

The squared frequencies ω_A^2 are obtained from the eigenvalues of this matrix as described in the text. Details for $N = 3$ and 4 will be found in ref 7.

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Properties of Two-Dimensional Polymers

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ABSTRACT: We have performed a series of Monte Carlo simulations for a two-dimensional polymer chain with monomers interacting via a Lennard-Jones potential. An analysis of a mean field theory, based on approximating the free energy as the sum of an elastic part and a fluid part, shows that in two dimensions there is a sharp collapse transition, at $T = \Theta$, but that there is no ideal or quasi-ideal behavior at the transition as there is in three dimensions. The simulations and mean field theory agree very well. While the simulations are not sensitive enough to extract precise values for the exponent ν , it is clear that it is close to the Flory values: $\nu = 3/4$, $T > \Theta$; $\nu = 1/2$, $T < \Theta$. The mean field theory also gives $\nu = 2/3$ at $T = \Theta$.

Introduction

The large-scale configurational properties of a polymer chain in a good solvent are determined by excluded volume interactions between distant segments of the chain, which cause the chain to swell relative to an ideal coil, where there are no interactions. In a poor solvent the net interaction between polymer segments is attractive, which causes the chain to contract relative to an ideal coil. These effects can be modeled by an effective interaction potential between polymer segments which has a strong short-range repulsive part and a weak attractive part. Then by varying the temperature, one can simulate the effects of a good solvent (high temperature) and a poor solvent (low temperature), just as in ordinary fluids where the repulsive part of the pair potential is most important at high temperatures and the attractive part is most important at low temperatures. In this work we shall use a truncated Lennard-Jones potential to represent the interaction between effectively independent polymer segments. Each segment then represents the average properties of many monomers.

Both theory and experiment indicate that in a good solvent the mean end-to-end distance of a polymer chain, R , depends on the number of polymer units, N , as $R = AN^\nu$, in the limit of large N . Here A is a constant that depends on the temperature or properties of the solvent. The exponent ν depends on the dimensionality of the system. Flory's theory¹ predicts that in three dimensions $\nu = 0.6$ and in two dimensions $\nu = 0.75$. Experiments,

simulation studies, and other theories also give numbers for ν close to these.²⁻⁴ These numbers reflect the more pronounced excluded volume effect in lower dimensions. In three dimensions a polymer segment can pass over or under another segment, but in two dimensions it is energetically unfavorable for two segments to cross.

In a poor solvent the polymer will confine itself to as small a region of space as is consistent with the excluded volume interaction. Assuming the density within this region is roughly uniform, then $N \propto R^d$, where d is the dimension of the system. Thus, we expect the power law dependence of the size of the chain R on the number of units N to be described by an exponent $\nu = 1/d$. For an ideal coil the power law dependence also holds with $\nu = 1/2$. Thus, in three dimensions the size of the polymer is a smaller power of N than the ideal coil, while in two dimensions the exponent ν is the same for the ideal coil and the collapsed coil. The "collapse" of a polymer in two dimensions may therefore be qualitatively different from that observed in three dimensions.

Monte Carlo simulations in three dimensions show that the change in R as the temperature is lowered near the collapse transition becomes steeper with increasing N .⁵ This suggests that for very long chains the collapse occurs over a very narrow temperature range. Experiments by Sun et al. indeed show this kind of phase transition for dilute solutions of polystyrene macromolecules in a cyclohexane solvent.⁶ Recently, Vilanove and Rondelez⁷ have measured the surface pressure for two-dimensional polymer chains and found values of ν given by 0.79 ± 0.01 and 0.56 ± 0.01 , respectively, for two different polymer solutions. The first value is close to the Flory value predicted theoretically for swollen chains and the second is more typical of a collapsed chain. If the error bars quoted are

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meaningful, then they suggest that the excluded volume exponent of Flory may be too small and that a very different theory is needed to describe a collapsed chain. Thus, investigation of two-dimensional polymers at this time takes on greater import.

