Critical Properties of Thin Films of Polymer Solutions

M. RIZZOTTO, I. SZLEIFER

Department of Chemistry, 560 Oval Drive, Purdue University, West Lafayette, Indiana 47907-1393

Received 5 April 2005; accepted 5 April 2005
DOI: 10.1002/polb.20483
Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The critical properties of polymer solutions confined in thin-film environments is studied with simple scaling arguments and a molecular theory. For purely repulsive surfaces, the critical volume fraction is a universal function of \( x = N^{1/2}/L \), where \( N \) is the chain length and \( L \) is the film thickness. The critical volume fraction is nonmonotonic in \( x \) and shows a deep minimum at a film thickness several times larger than the chain’s radius of gyration. This nonmonotonic behavior results from the interplay between the surface–polymer entropic repulsion and the tendency of the film to avoid large density gradients. The critical temperature is a monotonically increasing function of \( L \), as \( L \) goes from the two-dimensional limit to the three-dimensional limit.

Keywords: phase behavior; theory; thin films

The effect of confinement on the critical behavior of solutions is of general interest because it presents a systematic way of changing the dimensionality of the system and reducing the range of the fluctuations in the constrained direction to the system’s size. The confinement effect is particularly important in polymeric systems because of the constraint that surfaces present to the conformational degrees of freedom of the chain molecules.\(^1\)\(^2\) Therefore, it is important to understand how the interplay between the conformational statistics and thermodynamic state, as manifested in the critical behavior, is modified because of the confinement. Furthermore, it is an important applied problem as many devices that take advantage of nanoscale phenomena in complex mixtures are in confined geometries.\(^3\)

In this article, we report theoretical predictions for the variation of the critical volume fraction and critical temperature in polymer solutions confined between two parallel plates as a function of the distance between the two walls. Previous studies have looked at the critical properties of polymer solutions in three dimensions\(^4\)\(^–\)\(^6\) and two dimensions\(^7\) and at the effect of confinement in polymer blends phase separation.\(^8\)\(^–\)\(^10\) Here we present polymer solution films in which the walls present only excluded volume (repulsive) interactions to both the polymer chains and the low-molecular-weight solvent. The presence of the surfaces reduces the conformational space of the polymers that are close to them, and thus they present an effective repulsion (attraction) to the polymers (solvent), whose range is of the order of the chain dimensions, that is, the polymer radius of gyration \( R_g \).

What will be the effect of the surfaces on the critical point? We use simple scaling arguments to show that the critical volume fraction should show a nonmonotonic dependence on the film thickness. First, consider the case of a very thick film; that is, we start from a three-dimensional (3D) bulk system and confine it between two walls at a very large distance \( L \) from each other. The main effect of the surfaces is to deplete the polymers. The range of the depletion is of the order of the size of the polymer \( R_g \). The center of the film does not feel the presence of the surface in this limit, and therefore we expect the critical volume fraction to be reduced by an...
amount proportional to the fraction of the system that feels the surface:

$$\frac{\phi_c(L)}{\phi_{c,\text{bulk}}} = 1 - 4k_1 \frac{R_g^2}{L}, \quad L \to \infty$$

where \(\phi_c(L)\) is the critical volume fraction for films of thickness \(L\), \(\phi_{c,\text{bulk}}\) is the corresponding value in the bulk, \(k_1\) is a factor of order unity and 4 appears to account for the diameter of the polymers and the two surfaces. At the critical point, \(R_g\) of the polymer is close to the \(\theta\) temperature, and therefore the chain statistics is Gaussian. Thus, \(R_g\) is equal to \(CN^{1/2}\), with \(C\) a constant, \(N\) is the chain length, and \(\phi_c(L)/\phi_{c,\text{bulk}}\) is equal to \(1 - 4k_1N^{1/2}/L\).

