Simulation of Phase Equilibria for Lattice Polymers

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ABSTRACT: A new simulation method called the configurational-bias-vaporization method (CBV) is proposed which is designed for studying phase equilibria for lattice-polymer systems. A single simulation cell is used in this method where all polymers are introduced in the bottom portion of the cell upon initiation. Vaporization is then carried out by randomly eliminating a chain followed by generating a new chain through the configurational-bias method. Compositions of coexisting phases are then determined directly. The phase-equilibrium coexistence curves for polymer systems with chain lengths up to 200 have been obtained. Part of the results are compared with those from the test particle method and those reported by Madden et al. Corresponding predictions by the Flory−Huggins theory and the Freed theory have also been tested. The comparison shows that the Freed theory gives satisfactory critical temperatures while the Flory−Huggins theory shows a large discrepancy as expected. However, both theories give poor critical compositions.

I. Introduction

The most extensively used theory in the field of thermodynamics for polymer systems no doubt is the Flory−Huggins theory,[1,2] which was originally derived in the early 1940s based on a lattice model called the Flory−Huggins lattice. A variety of modifications have also been developed. However, most of them are based on a simple mean-field approximation. Therefore, they fail to describe the molecular origins of the entropic contribution and the concentration dependence of the experimental Flory interaction parameter. Recently, Freed and co-workers[3−5] have developed a lattice-cluster theory which in principle is an exact solution of the Flory−Huggins lattice. However, for practical reasons, the infinite series with respect to coordination number, temperature, and composition in this theory must be truncated at a certain order. The validity of the theory therefore should be tested by making comparison with computer simulation results.

Methodologies for the simulation of phase diagrams can be distinguished by two approaches, the indirect method and the direct method. The former determines compositions of coexistence phases indirectly from chemical potentials, while the latter determines equilibrium compositions directly.

For calculating chemical potentials, the grand canonical Monte Carlo method[6] and the Widom test particle method[7,8] are generally adopted. However, great difficulties have been met in dealing with long-chain molecules due to the very low insertion probability. Recently, two promising techniques appeared in the literature, which are attractive for polymer systems. The first one, proposed by Siepmann,[9] is based on the Widom test particle method[7] as well as the Rosenbluth and Rosenbluth growth algorithm.[10] The method has further been extended to free-space models.[11,12] The essentials of this method lie in a procedure to perform a configurational-bias insertion of a test chain molecule to calculate the chemical potential, which can be obtained from the following expression:

$$\mu^{\mathrm{r}} = -\frac{1}{\beta}\ln\langle W^{(n)}\exp(-\beta U_{\mathrm{g}})\rangle_N \tag{1}$$

where μ^{r} is the residual chemical potential of a chain, $W^{(n)}$ is the Rosenbluth weight of the testing chain during its growth, and U_{g} is the interactive energy between the chain and the rest of the system. The uncertainty of this method increases when the chain length increases. According to the authors, the limiting chain length is about 20−30 segments, which is far shorter than a normal polymer molecule.

Another method was proposed by Kumar et al.[13] With the so-called modified Widom technique, the chemical potential of chain molecules can be obtained from the incremental chemical potential,

$$\mu^{\mathrm{r}}_{\mathrm{incr}}(n) = \mu^{\mathrm{r}}(n+1) - \mu^{\mathrm{r}}(n) = -kT\ln\langle\exp(-\beta U^{+}_{n+1})\rangle \tag{2}$$

where U^{+}_{n+1} is the energy experienced during the growth of an existing chain by a single segment. The authors prove that this incremental chemical potential is chain length independent when the chain length is long enough (longer than about 30). The chemical potential can thus be expressed as

$$\mu^{\mathrm{r}} = (n - n_0)\mu^{\mathrm{r}}_{\mathrm{incr}}(n) + \mu^{\mathrm{r}}_{\mathrm{incr}}(n_0) \tag{3}$$

where n_0 is the chain-length threshold from which the incremental chemical potential can be viewed as chain length independent. By this method, chemical potentials and phase diagrams for both lattice models and free-space models have been obtained, with chain lengths up to $n = 50−100$.[14,15] However, because the dependence of the incremental chemical potential on chain length for shorter chains is neglected, the results are subject to some approximations.

