Monte Carlo Simulation of Phase Equilibria for Random Copolymers

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Received March 4, 1999; Revised Manuscript Received October 29, 1999

ABSTRACT: Configurational-bias-vaporization Monte Carlo simulation method developed previously has been used to simulate phase equilibria of AB random copolymer solutions based on a lattice model. Random copolymers are modeled as linear chains composed of segment A and segment B, for which the numbers of segments of them are r_A and r_B, respectively. Coexistence curves of random copolymer solutions with total chain length $r = r_A + r_B$ up to 200 and with chain composition varied are presented. Different sets of energy parameters are used. It is found that the critical density ρ_c is mainly determined by the total chain length r, while the reduced critical temperature T_c^* is determined by both the total chain length r and the chain composition f. Similar to Kambour et al. and Brinke et al.'s work, an effective interchange energy parameter ϵ^{eff} is introduced to treat the simulation results. Here ϵ^{eff} is a function of chain composition and various interchange energy parameters. With this measure, coexistence data of random copolymer solutions with different chain compositions can be mapped into a single curve for most cases. Phase behavior of these random copolymer solutions can then be predicted by coexistence curves of corresponding homopolymer solutions. However, the results are less satisfactory when monomers A and B are strongly repulsive toward each other.

1. Introduction

Computer simulation of phase equilibria for polymer solutions is an active field. Numerous methods have been developed. Among them, those direct methods that can obtain compositions of coexisting phases directly have attracted more attention due to their higher efficiency compared with those indirect methods. Most work put main interests on longer and longer chains aimed at testing the validity of various theories such as the Flory−Huggins theory[1,2] and the lattice-cluster theory of Freed.[3,4] Madden et al.[5] obtained phase diagrams for lattice homopolymers with chain length of 100 using a reptation and pseudokinetic algorithm. Mackie et al.[6] adopted the configurational-bias Gibbs ensemble method, with the chain length raised to 128. Yan et al.[7] developed a so-called configurational-bias-vaporization method, chain length raised to 200. Later, Frauenkron and Grassberger[8] were able to simulate homopolymer systems with chain lengths up to 2048 by a pruned-enriched Rosenbluth method combined with a histogram method. Similarly, Panagiotopoulos et al.[9] used histogram reweighting Monte Carlo simulation methods to study lattice homopolymers with chain lengths up to 1000. Recently, we were informed that Yan et al.[10] further raised the chain length to 4000 through a combination of expanded grand canonical simulations and histogram reweighting finite-size scaling analysis.

Although notable progress has appeared for the simulation of phase equilibria for homopolymers, simulations for copolymers are rarely reported in the literature. In this work, we studied the phase behavior of lattice random copolymers by using the configurational-bias-vaporization method proposed by Yan et al.[7] The influence of chain composition was mainly focused on. The whole paper is organized as follows. First we give briefly the model and methodology. We then report phase diagrams and corresponding critical properties for random copolymer solutions with chain lengths up to 200 and with different chain compositions using different sets of interaction energy parameters. We found that coexistence curves for random copolymers with different chain compositions can be mapped into a single curve in most cases by introducing an effective interchange energy parameter ϵ^{eff}. Finally we present conclusions.

2. Model and Simulation Method

Yan et al.'s configurational-bias-vaporization method is a direct method where two coexistence phases with an interface form automatically from a homogeneous fluid during the simulation.

Simulations are performed in a canonical ensemble of a simple cubic lattice. Dimensions of the simulation cell are $L_X \times L_Y \times L_Z = 32 \times 32 \times 256$ with periodic boundary conditions in all three directions. Random copolymers are represented by linear chains composed of monomers A and B; each of them occupies one site. Chain composition is defined by f, $f = r_A/(r_A + r_B) = r_A/r$, where r_A and r_B are numbers of segments of A and B, respectively, and r is the total chain length, $r = r_A + r_B$. All sites other than those occupied by copolymers are considered as solvent molecules or vacancies denoted by S; each of them also occupies one site. Only nearest-neighbor interactions are considered; therefore, six different interaction energy parameters ϵ_{AA}, ϵ_{AB}, ϵ_{BB}, ϵ_{AS}, ϵ_{BS}, and ϵ_{SS} are normally needed. However, for simplicity, only ϵ_{AA}, ϵ_{AB}, and ϵ_{BB} are assigned specific values with all others set to zero.

