PHYSICAL REVIEW E VOLUME 58, NUMBER 5 NOVEMBER 1998

First-order phase transition in unfolding a collapsed polymer: A histogram Monte Carlo simulation

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(Received 6 May 1998)

The phase transition associated with stretching a collapsed polymer chain (consisting of N monomers) is investigated in detail using the histogram Monte Carlo simulation method and the bond-fluctuation model. The distribution functions for the number of contacts and end-to-end distances are obtained. The free energy profile associated with the transition is explicitly computed. Our results on the energy cumulants and free energy profiles provide direct evidence for the first-order nature of the phase transition. The phase transition occurs in the whole poor solvent regime below the Θ point, $\chi > \chi_c$. The free energy barrier at the transition is found to scale with $N(\chi - \chi_c)$. Phase diagram for the first-order transition phase boundary is also obtained. We find that the mean-field theory results give only a qualitatively correct picture for the phase transition.
[S1063-651X(98)09011-4]

PACS number(s): 05.70.Fh, 05.70.Jk, 61.41.+e

I. INTRODUCTION

Previous studies on the deformation of a polymer chain were mostly concerned with the unwinding and stretching of a polymer chain under forces or flows for swollen or ideal polymer chains using scaling calculations [1–4]. These studies found that in these cases, the deformation of the chain is progressive and no sharp coil-stretch phase transition occurs. The theoretical interest in this subject has been further stimulated by current experimental techniques to manipulate and observe the configuration of a single DNA macromolecule under external stretching forces using fluorescence microscopy. These can be achieved by attaching a magnetic bead to the free end of an end-grafted DNA and subjected to magnetic [5] or hydrodynamic [5–8] forces and by micromechanical techniques [9]. In this study, we consider another more interesting situation, namely, the unwinding of a polymer collapsed in a bad solvent, i.e., below the Θ point [10–12]. Such a phenomenon may provide some understanding in the nature for protein folding, which can be crudely modeled as the reverse process if the external stretch is removed. Recent mean-field calculation [10,11] and stability analysis [13,14] of Flory-type models showed that in stretching a collapsed polymer coil in poor solvent, a first-order transition occurs as the stretching force is increased to some threshold value. However, the mean-field result could be wrong, even qualitatively, in predicting the nature of phase transitions. Examples of such failure include predicting a transition at a finite temperature for the Ising model regardless of the spatial dimension, and predicting first-order transitions in a two-dimensional Potts model even when the number of Potts states is not greater than 4 [15]. On the other hand, in some polymer systems such as demixing transition of a symmetric polymer mixture, mean-field behavior is correct [16] in the long chain limit. Therefore one should be careful about the results of mean-field theory in the nature of phase transitions. The nature of phase transitions can be very precisely studied by Monte Carlo simulation and hence the validity of theoretical predictions can be examined in detail. Furthermore, by unfolding these collapsed macromolecules, it may provide relevant information on the mechanism of protein folding and other related structures in biomolecules. Thus a knowledge of the free energy profile is useful in the understanding of the dynamics of protein folding. However, to calculate the free energy accurately and efficiently is nontrivial, even in a computer simulation. In this paper we apply the histogram Monte Carlo method [17,18] to our polymer system of interest and the free energy can be readily calculated.

From the viewpoint of statistical physics, such a system shows a variety of interesting phase transition phenomena which can provide experimental realizations and testing grounds for these theoretical models. The applicability of the histogram Monte Carlo method [17,18] is rather wide, from first-order to continuous phase transitions, from lattice models to continuum models, though most of the applications of the histogram Monte Carlo methods in the past were on the studies of phase transitions in spin systems such as Potts models. In particular, its applications to polymer systems are still rather limited [19,20]. Many polymer systems possess rich behaviors of phase transitions due to the complexity and large degrees of freedom in the system and hence the histogram method would provide a convenient way to investigate these phenomena. Furthermore, due to the complicated interactions among the monomers in a polymer system, the understanding of the free energy profile is essential in many macromolecular systems. The histogram method can compute the free energy profile with relative ease and is potentially ready to be applied to realistic macromolecules such as protein and DNA. An understanding of the free energy profile of these proteins or DNAs can provide valuable insights in the nature of protein folding and other relevant kinetic effects determined by the free energy profile.

II. MEAN-FIELD CALCULATIONS

The mean-field results of the system are briefly reviewed here for completeness; more details can be found in Ref.

