Monte Carlo simulation of phase separations of block copolymers and of corresponding blends

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SUMMARY:
The Monte Carlo method has been used to simulate the phase separations of block copolymers and of corresponding blends with very high concentration (sum of volume fractions of blocks A and B: \( \phi_A + \phi_B = 0.9545 \)). Our main findings are as follows: (1) The mixing is nonrandom even in the athermal limit. (2) The nonselective good solvent molecules (\( \phi_V = 0.0455 \)) are mostly located at the interface between A- and B-rich phases, thus, it is not true that solvent and monomeric units will remain mixed at all temperatures. (3) Even for the same microscopic A-B interaction energy, \( \varepsilon \), and at the same temperature, the Flory-Huggins parameter \( \chi \) of block copolymers is always higher than that of corresponding blends, and the \( \chi \) values of block copolymers and corresponding blends have different \( \varepsilon \)-dependencies. (4) The critical values of \( \chi \) both for block copolymer and corresponding blend are obtained and compared with the mean-field theoretical predictions. It is found that the ratio of \( \chi_c(\text{block})/\chi_c(\text{blend}) \) is qualitatively compatible with the prediction of the Flory-Leibler theory.

Introduction

It has been well-known for long time that the classic thermodynamic theory of polymer blends, the Flory-Huggins (FH) theory\(^1\)-\(^3\), involves drastic approximations. Besides the neglect of correlation in the occupancy of neighbor sites, which is due to the mean-field approximation, most of the excluded-volume restrictions are also neglected in the estimation of the configurational entropy of the chains. By Monte Carlo simulations, Sariban and Binder\(^4\),\(^5\) found results different from those given by the FH theory by a factor of 2.5 to 2 for symmetric blends. They attributed this huge discrepancy to the crude treatment of chain configurational statistics in the FH approximation. Furthermore, they found in their simulation that the FH interaction parameter \( \chi \) depends both on concentration and chain length. More careful theoretical analyses\(^6\)-\(^11\) have shown that \( \chi \) is not a purely energetic parameter as is given in the FH theory with \( \chi = z \varepsilon/(kT) \), where \( z \) is the coordination number of the lattice. Actually, the enthalpy term \( \chi \phi_A \cdot \phi_B \) in the FH theory involves entropic contributions which result in complex dependencies of \( \chi \) on concentration and chain length.

Copolymer melts show a spatial segregation at low temperatures. However, a macroscopic phase separation, which occurs, e.g., in polymer blends, can not occur, since the sequences are chemically connected. The phase separation happens on a mesoscopic scale where the microdomains of A- and B-rich regions emerge. As \( \chi \) is not a purely energetic parameter and involves entropic contributions, we can expect that \( \chi \) will have concentration and chain length dependencies different from those of corresponding blends even when the microscopic A-B nearest-neighbour interaction energies \( \varepsilon \) are identical for both systems. After the pioneering work by Meier\(^12\), later
on Helfand and Wassermann\textsuperscript{13–16}, Leibler\textsuperscript{17}, Ohata and Kawasaki\textsuperscript{18} and Fredrickson and Helfand\textsuperscript{19} have developed the statistical mechanical theory of micro phase separation in block copolymer bulk. The theoretical predictions have been checked thoroughly by Monte Carlo simulation of symmetric diblock copolymer melts in the presence of a solvent ($\phi_Y \geq 0.2$)\textsuperscript{20,21}, and it was found that the simulation results agree with the weak segregation theories at infinite temperature (the athermal limit). The quite good agreement seems to indicate that at infinite temperature the various approximations involved in the weak segregation theories are valid. At finite temperature, Fried and Binder\textsuperscript{21} found that the non-Gaussian conformation behavior of block copolymer chains due to the stretching (or elongation) of copolymer chain leads to the deviations of weak segregation theory from simulation results. Recently, Gauger et al.\textsuperscript{30} performed the first Monte Carlo simulation for a block copolymer system of unit density by using their own new algorithm. The obtained critical value of $\chi$ agrees with the theoretical prediction of Fredrickson and Helfand\textsuperscript{19} quite well. However, their data were calculated according to Flory’s definition of $\chi$, which has not been justified.