Chain molecules are first introduced into the bottom of the cell confined by two repulsive walls using the Rosenbluth−Rosenbluth growth technique.[11] The two repulsive walls are then removed, and the compressed chains are then gradually "vaporized" to form two coexisting phases. Five types of molecular motion, i.e., the Verdier−Stockmayer model[12] including end-rotation and L-flip (or kink jump motion), crankshaft motion, reptation, and the revised Rosenbluth−Rosenbluth

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10.1021/ma9903308 CCC: $19.00
Published on Web 02/12/2000

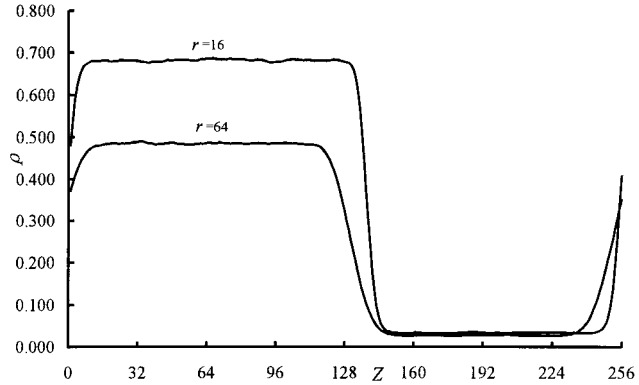

Figure 1. Simulated equilibrium density profile for lattice random copolymers ϵ_{AA}:ϵ_{AB}:ϵ_{BB} = 1.0:0.8:0.6. Upper curve: r = 16, f = 0.75, T^* = 2.0, ρ_g = 0.0330 ± 0.0008, and ρ_l = 0.6804 ± 0.0027. Lower curve: r = 64, f = 0.75, T^* = 2.55, ρ_g = 0.0271 ± 0.0008 and ρ_l = 0.4844 ± 0.0017.

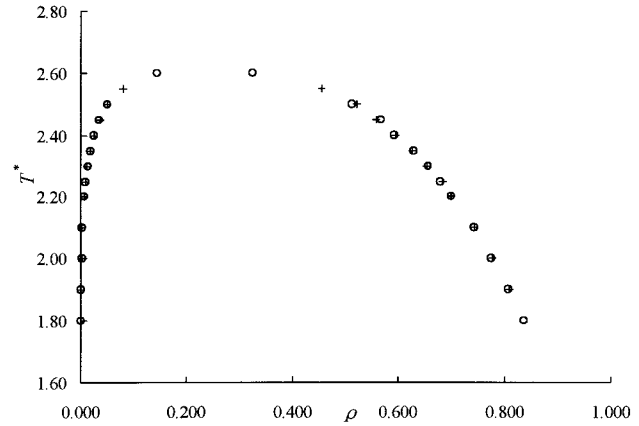

Figure 2. Simulated coexisting curves using different random-sequence introducing techniques: plus, technique 1; open square, technique 2. r = 32, f = 0.875, and other parameters are the same as those used in Figure 1.

growth (configurational-bias sampling) method proposed by Siepmann et al.[13] are used. After a great amount of trial moves, typically 4×10^7, two coexisting phases are formed. The density profile is calculated every 1000 steps; each step contains 20000−40000 trial moves. By taking the average, equilibrium densities of coexisting phases ρ_g and ρ_l are obtained. Standard errors $\Delta\rho_g$ and $\Delta\rho_l$ are calculated at the same time. Figure 1 shows two typical simulated equilibrium density profiles for lattice random copolymers with chain lengths r = 16 and 64, respectively. Parameters are shown in the figure caption, where reduced temperature $T^* = kT/\epsilon_{AA}$; this means that the solution of homopolymer A is selected as a reference.

For the initial packing of the random copolymers, we have used two different techniques. The first one is that we create arbitrary a random sequence prior to the insertion procedure with $r_A = fr$ and $r_B = (1 - f)r$. We then generate the chains using the Rosenbluth−Rosenbluth method according to that sequence. The second one is that when perform self-avoiding random walks on lattice to generate chains, we use random numbers to control the identity of monomers being inserted. The two insertion procedures are equivalent when chain length is infinite. For finite chain length, results of a random copolymer system with r = 32 and f = 0.875 using the two methods are shown in Figure 2. Almost the same coexistence curve within the statistical uncertainties is obtained. In the following simulations, we employ the first technique.

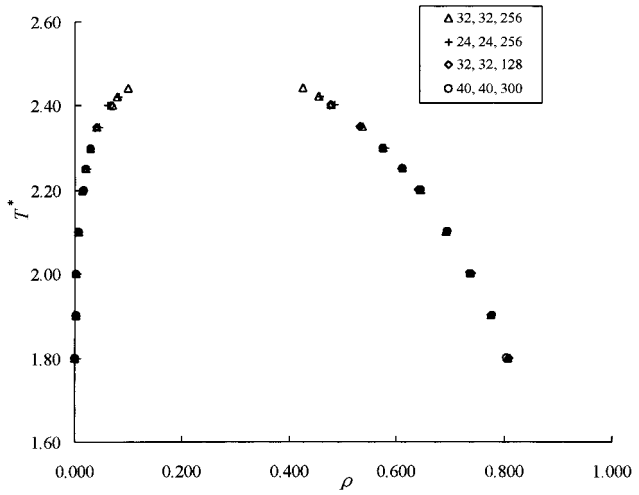

Figure 3. Finite-size effect. r = 32, f = 0.75, and other parameters are the same as those used in Figure 1.