Interesting progress in the calculation of chemical potentials was made by Kumar[16] using a modified real particle method which does not need any particle insertion. In that method, a randomly selected particle is removed from the system and then put back into the system near the original position. The chemical potential is determined by calculating the energy increment during this removal and insertion operation. Although it only treats simple atomic fluid systems at present,

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the method may be of great value when extended to polymer systems.

As an example of the direct method, the Gibbs ensemble[17,18] developed by Panagiotopoulos et al. is a typical and powerful one, especially when applied to small-molecule systems. However, great difficulties are met when applying this method to polymer systems, especially for lattice models. First, the Gibbs ensemble method also relies on insertions and removals of particles while the probability of a successful transfer for a long-chain molecule is very small. Although the problem has been partially solved by Laso, de Pablo, et al. by the so-called continuum-configurational-bias–Gibbs ensemble method,[19] the chain length is still limited to about 20. The other difficulty with the Gibbs ensemble is related to the volume exchange between two phases because of the discreteness of a lattice. Some tricks have been proposed to solve this problem. The typical one was proposed by Mackie et al.[20] They set the initial composition of the two cells to be at the center point of a tie line. No volume exchange is required because the final volume of the two phases must be the same. However, this method requires prior knowledge of the center point of a tie line, which is not easy to determine in a simulation.

Madden et al.[21] also report a direct method to determine the phase diagram for polymer systems. In their method, the system is separated into two phases in a single simulation box, with the polymer-rich phase condensed against an adhesive wall and the conjugate phase located at the other side of the simulation box. The system is perturbed by a reptation and pseudokinetic simulation algorithm, and the latter will produce a polydisperse sample. As is well known, the polydispersity will significantly affect the phase-equilibrium behavior of polymer systems, especially near the critical point. Some improvements have been suggested to reduce the polydispersity in Madden's approach, but they increase the complexity of the algorithm dramatically. Furthermore, only results for chain length $r = 100$ are available, which are inadequate to test theories.

Recently, Guo et al.[22] proposed a so-called equal-probability perturbation method (EPPM), which can be used to simulate coexisting phases in a single simulation cell with an explicit vapor–liquid interface. They successfully obtained phase diagrams for square-well fluids and simple Lennard-Jones fluids.

Most recently, Mackie et al.[25] reported a novel simulation technique, which successfully applied the Gibbs ensemble method to the simulation of lattice polymers. In their work, the configurational-bias method is used to cut all the chains across a randomly selected layer and to regrow them after a layer is added or removed. The difficulty due to the connectivity of the polymer chains can then be solved. However, for very long chains, a large number of segments may be involved during a trial move of the volume, and this may lead to a great perturbation and a very low acceptance ratio.

Enlightened by the above progress, especially by Madden et al., Guo et al., and Siepmann's revised Rosenbluth and Rosenbluth methods, in this work, we develop a new simulation method called the configurational-bias-vaporization method (CBV) for polymer systems on a Flory–Huggins lattice. Phase diagrams for homopolymers with chain lengths up to 200 are directly obtained in a single cell. Some of the results are compared with those obtained from the test particle method[23] and those reported by Madden et al.[21] Comparisons are also made with predictions from the Flory–Huggins theory and Freed's lattice-cluster theory. Although this work deals chiefly with binary homopolymer solutions on a lattice at present, it is expected to be of value in calculating phase diagrams for more complex systems, such as ternary systems, copolymers, amphiphiles, and free-space models.

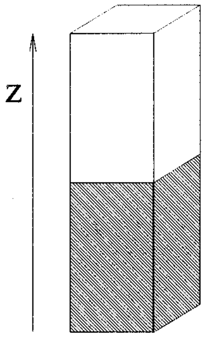

Figure 1. Schematic illustration of initial configuration.

II. Configurational-Bias-Vaporization Method

We use a single simulation cell with all the polymer chains located at the bottom upon initiation. We then vaporize the chains to form two coexisting phases in equilibrium.