The purpose of this paper is to obtain a better understanding of the properties of two-dimensional polymers by means of Monte Carlo simulations and an analysis based on Flory's theory and extensions by de Gennes⁸ and others.⁹

Computational Procedure

Our model chain is made up of $N + 1$ beads (i.e., N links) located at positions $\{r_i\}$ connected by rigid rods. The distance between nearest-neighbor beads is taken to be the unit of length. Any two beads along the chain interact via a Lennard-Jones potential $V(r_{ij})$ with a cutoff r_c shifted so that $V(r_c) = 0$; i.e.

$$V(r_{ij}) = 4\epsilon[(\sigma/r_{ij})^{12} - (\sigma/r_{ij})^6 + (\sigma/r_c)^6 - (\sigma/r_c)^{12}] \quad r_{ij} < r_c \quad (1a)$$

$$V(r_{ij}) = 0 \quad r_{ij} > r_c \quad (1b)$$

For most of our work $r_c = 2$ and $\sigma = 0.7$.

The ensemble of configurations was generated by a reptation Monte Carlo dynamics as explained in ref 5. Briefly, the method involves the usual Metropolis Monte Carlo scheme where a move is defined as taking a bead from one end of the chain and placing it at the other end, in a position such that the angle between the old last link and the new link is determined by the Boltzmann factor. This procedure works very well at high and medium temperatures, where the ends of the polymer have freedom to move around. At lower temperatures the procedure is less efficient since the end can get trapped in a position such that a bead cannot be added to it. This leads to a very low acceptance ratio which prevents us from going to very low temperatures.

Equilibrium averages are obtained by dividing the total sequence of Monte Carlo steps into 30 blocks, where each block contains 500($N + 1$) attempted moves. The final average and standard deviation is obtained by averaging over the block averages after discarding the first couple of blocks to allow the chain to come to equilibrium. We used values of $N + 1$ equal to 20, 40, and 80.

A variety of size and shape properties of the polymer was studied. In addition, we computed the configurational energy. In the next section we shall present our results for each property along with the mean field theory predictions and results from other studies.

Properties of Two-Dimensional Polymers

A. End-to-End Distance. A great deal of effort has been expended in trying to understand the dependence of the mean end-to-end distance on the number of monomer units. In our simulation, where there is no angular correlation between successive beads, each bead represents the average behavior of many such units. Thus, although our chains have a maximum size of 80 beads, we expect the chain to behave at least approximately as if it is in the asymptotic region of large N , and as reported below this seems to be the case.

A very successful and simple way of computing ν is the theory of Flory. Here the free energy is assumed to consist of two parts, an elastic part and a part due to the interactions of monomers independent of their chemical distance along the chain. (It has been shown that the Flory theory was not rigorous and in fact left out the largest part of the free energy.¹⁰ However, the parts left out appear

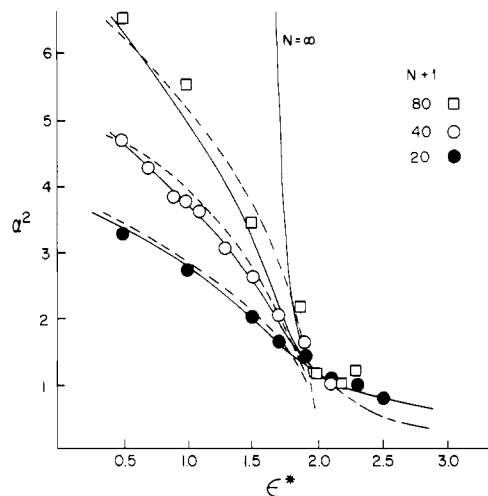


Figure 1. $\alpha^2 \equiv R^2/N$ for $N + 1$ beads from Monte Carlo simulation. The curves are from the Flory theory: (—) liquid part of free energy based on van der Waals approximation; (---) ($\epsilon^* < 2.0$) and (-.-) ($\epsilon^* > 2.0$), Flory theory up to third order in virial expansion; (···) Flory theory up to second order in virial expansion.

