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Collapse of a Polymer in a Polymeric Solvent

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ABSTRACT: A minimal model used previously to treat the collapse of a polymer of molecular weight n in monomeric solvents is extended to polymeric solvents of molecular weight x. This model reproduces the Flory results in the expanded polymer regime with the controlling variable $(1/2x - \chi)$ becoming zero at the Θ temperature. In the collapsed region the system shows a "tricritical point", with the polymer displaying a second-order transition at small molecular weight x which becomes first-order for x larger than a critical x_c. Surprisingly, for x and n large and equal, the dimensions approach the Θ temperature value, $\langle R^2\rangle_n = C_n n l^2$, with only a weak dependence on the value of χ. Recent experiments do show only a weak dependence of $\langle R^2\rangle$ on χ.

1. Introduction

A system of n molecules interacting with pairwise potentials and confined within a large volume V goes *through a first-order transition from the vapor to solid* phase as we lower the temperature from some large value to absolute zero (if the volume initially was not too large, first−order transitions from vapor to liquid and then to solid would occur). If as we lowered the temperature we also were to slowly decrease the volume, this would obviously not affect the character of the transitions. Now consider these n molecules to be covalently connected into a linear polymer. The effect of the covalent connections is to establish a volume V (for the system of n molecules) which changes slightly as we cool. The problem thus reduces to the one considered above, and so we expect that, given the proper energetics, the collapsing polymer system must show first-order phase transition behavior. The entropy reduction in forming the polymer has the effect of aiding the transition, not hindering it.

It was evidently an insight along the lines of the arguments in the above paragraph that led Ptitsyn and co-workers[1] to augment the venerable Flory theory[2] by a virial expansion which naturally led to a first-order phase transition during polymer collapse. De Gennes also, by use of a magnetic analogy,[3] showed the existence of first-order transitions during collapse as well as a tricritical point.

Neither of these works discusses collapse in polymer solvents. Flory did discuss the isolated polymer in a polymer solvent and derived the condition $1/2x - \chi = 0$ as the Θ condition. He thus observed that for a polymer in its own solvent $\chi = 1/2x$, while for a polymer in a monomeric solvent $\chi = {}^1/_2$ as Θ conditions.[2] In this paper we extend a very simple treatment given previously to polymeric solvents.[5] This treatment gives the Flory results in the expanded region but differs from the Flory treatment in that it is applicable to the collapsed region as well. We will discover that the collapse transition is second-order for small values of x, in agreement with the work of Sanchez,[4] but that for larger x the transition is first-order. Thus the system shows a "tricritical point". We use quotation marks because we are dealing with phase behavior in the $T-x$ plane rather than in the $T-P$ plane and because our second-order transition is in the Ehrenfest sense.

Our previous model for monomeric solvent[5] is a minimal model in that it is the simplest model that gives the correct results for the critical exponents in a universality class for linear polymers defined by the parameter space of chain length n, energy of interaction χ, and dimension d. The Sanchez model[4] from which our model[5] was derived is slightly more complicated because of its use of radius of gyration S rather than end-to-end length R as the measure of polymer size. It can also be considered to be a minimal model. The simplicity of the minimal model has allowed progress to be made when other effects are added in an attempt to make the model more representative of real systems. Three recent papers which have incorporated the above minimal models of excluded volume into realistic polymer problems are (1) an extension to star molecules,[6] (2) a polymer condensing to a liquid crystal droplet,[7] and (3) application to random copolymers and globular proteins.[8]

The minimal model of this paper extends the previous treatment[5] to include a linear polymeric solvent of arbitrary molecular weight x. The parameter space of this universality class[9] contains the four variables n, x, χ, and d. In this work the only order parameter describing a molecule is the end-to-end length R. The Lifshitz treatment[10] which allows for spatial density variation within the molecule will not be discussed. A recent set of four papers by Grosberg and Kuznetsov[11] provides a review of the collapse transition in polymers.