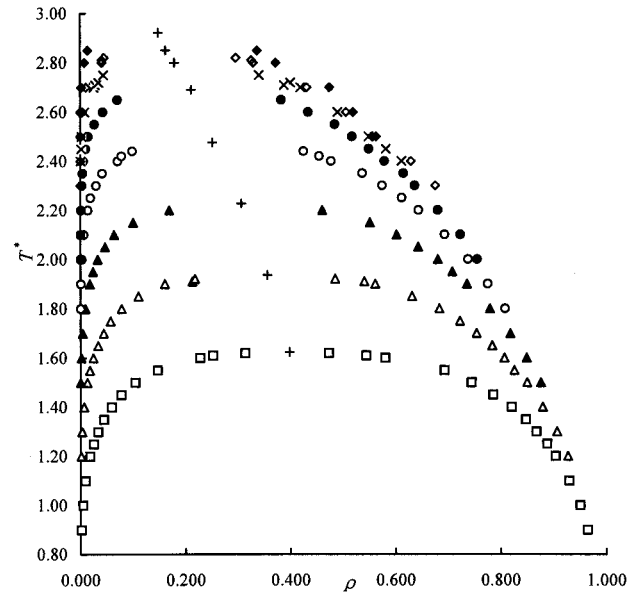

Figure 4. Simulated coexistence curves for lattice random copolymers with different chain lengths. f = 0.75, parameters are the same as those used in Figure 1. r : open square, 4; open triangle, 8; solid triangle, 16; open circle, 32; solid circle, 64; cross, 100; open diamond, 128; solid diamond, 200; plus, calculated critical points.

Test of finite-size effects is shown in Figure 3. It indicates that the finite-size effect could be neglected within the size of cells used in this work. Although the statistical error could be lower if a larger cell is used, however, the computation time will be dramatically increased. As a compromise, we use 32 × 32 × 256 as the cell size.

3. Results

3.1. The Influence of Chain Length on Phase Behavior. Coexistence curves for random copolymers with chain lengths r = 4−200 and chemical composition f = 0.75 are given in Figure 4, energy parameters are ϵ_{AA}:ϵ_{AB}:ϵ_{BB} = 1.0:0.8:0.6. Critical temperatures and densities were calculated by fitting the coexistence data

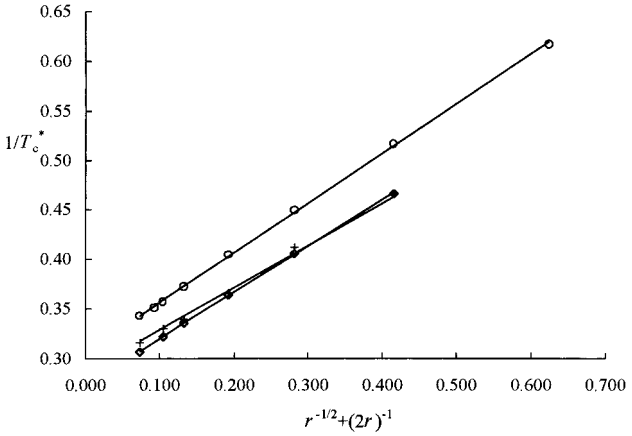

Figure 5. Schultz−Flory plot of lattice random copolymers. $1/T_c^* \sim r^{-1/2} + (2r)^{-1}$. Key: Open square, this work; plus, Yan et al.[7] for homopolymers; open diamond, Panagiotopoulos et al.[9] for homopolymers.

Table 1. Critical Temperatures and Densities for Different Chain Lengths for ϵ_{AA}:ϵ_{AB}:ϵ_{BB} = 1.0:0.8:0.6 and f = 0.75

r	T_c^*	ρ_c
4	1.623 ± 0.004	0.398 ± 0.004
8	1.936 ± 0.005	0.356 ± 0.006
16	2.227 ± 0.006	0.306 ± 0.002
32	2.476 ± 0.003	0.251 ± 0.003
64	2.691 ± 0.005	0.211 ± 0.002
100	2.800 ± 0.007	0.179 ± 0.005
128	2.851 ± 0.005	0.162 ± 0.004
200	2.922 ± 0.014	0.148 ± 0.008

to the following scaling relationships[14]

$$\rho_l - \rho_g = B(T_c^* - T^*)^\beta \quad (1)$$

$$\frac{\rho_l + \rho_g}{2} - \rho_c = A(T_c^* - T^*)^\mu \quad (2)$$

where β and μ are scaling exponents and A and B are parameters. In this work, we adopted $\beta = 0.326$ according to the Ising universality class and the Ising value $\mu = 0.875$ as Mackie et al.[6] did. Extrapolated critical points are also shown in Figure 4. Corresponding critical temperatures, critical densities and their errors are listed in Table 1.