Consider now the limit of very thin films, starting from the two-dimensional (2D) system and increasing the thickness of the film. According to de Gennes’s arguments, the critical volume fraction is the density at which there is overlap between the coils, that is, the crossover to the semidilute regime. For a film of thickness \(L \leq R_g\), the volume occupied by a chain is of order \(V \propto R_g^2L\), and thus \(\phi_c(L) \propto N^2/R_g^2L\). At the critical point, we can write for the 2D system \(R_g \propto N^{\nu_2D}\) and for the bulk 3D system \(\phi_{c,\text{bulk}} \propto N^{-\gamma}\). Then, in the thin-film limit,

$$\frac{\phi_c(L)}{\phi_{c,\text{bulk}}} = k_2 \frac{N^{1+y-2\nu_2D}}{L}, \quad L \to 0$$

where \(k_2\) is another constant of order unity. With the mean-field values \(y = \nu_2D = 1/2\), we get \(1 + y - 2\nu_2D = 1/2\), whereas using the recently determined non-mean-field exponents from Monte Carlo simulations, \(y = 0.39 \pm 0.02\) and \(\nu_2D = 0.56 \pm 0.01\), gives essentially the same value. Therefore, we can write for the thin-film limit \(\phi_c(L)/\phi_{c,\text{bulk}} = k_2N^{0.5}/L\).

The critical volume fraction decreases with increasing film thickness for very thin films (two dimensions) and increases with the film thickness for very thick ones (three dimensions). Therefore, there should be a film thickness at which the critical volume fraction is minimal. Furthermore, according to the arguments presented, the critical volume fraction at any thickness, scaled by its 3D value, is a universal function of \(x = N^{1/2}/L\), and in both limits, \(L \to \infty\) and \(L \to 0\), the dependence on the scaling variable is linear. Equating the results of thick and thin films, we obtain the crossover value of the film thickness as \(x_{\text{cross}} = 1/(k_2 + 4Ck_1)\), which should be smaller than 1, and thus we expect the crossover thickness to be larger than the radius of gyration of the bulk chains at the critical point.

These scaling arguments provide convincing arguments for the nonmonotonic variation of the critical volume fraction with the film thickness going continuously from three dimensions to two. However, that approach does not provide for a quantitative measure for the effect. In other words, what is the value of the minimal critical volume fraction and what is the polymer density profile at the critical point? Furthermore, the simple scaling arguments do not provide for the variation of the critical temperature with the film thickness.

To answer these questions, we apply a molecular mean-field theory that enables the study of the structural and thermodynamic properties of polymer solutions in inhomogeneous environments. This approach predicts the variation of the critical volume fraction with the chain length in bulk polymer solutions in reasonable agreement with experimental observations. Furthermore, the predictions of the theory for the structural and thermodynamic properties of chain molecules in confined environments are in excellent quantitative agreement with full-scale computer simulations and experimental observations. Therefore, this approach is expected to provide reliable results and the ability to study the films of interest in a systematic way. The basic idea of the theory is to treat each molecule with its intramolecular and surface interactions exactly (for each of their conformations), whereas the intermolecular interactions are treated within a mean-field approximation. The mean field depends on the local composition, and it is determined by the average properties of the chains. The starting point is to write the free energy functional of the system in terms of the polymer and solvent density profiles and the polymer probability distribution function (pdf) of chain conformations. The system of interest is composed of \(N_p\) polymers, each of length \(N\) in a lattice of \(L\) layers in the \(z\) direction and area \(A\). Thus, the total volume fraction of the polymer is \(\hat{\phi}_p = N_pN/LA\), and the local volume fraction of the solvent is denoted by \(\phi_s(z)\). The free energy per unit area is

$$\frac{\delta F(L)}{A} = L\hat{\phi}_p \ln \hat{\phi}_p + L\hat{\phi}_s \left( \sum_{\alpha} P(\alpha) \ln P(\alpha) + \chi \langle n_1 \rangle \right)$$

$$+ \frac{L^2 \hat{\phi}_p}{2N^2} \sum_{z=1}^{L} \langle n_{0,p}(z) \rangle \langle n_p(z) \rangle + \sum_{z=1}^{L} \phi_s(z) \ln \phi_s(z)$$