The present work is devoted to a study of the relation between the phenomenological FH interaction parameter $\chi$ and the microscopic monomer-monomer interaction energy $\varepsilon$ both for block copolymer and corresponding blend systems. Our most important finding concerns the nonrandom mixing of A and B monomeric units in block copolymers, which was also found for corresponding blends\textsuperscript{22}, even in the athermal limit. It is also found that even for the case of a nonselective good solvent, the vacancies (solvent molecules) are located at the interface between A- and B-rich phases. We attribute the nonrandomness of the mixing to the connectivity of monomeric units, forming chain-like molecules, resulting in a nonrandom contact between A and B units. Due to the neglect of excluded volume restrictions in estimating the configurational entropy of the chains, the accuracy of the expression for the configurational entropy per lattice site

\begin{equation}
\frac{S}{k} = \frac{1}{L_A} \phi_A \cdot \ln \phi_A + \frac{1}{L_B} \phi_B \cdot \ln \phi_B
\end{equation}

is not high and the validity of Eq. (1) is qualitative at best ($L_{A,B}$: length of the corresponding block).

We also find that the phenomenological FH interaction parameters for blends, $\chi$ (blend), and for diblock copolymers, $\chi$ (block), are different even if their microscopic monomer-monomer interaction energies, $\varepsilon$, are the same. In other words, $\chi$ shows different $\varepsilon$-dependencies for block copolymers and corresponding blends.

The organization of this paper is as follows: In the next section, we describe briefly the model and simulation procedure. Then we show the results of the simulation and present a comparison between the simulation results and the theoretical predictions in detail, while the last section summarizes our conclusions and contains some comments on the relevance of our findings for experimental work.
Model and simulation method

We perform the simulation in two-dimensional space. Cifra's simulation results have shown that there is no essential distinction in phase behavior between two- and three-dimensional systems\cite{22, 23}. Multiple-chain configurations were generated on a planar $41 \times 41$ square lattice which is considered as a Monte Carlo unit cell. The system was formed with 88 linear chains, each of which comprises 21 segments. Therefore, the concentration is as high as 0.9545, and our Monte Carlo studies can hence be regarded as in the bulk state. In the simulation, standard periodic boundary condition has been imposed on the lattice to mimic an infinite-size system\cite{24}. Due to the very high concentration of polymer segments, the "single-site bond fluctuation model" proposed by Larson et al.\cite{25, 26} and Carmesin et al.\cite{27} and the "vacancy diffusion algorithm" suggested by Lu et al.\cite{28} have been used in order to perform the Monte Carlo simulation efficiently. The model and the corresponding microrelaxation modes are schematically depicted in Fig. 1. It has been shown in refs.\cite{26, 27} that the model and the algorithm give the correct static and dynamic behaviors in quite an efficient manner. We avoid to use the traditional "slithering snake algorithm"\cite{29}, by which the vacancies are artificially located at the nearest neighbors of the chain ends during the simulation.

The system is relaxed from an arbitrary initial state to the equilibrium state by using the above mentioned algorithm in the athermal condition, i.e., with monomer-monomer and monomer-vacancy interaction energies $\varepsilon_{\text{AA}} = \varepsilon_{\text{BB}} = \varepsilon_{\text{VV}} = \varepsilon_{\text{VA}} = \varepsilon_{\text{VB}} = \varepsilon_{\text{AB}} = 0$, which corresponds to the case of infinite temperature. Then we designate a part of each chain as A segments and the remainders as B segments for the case of a block copolymer. For the case of a corresponding blend, the link between A and B blocks was cut off.