Figure 5 shows chain-length dependence of the critical temperature for random copolymers plotted according to the Shultz−Flory relationship[15]

$$\frac{1}{T_c(r)} - \frac{1}{T_c(\infty)} \propto \frac{1}{\sqrt{r}} + \frac{1}{2r} \quad (3)$$

Those for homopolymers by Yan et al.[7] and Panagiotopoulos et al.[9] are also plotted for comparison. The fitting of this work for r = 4−200 gives a correlation coefficient of 0.9998. Linear regression gives a reduced critical temperature for infinite-long random copolymer with f = 0.75 as $T_c^*(\infty)$ = 3.27 ± 0.01, while that for homopolymer is 3.45 and 3.71 by Yan et al. and Panagiotopoulos et al., respectively. Figure 6 shows the chain-length dependence of critical density by a log−log plot. Five data points with longer chain lengths are selected in the fitting that gives a slope of −0.30. A scaling relationship of $\rho_c \propto r^{-0.30}$ is obtained similar to those for homopolymers. For the latter, Mackie et al.[6] gave an exponent of 0.32−0.35. Corresponding results

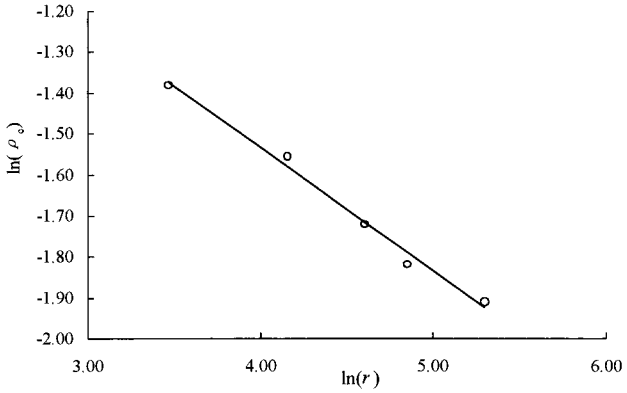

Figure 6. A ln−ln plot for chain-length dependence of critical density.

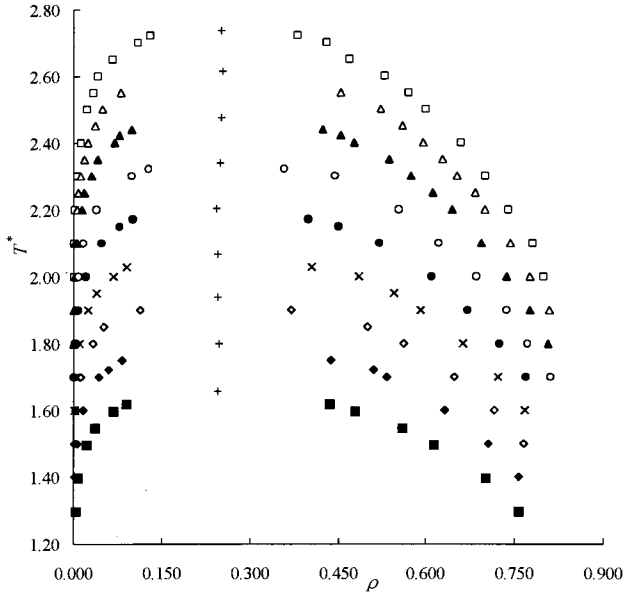

Figure 7. Simulated coexistence curves for lattice random copolymers with different chemical compositions. Energy parameters are the same as those used in Figures 1 and 4. r = 32. plus, calculated critical points. f: open square, 1.0; open triangle, 0.875; solid triangle, 0.75; open circle, 0.625; solid circle, 0.5; cross, 0.375; open diamond, 0.25; solid diamond, 0.125; solid square, 0. f = 1.0 from Yan et al.[7]

by Yan et al.,[7] Panagiotopoulos et al.,[9] Wilding et al.,[16] and Szleifer et al.[17] and the experimental value[14,18] are 0.27, 0.38, 0.369, 0.4, and 0.38−0.4, respectively.

The above results indicate that the chain-length dependence of the phase behavior of random copolymer systems is very similar to that of the homopolymer systems. The lower value of the reduced critical temperature for infinite long chain results from the relatively weaker attractive interaction energy between B−B and A−B in the copolymer. As for the lower value of the critical exponent, the limited chain length used in this work may be a matter of account.

3.2. The Influence of Chain Composition on Phase Behavior. Figure 7 shows the chain-composition dependence of coexistence curve for random copolymers with chain length r = 32, energy parameters are the same as those used in Figure 4. Critical points are calculated according to eqs 1 and 2. Critical temperatures, critical densities, and their errors are listed in Table 2. From the figure we can see that the critical temperature increases with increasing f. Figure 8 shows a linear relation with a correlation coefficient of 0.99992

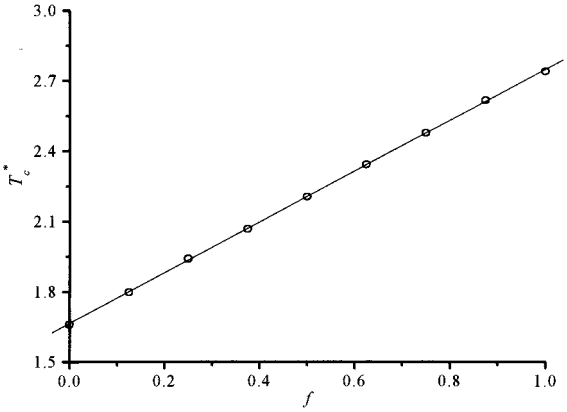

Figure 8. Critical temperature as a function of chain composition f. $r = 32$.

