1$ and has a depth of

$$N\Phi[-1] = U - \ln \mathrm{erf(a)} \approx U \tag{13}$$

The binodal condition occurs when the two minima are equally deep. This leads to

$$\begin{aligned} \frac{2a^*}{\sqrt{U}} &\approx 1 - \frac{1}{U^*}\ln(N\pi/2) \\ \frac{z_0^*}{N} &\approx \sqrt{\frac{u^*}{6}} - \frac{1}{\mathrm{N}\sqrt{6u^*}}\ln(N\pi/2) \end{aligned} \tag{14}$$

introducing the asterisk to specify that it is the value at the binodal. Inserting this result in eq 11 reveals that the transition in first approximation (for large fields) takes place at $\varphi^* = 0$, or equivalently, for $m^* = N/2$. More precisely however,

$$\begin{aligned} \varphi^* &\approx \frac{1}{U^*}\ln(N\pi/2) \\ \frac{m^*}{N} &\approx \frac{1}{2}\left(1 + \frac{1}{u^*N}\ln(N\pi/2)\right) \end{aligned} \tag{15}$$

The results of eqs 14 and 15 are consistent with the scaling analysis discussed above in the limit of $U \gg 1$. In fact there is a very large window where the scaling result is rather good. For extremely large field, however the finite extensibility effects distroy the scaling prediction.[19] An estimation for the onset of finite extensibility effects is easily found form eq 14b. Inserting the maximum value $z_0^* = N$, gives an upper limit for the Gaussian results $u^* = \sqrt{6}$. Equations 14 and 15 show that for small fields there are also some logarithmic corrections on the scaling predictions.

In Figure 5a, eq 14 is tested with the exact equation. For various degrees of polymerization we present $2a^*/\sqrt{U}$ as a function of $1/U^*$. From this figure it is clear that for high potentials the linear dependence is found to a good approximation. Inspection of the initial slope reveals that this slope is also exactly given by $-\ln(N\pi/2)$. Correspondingly, in Figure 5b, it is shown that in the same limit of large fields the position of the minimum in terms of the value of the order parameter is correctly predicted by eq 18. Again the initial slopes agree nicely with the predicted dependence on the chain length. In both parts a and b of Figure 5, it is seen that for small values of N the limiting behavior is lost rather quickly.

Binodal Weak Field. For weak fields $U < 1$, which are most important for polymers with a short length, it is necessary to analyze the binodal conditions for the case that the grafting point is close to the step in the potential. Inspection of this limit (cf. Figure 4b) reveals that it is possible for the chain to put the majority of its segments in the favorable half-space even though it starts in the unfavorable side. This means that it is appropriate to consider the limiting condition that $\varphi \approx 1$. In this limit eq 10b can be approximated by:

$$N\Phi[\varphi] \approx \ln(N\pi/2) + \frac{1}{2}\ln 2(1-\varphi) + \frac{2\mathrm{a}^2}{1-\varphi} + U\frac{1-\varphi}{2} \tag{16}$$

Provided that, $\mathrm{a} \ll 1/4\sqrt{U}$, a condition which is fully compatible with the limiting condition $\varphi^* \approx 1$, we find that the minimum of the Landau function is at $\varphi_{\min} = 1 - (2a)^2$, and the depth of the Landau function equals $N\Phi[\varphi_{\min}] = \ln(Na\pi\sqrt{2}) + 1/2 + 2Ua^2$. Again the other minimum remains at $\varphi = -1$ where the value of the Landau function equals $N\Phi[-1] = U - \ln(2a/\sqrt{\pi})$. Equating the values of the Landau function at the two minima results in the binodal line applicable for small displacements of the grafting point from the interface:

$$U^* = \frac{\frac{1}{2} + \ln(2(a^*)^2 N\sqrt{2\pi})}{1 - 2(\mathrm{a}^*)^2} \tag{17}$$

Let us estimate the crossover conditions from the finite size behavior of eq 17 to the thermodynamic limit given by eq 14. Inspection of eq 17 shows that when $2(a^*)^2 > 1$, the field becomes irrealistically negative. This suggests that the crossover condition is $a_c \approx 1$. Recalling that for high fields $\varphi = 0$, and in the low potential regime $\varphi \approx 1$, it is reasonable to take the crossover value $\varphi_c \approx 1/2$. Using this value in eq 15 leads to $U_c \approx \ln N^2$.