to cancel out for the most part so that Flory's theory gives quite accurate results. Our philosophy in using this theory is to assume that it is correct except for possibly small corrections to the exponent ν which are undetectable in our simulations and most experimental situations.) This free energy is then minimized with respect to the expansion factor $\alpha = R/N^{1/2}$. This leads to the result, in d dimensions, that

$$\alpha^{d+2} - \alpha^d = N^{2-d/2} \frac{1}{\rho} \frac{\partial}{\partial \rho} f(\rho, T) \quad (2)$$

where $f(\rho, T)$ is the (excess) free energy per particle of a fluid interacting with interparticle potential $V(r)$ at a density $\rho = (c/d)(N/R^d)$, where $c \simeq 1/\pi$ for $d = 2$, $c \simeq 3/4\pi$ for $d = 3$; i.e., the monomers are assumed to be distributed uniformly in a spherical volume of radius R . In the expanded state, $\rho \ll 1$ and $f(\rho, T) \sim \frac{1}{2}U_2(T)\rho^2$, where $U_2(T)$ is the second virial coefficient. In the simple Flory theory, therefore, one replaces the right side of (2) by $N^{2-d/2}U_2(T)$, giving

$$\alpha^{d+2} - \alpha^d = N^{2-d/2}U_2(T) \quad (3)$$

We then identify the Θ temperature, corresponding to the collapse transition, as occurring at $U_2(T) = 0$. While there are expected to be corrections to this simple picture, e.g., neighboring monomers are not independent even at small values of ρ , it nevertheless appears to give a good picture of the swollen chain when $U_2(T) > 0$ and $d < 4$. Note that in the absence of interactions $\alpha = 1$ for all d and we recover the ideal-coil results. If $U_2(\Theta) = 0$, then to first order we assume it to be of the form $U_2 \sim c(\epsilon_\Theta^* - \epsilon^*)$. Here $\epsilon^* = \epsilon/k_B T$ and ϵ_Θ^* is the value of ϵ^* at which the attractive part of the pair interaction potential compensates for the repulsive part. When $U_2(T) > 0$ and $d < 4$, then for large values of N the second term in eq 3 can be neglected. This gives $\nu = 3/(d + 2)$, which is very close to all experimental and numerical estimates. Using our high-temperature data shown in Figure 1 for $N = 40$, we find $\epsilon_\Theta^* = 1.93$, compared to the value of $\epsilon^* = 0.68$ where the second virial coefficient vanishes as determined by computing $U_2(T)$ numerically from the formula

$$U_2(T) = \int \{1 - \exp(-V/k_B T)\} d^2r \quad (4)$$

This huge discrepancy indicates that the bare binary interactions have very little to do with determining the

collapse of the two-dimensional polymer. This is different from three dimensions, where the collapse occurs at a temperature closer to the bare Θ temperature.

When we compute ν by a linear fitting of $\ln R$ vs. $\ln N$ for $N + 1 = 20, 40$, and 80 , we find $\nu = 0.76$ – 0.77 . It is difficult to give a reliable error bar for these data, but the trend suggests that the actual value of ν is very close to the Flory value of 0.75 . (Monte Carlo simulations of three-dimensional polymers have shown that finite size effects lead to slightly larger values of ν . This effect is probably also occurring here.¹¹) Renormalization group calculations give a slightly larger value for ν , namely, $\nu = 0.77$ in two dimensions.¹² However, Derrida¹³ recently used Nightingale's phenomenological scaling approach for the lattice polymer problem and found $\nu = 0.7503 \pm 0.0002$.

When $U_2(T)$ equals zero, eq 2 must be extended to include higher order virial coefficients. This leads to an equation of the form⁸

$$\alpha^{d+2} - \alpha^d - N \sum_{m \geq 3} U_m(T) N^{(m-1)(1-d/2)} \alpha^{-(m-2)d} = N^{2-d/2} U_2(T) \quad (5)$$

which in three dimensions reduces to⁸

$$\alpha^5 - \alpha^3 - \frac{U_3(T)}{\alpha^3} - \mathcal{O}\left(\frac{1}{N^{3/2}\alpha^6}\right) = N^{1/2} U_2(T) \quad (6)$$

and in two dimensions, however, to

$$\alpha^4 - \alpha^2 - N \sum_{m \geq 3} U_m(T) \alpha^{-2(m-2)} = N U_2(T) \quad (7)$$

