

Phase Transitions in a Collapsed Macromolecule: A Histogram Monte Carlo Simulation

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Using the histogram Monte Carlo simulation method and the bond-fluctuation model, I investigate the coil-globule collapse transition of a macromolecular chain under variable solvent conditions. The critical transition temperature (O-point) is accurately determined. Finite-size scaling results near the transition point are verified. Furthermore, the first-order transition associated with the freezing/crystallization of a polymer at a temperature below the O-point is also observed. The free energy profiles associated with these two transitions are explicitly computed.

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I. Introduction

The applicability of the histogram Monte Carlo Method [1,2] 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 limited [3,4]. To my knowledge, 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. In this paper, I investigate the well-known coil-globule phase transition of a polymer chain using the histogram method. The bond-fluctuation model (BFM) is employed in my simulation and the critical behavior as predicted in scaling and renormalization group theories are verified, and hence the universality of the collapse transition is explicitly demonstrated. Furthermore, due to the complicated interactions among the monomers in a polymer system, the understanding of the free energy profile of the polymer system is essential in many macromolecular systems. The histogram method can compute the free energy profile with relative ease and simplicity 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. As a first step, I demonstrate that the free energy profiles in the BFM associated with collapse transition and freezing transition can be readily computed.

II. BFM and the histogram Monte Carlo method

As in my previous studies on other polymer systems [5–7], I use the bond-fluctuation model (BFM) [8] to investigate the effects of solvent conditions on the structure of a polymer chain. 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 [4, 5] 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 $\exp(-\Delta\mathcal{H}/kT)$ is greater than a uniformly distributed random number between 0 and 1, where $\Delta\mathcal{H}$ is the energy change due to the move, k is the Boltzmann constant and T is the temperature. Henceforth I will use the reduced energies $X \equiv \epsilon/kT$ and $\epsilon = 1$ for convenience. $X = 0$ corresponds to the good solvent condition. A polymer chain of N monomers is placed in a sufficiently large box. Starting with a given value of X , 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.

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. The Hamiltonian \mathcal{H} of the system is

$$\mathcal{H}/kT = -XC \quad (1)$$

where C is the number of neighbor contacts. All the thermodynamic behavior of the system is determined entirely by the parameter X . Large values of X corresponds to poor solvent conditions. I am interested in the collapse phase transition and the order parameter characterizing the collapsed state is the density of the coil, defined as [9,10]

$$\rho \equiv N/\langle R_g \rangle^3 \quad (2)$$

where $\langle R_g \rangle$ is the mean radius of gyration of the chain. Since one needs to extrapolate physical quantities related to R_g and C , the histogram $H(C, R_g)$ will be recorded in the simulation. Following standard histogram Monte Carlo method [1], let $H_o(C, R_g)$ be the histogram recorded at X_o , then probability distribution at another value X is given by

$$P_X(C, R_g) = \frac{H_o(C, R_g) \exp[(X - X_o)C]}{\sum_{C, R_g} H_o(C, R_g) \exp[(X - X_o)C]} \quad (3)$$

Then for any physical quantity B (which is a function of C and/or R_g), its equilibrium average value at a value of X is

$$\langle B \rangle = \sum_{C, R_g} B P_{\chi}(C, R_g). \quad (4)$$

Thus by recording the histogram at χ_o , quantities at other values of X can be obtained. Of course the range of accurate extrapolation will be limited by the statistics of the histogram [1]. In this simulation study, by choosing χ_o close to the phase transition points I am interested in and recording H_o up to 10^8 samples, nice data for a sufficiently wide range of accurate extrapolation is obtained.