![Fig. 1. (a) The single-site bond fluctuation model; (b) two typical microrelaxation modes in the vacancy diffusion algorithm, where $\bigcirc$ represents a vacancy and the shaded area is occupied by other chain segments](image_url)
In addition to the simple volume exclusion interaction between the segments, an interaction energy, \( \varepsilon_{AB} = \varepsilon \), was introduced between A and B segments when they are nearest neighbors. We have specified the interaction energy between monomeric unit and vacancy (with small volume fraction, \( \phi_v = 0.0455 \)), \( \varepsilon_{VA} = \varepsilon_{VB} = \varepsilon_{VV} = \varepsilon_{AA} = \varepsilon_{BB} = 0 \). This choice, which corresponds to the vacancies acting as a nonselective good solvent, tends to favor the vacancies and the monomeric units to remain mixed at all temperatures according to the intuitive conjecture. In the next section, however, we will show that this is not the case. It must be noted especially that in the single-site bond fluctuation model within two dimensions, the coordination number is \( z = 8 \) instead of \( z = 4 \) in the usual square lattice chains. The athermal homopolymer system and miscible or immiscible systems can be simulated by designating the reduced interaction energies \( \varepsilon^* = \varepsilon/(kT) \) to be zero, negative or positive. For the system at finite temperature, each trial move is accepted or rejected according to the Metropolis sampling rule\(^{34} \). Not beyond the generality, our studies mainly aimed at a system of approximately symmetrical AB blends and AB diblock copolymers with A and B lengths \( L_A = 10 \) and \( L_B = 11 \).

The average number of heterocontacts per chain, \( N_{AB} \), in the AB diblock copolymer and AB blend is obtained simply by counting the total number of A-B nearest contact pairs in the system and then divided by the total number of chains, \( N_{ch} \), and finally averaged over the equilibrium ensembles. The phenomenological FH interaction parameter \( \chi \) and the real microscopic reduced interaction energy \( \varepsilon^* \) can be related through \( N_{AB} \) and \( N_{ch} \) by equating the enthalpic parts of the FH theory and the simulation system,

\[
\chi \phi_A \cdot \phi_B = N_{ch} \cdot \varepsilon^* N_{AB}(\varepsilon^*)/N_T
\]

where \( N_T \) is the total number of lattice sites in our model system; \( N_{AB}(\varepsilon^*) \) is the mean number of A-B contacts per chain with the interaction energy \( \varepsilon^* \).

In order to reduce the computational time, the simulation is started from an equilibrium state with \( \varepsilon^* = 0 \) (athermal system), and then \( \pm \Delta \varepsilon^* \) is added to simulate the finite temperature. The equilibrium state at the previous \( \varepsilon^* \) value is taken as the initial state for the simulation of the system with \( \varepsilon^* = \Delta \varepsilon^* \). In the region of phase transition, we choose the increment \( |\Delta \varepsilon^*| \leq 0.005 \). To estimate the location of the critical points, we used the maxima of the \( C_V/(kT) \) vs. \( \varepsilon^* \) curves. Of our, the finite-size scaling may still be important for our system, but we expect that the critical points determined here for systems as large as \( L \times L = 44 \times 44 \) will not suffer from large deviation. Certainly, the qualitative conclusions drawn here will not be altered.

Results and discussion

Nonrandomness of mixing

The averaged heterocontacts per chain, \( N_{AB}(\varepsilon^*) \), in the AB diblock copolymer and AB blend as a function of the reduced interaction energy \( \varepsilon^* \) is shown in Fig. 2. As is expected, in the miscible region, where \( \varepsilon^* < 0 \), the system is characterized by a large number of A-B contacts, while in the immiscible region, where \( \varepsilon^* > 0 \), the A-B contacts
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Fig. 2. The dependence of the average number of unlike contacts per chain, $N_{AB}$, on the reduced molecular interaction energy, $\epsilon^*$, for the system of AB blend and block copolymer with $L_A = 10, L_B = 11$. (□): AB block copolymer, $N_{ch} = 88$; (○): AB blend, $N_{ch} = 176$

are rare, which results from the phase separation. Snapshot pictures of corresponding microstructures are shown in Fig. 3. The unexpected finding of the present simulation is the nonrandom mixing in the athermal limit ($\epsilon^* = 0$), which can be clearly seen from the snapshot picture of the athermal system, Fig. 4. Compared with the case of an AB blend, for which Cifra also found a similar nonrandomness of mixing, the nonrandomness of mixing in the block copolymer system is much more pronounced. To show this nonrandomness quantitatively, Fig. 5 gives the number of A-B contacts as a function of composition for the block copolymer system. In Fig. 5, the solid line is calculated according to the random mixing assumption in FH theory,