Equation 17 is tested in Figure 6, for three values of the chain length. It is seen that eq 17 gives a good description of the binodal at small values of the external field and thus at small values for the grafting coordinate.

Spinodal Strong Field. Let us next estimate the spinodal line corresponding to the loss of metastable

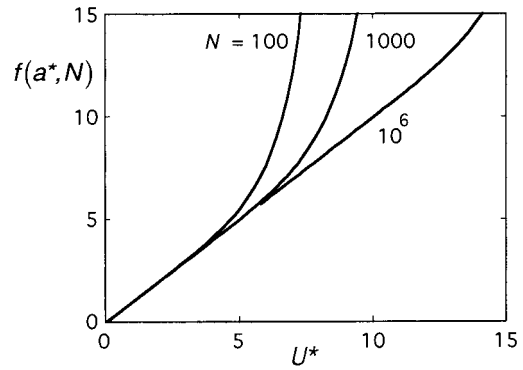

Figure 6. Dependence of the binodal at small values of the distance of grafting point from the interface. In this graph, $f(a^*,N) = (\ln 2(a^*)^2N\sqrt{2\pi e})/(1 - 2(a^*)^2)$ is plotted against the external field (cf. eq 17). Three values of the chain length have been used as indicated.

flowers. This condition can be identified as the point where the minimum in the Landau function just disappears. This occurs when both the second- and the first derivative of the Landau function with respect to the order parameter equals zero. As in both derivatives the $\ln(N)$ term is absent, it is immediately clear that the spinodal lacks an N-dependence other than hidden in the scaled variables a and U. Again it is convenient to consider the limit of strong external fields first. Putting the second derivative of the Landau function to zero $\partial^2\Phi[\varphi]/\partial\varphi^2 = 0$, leads to

$$\frac{1+\varphi^2}{(1+\varphi)^2} = \frac{4a^2}{1-\varphi} \tag{18}$$

It will be obvious that for strong fields the spinodal condition (we will use a double asterisk to refer to spinodal conditions) will be for $\varphi^{**} \approx -1$, i.e., where most of the segments are on the unfavorable side. In this limit, we find that the inflection point in the Landau function is given by

$$\varphi \approx -1 + \frac{1}{a}\left(1 - \frac{3}{4a}\right) \tag{19}$$

The combination of eq 18 with the condition that the first derivative of the Landau function is zero gives:

$$\frac{1}{(1+\varphi)^2} - \frac{\varphi}{(1-\varphi^2)} = U \tag{20}$$

Again, assuming that the spinodal condition is not far from $\varphi^{**} \approx -1$, leads to the spinodal equation:

$$\varphi^{**} \approx -1 + \frac{1}{\sqrt{U^{**}}}\left(1 + \frac{1}{4\sqrt{U^{**}}}\right) \tag{21}$$

The relation between the grafting distance and the external field consistent with eqs 19 and 20 is

$$a^{**} \approx -1 + \sqrt{U^{**}} \tag{22}$$

Interestingly, the spinodal value for the grafting coordinate is twice as far from the interface as the binodal (provided that the external field is large) and both these quantities are proportional to the chain length. As anticipated, the spinodal, in the $a(U)$ coordinates is independent of the chain length N and is thus universal.

Spinodal Weak Field. For small distances of the grafting point from the interface the spinodal condition will be found for positive order parameters. Now we can approximate eq 10b by

$$N\Phi[\varphi] \approx \ln(N\pi/2) + \frac{1}{2}\ln 2(1-\varphi) + \frac{2a^2}{1-\varphi} + U\frac{1-\varphi}{2} \tag{23}$$

where $\varphi \approx 1$. Setting the second derivative to zero gives $\varphi^{**} \approx 1 - 8(a^{**})^2$, which is only reasonable of course when $a \ll 1$, this result in the first derivative of the original eq 10b leads to

$$a^{**} = \frac{1}{4}\left(1/\sqrt{1 - \frac{1}{2}U^{**}}\right) \approx \frac{1}{4}\left(1 + \frac{1}{4}U^{**}\right) \tag{24}$$

This prediction shows that the spinodal becomes linearly dependent on the field when U is much smaller than unity. Correspondingly, $\varphi^{**} \approx 1/2 - U^{**}/4$.