We consider a system composed of N_p polymer molecules and N_s solvent molecules, where each polymer molecule occupies r sites and each solvent molecule occupies one site on a Flory–Huggins lattice. Three types of nearest-neighbor interactions, polymer segment–polymer segment, polymer segment–solvent molecule, and solvent molecule–solvent molecule, occur. They are represented by interaction potentials, $-\epsilon_{pp}$, $-\epsilon_{ps}$, and $-\epsilon_{ss}$, respectively. Because all of the mixing properties of the system are solely determined by an exchange-energy parameter defined as $\epsilon = \epsilon_{pp} + \epsilon_{ss} - 2\epsilon_{ps}$, we set both ϵ_{ps} and ϵ_{ss} to zero and use ϵ_{pp} as the only parameter to characterize the system. In this respect, the solvent molecules are treated as holes, and the incompressible polymer–solvent mixture is mapped onto a compressible lattice-polymer system.

Simulations are carried out in a single simulation cell whose height is much larger than its width and length. The typical cell size is 32 × 32 × 256. Periodic boundary conditions are used for all three directions. Similar to Guo et al., all N_p chain molecules are introduced into the lower portion of the cell upon initiation, while the upper portion is kept empty, as shown in Figure 1. To obtain the initial configuration, we put two repulsive walls in the simulation cell at the start, one at the bottom of the cell and the other at the middle. N_p chains are then introduced successively into the lower part of the cell by the Rosenbluth and Rosenbluth growth method. Thereafter, we remove the two repulsive walls. The chains can then move freely in the whole cell.

The procedure leading to a move of a chain is performed as follows. First we pick a chain randomly and eliminate it from the system. A new chain is then generated by a configurational-bias sampling method, which is a refined version of the Rosenbluth and Rosenbluth growth algorithm[10] revised by Siepmann.[9] Unlike the pseudokinetic method used by Madden et al., this method does not generate polydisperse samples. The position of the new chain is randomly selected without any relationship to the old one. If the growth procedure is successful, the transfer is accepted at a

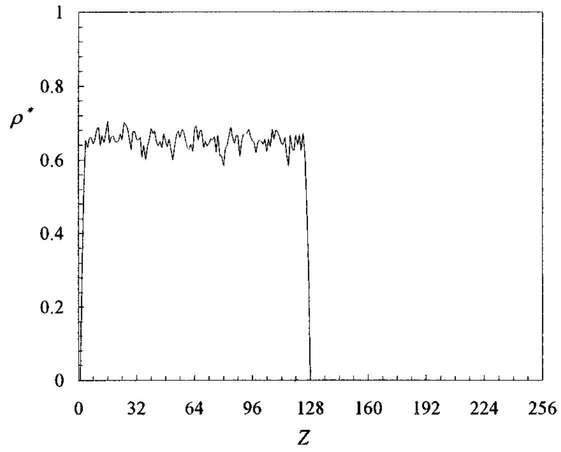

Figure 2. Initial density profile for $r = 32$.

Table 1. Acceptance Ratios during the Simulation

r	T^*	T^*/T^*_C	acceptance ratio
16	2.10	0.864	0.029
32	2.10	0.769	0.003
64	2.20	0.743	0.002
100	2.50	0.812	0.002
200	2.80	0.881	0.0004

ratio of

$$p_{\text{trans}} = \min\left(1, \frac{W_{\text{new}}}{W_{\text{old}}} \exp(-\beta\Delta E)\right) \tag{4}$$

where W_{new} and W_{old} are the Rosenbluth and Rosenbluth weight after and before the regrowth process and ΔE is the energy change of the system due to the chain regrowth. If the new configuration is not accepted, the old configuration is restored and is counted as usual.

After a great many chain moves, two coexisting phases are gradually formed with an explicit but irregular vapor–liquid interface which fluctuates randomly during the simulation. The difficulty inherent in the Gibbs ensemble method for a lattice-polymer system, the volume exchange of the two phases, is then avoided. The density profiles are calculated by a histogram algorithm every 1000 Monte Carlo steps. After equilibrium is achieved, the densities of the coexisting phases are obtained by taking averages from the profile directly.