2. Theory

2.1. Monomeric Solvent Case. We begin, as in the previous work, by expressing the Boltzmann factor, W, for a linear polymer chain as a product of three factors.

$$W = [R^2 \exp(-b^2R^2)][\Pi(1 - jl^2/R^3)][\exp(-n\chi(1 - nl^3/R^3))] \quad (1)$$

The first factor is proportional to the total number of random-walk configurations of a polymer of n segments whose end-to-end distance is R ($b^2 = 3/2C_n nl^2$, where l

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is the statistical length and C_n, the characteristic ratio, is a number between 1 and 10). The second factor corrects for excluded volume.[12] The third factor is the usual energetic term which measures the heat of mixing n polymer segments with $(R/l)^3 - n$ solvent molecules. The volume fraction of solvent is $1 - n(R/l)^3$ and the χ parameter is $\chi = z(\epsilon^{21} - (\epsilon^{22} + \epsilon^{11})/2)/kT$. The partition function, Q, can now be written as a sum over all allowed R and the Helmholtz free energy, F, from which all the thermodynamics can be derived is given by

$$F = -kT \ln Q, \quad Q = \sum_R W(R) \tag{2}$$

We simplify the problem considerably by representing the summation by the maximum term. The equation $\partial W/\partial R = 0$, or equivalently $\partial \ln W/\partial R = 0$, results in

$$\alpha^5/C_n - 2\alpha^3/3 = -n^{1/2}[n\alpha^6(\ln(1 - n^{-1/2}\alpha^{-3}) + n^{-1/2}\alpha^{-3}) + \chi] \tag{3}$$

which is an equation for determining R ($\alpha^2 = R^2/nl^2$). The standard formulas for the entropy and energy, $S = -\partial F/\partial T$ and $U = F - TS$, with S given by

$$S = -\partial F/\partial T|_{V,N,x} = \partial F/\partial T|_{V,N,x,R} + [\partial F/\partial R]|_{V,N,x,T}[\partial R/\partial T] = \partial F/\partial T|_{V,N,x,R} \tag{4}$$

result in

$$E = U/kTn\chi = 1 - n^{-1/2}\alpha^{-3} \tag{5}$$

In our previous paper[5] we showed that the energy displayed a second-order transition in the Ehrenfest sense (the U vs T curve is continuous, but the $\partial U/\partial T$ vs T curve is discontinuous). Also, eq 3 displays a collapse transition with polymer linear dimension varying as $n^{3/5}$ in the expanded region and $n^{1/3}$ in the collapsed region. The collapsed state is of less than close-packed density, however.

2.2. Polymeric Solvent Case. In order to treat the polymer solvent case, we envisage a background lattice onto which we have placed the n-mer. The first two terms of eq 1 are the number of ways to place the molecule onto the lattice. After this is done, the monomeric solvent can be placed onto the lattice in only one way. However, in treating the polymeric solvent we must take into account the number of ways to place the polymeric solvent onto the lattice after the n-mer is put down. Let the total number of x-mers be n_x, n_1 of them residing within the confines of the n-mer and n_2 of them residing outside.

$$n_x = n_1 + n_2 \tag{6}$$

Another equation of constraint among the n's is a volume constraint.

$$n + xn_1 = 4\pi R^3/3l^3 \tag{7}$$

This is the statement that the total volume of one n-mer plus n_1 x-mers is $4\pi R^3/3l^3$, which is the volume of the sphere defined by the R of the n-mer. The total weighting factor for placing one n-mer of end-to-end length R plus n_x x-mers is

$$W^{\mathrm{T}} = [R^2 \exp(-b^2R^2)][\Pi(1 - jl^2/R^3)][\exp(-n\chi(1 - nl^3/R^3))]P_1P_2 = WP_1P_2 \tag{8}$$

where P_1 is the number of ways to fill the volume spanned by the one n-mer with the n_1 x-mers, and P_2 is the number of ways to fill up the rest of the lattice with the remaining n_2 x-mers. Note that both P_1 and P_2 must appear as factors because they each are functions of R by virtue of the equations of constraint.