Table 2. Chain-Composition Dependence of Critical Temperature and Density for ϵ_{AA}:ϵ_{AB}:ϵ_{BB} = 1.0:0.8:0.6 and r = 32

f	T_c^*	ρ_c
1.0	2.735 ± 0.004	0.257 ± 0.004
0.875	2.616 ± 0.004	0.253 ± 0.003
0.75	2.476 ± 0.003	0.251 ± 0.003
0.625	2.341 ± 0.006	0.249 ± 0.008
0.5	2.204 ± 0.008	0.244 ± 0.005
0.375	2.068 ± 0.007	0.245 ± 0.007
0.25	1.940 ± 0.008	0.245 ± 0.004
0.125	1.798 ± 0.009	0.247 ± 0.005
0	1.658 ± 0.009	0.246 ± 0.004

and a slope of 1.082. On the other hand, the critical density is nearly constant within the statistical error.

3.3. Effective Interchange Energy Parameter. As we have mentioned in section 3.1, random copolymers are similar to homopolymers in the phase behavior. Figures 7 and 8 further indicate that there may be a simple relation between critical properties and chain compositions of the copolymer. For mixtures of homopolymers and random copolymers, Kambour et al.[19] also formulated a theory of Flory−Huggins type with an effective Flory−Huggins parameter χ_{blend} as a function of chain compositions of copolymers. Brinke, Karasz, and MacKnight[20] then extended this theory and applied it to blends of random copolymers. Enlightened by the above developments, we also introduce an effective parameter to treat the simulation results.

For systems composed of a solvent and a random copolymer, similar to Kambour et al. and Brinke et al.'s work, the effective interchange energy parameter ϵ^{eff} is defined by

$$\epsilon^{eff} \equiv f\overline{\epsilon_{SA}} + (1-f)\overline{\epsilon_{SB}} - f(1-f)\overline{\epsilon_{AB}} \qquad (4)$$

where S denotes the solvent molecule and $\overline{\epsilon_{SA}}$, $\overline{\epsilon_{SB}}$, and $\overline{\epsilon_{AB}}$ are interchange energy parameters defined as follows:

$$\begin{aligned} \overline{\epsilon_{SA}} &= \epsilon_{SS} + \epsilon_{AA} - 2\epsilon_{SA} \\ \overline{\epsilon_{SB}} &= \epsilon_{SS} + \epsilon_{BB} - 2\epsilon_{SB} \\ \overline{\epsilon_{AB}} &= \epsilon_{AA} + \epsilon_{BB} - 2\epsilon_{AB} \end{aligned} \qquad (5)$$

In simulations of this work, solvent molecules are regarded as voids as usual; therefore, $\epsilon_{SS} = \epsilon_{SA} = \epsilon_{SB} =$ 0 and eq 4 becomes

$$\epsilon^{eff} = f^2\epsilon_{AA} + (1-f)^2\epsilon_{BB} + 2f(1-f)\epsilon_{AB} \qquad (6)$$

ϵ^{eff} is a quadratic function of f. For solutions of homopolymer A or B, $\epsilon^{eff} = \overline{\epsilon_{SA}} = \epsilon_{AA}$ or $\epsilon^{eff} = \overline{\epsilon_{SB}} = \epsilon_{BB}$. The effective reduced temperature T^{**} is then calculated by

$$T^{**} = kT/\epsilon^{eff} = \overline{\epsilon_{SA}}T^*/\epsilon^{eff} = \epsilon_{AA}T^*/\epsilon^{eff} \qquad (7)$$

where $T^* = kT/\epsilon_{AA}$ is the ordinary reduced temperature. The following three typical cases are then considered.

3.3.1. $\overline{\epsilon_{AB}} = 0$, $\epsilon_{AB} = (\epsilon_{AA} + \epsilon_{BB})/2$. For systems when ϵ_{AB} equals the arithmetical mean of ϵ_{AA} and ϵ_{BB}, eq 6 can be simplified as

$$\epsilon^{eff} = f\epsilon_{AA} + (1-f)\epsilon_{BB} \qquad (8)$$

Now ϵ^{eff} is a linear function of f. Obviously the linear relationship between T_c^* and f in Figure 8 is just due to this linear behavior. For Figure 7, ϵ_{AA}:ϵ_{AB}:ϵ_{BB} = 1.0:0.8:0.6. When f = 1.0, 0.75, 0.5, 0.25, and 0, $\epsilon^{eff}/\epsilon_{AA}$ = 1.0, 0.9, 0.8, 0.7, and 0.6. After transforming T^* to T^{**} using eqs 7 and 8, we plot the coexistence data of Figure 7 again. Figure 9 shows the results. The five coexistence curves of Figure 7 are now mapped into a single curve. The coexistence curve of random copolymer solutions can then be predicted by the coexistence curve of the corresponding homopolymer solutions if $\overline{\epsilon_{AB}} = 0$.