III. Results and Discussion

Table 1 shows the acceptance ratios during simulations at low temperatures for chain molecules with various chain lengths. The magnitude is about 10^{-3}–10^{-4} when r varies from 32 to 200. As we usually carry out about 10^9 trial moves for those long chains, around 10^5–10^6 effective moves actually take place, which is sufficient to yield a reliable average. However, the acceptance ratio declines dramatically as the chain length increases. The simulation will be very difficult when the chain length is greater than 200.

Figure 2 indicates a typical initial density profile along the z direction produced by the initiation algorithm. As we can see in the figure, the repulsive walls produce a sharp density drop at the interface, which facilitates the evolution of a phase-equilibrium system thereafter. This is why we use repulsive walls rather than attractive walls. In principle, we can use any initial density, so long as the initial configuration is thermodynamically unstable. However, if we set the initial overall density near the center point of the tie line, equilibrium can be achieved more quickly. This center point can be guessed by some theories, such as the Flory–Huggins theory.

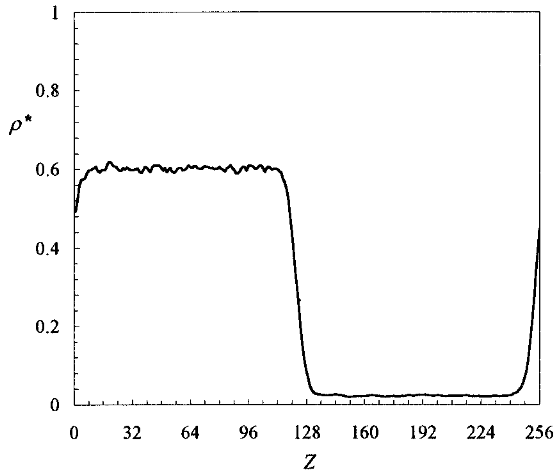

Figure 3. Density profile for $r = 32$ at $T^* = 2.5$.

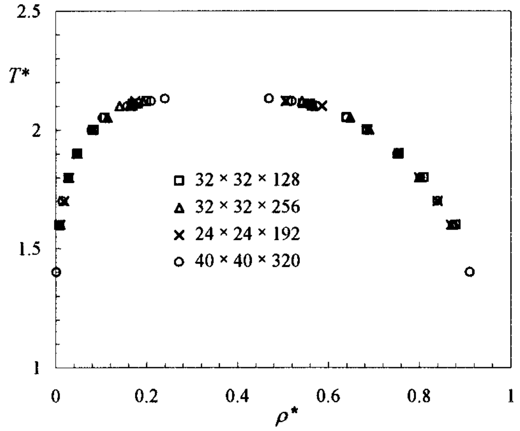

Figure 4. Finite-size effect in simulation.

Figure 3 shows a typical equilibrium density profile for a lattice-polymer system with chain length $r = 32$ at $T^* = 2.5$ from the simulation. Two flat compartments in the density profile represent the two coexisting phases in equilibrium. The higher one is for the liquid phase, or the polymer-rich phase, while the lower one is for the vapor phase, or the solvent-rich phase. The compositions for coexisting phases can be obtained directly from the figure. In this case, they are $\rho^*_L = 0.60$ and $\rho^*_V = 0.022$, respectively. Fluctuations occur naturally in the density profile. They become more serious when the temperature becomes higher, especially for long-chain molecules. To alleviate those strong fluctuations, we carry out multiple runs and take the average of them.

Figure 4 shows simulation results for coexisting phases of a lattice-polymer system with chain length $r = 8$ obtained in simulation boxes with various sizes. No distinct differences can be found in the results when simulation boxes with different sizes are adopted, except those near the critical temperature. The finite-size effect is practically negligible if the box size is greater than 24. The statistical error could be lower if we use a larger simulation box with the cost of dramatically increasing the computing time ($t \propto \rho L^3$). As a compromise for both computer time and statistical efficiency, we use a 32 × 32 × 256 box size in the remaining portions of this work.