(3)
where the first (last) term is the mixing entropy of the polymers (solvent) and the second is the conformational entropy of the chains, with \( P(\alpha) \) denoting the probability that a polymer chain is found in conformation \( \alpha \). The third is the intramolecular energy of the polymer, with \( \langle n_k \rangle \) the average number of intramolecular contacts, and \( \chi \propto 1/T \) measures the strength of monomer–monomer attractions, \( T \) being the temperature. The fourth term is the polymer–polymer intermolecular attraction, \( \langle n_{n,p}(z) \rangle = \sum_{\alpha} P(\alpha)n_{n,p}(z;\alpha) \), is the average number of open contacts that the polymer chains have in layer \( z \), and \( \langle n_p(z) \rangle \) is the average number of segments at \( z \). The repulsive interactions are included through packing constraints. That is, each lattice site is occupied either by a polymer segment or a solvent molecule. Under the assumption of inhomogeneity in the \( z \) direction, the constraint for \( 1 \leq z \leq L \) is written as the sum of the local polymer and solvent volume fraction:

\[
\langle \phi_p(z) \rangle + \phi_s(z) = L \frac{\Phi_p}{N} \sum_{\alpha} P(\alpha)n_p(z;\alpha) + \phi_s(z) = 1 \tag{4}
\]

The pdf of chain conformations and the solvent density profiles are found by the minimization of the free energy (eq 3) subject to the packing constraints (eq 4). Introducing Lagrange multipliers \( \beta \pi(z) \), the minimization gives

\[
P(\alpha) = \frac{1}{q} \exp \left[ -\beta \sum_{z=1}^{L} \pi(z)n_p(z;\alpha) - \chi n(\alpha) - \frac{L\chi \Phi_p}{2} \sum_{z=1}^{L} (n_{n,p}(z;\alpha)p(n_p(z)) + \langle n_{n,p}(z) \rangle n_p(z;\alpha)) \right] \tag{5}
\]

for the pdf, where \( q \) is the normalization constant (single-chain partition function). For the solvent, we have

\[
\phi_s(z) = \exp[-\beta\pi(z)] \tag{6}
\]

Now we need to determine the Lagrange multipliers, and then we can calculate the free energy for any thermodynamic state and film thickness. Replacing the explicit expression for the pdf (eq 5) and the solvent density profile (eq 6) into the constraint equations (eq 4) gives a set of \( L \) coupled nonlinear equations, from which we can determine the Lagrange multipliers and self-consistently the values of \( \langle n_{n,p}(z) \rangle \) necessary to determine the free energy and any desired average property of the system, including the polymer density (volume fraction) profile. The input necessary to solve the equations is the set of polymer chain conformations and the values of \( \phi_p \), \( \chi \), and \( L \). For the polymer chains, we generate a set of \( 10^6 \) independent conformations, in which the position of the first segment is randomly chosen within the film, using the Rosenbluth and Rosenbluth method for chains in a simple cubic lattice with hard walls at \( z = 0 \) and \( z = L + 1 \). The critical volume fraction and temperature are determined by the equating of the second and third derivatives of the free energy to zero. To show the quality of the theory, we show in Figure 1 a comparison of the predictions of the volume fraction profile at the critical point as predicted with the theory and from Monte Carlo simulations. The agreement between the two is very good, supporting the validity of the predictions from the theory.

Figure 2 presents the predictions for the variation of the critical volume fraction of the thin film, scaled by the \( N \)-dependent bulk value, as a function of the scaled film thickness. There are nine different chain lengths shown in the figure, and all but the two smallest ones show scaling with the variable predicted by the simple arguments presented previously. Furthermore, the reduction in the critical volume fraction at the minimum is approximately 25%. In other words,
the effect of confinement on the critical density for phase separation is very large. Note also the two limiting cases of approaching the 3D and 2D limit, for which the volume fraction varies linearly with the scaled inverse film thickness.

The question that arises is what are the differences in the structures of the films in the different regimes. Before showing those results, we should mention that the molecular mean-field theory cannot be applied in the limit in which the film thickness is smaller than the radius of the chains. The reason is that in the 2D limit, the mean-field approximation becomes poor. Therefore, all the results shown are for film thicknesses that are larger than the bulk radius of gyration of the chains, that is, \( x > 1 \).

