

Critical behavior of lattice polymers studied by Monte Carlo simulations

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A newly developed expanded grand-canonical formalism is applied to locate the critical point of systems of long polymeric molecules. Two polymer systems are investigated in this work; the first consists of chains in a simple cubic lattice, the second consists of bond-fluctuating molecules. For the former we simulate molecules of up to 16 000 sites, and for the latter we study molecules of up to 500 sites. These chain lengths are well above those investigated by all prior simulation studies of critical phenomena in polymer solutions. Critical parameters are determined as a function of chain length by means of field-mixing finite-size scaling techniques. Our results for the scaling behavior of the critical temperature are consistent with literature values. Our results for the scaling of the critical density, however, indicate that the corresponding critical exponent is higher than that reported by previous authors. The leading logarithmic term of the finite-chain-length correction to the critical density is confirmed by our results. © 2000 American Institute of Physics. [S0021-9606(00)50438-3]

I. INTRODUCTION

There has been a recent, revived interest in the critical properties of polymer solutions. For polymer solutions, the well-known Ising-like critical scaling laws are found to include prefactors that depend on the degree of polymerization, n . The following three relationships have been widely studied theoretically, experimentally and, more recently, by computer simulations:

$$\phi_{\text{coex}}^2 - \phi_{\text{coex}}^1 \propto n^{-x_1} \tau^\beta, \quad \tau = 1 - T/T_c(n), \quad (1)$$

$$\phi_c \propto n^{-x_2}, \quad (2)$$

$$T_\Theta - T_c \propto n^{-x_3}. \quad (3)$$

Equation (1) describes the shape of the coexistence curve; the exponent β is well known to be the same as that for the 3D Ising model, $\beta = 0.325$. The width of the curve, however, does depend on chain length. Experimental data^{1–3} suggest that $x_1 = 0.23–0.34$. Recent simulation results⁴ give $x_1 = 0.20–0.22$.

Equation (2) describes the scaling behavior of the critical density as a function of chain length. Experimental data¹ show that $x_2 = 0.38 \pm 0.01$. Recent simulation results^{4–6} for reasonably long chains also give $x_2 = 0.38 \pm 0.01$; earlier simulation data gave much lower values for x_2 , but the chain lengths involved in those simulations were not long enough to be in the scaling regime.^{7–11}

Equation (3) describes the scaling behavior of the critical temperature as a function of chain length. All reported results from experiments and computer simulations agree that the exponent is $x_3 = 0.5$.

Theoretical estimates for these scaling exponents, however, are controversial. Mean-field theories¹² predict $x_1 = 0.25$, $x_2 = 0.5$, $x_3 = 0.5$; de Gennes¹³ suggested from renormalization group arguments that $x_1 = (1 - \beta)/2 = 0.34$, $x_2 = 0.5$, $x_3 = 0.5$; Cherayil¹⁴ suggested that these exponents are

governed by the following relations

$$x_2 + x_3 = 1, \quad x_1 = x_3(1 - \beta), \quad (4)$$

which conflicts with the experimental results. Muthukumar¹⁵ proposed that $x_1 = x_3 = 2/9$ and $x_2 = 1/3$; Most recently, Frauenkron and Grassberger⁶ suggested another relation:

$$x_3 y \leq x_2, \quad (5)$$

where y is the universal exponent which governs the density of an infinitely long chain coil as a function of temperature. The most likely value of y is found to be 1 from simulation results for extremely long chains of n up to 10^6 . This new relationship also appears to be in conflict with experimental results.

To reconcile these contradictions, Frauenkron and Grassberger⁶ suggested that the limiting value of x_2 should actually be 0.5. The apparent, observed lower value of x_2 from experiments and computer simulations of moderately long chains arises from large logarithmic corrections. Experimental data for much longer, monodisperse polymers could help validate Frauenkron and Grassberger's arguments. Unfortunately, such experiments would be difficult. It is therefore of interest to ask whether recently developed simulation techniques can be used to generate critical-scaling data for ultra-high molecular weight polymers and, if so, can such data provide more definite answers about the critical behavior of polymer solutions?