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[11]. The system consists of a polymer chain with $N \gg 1$ monomers collapsed in a poor solvent with one end fixed at some point in space (taken to be the $z=0$ plane). A force f pulls on its free end in the z direction which tends to unwind the chain. Let z denote the end-to-end distance (also the height of the free-end monomer) of the chain, then the total phenomenological reduced free energy is composed of three terms corresponding to the elastic free energy, mixing free energy and the potential energy due to f as follows:

$$\frac{F}{kT}=F_{\mathrm{el}}+\frac{1}{a^3}\int d^3r\, F_{\mathrm{mix}}[\Phi]-\varphi z, \tag{1}$$

where k is the Boltzmann constant, T is the temperature, $\varphi \equiv f/(kT)$, a is the monomer size, and F_{el} is the elastic free energy. In the poor solvent regime, the elastic free energy [21] consists of two terms

$$F_{\mathrm{el}}=\frac{1}{a}\int_0^z \mathcal{L}^{-1}\left(\frac{u}{Na}\right)du+\frac{3}{2}\frac{Na^2}{z^2}, \tag{2}$$

where $\mathcal{L}(x)=\coth x-1/x$ is the Langevin function. The first term in F_{el} takes into account the finite extensibility of the chain [22] which is important for strongly stretched configurations whereas the second term dominates for collapsed configurations. F_{mix} is the Flory mixing free energy [22,23]

$$F_{\mathrm{mix}}(\Phi)=(1-\Phi)\ln(1-\Phi)+\chi\Phi(1-\Phi), \tag{3}$$

where χ is the usual Flory interaction parameter and Φ is the monomer volume fraction. As in the usual Flory mean-field calculation, Φ is approximated by a constant. In the absence of external force, the chain has a spherical shape and it has been shown that a second-order transition from the swollen state to the collapsed state [23,24] occurs at $\chi_c=1/2$. For $\chi<1/2$, the polymer coil is in a swollen state with a linear dimension $\sim aN^{3/5}$. At the Θ point, $\chi=\chi_c=1/2$, the polymer chain behaves like an ideal coil with size $\sim aN^{1/2}$. And for $\chi>1/2$ the chain has a collapsed configuration with a linear dimension $\simeq aN^{1/3}$. Under a strong enough unwinding force, the polymer will be stretched. The collapsed and stretched states are distinguished by the order parameter, in units of a, defined by $\eta \equiv z/N$. Henceforth, a will also be absorbed in the unit of φ for convenience. The stable state is given by the global minimum of the free energy. This model was solved [11] exactly in the $N\rightarrow\infty$ limit to give

$$\langle \eta \rangle=\begin{cases}0 & \text{for } \varphi\leqslant\varphi^* \\ \mathcal{L}(\varphi) & \text{for } \varphi>\varphi^*\end{cases}. \tag{4}$$

Furthermore for a given value of χ, φ^* can be solved in the $N\rightarrow\infty$ limit to obtain the equation for the first-order phase transition boundary [11]

$$\varphi^*=e^{\chi^*-\chi}\sinh\varphi^*, \tag{5}$$

with $\chi^*=2\chi_c=1$. Moreover, there is no abrupt change in the $\chi_c<\chi<\chi^*$ poor solvent regime, with

$$\langle \eta \rangle=\mathcal{L}(\varphi) \quad \text{for all } \varphi\geqslant 0 \quad \text{and } \chi_c\leqslant\chi\leqslant\chi^*, \tag{6}$$

the polymer globule is elongated progressively and continuously.

For $\chi>\chi^*=1$, the free energy $F(\eta)$ possesses two minima separated by a free energy barrier. For $\varphi<\varphi^*$, the stretched state is metastable and the characteristic time for it to transit to the stable collapsed state depends on the free energy barrier height. The free energy barrier is maximal at $\varphi=\varphi^*$ and is given by [11]

$$\frac{\Delta F}{NkT}=\chi-\chi^*-\frac{\sqrt{\varphi^*(\chi-\chi_c)}}{N^{1/3}} \tag{7}$$

in the large N limit. The tunneling time can be estimated from $\tau\sim\exp(\Delta F/kT)$. The existence of metastable states in a first-order transition is manifested experimentally by the presence of hysteresis loop if the observation time is not much greater than the lifetime of metastable states [10].