$$N_{AB} = N_T \cdot (\xi - 2) \phi_A \cdot \phi_B / N_{ch}$$

which corresponds to the athermal limit ($\epsilon^* = 0$). Obviously, $N_{AB}$ predicted by the random mixing assumption in the symmetric block copolymer system is higher by a factor of 1.7 (1.4 for the corresponding homopolymer blend) than the simulation results. We attribute this nonrandomness of mixing to the connectivity of monomers to form the chain-like molecule. We have further confirmed this arguments by simulating the athermal system of an AB monomeric mixture: it is found that the number of A-B contacts in the athermal limit follows Eq. (3) properly. Therefore, we can expect that the FH configurational entropy, Eq. (1), does not describe properly the entropy of mixing for chain-like molecules. This agrees with the theoretical analysis given by Freed.

Another unexpected finding of this simulation is the nonrandom location of the vacancies (solvents) despite the fact that our solvent is a nonselective good solvent, i.e., $\varepsilon_{AB} = \varepsilon > 0$ and $\varepsilon_{AA} = \varepsilon_{BB} = \varepsilon_{VV} = \varepsilon_{VA} = \varepsilon_{VB} = 0$. It was expected that a nonselective good solvent tends to favor the vacancies and monomeric units to remain mixed at all temperatures and that a bulk phase separation into two phases with one rich and one poor in vacancies will not occur. However, it can be seen from Fig. 3 that
the vacancies ($\phi_v = 0.0455$) in the blend and block copolymer systems are aggregated when $\varepsilon^* < 0$ as expected, but we should emphasize that the vacancies are mostly located at the interface between A- and B-rich phases for the case of $\varepsilon^* > 0$, which corresponds to a nonselective good solvent. Obviously, the aggregation of vacancies when $\varepsilon^* < 0$ can be interpreted through the negative mixing volume for the negative $\chi$ observed experimentally, i.e.,

$$V_m < V_A^0 + V_B^0$$  \hspace{1cm} (4)
Fig. 5. Average number of unlike contacts per chain in the bulk copolymer, $N_{AB}$, as a function of composition $\phi_A$ for three different $\varepsilon^*$. The solid line is calculated according to the random mixing assumption, Eq. (3)

where $V_m$ is the volume of the mixture, $V_A^0$ and $V_B^0$ are the volumes of pure A and B, respectively. However, the nonrandomness of the vacancy location for the case of $\varepsilon^* > 0$ might also result from the nonrandomness of A-B mixing existing even in the athermal system. Certainly, we are not yet in a position to draw final conclusions about it.

Relation between $\chi$ and $\varepsilon^*$

Following the assumption that $\chi$ represents a local (microscopic) interaction among monomer species, the FH interaction parameter of a symmetric AB diblock copolymer melt should be identical with that of a symmetric AB homopolymer blend when both systems are at the same temperature. In addition to that, the FH interaction parameter should also be linearly proportional to the reduced microscopic A-B interaction energy $\varepsilon^*$. However, Sariban and Binder's simulation results$^{4,5}$ have shown that $\chi$ depends on concentration and chain length for an AB homopolymer blend with solvent ($\phi_V \geq 0.2$). Freed et al.$^6$ have analyzed the FH model in great detail; they found that $\chi$ is just a phenomenological parameter instead of a local (microscopic) interaction among monomer species and it shows quite complicated dependencies on chain length and concentration. By including the higher-order corrections, Bawendi and Freed$^7$ proved that $\chi$ should be written as follows,

$$
\chi = \frac{\varepsilon^* (z - 2)}{2} + \frac{z \varepsilon^* \varepsilon^*}{4} + \varepsilon^* \left[ \frac{2}{L_A + 1} - \frac{1}{L_B + 1} \right] + \left( \frac{1}{L_A} - \frac{1}{L_B} \right)^2 \frac{z + 4}{z^2} \phi_A \cdot (1 - \phi_B) + O(z^{-3}, z^{-1} \varepsilon^*, \varepsilon^* \varepsilon^*, \frac{L_A^{-3}}{L_B^{-3}})
$$

for an AB blend with $\phi_A + \phi_B = 1$.