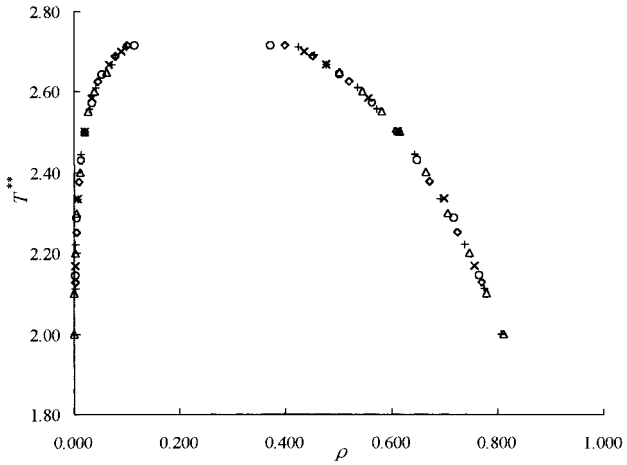

Figure 9. Plot of coexistence data for copolymer systems with different compositions using effective reduced temperature. Energy parameters are the same as those used in Figures 1 and 4; r = 32. f: open triangle, 1.0; plus, 0.75; open diamond, 0.50; open square, 0.25; cross, 0.

3.3.2. $\overline{\epsilon_{AB}} < 0$, $\epsilon_{AB} > (\epsilon_{AA} + \epsilon_{BB})/2$. $\overline{\epsilon_{AB}} < 0$ means that A and B are more attractive toward each other than toward A and B themselves. Figure 10 shows the results for a system of this category; energy parameters are ϵ_{AA}:ϵ_{AB}:ϵ_{BB} = 1.0:1.2:0.6, $\overline{\epsilon_{AB}}$:ϵ_{AA} = −0.8, and chain length r = 32. Equation 6 should be used in this case to calculate ϵ^{eff}. When f = 1.0, 0.75, 0.5, 0.25, and 0, $\epsilon^{eff}/\epsilon_{AA}$ = 1.0, 1.05, 1.0, 0.85, and 0.6. From the figure we can see that the coexistence data of five different chain compositions can still be incorporated into a single curve. Although the single curve obtained is not as satisfactory as that of Figure 9, it is still good enough except near the critical region. Figure 11 shows results for a similar system, energy parameters are ϵ_{AA}:ϵ_{AB}:ϵ_{BB} = 1.0:0.8:0.4, $\overline{\epsilon_{AB}}$:ϵ_{AA} = −0.2, and chain length r = 64. When f = 1.0, 0.75,

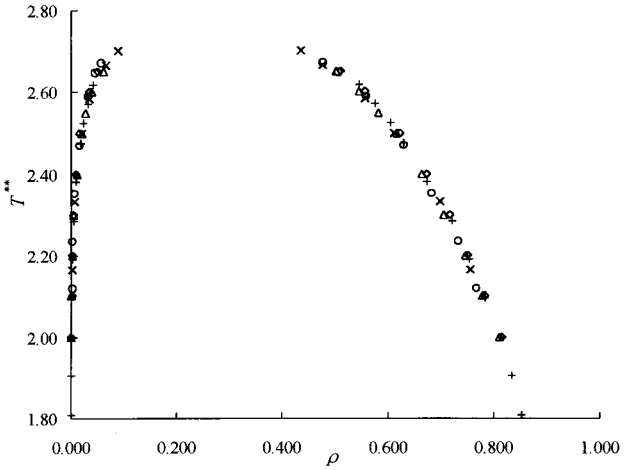

Figure 10. Plot of coexistence data for copolymer systems with different composition using effective reduced temperature. Energy parameters are ϵ_{AA}:ϵ_{AB}:ϵ_{BB} = 1.0:1.2:0.6; r = 32. f: open triangle, 1.0; plus, 0.75; open diamond, 0.50; open square, 0.25; cross, 0.

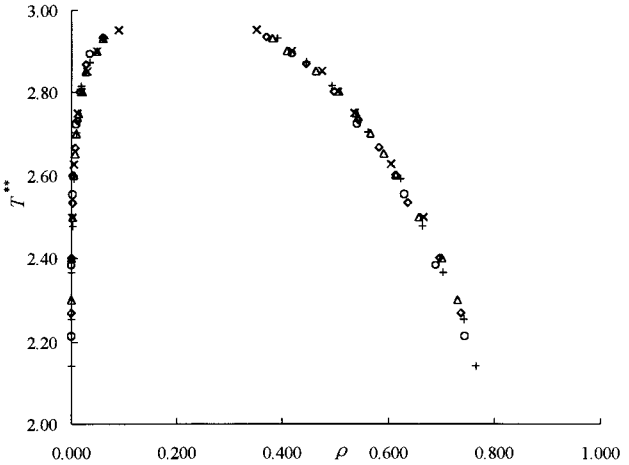

Figure 11. Plot of coexistence data for copolymer systems with different composition using effective reduced temperature. Energy parameters are ϵ_{AA}:ϵ_{AB}:ϵ_{BB} = 1.0:0.8:0.4; r = 64. f: open triangle, 1.0; plus, 0.75; open diamond, 0.50; open square, 0.25; cross, 0.