In this paper we employ a newly developed expanded grand-canonical formalism¹⁶ to study the phase behavior and critical scaling of polymer solutions on a lattice. The molecular weights studied in this work are significantly higher than those studied by previous authors. The results should therefore provide much-needed insights regarding the crossover (if such a crossover exists) from the experimentally observed $x_2 = 0.38$ to the recently proposed scaling of

$x_2=0.5$. Two models are employed in our simulations: the bond-fluctuation model and a simple cubic lattice model. For the first model, we simulate chains of up to 500 sites; for the latter model, we simulate chains of up to 16 000 sites.

II. MODELS AND SIMULATION METHOD

We implement our simulations for both, the simple cubic lattice (SC) model and the bond-fluctuation (BF) model.^{17,18} In the SC model, each lattice site is occupied by either a polymer monomer or a monomeric solvent particle. Only nearest-neighbors interact with each other. In this work we simulate SC model chains of up to 16 000 segments.

In the BF model,¹⁸ polymer chains are represented by N monomer units, each occupying a unit cell of a simple cubic lattice (eight lattice sites in 3D). Successive monomers are connected by bonds that are allowed to take one of 108 possible values. The set of allowed bonds is selected so that the bond length lies in a prescribed range ($2-\sqrt{10}$); no two bonds can cut through each other. All monomer pairs at a distance less than $\sqrt{6}$ from each other, bonded or unbonded, experience a constant interaction energy. In this work we simulate BF chains of up to 500 segments.

For SC model simulations, we use a combination of crankshaft and kink-jump moves to displace molecules. For BF model simulations, a combination of reptation and monomer-hopping moves is used to relax configurations. For details regarding these trial moves, readers are referred to the literature.^{17,18}

For both lattice models, we use an expanded grand-canonical ensemble formalism, proposed earlier in our group¹⁶ for fast insertion/destruction of chain molecules. During the simulation, a system consisting of N normal chains and a tagged chain. The length of the tagged chain is allowed to fluctuate. Instead of creating or annihilating a whole chain at a time, growing or shrinking attempts are made for the tagged chain. In this work, we have optimized the formalism by carefully choosing the ‘‘chunk-size’’ by which the tagged chain is allowed to grow or shrink during a trial move.

For both models, the box sizes are chosen such that the average number of chains corresponding to the critical density is between 30 and 40. For the longest chain ($n=16\,000$) studied in this work, the box size is 300, which implies that the average number of chains is 38 at the critical density ($\phi_c=0.0225$). The number of Monte Carlo steps used to generate the results ranges from 10^7 to 6×10^7 ; each step consists of 500 to 4000 updates, depending on the chain length. For the longest chains, a simulation takes about 2 weeks on an Alpha 600 MHz workstation.

Histograms for the joint distribution of number of particles and total configurational energy are collected during the simulations. Multiple overlapping histograms are generated for different temperatures and chemical potentials. These histograms are then combined using reweighting techniques.¹⁹ These techniques are also used to determine the binodal curve for the systems of interest. Mixed-field finite-size scaling methods^{20–22} are employed to locate the precise coordinates of the critical solution point.

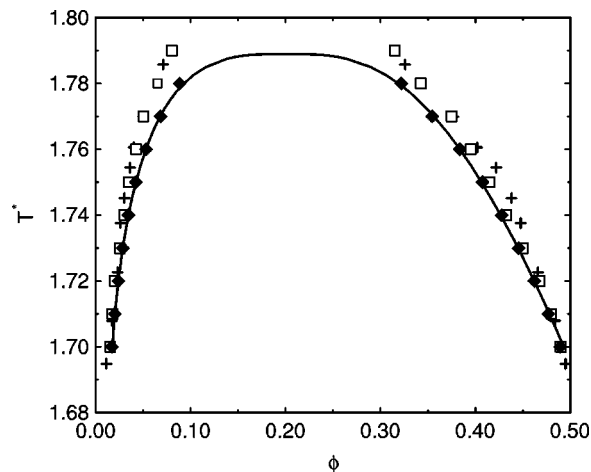


FIG. 1. Binodal curve for the BF model with $n=20$. The crosses show data by Wilding *et al.*; the diamonds are data from this work; and the squares are ‘‘peak’’ values calculated in this work.