$$P_1 = (\prod_{j=1}^{n_1} \nu_j)/n_1! \tag{9}$$

$$\nu_{j+1} = (xn_1 - xj)[(xn_1 - xj)/(xn_1 + n)]^{x-1}z(z - 1)^{x-2} \tag{10}$$

$$P_2 = (\prod_{j=1}^{n_2} \mu_j)/n_2! \tag{11}$$

$$\mu_{j+1} = (xn_2 - xj)[(xn_2 - xj)/(xn_2)]^{x-1}z(z - 1)^{x-2} \tag{12}$$

To obtain P_1, we place the molecules one at a time onto the lattice until the volume of the n-mer is filled up. ν_{j+1} is the number of ways to place the $(j + 1)$th molecule given that the previous j molecules have to be placed. To calculate ν_{j+1}, we place the first segment of the molecule onto the lattice on any one of the $xn_1 - xj$ remaining sites. The probability of placing the remaining $x - 1$ monomers of the molecule is equal to the probability that $x - 1$ contiguous linearly connected lattice sites are all empty. This is estimated as the product of the probabilities that each site is empty, which in turn is given by the volume fraction $(xn_1 - xj)/(xn_1 + n)$. The factor $z(z - 1)^{x-2}$ accounts for the flexibility of the molecule.

To evaluate R, one maximizes W_{T} subject to the equations of constraint. It is best to work with the ln W_{T} and use eqs 6 and 7 to eliminate n_1 and n_2 before taking the derivative. The summations over j are evaluated using

$$\int \ln(A - Bj)\, dj = -((A - Bn_2)/B) \ln(A - Bn_2) - n_2 + (A/B) \ln A \tag{13}$$

After several pages of tedious but straightforward computation one obtains (notes available on request) a simple generalization of eq 1.

$$\alpha^5/C_n - 2\alpha^3/3 = -n^{1/2}[(n/x)\alpha^6(\ln(1 - n^{-1/2}\alpha^{-3}) + n^{-1/2}\alpha^{-3}) + \chi] \tag{14}$$

The expression for energy is again given by eq 5.

Figure 1 is a plot of α (calculated from eq 14) versus ϵ for a polymer of chain length $n = 10^5$ for different values of the solvent molecular weight. ϵ is a normalized interaction parameter defined as $\epsilon = (\chi_c - \chi)/\chi_c$ with $\chi_c = 1/2x$. ϵ is equivalent to the normalized temperature $(T - T_c)/T_c$ from classical discussions of critical phenomena. It is necessary to plot α versus ϵ because the point where $\alpha = 1$ for the different curves in Figure 1 depends on the solvent molecular weight, an issue which was not important in previous work on the collapse transition in low molecular weight (monomeric) solvents. One immediately sees that a first-order transition occurs at a critical value of x (x_c). This value is obtained by asking when $\partial\alpha/\partial\chi$ first becomes infinite as we raise x. From eq 14 we obtain by using the formula for the derivative of an implicit function a formula for x_c.