The dependence of $\chi$ on $\varepsilon^*$ can be obtained according to Eq. (2) in our simulation, which is shown in Fig. 6. It should be pointed out emphatically that for the same microscopic molecular interaction parameter $\varepsilon^*$ and AB composition, the $\chi$ value of the block copolymer is usually higher than that of the corresponding blend. It is confirmed again that $\chi$ is just a phenomenological parameter. It is not difficult to
understand that the entropic contribution to $\chi$ for a block copolymer is different from that of a blend due to the chemically bonded A and B sequences and thus results in different $\varepsilon^*$ dependencies of $\chi_{\text{block}}$ and $\chi_{\text{blend}}$. It also indicates that the microscopic origin of this difference is due to the difference of the mixing randomness between block copolymers and the corresponding blend systems.

The comparison between the theoretical prediction, Eq. (5), and the simulated results for the AB homopolymer blend is given in Fig. 7, where the contribution from the vacancies has been neglected due to their low concentration ($\phi_v = 0.0455$). It is shown that the agreement is quite good for the region of $\varepsilon^* > 0$, however the deviation is large for negative $\varepsilon^*$. The existing deviation might be due to the relative low order of correction in Eq. (5). For the block copolymer system, there is no corresponding theoretical formula for comparison.

Finally, we performed the simulation for a largely asymmetric block copolymer system with $L_A = 5$ and $L_B = 16$. The results are shown in Fig. 8. It seems that $\chi$ vs. $\varepsilon^*$ has no strong dependence on the composition for the block copolymer system. However, this is not conclusive and it needs more extensive studies on longer chain lengths and various AB compositions.

**Critical temperature of phase separation**

Our simulation gives the critical values of $\varepsilon^*$ and $\chi$ at the phase transition point, $\varepsilon_c^*(\text{blend}) = 0.025 \pm 0.002$, $\varepsilon_c^*(\text{block}) = 0.125 \pm 0.002$, and $\chi_c(\text{blend}) = 0.10 \pm 0.01$, $\chi_c(\text{block}) = 0.41 \pm 0.01$, for the systems with $L_A = 10$ and $L_B = 11$. Sariban and Binder\textsuperscript{4,5,20,21} have shown the large discrepancy between the prediction for the critical temperature $kT_c/\varepsilon$ resulting from the FH theory and the simulated critical temperature; the FH theory predicts a $T_c$ which is too high by a factor of 2 to 2.5, and it is expected that this will persist in the limit of infinite chain length. For the symmetric AB blend, the location of the transition in the Flory theory\textsuperscript{11} is predicted to be

$$\chi_c(\text{blend}) \cdot L = 2$$

(6)
The comparison between theoretically calculated results and Monte Carlo simulation outputs of $\chi$ vs. $\varepsilon^*$ for an AB blend with $L_A = 10$, $L_B = 11$. The solid line is calculated according to Eq. (5), while the symbols are corresponding Monte Carlo data.

Fig. 8. Relationship between $\chi$ and $\varepsilon^*$ in AB block copolymer systems with different composition. (□): $L_A = 10$, $L_B = 11$, $N_{ch} = 88$; (○): $L_A = 5$, $L_B = 16$, $N_{ch} = 88$

while the weak segregation theory of Leibler$^{17}$, Ohata et al.$^{18}$ and their Hatree corrections given by Fredrickson and Helfand$^{19}$ lead to the prediction of

$$\chi_c(\text{block}) \cdot L = 10,5 + 41/L^{1/3}$$

for the location of the microphase separation transition of symmetric block copolymers.

Apparently, Flory's theoretical prediction for the AB blend is higher by approximately a factor of 2 compared with our simulated results, and the Monte Carlo results of Sariban and Binder$^{4,5}$ agree with ours quite well. Concerning the AB block copolymer system, Eq. (7) is also too high by a factor of 3 compared with our results.