Here $U_m(T)$ is proportional to the m th virial coefficient. As can be seen, the structure of the extended Flory theory is quite different in two dimensions from that in three dimensions. In three dimensions only the third virial coefficient is necessary at $T = \Theta$ since all other terms are of higher order in $N^{-1/2}$. The resulting equation is then of the same form as that describing tricritical points and thus the collapse has been theoretically described in this way.^{15,16} In two dimensions, however, all terms in the series are proportional to N and hence near the collapse higher order terms are more important than in three dimensions. In the language of the renormalization group all the terms are relevant. Physically, this corresponds to the restriction of configuration space in two dimensions causing the polymer to intersect itself many times.¹⁶

We fitted the data for $N + 1 = 40$ to an equation with the functional form of eq 7 where $U_2(T) = c(\epsilon_0^* - \epsilon^*)$, $U_3(T) = \text{const}$ and $U_m(T) \equiv 0$ for $m \geq 4$. The same values for ϵ_0^* , c and $U_3(T)$ were then used to generate the curves in Figure 1 for $N + 1 = 20, 40$, and 80 beads. This functional form fits the data well below $\epsilon_0^* = 1.63$ but does less well above ϵ_0^* . This suggests that the density of monomer units within the region of the polymer is too great and that more terms in the expansion are needed.

A more realistic way to represent the liquid-like behavior of the polymer units is to use an approximate free energy such as the van der Waals theory, which we write as¹⁷

$$\frac{F}{k_B T} = \frac{F_{\text{ideal}}}{k_B T} - N \ln \frac{(1 - Nb)}{V} - \frac{N^2 a}{V} \quad (8)$$

Here b is a parameter that represents the hard-core volume of a polymer segment and a is another parameter that determines the Θ temperature. Using this model free energy in the Flory theory, one finds the following:

Three Dimensions

$$\alpha^5 - \alpha^3 - \frac{b^2}{2k(k\alpha^3 - bN^{1/2})} = \frac{b - a}{2} N^{1/2} \quad (9)$$

Two Dimensions

$$\alpha^4 - \alpha^2 - \frac{Nb^2}{3k(k\alpha^2 - b)} = \frac{b - a}{3} N \quad (10)$$

where k is defined such that the volume (or area in two dimensions) is $V = kR^d$. There is not much change in the structure of these equations for large N at high and medium temperatures from that given in eq 5–7 as is shown by the curves in Figure 1. At low temperatures the van der Waals equation does give a better fit to the data than eq 7 using only up to the third virial coefficient. The fit to the 40-bead data gives $b = 1.8$, $a = 1.1\epsilon^*$, and $k = 3.5$, which are all reasonable values. For example, the hard-core area is roughly $\pi(\sigma/2)^2$, which equals 1.54 for $\sigma = 0.7$. ϵ_0^* is found by identifying $c(\epsilon_0^* - \epsilon^*) = (b - a)/3$, which gives $\epsilon_0^* = 1.66$ for our fit.

We see that eq 10 fits the data very well at both high and low temperatures. Also shown in Figure 1 is the prediction from eq 10 for the expansion factor for $N \rightarrow \infty$ and $\epsilon^* > \epsilon_0^*$. This curve shows that there is a very sharp transition from the excluded volume region to the collapsed chain region. Since the Monte Carlo data fit this equation, there is some reason to believe that a sharp transition does indeed exist for $d = 2$. The same result was found by Derrida for a lattice model with attractive interactions. He uses a finite-width, infinite-length strip and finds that ν goes from 0.75 to 0.5 in a narrow region of ϵ^* . The curves get sharper as the width increases.¹⁸ Also of interest is the fact that right at $\epsilon^* = \epsilon_0^*$ we find that the first and third terms of eq 10 are dominant and that $\nu = 0.66667$, instead of $\nu = 0.5$, which occurs in three dimensions at the collapse transition. (Derrida¹⁸ finds that curves of $\nu(T)$ as a function of width cross at a $\nu \approx 0.55$ – 0.58 .) This suggests that the two-dimensional polymer does not have a region of quasi-ideal behavior as is found for the three-dimensional chain. Thus, the two-dimensional polymer goes directly from an excluded volume state to a collapsed state. For $\epsilon^* > \epsilon_0^*$ the value of the expansion factor, α , is constant in the limit of large N and is given implicitly by the equation

$$\alpha^2 = \frac{b}{k} + \frac{b^2}{k^2(a - b)} \left[1 - \frac{3(\alpha^4 - \alpha^2)}{N(a - b)} \right] \quad (11)$$