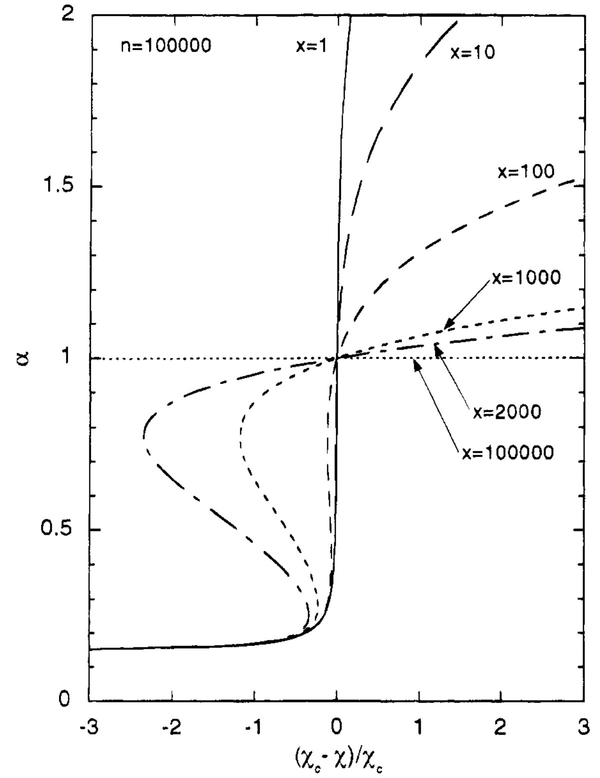

Figure 1. Expansion factor $\alpha = R/N^{1/2}l$ vs ϵ for a polymer molecule of length n (n-mer) imbedded in a polymeric solvent of x-mers. For molecular weights greater than about $10x^{1/2}$ the transition is first-order, while for smaller molecular weights the transition is second-order.

$$5\alpha^2/C_n - 2 + 3(n/x_c)[2Y\ln(1 - 1/Y) + 2 + 1/(Y - 1)] = 0, \quad Y = n^{1/2}\alpha^3 \qquad (15)$$

Retaining the first three terms in the expansion of the logarithm, we obtain

$$5\alpha^2/C_n + n^{1/2}/x\alpha^3 = 2 \qquad (16)$$

Depending on the values of x, n, and C_n, this equation has no solution (small x), one solution (at x_c), or two solutions ($x > x_c$). To find the critical x_c, we find the value of α which gives a minimum for the left-hand side of eq 16 and place it into eq 16 to obtain

$$x_c = 10.6n^{1/2}/C_n \qquad (17)$$

If we had used 3 rather than 2 in the right-hand side of eq 16, which corresponds to maximizing RW_T in eq 8 (this procedure gives a Flory coefficient of 1 rather than $^2/_3$ in the second term of the left-hand side of eq 14), the numerical factor on the right-hand side would be 3.9.

3. Results and Discussion

If we expand the right-hand side of eq 14 by expanding the logarithm, we have for large n, and for $(^1/_2x - \chi) > 0$,

$$\alpha^5/C_n - 2\alpha^3/3 = n^{1/2}[1/2x - \chi] \qquad (18)$$

which is the Flory result. This equation gives the insight that $\chi = {}^1/_2$ for Θ conditions in monomeric solvent and $\chi = 1/2x$ for Θ conditions when a large molecular weight polymer is in a bath of like polymer. Perhaps even more important, the dimensions of a high molecular weight polymer in a bath of high molecular weight polymer are almost independent of the value of χ as Figure 1 nicely shows. Experiments by Briber, Bauer, and Hammouda[13] seem to be in accord with this prediction. For polystyrene molecules in dilute concentration in a matrix of poly(vinylmethyl ether) of similar chain length, the polystyrene molecule is observed to be only slightly expanded. Only a weak temperature dependence in α was observed.

The prediction of the first-order transition is certainly very interesting since it makes the important testable statement that collapse is dependent on the molecular weight of solvent through eq 17 (really eq 15).

In our derivation we assumed that the x-mer was either inside or outside of the n-mer. In reality the x-mer can span the space between inside and outside, especially when x is large. We are unable to address this problem at this time.

In summary, we have presented an extremely simple model which reproduces the Flory results in the expanded region and also is applicable to the collapsed region. This model has already proved useful in the $x = 1$ version[4,5] in solving collapse in polymer stars,[6] collapse into liquid crystal droplets,[7] and the coil to globule collapse transition.[8] Our expanded treatment should continue to prove useful in solving those larger polymer problems in which excluded volume is only one part of the total problem.

References and Notes

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(9) A universality class is a set of objects which are distinguished from one another by allowing each member of the set to correspond to different points in parameter space (or more correctly on the parameter manifold). The common feature or features which define the set is what the minimal model explains. If all of the common features are explained in the simplest way possible, we have *the* minimal model. If some but not all of the common features are explained in the simplest possible way, we have *a* minimal model. Some use of the words "a minimal model" for any simple explanation which explains any essential feature of a set.
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