Interestingly, the minimum in the critical volume fraction is at \( x = N^{1/2}/L = 0.28 \), which is more than four times the radius of gyration of the chains at the bulk critical point. Figure 3 shows the profiles for two values of the scaling variable \( x \). First, at the two values of the scaled film thickness, the density profiles show almost perfect scaling for the different molecular weights shown in each case. Second, there is a qualitative change in the shape of the profiles in the crossover thickness in comparison with the onset of the thick-film regime.

The change in the shape of the profiles is a result of the competition between the effective surface interactions and the free energy cost associated with gradients in the density. In the limit of thin films, surface interactions are dominant, whereas in the thick-film limit, the gradients will be the determining factor. In the two limits, both effects are relevant, even though one is more dominant than the other. The profiles in the minimum show the dominant effect of the surface repulsions. The profiles close to the surfaces (\( d = 0 \) and \( d = 1 \), where \( d \) is the scaled distance) are concave, with a sharp maximum in the density in the middle of the film. At all distances, there are large gradients of the
density. For thicker films, the surface effect is not that dominant, mostly because it represents a smaller fraction of the film, and therefore we see that the profiles flatten in the middle of the film to reduce the free energy cost associated with the gradients. This pattern continues as the films become thicker and leads to the scaling picture of an (almost) homogeneous large middle film with regions depleted of polymers close to the surfaces, whose sizes are of the order of the radius of gyration.

The region between the minimal critical volume fraction and the 2D film has a density profile that looks qualitatively like the one from the minimum shown in Figure 3 (results not shown). The main difference is that as the distance between the walls becomes smaller, the value of the density at contact increases. For both cases shown in Figure 3, the volume fraction at the surface is very small.

The last quantity that we report is the critical \( \chi \) parameter and its variation with the film thickness. The aforementioned simple scaling arguments cannot be directly applied for the variation of the critical temperature. However, in the limit of very thick films, \( L \to \infty \), one would expect the shift in the critical temperature to scale with the film thickness as predicted for simple liquids,\(^1\) that is, \( \chi_{c(L)} - \chi_{c,\text{bulk}} \propto 1/ L^2 \). Furthermore, because the natural length scale in the polymers is \( N^{1/2} \), we plot the distance of the critical point as a function of \( N^{1/2}/ L^2 \). Figure 4 shows that all the results scale very nicely with this variable, and furthermore, the approach to the 3D limit is linear as expected in cases in which the polymeric nature of the molecules becomes a minor issue. Furthermore, the shift in the critical temperature is monotonic with the film thickness, and the presence of confinement always stabilizes the solution. That is, the critical temperature decreases monotonically as the film thickness decreases from the 3D limit to the 2D limit.

In conclusion, we have shown, using simple scaling arguments and molecular mean-field theory, that the confinement of polymer solutions between two parallel purely repulsive walls results in a nonmonotonic variation of the critical volume fraction as a function of the film thickness. The reduction in the critical volume function can be as large as 25\% for film thicknesses corresponding to several times the radius of gyration of the chain. The shift in the phase behavior may have important consequences for the design of nanoscale devices for which the typical confinement is of the sizes studied here. The physical origin of the minimum arises from the competition between the effective long-range surface repulsions, which result from the reduction of the conformational space of the polymers, and the free energy price associated with gradients in density. This is confirmed by our preliminary results (not shown) that predict that adding an attractive interaction between the polymer segments and the surface can lead to a monotonic variation of the critical volume fraction with the film thickness. This opens a route for the rational design of confined environments for the stabilization of polymer solutions.

The authors thank O. J. Hehmeyer, G. Arya, and A. Z. Panagiotopoulos (ref. 7) for providing the raw data for the comparison in Figure 1. This material is based on work supported by the National Science Foundation (grant CTS-0338377) and by the Indiana 21st Century Fund.

REFERENCES AND NOTES