III. RESULTS

Figure 1 shows the binodal curve for a $n=20$ bond-fluctuation model chain. Results reported by Wilding *et al.*⁵ are also included in the figure for reference. At first glance, there appear to be some deviations between the two sets of data. However, it turns out that the discrepancies between them is due to the different definition of coexistence density employed by Wilding *et al.* and by ourselves. In our work, we define the coexistence density via the mean value under a distribution peak; Wilding *et al.* identified it via the peak value. After calculating peak densities, we found that our results are in good agreement with those reported by Wilding *et al.* This comparison serves to establish the correctness of our simulations.

In order to take finite-size effects into account, we calculate the critical temperature and critical composition for each chain length at several, different box sizes. According to the theory of finite-size scaling,^{20–22} a plot of critical composition ϕ_c versus $L^{-(1-\alpha)/\nu}$ should be a straight line, where L is the simulation box size, and $\alpha \approx 0.11$ and $\nu \approx 0.629$ are universal exponents. Extrapolating the line to infinite system size provides an estimate of the ‘‘true’’ critical composition. Figure 2 shows results for four different chain lengths. Two important features can be extracted from that plot. First, within the statistical uncertainty of our simulations, these lines have the same slope. This fact can be used to estimate the ‘‘true’’ critical parameters for longer chains, where it is too expensive to run several simulations with larger box sizes. Second, we also note that the magnitude of the resulting ‘‘finite-size’’ correction is in fact smaller than the statistical uncertainty of our simulation results. These findings suggest that finite-size effects will not alter the conclusions of this work.

Figure 3 shows simulated critical temperatures as a function of chain length for both lattice models. The plot follows the Shultz–Flory relationship

$$\frac{1}{T_c(n)} - \frac{1}{T_c(\infty)} \propto \frac{1}{\sqrt{n}} + \frac{1}{2n}. \quad (6)$$

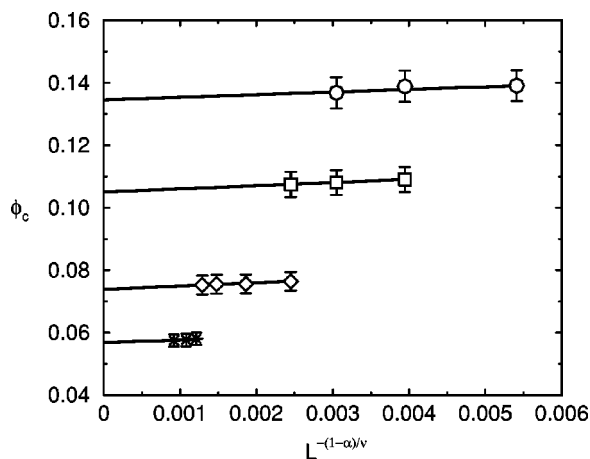


FIG. 2. Finite-size scaling of critical composition for four different chain lengths. The circles show data for $n=200$; the squares show data for $n=400$; the diamonds show data for $n=1000$; and the stars show data for $n=2000$. The lines were fitted to the numerical data.

Least-square fits of the data indicate that the critical temperature for infinitely long chains is $T_c(\infty)=3.71\pm 0.01$ for the SC model and $T_c(\infty)=2.08\pm 0.01$ for the BF model. Both are in good agreement with previously reported values.^{4,6} The high linearities in the figure confirm that $x_3=0.5$.