III. BOND-FLUCTUATION MODEL AND THE HISTOGRAM MONTE CARLO METHOD

The bond-fluctuation model (BFM) [25] for polymer chains is employed to investigate the system by Monte Carlo simulations. In the BFM, a cube of eight lattice sites represents each effective monomer on a simple cubic lattice. Self-avoidance is modeled by the requirement that no two monomers can share a common site. The 108 allowed bond vectors connecting two consecutive monomers along a chain are obtainable from the set {(2,0,0), (2,1,0), (2,1,1), (2,2,1), (3,0,0), (3,1,0)} by the symmetry operations of the cubic lattice, i.e., (2,0,0) represents $(\pm 2,0,0)$, $(0,\pm 2,0)$, and $(0,0,\pm 2)$, etc. To model the poor solvent condition, an attractive interaction among the monomers is modeled by an energy cost $-\epsilon<0$ if two monomers are neighbors of each other. Two monomers are considered as neighbors [20,26,27] if they are separated by one of the displacement vectors {(2,0,0), (2,1,0), (2,1,1)} (plus those obtained from symmetry operations) and there is no distinction for the energy cost for these three types of bond vectors. The Monte Carlo procedure starts by choosing a monomer at random and trying to move it one lattice spacing in one of the randomly selected directions: $\pm x, \pm y, \pm z$. The move will be accepted only if (i) self-avoidance is satisfied, (ii) the new bonds still belong to the allowed set, and (iii) the Boltzmann factor $\exp(-\Delta E/kT)$ is greater than a uniformly distributed random number between 0 and 1, where ΔE is the energy change due to the move. Henceforth the reduced energy $\chi\equiv\epsilon/kT$ and $\epsilon=1$ will be used for convenience. χ defined here in our simulation model has the same physical meaning as the one in mean-field theory in the preceding section, though numerically it can be different. $\chi=0$ corresponds to the good solvent condition. In this BFM, the Θ point corresponds to $\chi_c=0.52$ [28].

The stretching force acting in the z direction is implemented by fixing one end of the polymer in space at an altitude $z=0$ and a potential energy $-fz$ is associated with the free-end monomer at a height z. A polymer chain of N monomers is placed in a sufficiently large box. The initial configuration of the chain is grown by random self-avoiding walk to the desired length under good solvent condition and no external force. Then the polymer is slowly annealed to the desired values of χ and f. Starting with given values of χ and f, the system is allowed to equilibrate for a long time (typically five times the relaxation time) and then the histogram for the relevant physical quantities and other ensemble averages are taken from runs over an even longer period of time. Time is measured in units of Monte Carlo steps per monomer (MCS/monomer). One MCS/monomer means that on average every monomer has attempted to make one trial move.

In the model for the coil-globule collapse transition, the solvent quality is modeled by an attractive energy cost when the monomers are neighbors of each other. In the presence of an external stretching force, the Hamiltonian or the total energy E of the system is

$$E/kT = -\chi\mathcal{C} - \varphi z, \tag{8}$$

where $\mathcal{C}$ is the number of neighbor contact pairs and z is the position of the free-end monomer (which is also the z component of the end-to-end distance). All the thermodynamic behavior of the system is determined solely by the parameters χ and φ. Large values of χ correspond to poor solvent conditions. We are interested in the phase transition from a collapsed polymer to a stretched polymer; these two states can be characterized by the stretch parameter [29], defined as in the preceding section, as

$$\eta \equiv z/N \tag{9}$$

and/or the collapsed parameter

$$\psi \equiv \mathcal{C}/N. \tag{10}$$

We shall use the stretched parameter η as the order parameter in the analysis of the simulation data. Since one needs to extrapolate physical quantities related to η and ψ, the histogram $H(\psi,\eta)$ will be recorded in the simulation. Following standard histogram Monte Carlo method [17], let $H_0(\psi,\eta)$ be the histogram recorded at χ_0 and φ_0, then the probability distribution at another (χ,φ) is given by

$$P_{\chi\varphi}(\psi,\eta) = \frac{H_0(\psi,\eta)\exp\{N[(\chi-\chi_0)\psi + (\varphi-\varphi_0)\eta]\}}{\sum_{\psi,\eta} H_0(\psi,\eta)\exp\{N[(\chi-\chi_0)\psi + (\varphi-\varphi_0)\eta]\}}. \tag{11}$$

Then for any physical quantity B (which is a function of ψ and/or η), its equilibrium average value at χ and φ is

$$\langle B\rangle = \sum_{\psi,\eta} B P_{\chi\varphi}(\psi,\eta). \tag{12}$$

Thus by recording the histogram at (χ_0,φ_0), quantities at other values of (χ,φ) can be obtained. Of course the range of accurate extrapolation will be limited by the statistics of the histogram [17]. In this simulation study, by choosing (χ_0,φ_0) close to the phase transition points of interest and recording H_0 up to 10^9 samples, nice data for a sufficiently wide range of accurate extrapolation are obtained. The multihistogram method [18] can also be used to extend the range of accurate extrapolation.