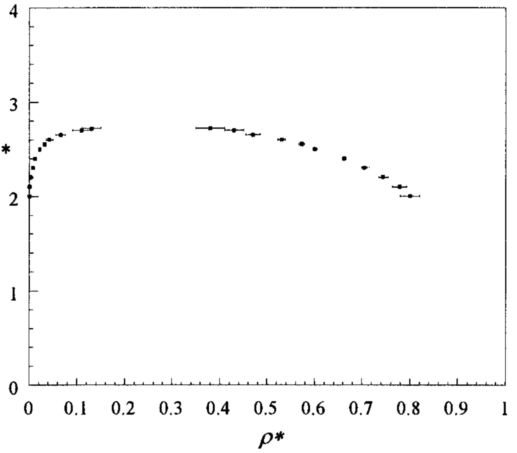

Figure 5. Statistical error in simulation for $r = 32$.

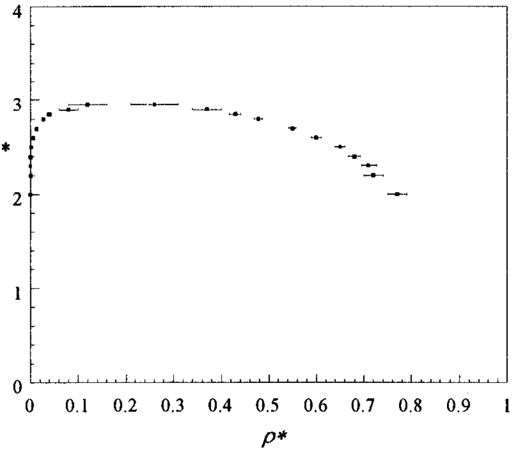

Figure 6. Statistical error in simulation for $r = 64$.

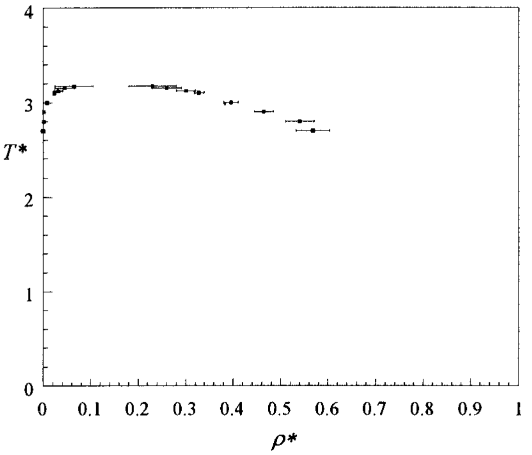

Figure 7. Statistical error in simulation for $r = 200$.

Figures 5−7 show densities of coexisting phases with statistical error bars for lattice-polymer systems with chain lengths $r = 32$, 64, and 200, respectively. The statistical error exhibits a minimum at the intermediate temperature range. It grows for both higher and lower temperatures and has a maximum near the critical point. The statistical error increases when the chain length is increased.

Figure 8 compares the results of this work and those from the test particle method for a lattice-polymer system with chain length $r = 8$. The two sets of data coincide with each other within the error range, except those near the critical temperature. Because a 16 × 16 × 16 simulation box is used in the test particle method, which is smaller than that of the present work, the discrepancy may result from the finite-size effect.

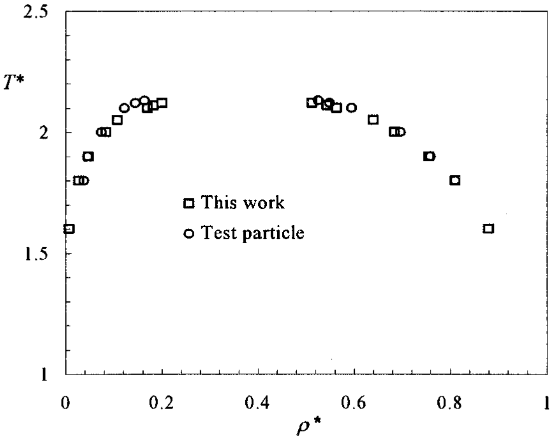

Figure 8. Phase diagram for chain length $r = 8$.