In the final graphs (Figure 7) we present the numerical evaluation of the spinodal in the system. In Figure 7a, we plot $a^{**}(\sqrt{U^{**}})$, according to eq 22. Again, the analytical predictions for the spinodal are very accurate. The inset shows that at small values of the external field there is an almost linear dependence of a^{**} on the external field. This follows approximately the prediction of eq 24. The value of the order parameter at the spinodal condition is presented in Figure 7b. The dependence of the order parameter at large fields (inset in Figure 7b) is nicely recovered. At small fields the order parameter is slightly over-estimated by the asymptotic analysis. This can easily be traced back to the use of eq 23 which is correct near $\varphi = 1$, but it is clear that the order parameter remains well below this value.

When the field $U^{**} = 0$, i.e., in the "rolling" domain, there exists a distance a^{**} from the interface, from which the Landau function goes over from having two (trivial) minima to having just one. This may formally be identified with a spinodal point; however, the physical interpretation is much less clear. In this limit the chains do not feel any field and the flower conformations as such only exist as spontaneous conformation fluctuations. Only above the threshold $U^{**} = 1$ do the flower-like conformations develop and the meaning of the spinodal states becomes clear.

Discussion

A Landau analysis of phase transitions critically relies on the fact whether of not the correct Landau function and the corresponding order parameter are found. Of course the quality of the results predicted from a particular choice gives support for it. In polymer problems it is always tempting to use the relation between the end-point distribution $P(z,N)$ (which obeys the Edwards diffusion equation) and the partition function Q:

$$Q = \exp(-F) = \int_{-\infty}^{\infty} P(z,N)\,dz = \int_{-\infty}^{\infty} e^{\ln(P(z,N))}\,dz \tag{25}$$

to suggest a Landau function of the form:

$$\Phi[\dot{z}] = -\ln(P(z,N)) \tag{26}$$

where z should be related to the order parameter. The identification of eq 26 is, however, not particularly

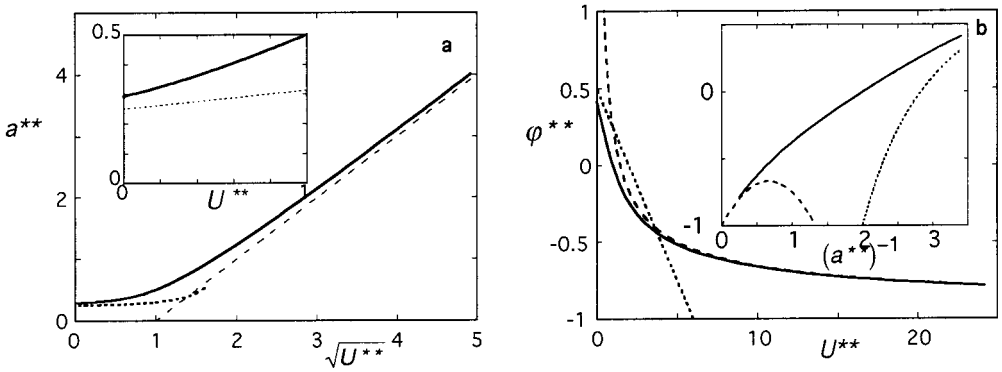

Figure 7. (a) Spinodal in terms of a**($\sqrt{U^{**}}$): the dashed line gives the asymptote for high fields (cf. eq 22), and the dotted line is eq 24. In the inset, the same data are shown in coordinates a**(U^{**}), and the dotted line is eq 24 in linearized form. (b) Value of the order parameter φ^{**} as a function of U^{**}. The dashed line is eq 21, and the dotted line is $\varphi^{**} \approx 1/2 - 1/4U^{**}$. In the inset, φ^{**} is plotted as a function of the inverse distance of the grafting point to the interface. The dashed line is the predicted asymptote from eq 19, and the dotted one is $\varphi^{**} \approx 1 - 8(a^{**})^2$.

useful. We can formulate at least four objections against the identification as specified in eq 26: (i) In eq 26 we have used the free energy and not the free energy per segment. (ii) The proper normalization of the z-coordinate to generate an order parameter which varies from -1 to 1 is not obvious. (iii) In ref 7, we have argued that the end-point distribution $P(z,N)$ is a function with a single maximum. Therefore the Landau function as defined by eq 26 is a function with a single minimum. This is in direct conflict with the observation that the phase transition found in this system. (iv) It is possible to analyze the problem of a Gaussian chain which is restricted by both its ends to the same plane $z = 0$. For this problem the exact partition function is available as well and also for this system there is a rolling transition. In this case, the end-point distribution reduces to a δ function which is for trivial reasons not a possible Landau function. Therefore the Landau function as discussed above is without doubt a better choice.