0.5, 0.25, and 0, $\epsilon^{eff}/\epsilon_{AA}$ = 1.0, 0.8875, 0.75, 0.5875, and 0.4. The single curve obtained is also satisfactory. The two figures indicate that for $\overline{\epsilon_{AB}} < 0$, the coexistence curve of random copolymer solutions can still be predicted by the coexistence curve of the corresponding homopolymer solutions.

3.3.3. $\overline{\epsilon_{AB}} > 0$, $\epsilon_{AB} < (\epsilon_{AA} + \epsilon_{BB})/2$. $\overline{\epsilon_{AB}} > 0$ means that A and B are more repulsive toward each other than A and B themselves. Figure 12 shows a system of this category, energy parameters are ϵ_{AA}:ϵ_{AB}:ϵ_{BB} = 1.0:0.5:0.4, $\overline{\epsilon_{AB}}$:ϵ_{AA} = 0.4, and chain length r = 32. Again eq 6 should be used in this case to calculate ϵ^{eff}. When f = 1.0, 0.75, 0.5, 0.25 and 0, $\epsilon^{eff}/\epsilon_{AA}$ = 1.0, 0.775, 0.6, 0.475, and 0.4. The results shown in the figure indicate that the introduction of ϵ^{eff} by eq 6 is still acceptable. All coexistence data for different chain compositions can still be incorporated into a single curve.

Figures 13 and 14 show similar systems but with larger $\overline{\epsilon_{AB}}$. For the former, energy parameters are ϵ_{AA}:ϵ_{AB}:ϵ_{BB} = 1.0:0.4:0.6, $\overline{\epsilon_{AB}}$:ϵ_{AA} = 0.8, and chain length r = 32. When f = 1.0, 0.75, 0.5, 0.25, and 0, $\epsilon^{eff}/\epsilon_{AA}$ = 1.0, 0.75, 0.6, 0.55, and 0.6. For the latter, energy parameters are ϵ_{AA}:ϵ_{AB}:ϵ_{BB} = 1.0:0.2:0.6, $\overline{\epsilon_{AB}}$:ϵ_{AA} = 1.2, and

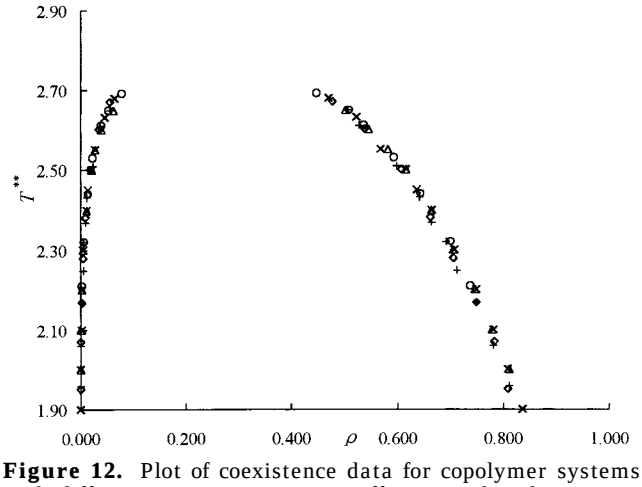

Figure 12. Plot of coexistence data for copolymer systems with different composition using effective reduced temperature. Energy parameters are ϵ_{AA}:ϵ_{AB}:ϵ_{BB} = 1.0:0.5:0.4; r = 32. f: open triangle, 1.0; plus, 0.75; open diamond, 0.50; open square, 0.25; cross, 0.

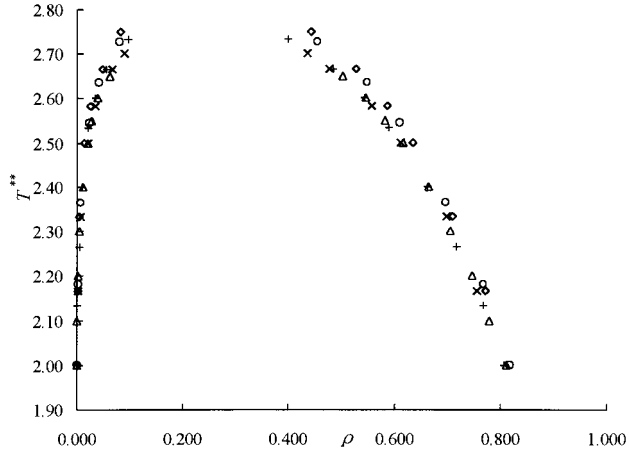

Figure 13. Plot of coexistence data for copolymer systems with different composition using effective reduced temperature. Energy parameters are ϵ_{AA}:ϵ_{AB}:ϵ_{BB} = 1.0:0.4:0.6; r = 32. f: open triangle, 1.0; plus, 0.75; open diamond, 0.50; open square, 0.25; cross, 0.