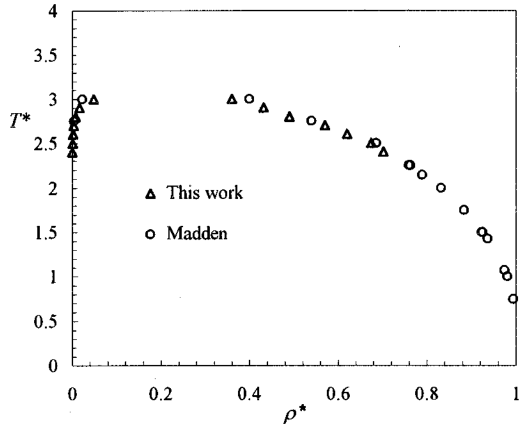

Figure 9. Phase diagram for chain length $r = 100$.

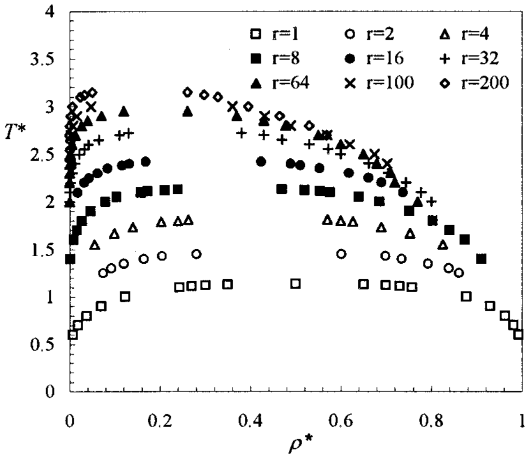

Figure 10. Phase diagram of lattice-polymer systems with chain length $r = 1-200$.

Figure 9 compares compositions of coexisting phases in this work and those reported by Madden et al.[21] for a lattice-polymer system with chain length $r = 100$. Data in this work are a little lower than those of Madden et al. in the polymer-rich phase and a little higher in the solvent-rich phase, especially near the critical temperature. The discrepancy may result from the polydispersity involved in Madden et al.'s work. As mentioned by them, a polydispersity $M_w/M_n = 1.067$ appears in their work.

Figure 10 summarizes all the data obtained in this work for lattice-polymer systems with chain lengths

Table 2. Phase Equilibria Data of Lattice-Polymer Systems with Chain Length $r = 8-200$

T^*	ρ^*_V	ρ^*_L
	$r = 8$	
1.40	0.002	0.91
1.60	0.010	0.87
1.70	0.016	0.84
1.80	0.028	0.80
1.90	0.047	0.75
2.00	0.079	0.69
2.05	0.104	0.64
2.10	0.158	0.58
2.11	0.172	0.55
2.12	0.210	0.52
2.13	0.240	0.47
	$r = 16$	
2.10	0.018	0.74
2.20	0.032	0.69
2.25	0.043	0.66
2.30	0.062	0.62
2.35	0.084	0.55
2.38	0.116	0.51
2.40	0.132	0.49
2.42	0.168	0.42
	$r = 32$	
2.00	0.0004	0.80
2.10	0.001	0.78
2.20	0.003	0.74
2.30	0.007	0.70
2.40	0.012	0.66
2.50	0.022	0.60
2.55	0.032	0.57
2.60	0.042	0.53
2.65	0.065	0.47
2.70	0.110	0.43
2.72	0.130	0.38
	$r = 64$	
2.00	0.00001	0.77
2.20	0.0001	0.72
2.30	0.0003	0.71
2.40	0.0008	0.68
2.50	0.002	0.65
2.60	0.006	0.60
2.70	0.013	0.55
2.80	0.027	0.48
2.85	0.040	0.43
2.90	0.070	0.37
2.95	0.120	0.26
	$r = 100$	
2.40	0.0002	0.70
2.50	0.0006	0.68
2.60	0.0016	0.62
2.70	0.0028	0.57
2.80	0.008	0.49
2.90	0.016	0.43
3.00	0.048	0.36
	$r = 200$	
2.70	0	0.57
2.80	0.0012	0.53
2.90	0.0025	0.47
3.00	0.007	0.40
3.10	0.024	0.33
3.12	0.032	0.30
3.15	0.050	0.26

varies from 1 to 200. Data for $r = 1-4$ are obtained from the test particle method.[23,24] The data are also listed in Table 2. It is a systematic report of phase-equilibrium data for lattice-polymer systems over a wide range of chain length.