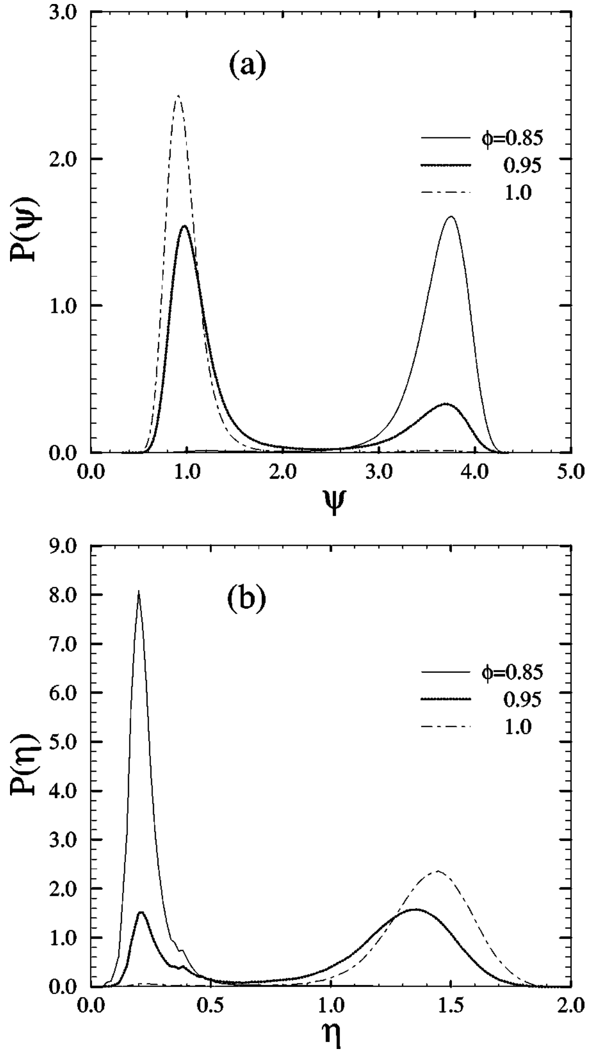


FIG. 1. Probability distributions of a chain of length $N=60$ and at $\chi=1.0$ for three values of φ. (a) $P(\psi)\equiv\int P_{\chi\varphi}(\psi,\eta)d\eta$, (b) $P(\eta)\equiv\int P_{\chi\varphi}(\psi,\eta)d\psi$. The distributions are normalized.

Since one expects a first-order transition in stretching the collapsed chain, a knowledge of the order of magnitude of the tunneling time between the collapsed and stretched states in advance would be desirable. This can be estimated from our previous study [10] (without using the histogram method) for $N=40$, with the longest relaxation time found to be of the order of 10^6 MCS/monomer at $\chi=1$ and near the threshold force. The order of magnitude of tunneling times at other values of χ and chain lengths can then be estimated from Eq. (7). Finally, one can make sure that the simulation period is long enough (much greater than tunneling time) from results on the distribution functions (see next section) which should be smooth and characterized by the double-peak feature of a typical first-order phase transition.

IV. DISTRIBUTION FUNCTIONS AND ORDER PARAMETER

Extensive simulations are carried out to obtain the histograms for various values of (χ_0,φ_0) near the phase transition points for chains of different lengths. $P_{\chi\varphi}(\psi,\eta)$ can be obtained from the histogram $H_0(\psi,\eta)$ through Eq. (10),

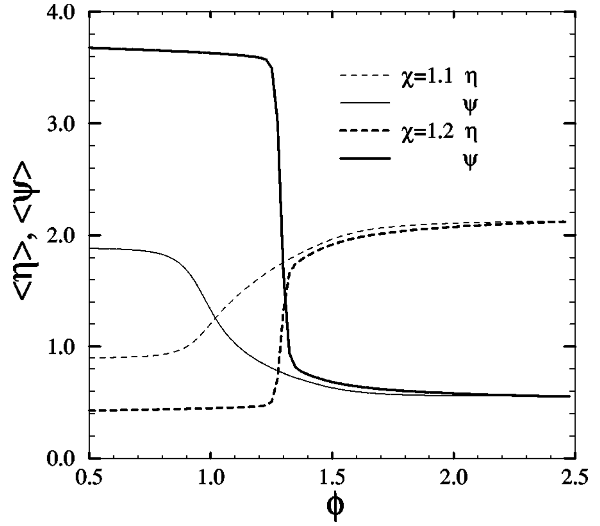


FIG. 2. The order parameter $\langle \eta \rangle$ and the collapsed parameter $\langle \psi \rangle$ versus φ at two values of χ. $N=80$.