Thus, coming from the low-temperature side (large ϵ^*), we see that α^2 diverges for $N = \infty$ (since as $\epsilon^* \rightarrow \epsilon_0^*$, $\alpha - b \rightarrow 0$) and is not constant as it would be for the quasi-ideal coil.

The reason for a lack of ideal behavior in two dimensions is probably due to the topological constraints on the allowable configurations. These constraints could also lead to nonideal behavior of polymer melts, unlike their three-dimensional counterparts, where it has been argued that the single chain in a melt does in fact behave as an ideal chain.¹⁹

B. Radius of Gyration. The mean radius of gyration is defined as

$$S^2 \equiv \sum_i \sum_{j \neq i} r_{ij}^2 \quad (12)$$

Fits to the data for S are also possible as was done for R . The results are similar, with slightly different values of the parameters b , a , and k needed for the best fit. (Here the natural variable to replace α^2 is $\phi^2 = 6S^2/N$.)

In Figure 2 we plot the values of R^2/S^2 as a function of ϵ^* . Since this ratio is independent of N , the form of $\phi^2(N)$ is the same as that of $\alpha^2(N)$. The asymptotic value for high temperatures is about 7.5 , which is similar to the value

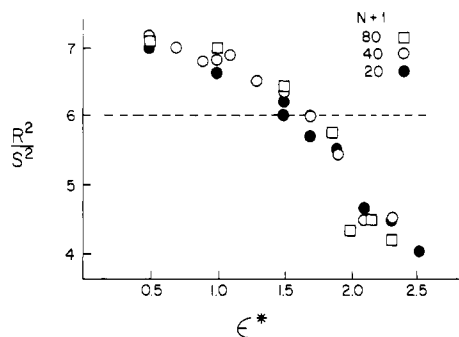


Figure 2. Data from Monte Carlo calculations for R^2/S^2 .

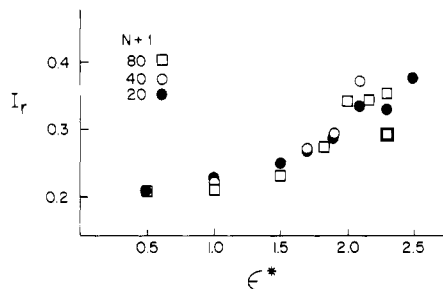


Figure 3. Data from Monte Carlo calculations for $I_r = \langle I_{\min}/I_{\max} \rangle$, where I_{\min} (I_{\max}) is the smallest (largest) principal moment of inertia.

obtained by Monte Carlo calculations on a square lattice, which gave $R^2/S^2 = 6.9$. It is larger than that obtained for three-dimensional lattices, where R^2/S^2 is around 6.4.^{20,21} Also, one expects that the value of this ratio should equal 6 for an ideal chain. This occurs for ϵ^* around 1.7, which is very close to the ϵ_{θ}^* found by fitting the 40-bead data. It is not clear whether this means that the chain is ideal. We argued against this possibility in the last section. More likely, this ratio must be greater than 6 in the excluded volume region and less than 6 in the collapsed region, and thus near the transition the ratio must pass through 6.

C. Principal Moments of Inertia. We have also computed the ratio of the principal moments of inertia and the results are shown in Figure 3. We define I_r as $\langle I_{\min}/I_{\max} \rangle$. In the excluded volume regime we expect elongated chains, leading to small values of I_r . We find that this is the case with I_r about equal to 0.2 for high temperatures and independent of N . In the collapsed regime we expect I_r to be closer to unity, which is its value for a disk. Our results show a smooth though rapid crossover near the fitted value of ϵ_{θ}^* .