III. Collapse transition

Extensive simulations are carried out to obtain the histograms for $\chi_o = 0.5$ for different chain lengths. Fig. 1 displays the size distribution $P(R_g)$ at $\chi_o = 0.5$. At $\chi_o = 0.5$, the coil is still in a swollen state. Using the histogram extrapolation technique, the order parameter ρ at different values of X near $\chi_o = 0.5$ is obtained smoothly. The results for different values of N are shown in Fig. 2. ρ starts to increase rapidly for X larger than 0.5 and the change becomes sharper as N increases indicating a phase transition to the order (collapsed) state. To determine the phase transition temperature, i.e. the Θ -temperature, I make use of the finite-size scaling theory for the collapse transition [9] which gives

$$\langle R_g \rangle = N^{1/2} f(tN^{1/2}) \quad (5)$$

where $t \equiv T/T_{\Theta} - 1$ is the deviation from the critical point and f is some scaling function. Thus a plot of $\langle R_g \rangle / N^{1/2}$ versus X for different values of N will intersect at a common

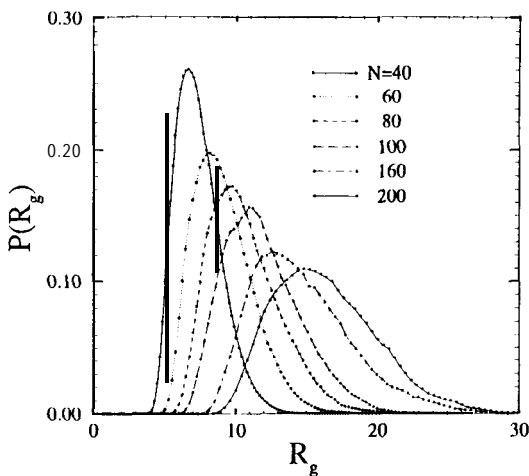


FIG. 1. Probability distribution for the radius of gyration of a polymer at $\chi = 0.5$ for different chain lengths. The distribution is normalized.

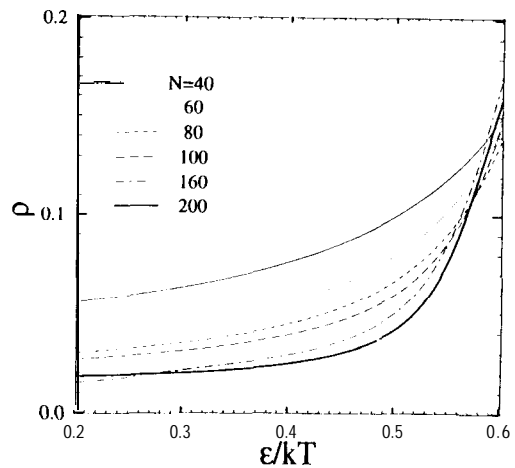


FIG. 2. The order parameter ρ in the collapse transition versus χ for polymer of different chain lengths.

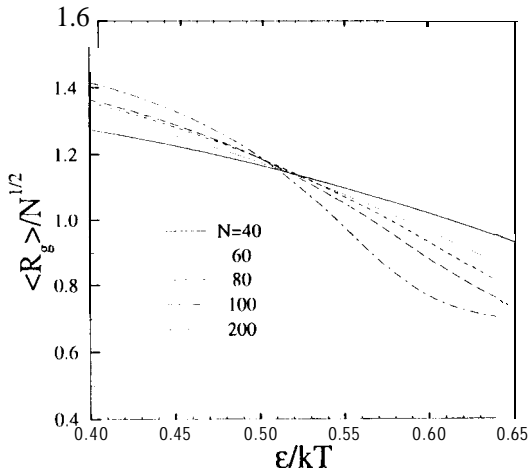


FIG. 3. $\langle R_g \rangle / N^{1/2}$ versus χ for chains of different lengths.

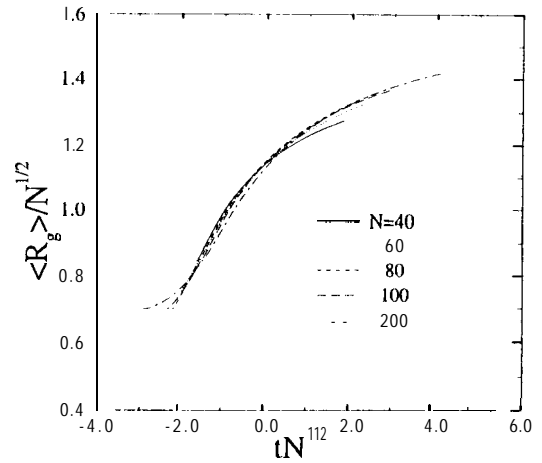


FIG. 4. Scaling plot of $\langle R_g \rangle / N^{1/2}$ versus $tN^{1/2}$ as suggested in Eqn. (5). $t \equiv T/T_\Theta - 1$ and $T_\Theta = 0.52$ is used.