The phase diagram shows that the binodal is found for grafting point distances that are proportional to the chain length. With decreasing distance of the grafting point from the interface, the external potential needed to find the coil-to-flower transition decreases. The coil-to-flower transition transforms to the rolling transition exactly at the point $(U,z_0) = (0,0)$. Next, for negative values of the grafting point there is no phase transition any more. Thus the line of first-order coil-to-flower phase transitions stops at the point of the rolling transition. The end point of a line of first-order phase transitions is of course special. It cannot be a point with a true first-order character. More exactly it must be a critical point. Interestingly, for this critical point we have an exact solution in the Gaussian chain approximation and its analysis has been published before.[6]

Above we only have analyzed the spinodal state that corresponds to the loss of the metastable flower states. Of course there exists another spinodal condition, namely the point where the metastable coil state is lost in favor of only flower states. This spinodal line can be estimated from the condition that the minimum at $\varphi = -1$ is lost. This means that the Landau function levels off near $\varphi = -1$, or mathematically: $\Phi[-1] = \Phi[-1 + 1/N]$. This equality can only be realized when z_0 is of order unity, a result which is virtually independent of both N and U. Thus the phase diagram of Figure 4a should be complemented with a second almost horizontal spinodal line which, in essence, overlaps with the $a = 0$ axis. It is useful, however, to consider the effect of fluctuations on this last result. In principle fluctuations may overcome energy barriers of order k_BT. Therefore, it is sufficient that the local minimum at $\varphi = -1$ and the nearby local maximum differ only in the order of k_BT. In ref 19, it is shown that this condition leads to a spinodal $z_0^{++} \sim R_g$ (here the ++ notation is used to distinguish this spinodal condition from the one discussed above). This means that when the chain is placed closer to the surface than R_g, fluctuations may cause the chain to become unstable in favor of stable flowers. This spinodal condition is expected to depend only very weakly on the value of the external field.

Upon crossing the binodal line, the jump in the order parameter $\Delta\varphi$ is of the order of unity for large external fields and grows in the region of small systems monotonically up to $\Delta\varphi = 2$ at the critical point where the rolling transition is found. In principle this behavior of the order parameter is odd: typically one would like the jump in the order parameter to vanish at the critical point. This observation is of particular relevance when one becomes interested in the system from a dynamical point of view. The parameter space between the binodal and spinodal is the region where metastable states exist. The origin of the metastable states is the maximum in the Landau function as a function of the order parameter. In the thermodynamic limit, this maximum is such that the system can remain indefinitely long in a local minimum. For polymer chains however, the finite chain length case is of considerable more interest. Then the lifetime for a chain to remain in a local minimum will be finite. The metastable states (and spinodal lines) vanish in the limit of the rolling transition indicating a relatively fast equilibration. However, as noticed above the conformational changes that are necessary are most dramatic in the rolling case: $\Delta\varphi = 2$. The overall evaluation of the kinetics of the phase transitions is therefore far from trivial. The ideal method to perform a dynamic analysis is in a Landau function framework. Most likely it requires further elaboration on the choice of the (dynamic) order parameter where the conformational change and the height of the barrier are both included.[19] This will be the subject of forthcoming work.

Both the rolling transition and the coil-to-flower transition are of course discussed in an idealized setting, i.e., where the interface is represented as a step func-

tion. These types of interfaces may be approximately present in systems where two media are put next to each other. For example one can consider the interface between two polymer gels with differ in polymer density. Chains from a higher density gel may form flowerlike conformations and penetrate into the gel with the lower density. Another application for the coil-to-flower transition may be found as a sub-problem for finding a (close to) exact model for the adsorption-to-flower transition for a minority chain grafted into a polymer brush. It was shown before that in this system there exists a first-order adsorption to flower transition where the minority chain adsorbs on the solid substrate inside the brush and upon changing conditions can go to the flower conformation. In this case, the flower consists of a strongly stretched stem crossing the brush and a perturbed coillike conformation outside the brush. The introduction of a solid substrate into the coil-to-flower model is a next step which will be the subject of a future study as well.