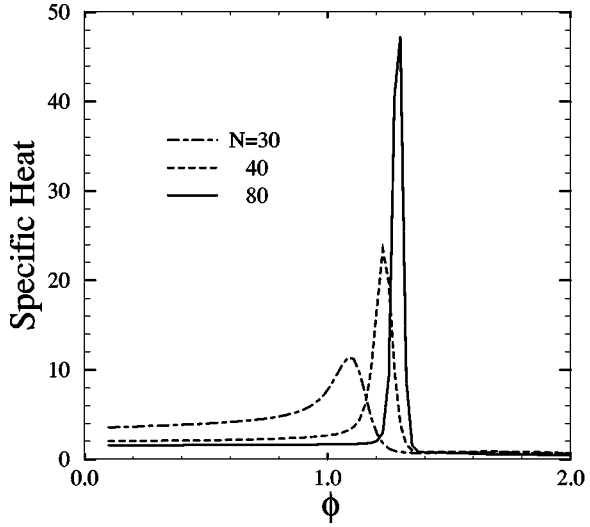


FIG. 4. Specific heat (in units of k) versus φ for chains of various lengths at $\chi=1.2$.

hence the probability distributions for the number of contacts $P(\psi)$ and the z position of the free-end monomer $P(\eta)$ are also obtained. Figure 1 displays these distributions with a given value of $\chi=1$, but with three different values of φ. At $\chi=1$, the polymer is in a rather poor solvent and is strongly collapsed in the absence of external unwinding force (the Θ point for this model is $\chi_c=0.52$). In Fig. 1(a), $P(\psi)$ has a single peak for $\varphi=0.85$ which is below the transition to the stretched state. The average number of neighbors per monomer peaks narrowly around $\psi\simeq 3.8$, characteristic of a collapsed state. As the stretching force is increased to $\varphi=0.95$, very close to the transition point, $P(\psi)$ shows a prominent double-peak character with an extra peak at $\psi\simeq 1$ signaling the emergence of the coexisting stretched state. This characteristic of a first-order transition can also be observed [Fig. 1(b)] from the change of a single peak in $P(\eta)$ below the threshold force to the emergence of a second peak near the transition point. The threshold force at the transition point, denoted by φ_N^*, is defined in the simulation to be the value of φ such that the two minima in the free energy profile are of the same depth [or the two peaks in $P(\eta)$ are of the same height]. The true phase transition threshold value in the $N \rightarrow \infty$ limit is denoted by φ^*. Using the histogram extrapolation technique, the variation of the order parameter $\langle \eta \rangle$ and the collapsed parameter $\langle \psi \rangle$ are calculated as a function of φ for fixed values of χ. The results for different values of χ are shown in Fig. 2 for a chain of $N=80$. For $\chi=1.2$, a sharp jump in the order parameter occurs at $\varphi_N^* \simeq 1.3$, typical in a first-order transition. A sharp decrease in $\langle \psi \rangle$ also occurs at φ_N^*. However, for $\chi=1.1$ the changes in the order parameter and $\langle \psi \rangle$ are much less abrupt, suggesting a weak first-order transition. More detailed analyses on the free energy profile and energy cumulant are carried out in the next section in order to determine the existence of a first-order transition.

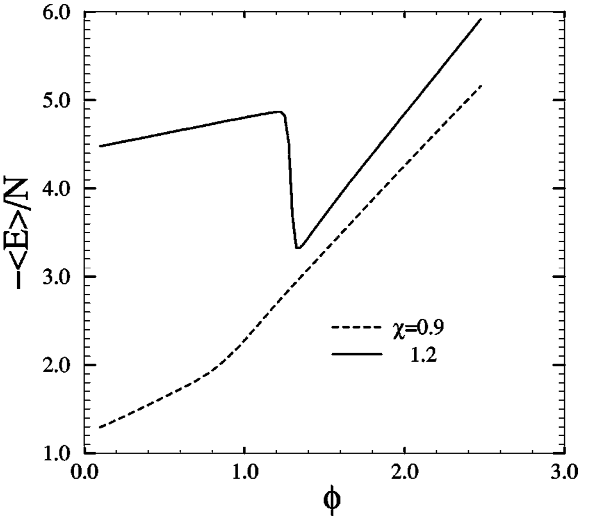


FIG. 3. Mean energy per monomer (in units of kT) versus φ for two values of χ. $N=80$.

V. ENERGY CUMULANTS AND FREE ENERGY PROFILE

The average total energy of the system [given by Eq. (8)] can be readily computed from the histogram method. Figure 3 displays the mean energy per monomer of a chain of length $N=80$ as a function of φ for two fixed values of χ. For $\chi=0.9$, $\langle E \rangle$ continuously increases with φ suggesting the absence of a (or weak) first-order phase transition. But for $\chi=1.2$, $\langle E \rangle$ shows a sharp drop at $\varphi_N^* \simeq 1.3$ signaling a first-order phase transition. The specific heat can also be easily computed by the mean square energy deviation and the results are shown in Fig. 4 as a function of φ for chains of different lengths. The peak of the specific heat grows rapidly as the length increases, suggesting a phase transition in the thermodynamic limit. The nature of the phase transition can be investigated by finite-size analysis of Binder's energy cumulant [30] defined as

$$V_N \equiv 1 - \frac{\langle E^4 \rangle_N}{3\langle E^2 \rangle_N^2}, \tag{13}$$

where $\langle\ \rangle_N$ denotes thermal average of a chain of length N. For first-order transition, $V_N - 2/3 \neq 0$ at $\varphi=\varphi^*$ as $N \rightarrow \infty$,