Figure 4 shows a log-log plot of critical compositions as a function of chain length. A small curvature of the data for both models can be inferred from the figure. This suggests that a simple power-law fit to the data is not appropriate. At any rate, such a fit gives an exponent $x_2=0.35-0.48$, depending on the interval of data employed for regression. To take the curvature into account explicitly, we used a functional form suggested by Wilding *et al.*,⁵ namely $\phi_c(n)=(b_1+b_2n^{x_2})^{-1}$. In such a fit, we obtained the exponent $x_2=0.51\pm 0.03$ for the BF model, and $x_2=0.47\pm 0.03$ for the SC model. These values are clearly much larger than

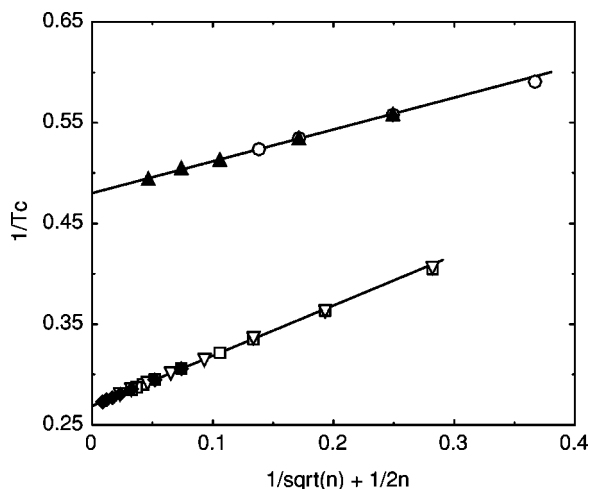


FIG. 3. Shultz-Flory plot of the scaling of critical temperature with chain length. The filled triangles show our results for the BF model; the circles are results reported by Wilding *et al.* (1996); the diamonds are our results for the SC model, the open triangles are results reported by Frauenkron *et al.* (1997), and the squares are results reported by Panagiotopoulos *et al.* (1998). The lines are least-square fits of our simulation results. Error bars are smaller than the symbol size.

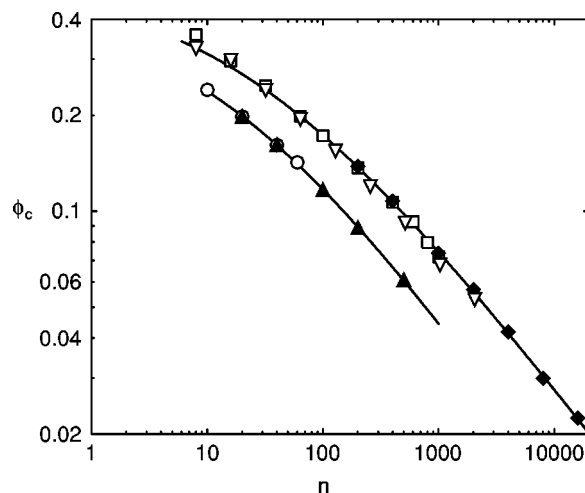


FIG. 4. Scaling of the critical density with chain length. The filled triangles show our results for the BF model; the circles are results reported by Wilding *et al.* (1996); the diamonds show our results for the SC model; the open triangles are results reported by Frauenkron *et al.* (1997), and the squares are results reported by Panagiotopoulos *et al.* (1998). The curves are fits to our simulation results (using the functional form $\phi_c(n)=(b_1+b_2n^{x_2})^{-1}$). The uncertainty of critical density is of approximately the same size as the symbols.

those inferred from experimental data and previously reported simulation results, but within the uncertainty range, it is in agreement with that predicted by the mean-field theories, that is $x_2=0.5$.

As mentioned in the introduction, Frauenkron and Grassberger⁶ have recently argued that the deviation between the exponent from experiments and that from mean-field considerations is due to finite-chain-length corrections, and should therefore vanish in the limit $n\rightarrow\infty$. The longest polymers employed in the experiments of Dobashi *et al.* was approximately equivalent to $n=2000$ in our SC model. If we use the results of simulations only up to that limit, a power-law fit also gives $x_2\approx 0.38$, which is consistent with previous analyses of experimental data. The simulations reported here correspond to much longer chains; we believe that the curvature feature observed in the new results lends credence to the fact that the true asymptotic limit of x_2 should be 0.5.