Experimental observations for the transitions mentioned above are of considerable interest. Of course experimental systems are typically more complex as the model system discussed above, but we believe that the present models will serve as accurate guides to help understand the experimental results. Moreover, in the freely jointed-chain case, one can push the modeling often more close to the experimental conditions. For example, in the freely jointed-chain model the molecular nature of the interface can be reintroduced using the Scheutjens−Fleer model.[1] We therefore encourage experimental work in this area.

Conclusions

A polymer chain pinned with one of its ends at the unfavorable side of a penetrable interface, shows a conformational phase transition upon variation of the grafting distance. The two types of conformations that can coexist are the coil- and the flower state. The last one is a conformation with a strongly stretched stem from the grafting point to the interface and a crown which is a perturbed coil living on the favorable side. We have shown that it is possible to analyze the coil-to-flower transition by means of a Landau function. Accurate estimates for the asymptotic behavior of the binodal and spinodal lines of this first-order phase transition were obtained. In this phase diagram, one binodal and two spinodal lines are identified and therefore information is available in which region of parameter space one can have metastable states, i.e., (i) the coil state that is present in the unfavorable part of the interface, while thermodynamically a flower state is more favorable or (ii) the flower state is present even though the coil has a lower free energy. The line of first-order phase transitions, i.e., the binodal line, in the phase diagram stops at $(z_0,U) = (0,0)$. For this reason the rolling transition, which is the name of the transition exactly at this point, is not a first-order phase transition but necessarily a critical point. For this critical point the exact partition function is known for all values of the chain length. Using the Landau function it was further possible to show that in the limit of strong fields, $U > 1$, the force necessary to keep a chain localized at a specified position is independent of the chain length and the position of the grafting point. From this a simple scaling picture of the coil-to-flower transition is suggested where the stem is a string of blobs in equilibrium with a coil sitting on the favorable side of the interface.

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References and Notes

(1) Fleer, G. J.; Scheutjens, J. M. H. M.; Cohen Stuart, M. A.; Cosgrove, T.; Vincent, B. *Polymers at interfaces;* Chapman & Hall: London, 1993.
(2) Feller, W. *An introduction to probability theory and its applications*; John Wiley & Sons: New York, 1950.
(3) Lepine, Y.; Caillé, A. *Can. J. Phys.* **1978**, *56*, 403.
(4) Eisenriegler; E. Kremer, K.; Binder, K. *J. Chem. Phys.* **1982**, *77*, 6296.
(5) Gorbunov, A. A.; Skvortsov, A. M. *J. Chem. Phys.* **1992**, *98*, 5961−5970.
(6) Skvortsov, A. M.; van Male, J.; Leermakers, F. A. M. *Physica A* **2001**, *290*, 445−452.
(7) Skvortsov, A. M.; Klushin, L. I.; van Male, J.; Leermakers, F. A. M. *J. Chem. Phys* **2000**, *112*, 7238.
(8) Lee, T. D.; Yang, C. N. *Phys. Rev.* **1952**, *87*, 410.
(9) Fisher, M. E.; Nelson, D. R. *Phys. Rev. Lett.* **1974**, *32*, 1350.
(10) Landau, L. D.; Lifshitz, E. M. *Statistical Physics*; Nauka: Moscow, 1976.
(11) Subramanian, G.; Williams, D. R. M.; Pincus, P. A. *Europhys. Lett.* **1995** *2*, 285.
(12) Williams, D. R. M.; MacKintosh, F. C. *J. Phys. 2* **1995**, *9*, 1417.
(13) Gufford, M. C.; Williams, D. R. M.; Sevick, E. M. *Langmuir* **1997**, *21*, 55691.
(14) Steels, B. M.; Leermakers, F. A. M.; Haynes, C. A. J. *Chromatogr. B* **2000**, *113*, 31.
(15) Jimenez, J.; Rajagopalan, R. *Langmuir* **1998**, *14*, 2598.
(16) Milchev, A.; Yamakov, V.; Binder, K. *Europhys. Lett*, **1999**, *47*, 675, *Phys. Chem. Chem. Phys.* **1999**, *1*, 2083.
(17) Sevick, E. M.; Williams, D. R. M. *Macromolecles* **1999**, *32*, 6841.
(18) Skvortsov, A. M.; Gorbunov, A. A.; Leermakers, F. A. M.; Fleer, G. J. *Macromolecules* **1999**, *32*, 2004.
(19) Skvortsov, A. M.; Klushin, L. I.; van Male, J.; Leermakers, F. A. M. *J. Chem. Phys* **2001**, *34*, 0000.

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