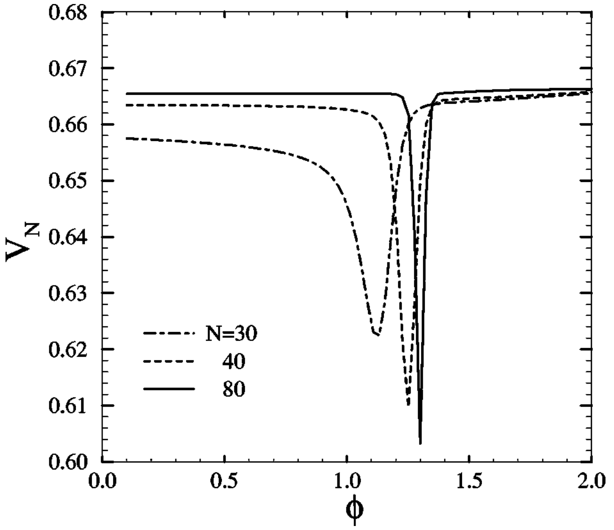


FIG. 5. Energy cumulant V_N versus φ for chains of various lengths at $\chi=1.2$.

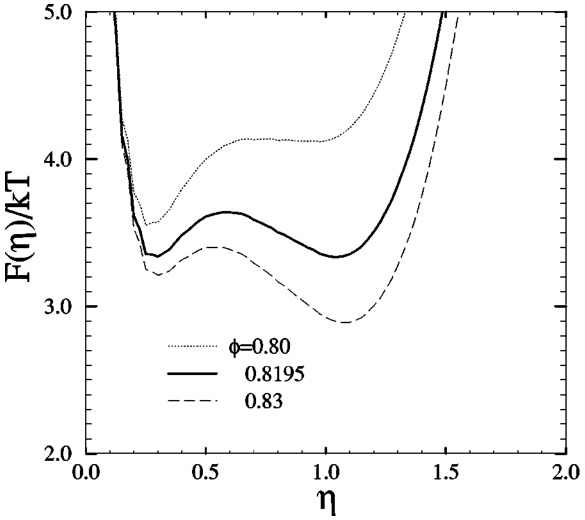


FIG. 6. Reduced free energy profile F/kT as a function of the order parameter η for $N=40$ and $\chi=1$, for different values of φ below, close to, and above the first-order transition. $\varphi^*\simeq 0.8195$.

whereas for higher-order transitions $V_N=2/3$ as $N\to\infty$ even at the transition point φ^*. As shown in Fig. 5, V_N has a deeper and narrower minimum as the system size increases, indicating the typical feature of a first-order transition.

Direct evidence of the first-order nature of the phase transition at φ^* can be obtained from the free energy profile as a function of the order parameter η. An important advantage in using the histogram method is that the free energy landscape associated with the phase transition can be readily calculated using the technique developed by Lee and Kosterlitz [31] in the study of the Potts model. The free energy as a function of the order parameter $F(\eta)$ at any given (χ,φ) can be computed, up to an additive constant, from the histogram method as

$$\frac{F(\eta)}{kT}=-\ln\sum_{\psi} H_0(\psi,\eta)\exp\{N[(\chi-\chi_0)\psi+(\varphi-\varphi_0)\eta]\}. \tag{14}$$

Figure 6 shows the result of $F(\eta)$ for various values of φ for $\chi=1$ extrapolated from the $(\chi_0,\varphi_0)=(1,0.805)$ histogram with $N=40$. The double minima separated by a free energy profile provide direct evidence for the first-order nature of the transition. The minimum at small value of η is the collapsed state and the one at larger η corresponds to the stretched state. For $\varphi<\varphi_N^*$, the stretched state is the metastable state while for $\varphi>\varphi_N^*$, the collapse state becomes metastable. As φ increases, the global minimum jumps from the collapse to the stretched state. The two minima have the same depth at $\varphi_N^*\simeq 0.8195$. The jump in the order parameter will of course depend on the given value of χ, the jump will be larger for a poorer solvent (larger χ).