A few comments on the nature of finite-chain-length corrections are in order. According to a renormalization group analysis,^{6,23} the leading term of the finite-chain-length corrections to the critical density is given by

$$\phi_c \propto (\ln n/n)^{1/2}. \quad (7)$$

To take molecular interaction into account, the n in Eq. (7) can be replaced by n/n_0 , where n_0 is the persistence length. According to this equation, we should get a straight line if we plot $n\phi_c^2$ as a function of $\ln n$. Figure 5 shows such a plot; the linearity of our two sets of simulation results is satisfactory. Note that Fig. 5 only shows the corrections to the mean-field prediction; small deviations of the critical density can therefore lead to large uncertainties in that plot. The lines in Fig. 5 correspond to best fits of simulation data, which correspond to $n_0=3.3\pm 0.8$ for the SC model, and $n_0=1.7\pm 0.3$ for the BF model. We have also determined the persistence length of our SC chains at the critical point directly

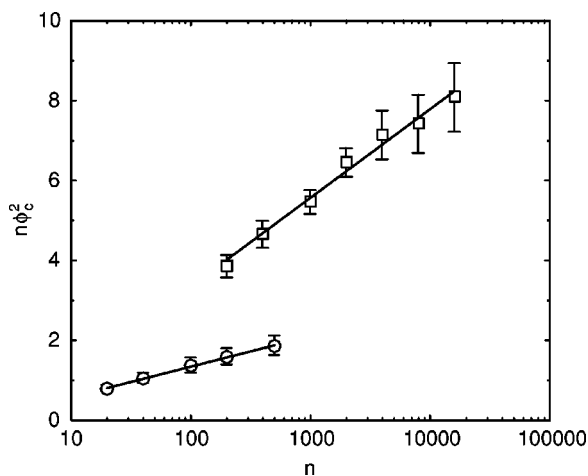


FIG. 5. The leading logarithmic correction to the scaling behavior of the critical density. The squares are simulation results for the SC model; the circles are results for the BF model; lines are least-square fits to the simulation results.

from simulations; the values obtained in this manner range from 3.0 to 3.9, depending on chain length. These numbers are consistent with the best-fit values of Fig. 5. The level of agreement shown in the figure provides direct numerical evidence in support of Eq. (7). Again, this suggests, as implied by Eq. (7), that the asymptotic value of x_2 is 0.5.

A recent study²⁴ of dilute polymer solutions has indicated that the subleading $\ln(\ln n)/\ln^2 n$ term of the finite-chain-length corrections for a number of properties of single θ -chains is of the same order of magnitude as the leading term, even for relatively long chains. That analysis, however, was performed on a different model (Domb–Joyce-like) and at this point it is unclear how it would influence the corrections to the critical density observed in our simulations, because the numerical prefactors for our model are not available. It is still interesting to point out that the leading term [Eq. (7)] is sufficient to provide a good description of finite-chain-length corrections for our simulations.

IV. CONCLUSION

We have applied our newly proposed expanded grand canonical ensemble simulation method to simulate the critical behavior of polymer solutions. This method has permitted study of ultra-high molecular weight chains; the length of the molecules that we have been able to study for the cubic lattice model of polymer solutions is an order of magnitude longer than that examined by previous simulations, and

longer than that of the polymers employed in experimental studies of critical demixing. The scaling behavior of the critical temperature is shown to be as predicted by mean-field arguments. More interestingly, in contrast to previous results of simulations and experiments, our results for the scaling behavior of the critical density are shown to exhibit a crossover to mean-field behavior in the limit of ultra-high molecular weight polymers. A fit to the simulation results gives the exponents $x_2 = 0.51 \pm 0.03$ and $x_2 = 0.47 \pm 0.03$ for the BF and the SC models, respectively. Our simulation results are also consistent with the leading term of the finite-chain-length corrections to the critical density deduced from renormalization-group arguments. Note, however, that higher order corrections could be as important and contribute to the deviations from mean-field behavior observed in this work.

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