Figure 11 shows a Shultz–Flory plot of the simulated critical temperatures as a function of chain length. Linearity similar to that predicted by the Flory–Huggins theory is indicated. Extrapolation gives an estimate $T_C^{*,\infty} = 3.45$ for the critical temperature of a polymer with an infinite molecular mass. The figure also compares the simulation results with the predictions from the Freed theory and the Flory–Huggins theory. It is shown that the Flory–Huggins theory gives much higher predictions of critical temperatures as expected, while the Freed theory is much more satisfactory, but still a little higher than the simulation data, especially for short chain lengths. Similar to Mackie et al.'s work,[25] the discrepancies between simulations and mean-field theories become slightly smaller for longer chains.

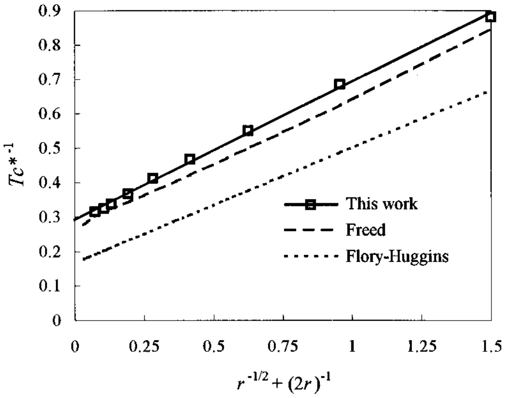

Figure 11. Comparison of critical temperature for lattice-polymer systems from the Monte Carlo method with those predicted by theories.

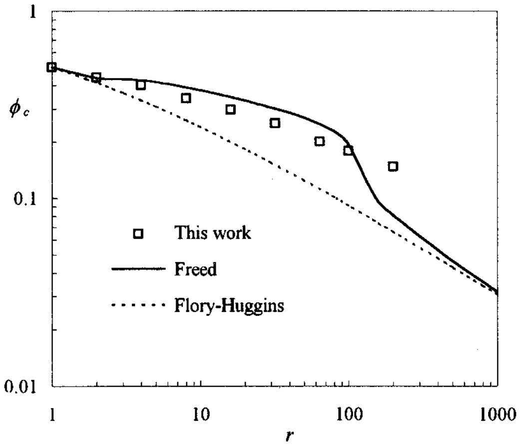

Figure 12. Comparison of critical composition for lattice-polymer systems from the Monte Carlo method with those predicted by theories.

Figure 12 is a log–log plot of the simulated critical compositions as a function of chain length. Those predicted by the Freed theory and the Flory–Huggins theory are also depicted for comparison. It is shown that the Flory–Huggins theory gives poor predictions, which does not surprise us. However, the Freed theory is also not very satisfactory, which produces a strangely shaped curve with an arched segment in the chain-length range $2 \leq r \leq 200$. The curve crosses the simulation results at $r = 100$, which is by chance the one Madden et al.[21] used to do their simulation work and to test the Freed theory. On the other hand, when r is greater than 100, predictions of both theories approach each other but are remarkably different from the present simulation results. A least squares fit of the chain-length dependence of critical compositions in this work gives a scaling of $\phi_c \propto r^{-0.27}$ similar to $\phi_c \propto r^{-0.32}$ in Mackie et al.'s work,[25] while the Flory–Huggins theory gives $\phi_c \propto r^{-0.5}$. Obviously, both Mackie et al.'s work and this work imply that more theoretical effort is still required. Perhaps the truncation in the Freed theory is made too soon.