The free energy barrier is essential to the lifetime of the metastable states which is in turn related to the memory or hysteresis effect. This can be measured by the maximum of the free energy barrier ΔF which occurs at $\varphi=\varphi_N^*$. The lifetime of the metastable states can be characterized by $\tau \sim \exp[\Delta F/kT]$. From the mean-field theory prediction in Eq. (7), ΔF is positive for $\chi>\chi^*$ and this can be tested with our simulation data. Figure 7 shows ΔF at the transition point as a function of χ for chains of different lengths. The linear behavior of ΔF agrees with the mean-field result. Furthermore Eq. (7) predicts that the slope of the straight line is proportional to N. The slopes for the data in Fig. 7 are plotted as a function of N in Fig. 8(a). The slopes show very nicely a linear behavior passing through the origin, in good agreement with the prediction. In the simulation of a polymer of finite chain length, the value of χ below which there is no transition is denoted by χ_N^*. The x intercept in Fig. 7 will give the value of χ_N^*. To extrapolate to the large N limit, χ_N^* is plotted against $1/N$ in Fig. 8(b). The data in Fig. 8(b) fall roughly on a straight line indicating an approximate $1/N$ finite-size effect instead of the $1/N^3$ finite-size correction predicted by Eq. (7). Thus our data suggest the free energy barrier at the first-order transition point can be estimated as

$$\frac{\Delta F}{NkT}=A(\chi-\chi^*)-\frac{\text{const}}{N} \tag{15}$$

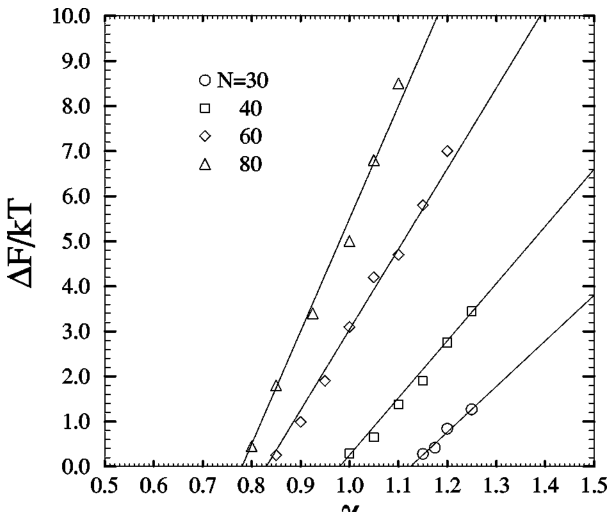
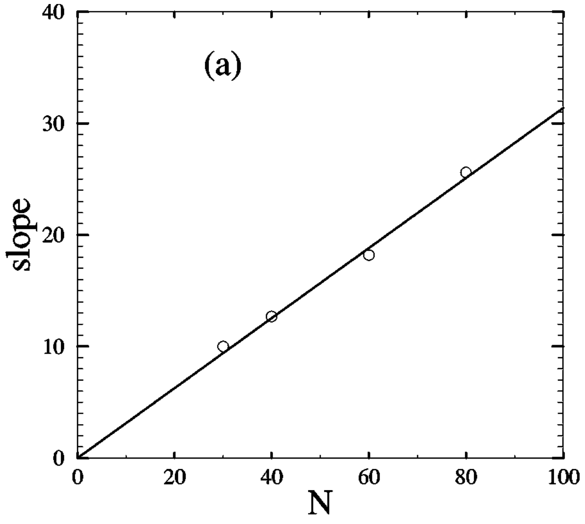


FIG. 7. Reduced free energy barrier $\Delta F/kT$ at the transition point φ^* versus χ for chains of different lengths. Error bars are about the sizes of the symbols.



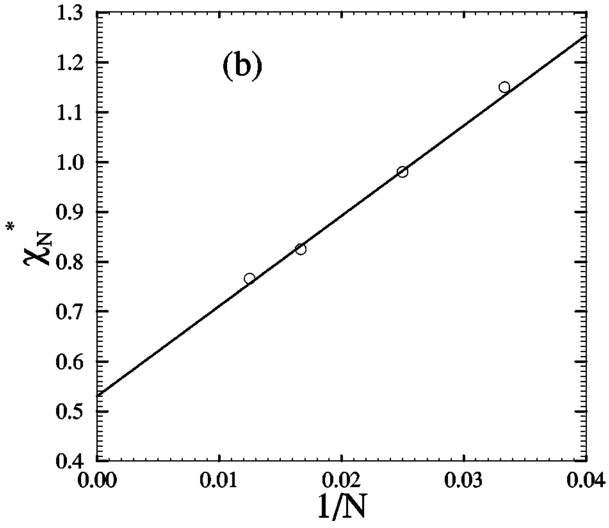


FIG. 8. (a) The slopes of the data in Fig. 7 versus N. (b) χ_N^* versus $1/N$ for chains of lengths $N=30$, 40, 60, and 80. χ^* is extrapolated from the $N\rightarrow\infty$ limit to be 0.53 ± 0.03. Error bars are about the sizes of the symbols. Straight lines are best fits to the data.