The mean-field prediction for symmetric diblock copolymer melts$^{17,18}$ and symmetric blends$^{19}$ of associated homopolymers at their respective phase separation transition is

$$\chi_c(\text{block})/\chi_c(\text{blend}) = 5,25 \quad (L \rightarrow \infty)$$

or for finite chain length$^{18}$,

$$\chi_c(\text{block})/\chi_c(\text{blend}) = (10,5 + 41L^{-1/3})/2 \approx 12,7 \quad (L = 21)$$

However, our simulations give

$$\chi_c(\text{block})/\chi_c(\text{blend}) = 4,1$$
which seems qualitatively compatible with the mean-field theoretical prediction of the Flory-Leibler theory, Eq. (8). It should be emphasized that this qualitative agreement can not attribute too much physical meaning to the microscopic interaction origin of $\chi$ in the mean-field theory. It is simply due to the nonrandomness of the mixing discussed before and the different $\varepsilon^*$ dependencies of $\chi$ for the block copolymer and corresponding blend systems.

**Conclusions**

The main results of our simulation for AB block copolymers and corresponding blends in very high concentration ($\phi_A + \phi_B = 0.9545$) can be summarized as follows:

1. It is found that the monomer-monomer mixing is not random even for athermal (i.e., $\varepsilon^* = 0$) block copolymer and corresponding blend systems. We have attributed this nonrandomness of mixing to the chain-like character of polymers which results in nonrandom A-B contacts. Due to the same reason, the FH configurational entropy contains some inaccuracies for mixtures of chain-like molecules. In other words, these inaccuracies are introduced through the neglect of most of the excluded volume restrictions in the estimation of configurational entropy.

2. It is also found that even for the case of nonselective good solvent, the vacancies (solvent molecules) are located at the interface between A- and B-rich phases. This is beyond the intuitive expectation that monomeric units and vacancies will remain mixed at all temperatures. The nonrandomness of vacancy location might also result from the nonrandom mixing of AB units in block copolymer and homopolymer blend systems which even shows up in the athermal limit.

3. The entropic contribution to the phenomenological Flory-Huggins interaction parameter $\chi$ has been further confirmed by the present simulation. It is shown that the $\varepsilon^*$ dependence of $\chi$ is quite complicated and the values for the cases of block copolymer and corresponding homopolymer blend systems are different. We found that the $\chi$ value of diblock copolymers is always higher than that of corresponding blends while their reduced microscopic A-B interaction energies, $\varepsilon^*$, are the same. In other words, the experimental value of $\chi$ of a blend at a certain temperature will be lower than that of the corresponding block copolymer. Therefore, we must note that the $\chi$ value obtained experimentally by fitting the Flory formula for an AB blend can not be directly applied to the corresponding AB block copolymer even when both systems have the same chemical moieties (i.e. the same $\varepsilon_{AB}$), the same composition and are at the same temperature.

4. The critical values of $\varepsilon^*$ and $\chi$ both for block copolymer and blend systems at the phase separation transition are obtained. By comparison with the mean-field theoretical predictions, we found that the theoretical prediction by Flory for the AB blend is too high by approximately a factor of 2 and that Fredrickson and Helfand's theoretical prediction for diblock copolymers is also too high by approximately a factor of 3. However, the ratio of $\chi_c$(block)/$\chi_c$(blend) = 4.1 obtained in this work is qualitatively compatible with the mean-field theoretical prediction, $\chi_c$(block)/$\chi_c$(blend) = 5.25, of the Flory-Leibler theory.

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Obviously, the present results are quite preliminary and we are not yet in a position to draw final conclusions on many matters. Further work on these important points is certainly needed. We are planning to perform additional simulations for various chain lengths and different AB compositions and to carry out a detailed comparison to the theory and pertinent experiments in the future work.

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2) M. Huggins, J. Am. Chem. Soc. 64, 1712 (1942)
5) A. Sariban, K. Binder, Macromolecules 21, 711 (1988)
13) E. Helfand, Macromolecules 8, 552 (1975)
14) E. Helfand, Z. R. Wassermann, Macromolecules 9, 879 (1976)
17) L. Leibler, Macromolecules 13, 1602 (1980)
22) P. Cifra, F. E. Karasz, W. J. MacKnight, Macromolecules 21, 446 (1988)