D. Fluctuations in S^2 . We also computed the quantity $\langle \Delta S^2 \rangle = \langle S^4 \rangle - \langle S^2 \rangle^2$. One expects that $\langle \Delta S^2 \rangle$ will decrease dramatically at the collapse transition since the size of the chain should not fluctuate nearly as much for a collapsed glob as an extended chain. However, we observe a gradual change with temperature. This may just mean that S^2 is largely a measure of internal polymer properties as well as global properties and that these do not change significantly at the transition.

E. Angle between Two Halves of the Polymer. If we consider a polymer as being composed of two halves, then the mean end-to-end distance is related to the distance from one end to the middle and the distance from the other end to the middle as

$$R^2 = (\vec{R}_1 + \vec{R}_2)^2 = 2R_1^2 + 2\vec{R}_1 \cdot \vec{R}_2 \quad (13)$$

where $\vec{R}_1 = \vec{r}_1 - \vec{r}_{N/2}$ and $\vec{R}_2 = \vec{r}_{N/2} - \vec{r}_N$. For long chains $R = AN^\nu$ and $R_1 = R_2 = A(N/2)^\nu$. Thus, eq 13 gives

$$\langle \vec{R}_1 \cdot \vec{R}_2 \rangle / \langle R_1^2 \rangle = \frac{1}{2}(2^{2\nu} - 2) \quad (14)$$

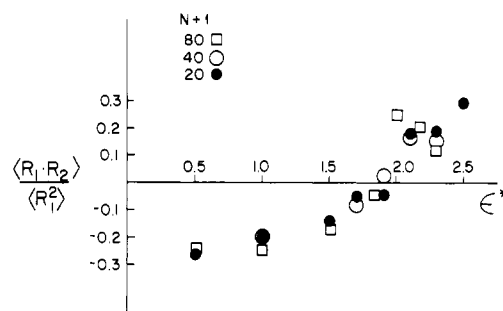


Figure 4. Data from Monte Carlo calculations for the ratio $\langle \vec{R}_1 \cdot \vec{R}_2 \rangle / \langle R_1^2 \rangle$, where $\vec{R}_1 = \vec{r}_1 - \vec{r}_{N/2}$ and $\vec{R}_2 = \vec{r}_{N/2} - \vec{r}_N$.

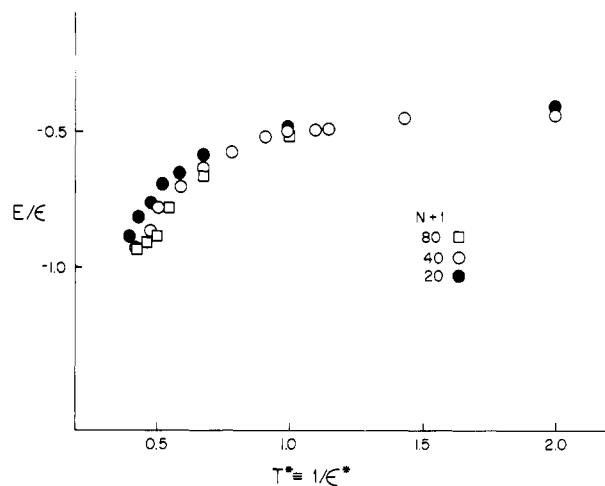


Figure 5. Data from Monte Carlo calculations for the energy per bead vs. reduced temperature.

This quantity cannot be used to get a reliable value of ν because end effects are too important even in the excluded volume region. However, $\langle \vec{R}_1 \cdot \vec{R}_2 \rangle$ should equal zero when $\nu = 0.5$ and thus can be used to locate the θ temperature. This occurs at $\epsilon^* = 1.9$, as can be seen in Figure 4. This value is somewhat higher than our other estimates of the collapse temperatures. Also, we note that for $\epsilon^* > \epsilon_{\theta}^*$, $\langle \vec{R}_1 \cdot \vec{R}_2 \rangle$ should equal 0 since $\nu = 0.5$. But this is not the case due to the fact that R_1 and R_2 are very highly correlated so that half the chain cannot be treated as a long chain by itself, as assumed in the derivation of eq 14.