for some model dependent constant A. The free energy barrier is extensive to leading order in N as expected. Extrapolating to large N, we get an estimate of $\chi^*\simeq0.53\pm0.03$ by least squares fitting. The value of χ^* is remarkably close to the Θ point of our model $\chi_c\simeq0.52\pm0.01$ [28] suggesting $\chi^*=\chi_c$. Thus the mean-field result in Eq. (7) is correct only qualitatively. Our simulation data suggest that $\chi^*=\chi_c$ and first-order transition exists in the whole poor solvent regime $\chi>\chi_c$. The lifetime of the metastable state is hence given by, to leading order in N,

$$\tau=\tau_0\exp[A(\chi-\chi_c)N] \tag{16}$$

for some microscopic time scale τ_0. The value of the model dependent constant A is obtained from least squares fitting of the data in Fig. 8(a) to be $A\simeq0.314\pm0.02$. Because of the exponential increase factor in the chain length N, τ can be macroscopic or even astronomical in a realistic long polymer chain.

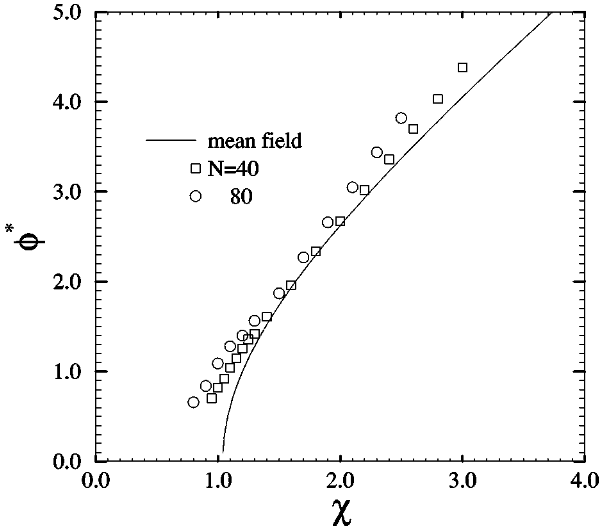


FIG. 9. Phase diagram of the reduced threshold force φ^* versus χ. Solid line is the result from the mean-field theory by taking $\chi^*=2\chi_c=1.04$. Symbols are Monte Carlo data for chains of length $N=40$ and 80.

VI. SUMMARY AND DISCUSSION

In this paper the phase transition in unwinding a collapse polymer in a poor solvent condition was investigated in detail using the histogram Monte Carlo method. Our results on the energy cumulants and free energy profiles provided good evidence for the first-order nature of this phase transition. By increasing the external unwinding force, the linear dimension of a long polymer coil can vary over several orders of magnitude abruptly. This may be useful in some applications on chemical/biochemical engineering in designing a molecular gateway in which the gate is closed by stretching the polymer chain to block the path. By performing careful finite-size analysis of the free energy profile data, we showed that such a transition occurs for a polymer chain in the entire poor solvent regime below the Θ point ($\chi>\chi_c$). Mean-field theory predicts correctly the first-order nature of the transition, but this transition occurs only in the $\chi>2\chi_c$ regime. The discrepancy is due to the corrections to mean-field behavior.

On the other hand, the first-order phase boundary separating the collapse and stretched states can be computed from the histogram Monte Carlo extrapolation. Figure 9 displays the phase diagram obtained from data of $N=80$ polymer chain. The collapse state is in the large χ region while the stretched state lies in the small χ regime. The prediction of the phase boundary from mean field theory in Eq. (5), using $\chi^*=2\chi_c=1.04$, is also shown for comparison. The mean-field result can only describe the phase boundary qualitatively. The prediction is better in the larger χ behavior. More significant deviation is observed for data near χ^*. Naively extrapolating the simulation data for $N=40$ and 80 in Fig. 9 to the χ axis gives $\chi^*\sim0.5$ consistent with the value obtained from finite-size analysis in the preceding section.

This first-order phase transition can be understood intuitively from the following physical picture: the monomers are attracted rather strongly to each other in the collapsed situation, the external force acting on the ends of the polymer which tends to unfold the polymer will increase the tension along the chain and try to pull the monomers apart from each other. As the external unwinding force becomes strong enough, the monomer attraction will be overcome and the separation between monomers increased. Since the attraction among the monomers is short ranged, and provided the tension along the chain is uniform (this is true if the unwinding force increases slowly enough and the chain has sufficient time to equilibrate), the restoring force will disappear suddenly once the separation between the monomers exceeds the range of attraction. As a result, the polymer will be stretched abruptly leading to a first-order phase transition. The above picture suggests that this first-order transition may be smoothed off to a higher-order or even no phase transition if the range of monomer attraction is sufficiently long. This will be tested by our future simulations.

ACKNOWLEDGMENTS

I thank the National Council of Science of Taiwan for support under Grant No. NSC 88-2112-M-008-017. Computing time, provided by the Simulation Physics Laboratory, National Central University, is acknowledged

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