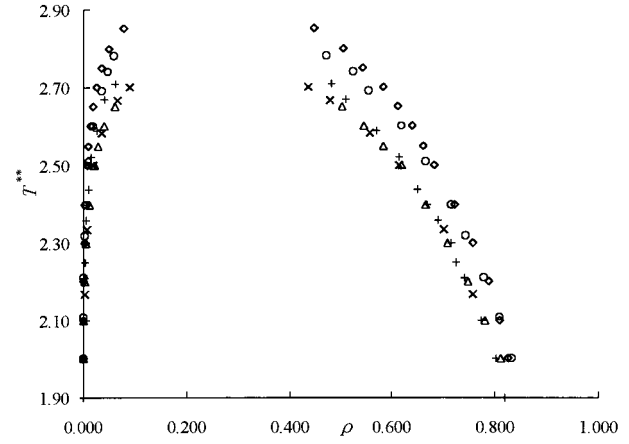

Figure 14. Plot of coexistence data for copolymer systems with different composition using effective reduced temperature. Energy parameters are ϵ_{AA}:ϵ_{AB}:ϵ_{BB} = 1.0:0.2:0.6; r = 32. f: open triangle, 1.0; plus, 0.75; open diamond, 0.50; open square, 0.25; cross, 0.

chain length r = 32. When f = 1.0, 0.75, 0.5, 0.25, and 0, $\epsilon^{eff}/\epsilon_{AA}$ = 1.0, 0.675, 0.5, 0.475, and 0.6. It is seen obviously from these figures that the coexistence data for different chain compositions now fail to form a single

Table 3. Reduced Critical Temperatures for Random Copolymer Systems for ϵ_{AA}:ϵ_{AB}:ϵ_{BB} = 1.0:0.4:0.6 and r = 32

f	T_c^*	f	T_c^*
1.0	2.737 ± 0.004	0.25	1.551 ± 0.010
0.75	2.084 ± 0.007	0	1.658 ± 0.009
0.5	1.692 ± 0.006		

Table 4. Reduced Critical Temperatures for Random Copolymer Systems for ϵ_{AA}:ϵ_{AB}:ϵ_{BB} = 1.0:0.2:0.6 and r = 32

f	T_c^*	f	T_c^*
1.0	2.737 ± 0.004	0.25	1.380 ± 0.010
0.75	1.906 ± 0.006	0	1.658 ± 0.009
0.5	1.468 ± 0.005		

curve. The larger $\overline{\epsilon_{AB}}$, the more scattered the data points will be, especially near the critical region. Tables 3 and 4 list reduced critical temperatures for the above two systems, respectively.

The results of Figures 13 and 14 indicate that eqs 4 or 6 for the effective interchange energy parameter is only suitable for random copolymer systems with smaller or negative $\overline{\epsilon_{AB}}$. For larger positive $\overline{\epsilon_{AB}}$, the simple expression for the effective interchange energy parameter must be revised in order to achieve more satisfactory mapping results.

4. Conclusion

The configurational-bias-vaporization Monte Carlo simulation method developed previously is used to simulate phase behavior of AB random copolymers based on a lattice model. Coexistence curves for random copolymers with chain lengths up to 200 and with different chain compositions are presented using different energy parameters. Critical parameters are also presented.

It is found that the critical density ρ_c is mainly determined by the total chain length r, while the critical temperature T_c^* is determined by both the chain length r and the chain composition f. The phase behavior of random copolymer systems is very similar to that of homopolymer systems. This fact indicates that with reasonable parameter transformation, the coexistence curves of random copolymer systems may be related to those coexistence curves of the corresponding homopolymer systems.

Enlightened by Kambour et al.[19] and Brinke et al.'s[20] work, an effective interchange energy parameter ϵ^{eff} is introduced which is a simple function of chain composition and corresponding pair interaction energy parameters. With this ϵ^{eff} used, for $\overline{\epsilon_{AB}} \leq 0$ or $\overline{\epsilon_{AB}} > 0$ but is relatively small, nearly all coexistence data for random copolymer systems with different chain compositions can be mapped into a single curve. This allows us to predict the phase behavior of random copolymer systems using information on the corresponding homopolymer systems. However, for larger $\overline{\epsilon_{AB}}$, the mapping results are less satisfactory, indicating that the simple expression of the introduced effective interchange energy parameter ϵ^{eff} should be revised.

Although some interesting results have been presented, this article is still a rudimentary work about random copolymers and is far from perfect. More simulations for longer chains and using wider range of energy parameters should be carried out.

Acknowledgment. This work is supported by the Chinese National Science Foundation and by the Doctoral Research Foundation sponsored by the Chinese Ministry of Education. In addition, the reviewer's comments are very much appreciated because of their valuable contribution to the revision of the manuscript.

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MA9903308