F. Energy and Specific Heat. The total internal energy of the polymer as a function of temperature is shown in Figure 5. The slope of this curve is the specific heat. If there is a specific heat peak near the collapse, it is difficult to see. Baumgartner²² found no peak in the three-dimensional case except at very low temperatures corresponding to a liquid-solid transition. Derrida,¹⁷ however, found a peak in two dimensions for his lattice model. To pin down the energy in our model we need to go to lower temperatures than we are capable of at the moment. One significant feature of the curves is that they are largely N independent, with at least some of the N dependence due to end effects.

G. Snapshots of Polymer Configurations. Another way to gain a qualitative feel for what is going on in the polymer as the temperature is lowered is to look at snapshots of polymer configurations. We have looked at many configurations and show a few in Figure 6. These pictures show that the primary difference is the number of contacts between beads, which increases as the temperature is lowered. Another difference is that the extended chain moves through a large sequence of varying shapes, whereas the collapsed chain will change its shape much more slowly

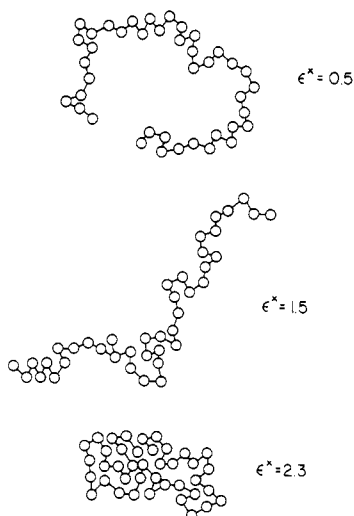


Figure 6. Snapshot configurations of 40-bead polymers from Monte Carlo simulations. These were hand drawn; thus some of the distances between beads appear unequal.

and is unlikely to exhibit any very extended shapes.

Conclusion

We conclude that a free energy consisting of two parts, an elastic part and a liquid-like part, in the spirit of Flory's mean field theory, describes a two-dimensional polymer very well in both the excluded volume and collapsed regimes. This theory predicts a sharp transition but does not predict ideal coil behavior at the transition, which distinguishes it from three dimensions, where it is thought that there is quasi-ideal behavior at the Θ temperature. Consistent with this prediction our Monte Carlo data give no indication of a crossover from excluded volume behavior to ideal coil behavior as found in the three-dimensional simulation.⁵ Although our data are not sufficient to rule out other exponents than those derived by Flory, it is clear that these exponents are very close to the correct values.

Acknowledgment. We thank B. Derrida for making his results available to us prior to publication. This work is supported in part by AFOSR Grant No. 78-3522 and by

U.S. DOE Contract DE-AC02-76ER03077. Acknowledgment is also made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

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Photon Correlation Spectroscopy on Polystyrene Solutions under High Pressure

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Received September 1, 1981*

ABSTRACT: The diffusion coefficient D of a narrow-fraction polystyrene ($\bar{M}_w = 111\,000$, $\bar{M}_w/\bar{M}_n \leq 1.06$) in toluene has been studied as a function of pressure from 1 up to 5000 atm for both dilute and semidilute solutions by using the photon correlation spectroscopy technique. In dilute solution the value of the coefficient k_D , representing the concentration dependence of D , was found to be independent of pressure. Likewise, the hydrodynamic radius R_H , obtained from the value of D at infinite dilution, was observed to be independent of pressure. The observed decrease in D with increasing pressure is, for all concentrations, completely correlated to the pressure dependence of the solvent viscosity.

Introduction

Although there are a number of total intensity light scattering investigations¹⁻⁹ dealing with the effect of pressure on, for example, the second virial coefficient and the radius of gyration of polymer chains in dilute solution, little attention¹⁰ has been paid to the pressure dependence

of dynamical properties in polymer systems. The main objective of the present paper is to study the effect of pressure on the diffusion features in dilute and semidilute polymer solutions.

In recent years photon correlation spectroscopy (PCS) has been extensively used to study dynamic features of