IV. Conclusions

1. A new simulation method called the configurational-bias-vaporization method (CBV) for lattice-polymer systems is proposed. The simulation is performed in a single cell with all chains located at the bottom upon initiation. Vaporization is then carried out by randomly eliminating a chain followed by generating a new chain through the configurational-bias method. Compositions of the coexisting phases are then determined directly.
2. The finite-size effect is studied by comparing the results obtained from different simulation boxes with different sizes. The effect can be neglected in the simulations performed in this work.
3. The simulation method is also checked by comparing the results with those from the test particle method and those from Madden et al.'s work.[21] Good agreement is achieved, if we take the statistical error and the inherent characteristics of different simulation methods into account.
4. Simulation results for phase equilibria of lattice-polymer systems with chain lengths $r = 1-200$ are reported.
5. Comparison between predictions of the Flory–Huggins theory and the Freed theory with the simulation results are also presented. The Freed theory gives satisfactory critical temperatures while the Flory–Huggins theory shows a large discrepancy. However, both theories give poor critical compositions.

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References and Notes

(1) Flory, P. J. *J. Chem. Phys.* **1942**, *10*, 51.
(2) Huggins, M. L. *J. Chem. Phys.* **1942**, *46*, 151.
(3) Freed, K. F. *J. Phys. A* **1985**, *18*, 871.
(4) Bawendi, M. G.; Freed, K. F. *J. Chem. Phys.* **1986**, *84*, 7036; **1987**, *86*, 3720; **1988**, *88*, 2741.
(5) Freed, K. F.; Bawendi, M. G. *J. Phys. Chem.* **1989**, *93*, 2194.
(6) Norman, G. E.; Filinov, V. S. *High Temp.* **1969**, *7*, 216.
(7) Widom, B. *J. Chem. Phys.* **1963**, *39*, 2808.
(8) Shing, K. S.; Gubbins, K. E. *Mol. Phys.* **1982**, *46*, 1109.
(9) Siepmann, J. I. *Mol. Phys.* **1990**, *70*, 1145.
(10) Rosenbluth, M. N.; Rosenbluth, A. W. *J. Chem. Phys.* **1955**, *23*, 356.
(11) de Pablo, J. J.; Laso, M.; Suter, U. W. *J. Chem. Phys.* **1992**, *96*, 2395.
(12) Frenkel, D.; Smit, B. *Mol. Phys.* **1992**, *75*, 983.
(13) Kumar, S. K.; Szleifer, I.; Panagiotopoulos, A. Z. *Phys. Rev. Lett.* **1991**, *66*, 2935.
(14) Szleifer, I.; Panagiotopoulos, A. Z. *J. Chem. Phys.* **1992**, *94*, 6666.
(15) Panagiotopoulos, A. Z.; Szleifer, I. *Polym. Prepr.* **1992**, 547.
(16) Kumar, S. K. *J. Chem. Phys.* **1992**, *97*, 3550.
(17) Panagiotopoulos, A. Z. *Mol. Phys.* **1987**, *61*, 813.
(18) Panagiotopoulos, A. Z.; Quirke, N.; Stapleton, M.; Tildesley, D. J. *Mol. Phys.* **1988**, *63*, 527.
(19) Laso, M.; de Pablo, J. J.; Suter, U. W. *J. Chem. Phys.* **1992**, *97*, 2817.
(20) Mackie, A. D.; O'Toole, E. M.; Hammer, D. A.; Panagiotopoulos, A. Z. *Fluid Phase Equilib.* **1993**, *82*, 251.
(21) Madden, W. G.; Pesci, A. I.; Freed, K. F. *Macromolecules* **1990**, *23*, 1181.
(22) Guo, M. X.; Li, Y. G. *J. Chem. Ind. Eng.* (*China*) **1994**, *45*, 448.
(23) Yan, Q. L.; Jiang, J. W.; Hu, Y. *Proceedings of the 2nd International Symposium on Thermodynamics in Chemical Engineering and Industry. Beijing* **1994**, 263–267.
(24) Yan, Q. L.; Jiang, J. W.; Liu, H. L.; Hu, Y. *J. Chem. Ind. Eng. (China)* **1995**, *46*, 517.
(25) Mackie, A. D.; Panagiotopoulos, A. Z.; Kumar, S. K. *J. Chem. Phys.* **1995**, *102*, 1014.

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