intersection point $\chi_c \equiv \epsilon/kT_\Theta$. Fig. 3 shows such a plot using histogram extrapolation. Indeed the curves for various values of N intersect very closely and $\chi_c \approx 0.52 \pm 0.01$ which corresponds to $kT_\Theta \approx 1.92 \pm 0.04$. Using this value for T_Θ , a scaling plot for data collapsing into an universal curve is shown in Fig. 4 verifying the finite-size scaling prediction in Eqn. (5).

Another 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 [11] in the study of the Potts model. The free energy as a function of the order parameter $F(\rho)$ at arbitrary X can be computed, up to an additive constant, from the histogram method as

$$\frac{F(\rho)}{kT} = -\ell n \sum_{\mathcal{C}} H_o(\mathcal{C}, R_g) \exp[(\chi - \chi_o)\mathcal{C}] \quad (6)$$

through the relation $p = N/R_g^3$. Fig. 5 shows the result of $F(p)$ for various values of X extrapolated from the $\chi_o = 0.5$ histogram with $N = 200$. For smaller values of X up to 0.5, $F(p)$ has a minimum at ρ close to 0 indicating the stable equilibrium state is the swollen state. As X increases, the minimum shifts for larger values of ρ continuously indicating a continuous phase transition. For $X = 0.55$, the minimum is at $\rho \approx 0.15$ showing that the polymer is in a poor solvent below the Θ point.

IV. Freezing/Crystallization transition

For sufficiently large values of X (or low T), the attraction between monomers becomes relatively very strong. For real polymers, this corresponds to the extremely poor solvent condition and basically the polymers have no solvent molecules inside them and is in a polymer melt condition. At this sufficiently low temperature, the polymer melt will freeze

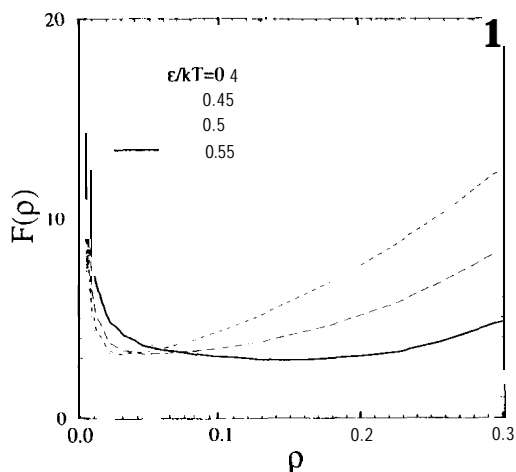


FIG. 5. The reduced free energy F/kT as a function of the order parameter ρ in the collapse transition for various values of χ .

or “crystallize”. In the BFM, this freezing transition can also be studied rather conveniently because of the bond lengths in this model is not fixed, contrary to conventional lattice polymer models. Such freezing transition occurs even for a single chain of sufficiently long chain length. This freezing transition is due to the cooperative effects of attraction of neighbor particles similar to freezing transition in ordinary liquids. In the current model, this freezing transition can be observed only for large N and one expects it to occur for a value larger than $\chi_c = 0.52$. I performed simulations and recorded the histogram for $\chi_o = 0.65$ to study this freezing transition for a single polymer chain. Fig. 6 displays the mean energy per monomer as a function of X for polymer of different chain lengths. At long enough chain length, the discontinuity in the energy (latent heat) across the freezing point is rather prominent signaling a first order transition. Using the histogram method, the freezing temperature can be readily obtained by computing the free energy (via Eqn. (6)) as a function of the energy (which is proportional to C) extrapolated to different values of X . The free energy profiles are shown in Fig. 7. As expected for a typical first order transition, the free energy profile shows a double well feature. The local free energy maxima are truncated to give a better view for the local minima. For lower values of X , the global minimum is located at a higher energy (less negative) while the other local minimum at a lower energy (i.e. the frozen state). As X increases, the lower energy local minimum deepens while the higher energy one becomes more shallow. At the freezing point $\chi_f \simeq 0.644$, the two local minima are of the same depth and the systems jumps to the frozen state.

This freezing transition can also be understood from the data on the mean square bond lengths, $\langle \ell^2 \rangle$, of the chain. From my data, $\langle \ell^2 \rangle$ decreases with increasing X . $\langle \ell^2 \rangle$ drops discontinuously from $\simeq 6.5$ to $\simeq 5.6$ at χ_f signaling the freezing transition. The same behavior has also been observed in my previous studies on grafted chains in poor solvents [5] using the same model. In the BFM, the values of ℓ^2 for the bond vectors $\{(2,0,0), (2,1,0), (2,1,1), (2,2,1), (3,0,0), (3,1,0)\}$ are 4, 5, 6, 9, 9, 10 respectively. Only the first three bond vectors (i.e. the shorter bonds) are considered as neighbors who cost an attractive energy

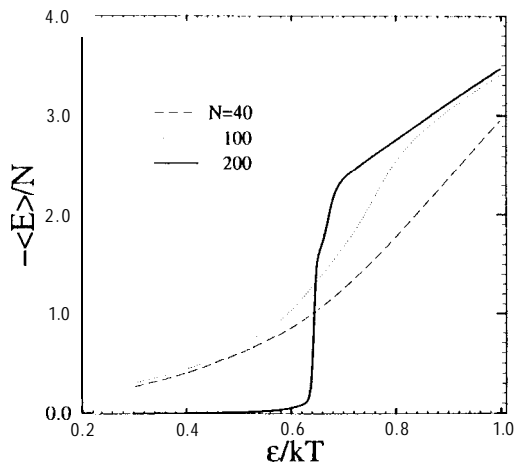


FIG. 6. The mean energy per monomer $-\langle E \rangle/N$ as a function of χ in the freezing transition for chains of different chain lengths.

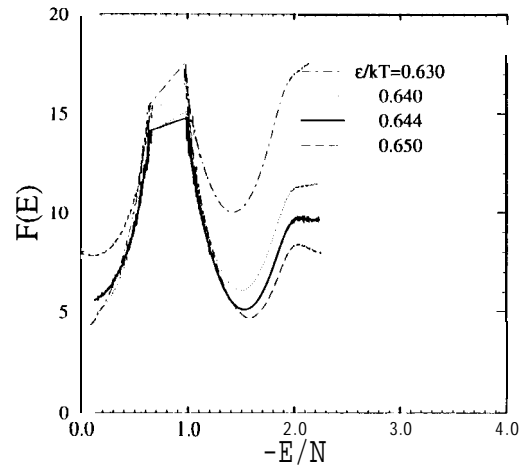


FIG. 7. The reduced free energy F/kT as a function of energy E in the freezing transition for various values of χ . The peak of each free energy barrier is truncated.

in this model. Therefore, from my simulation results, one can conclude that there is no “longer bonds” for $X > X_f$ (i.e. below the freezing temperature) since $\langle \ell^2 \rangle < 6$ in this regime. This suggests that the freezing or crystallization is associated with the abrupt “shrinking” of bonds as the polymer crystallizes.

V. Conclusion and outlook

In this paper, I demonstrated the application of the histogram Monte Carlo method to study phase transitions in a polymer system. The collapse and freezing transitions are analyzed rather conveniently and easily. Free energy profiles and hence the nature of these transitions can be investigated in detail. This provides a route to the direct simulation of more realistic macromolecules such as proteins and DNAs to achieve deeper understanding of the kinetics and dynamics of many complicated phenomena such as protein folding. Also applications to other model polymer systems which show interesting phase transition behaviors can be applied directly, such as the first-order transition in the unfolding of a collapsed polymer [7, 12] is under current investigation.

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