Graphical Abstract

Quantitative Study of Fluctuation Effects by Fast Lattice Monte Carlo Simulations. VI. Phase Behavior of Incompressible Symmetric Binary Homopolymer Blends

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August 5, 2016

Abstract

We reported the first Monte Carlo study of incompressible symmetric binary homopolymer blends. Using fast lattice Monte Carlo simulations (Q. Wang, *Soft Matter* 5 (2009) 4564) in a semi-grand-canonical ensemble with the cooperative motion

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algorithm generalized in our previous work (P. Zhang, Q. Wang, J. Phys. Chem. B 118 (2014) 12059-12067) and the finite-size scaling theory, we studied the critical properties of incompressible symmetric blends on the hexagonal lattice. We also used the replica-exchange scheme to greatly improve our sampling, and the multiple histogram reweighting technique to accurately locate the critical point. Instead of the self- and mutual-avoiding walk chain model and the nearest-neighbor interaction used in conventional lattice simulations, here we adopt the model system with multiple occupancy of lattice sites and the Kronecker δ -function interaction, which is the lattice counterpart of the standard model of incompressible binary homopolymer blends used in continuum polymer field theories. This enables direct comparisons between our simulation results and mean-field (Flory-Huggins) predictions without any parameter-fitting (e.g., to determine the Flory-Huggins χ -parameter). The effects of system fluctuations/correlations on the critical point and phase diagram of incompressible symmetric blends are therefore quantitatively and unambiguously revealed in this work.

Keywords: Polymer Blends, Cooperative Motion Algorithm, Flory-Huggins Theory, Fluctuation/Correlation Effects.

1 Introduction

This is the sixth paper in our series of study,¹⁻⁵ where fast lattice Monte Carlo (FLMC) simulations⁶ are directly compared with the corresponding polymer lattice field theories based on the same model system (Hamiltonian), thus without any parameter-fitting, to unambiguously and quantitatively reveal the effects of fluctuations/correlations either neglected or treated approximately in the theories. In the preceding paper in this series,⁵ we generalized the cooperative motion algorithm (CMA), the *only* Monte Carlo (MC) method for simulating incompressible and monodisperse polymer melts, originally proposed by Pukula⁷ for the self- and mutual-avoiding walk (SMAW) to the case of multiple occupancy of lattice sites (MOLS),⁶ and quantified the Gaussian and non-Gaussian fluctuations/correlations in the incompressible homopolymer melts in two dimensions (2D). We found that FLMC results approach the lattice Gaussian-fluctuation predictions with increasing ρ_0 (the total number of polymer segments on each lattice site), and that the leading order of non-Gaussian fluctuation effects on the single-chain properties is inversely proportional to ρ_0^2 .⁵ The effects of fluctuations/correlations, however, are extremely important for systems close to a phase transition point and dominate their thermodynamic and dynamic properties. Two well-known examples are polymer blends (in the melt state) near the critical point and diblock copolymer melts near the order-disorder transition. By virtue of the generalized CMA,⁵ we study in this work the effects of fluctuations/correlations on the critical point and phase diagram of incompressible symmetric binary homopolymer blends on the 2D hexagonal lattice, where the system fluctuations/correlations are expected to be much stronger than those in three dimensions (3D).

Binary homopolymer blends A/B undergo phase separation with increasing immiscibility between chains of different types. For symmetric blends where the only difference between A and B chains is their labeling, the well-known Flory-Huggins (FH) theory⁸ predicts a critical point at $(\chi N)_c = 2$, where χ is the FH interaction parameter between A and B segments and N the total number of segments on each chain. As a mean-field theory, however, FH theory neglects the system fluctuations/correlations, which are crucial near the critical point. As many groups have reported experimental, theoretical, and simulation studies of binary homopolymer blends,⁹ in the following we briefly summarize only molecular simulation studies on the phase behavior of symmetric blends in the melt state that are closely related to our work.

Independent of yet complementary to experiment and theory, molecular simulation can provide the “exact” properties of a model system within controllable statistical errors and finite-size effects,¹⁰ and is therefore best suited to test theoretical predictions. Using MC simulations of SMAW chains on the simple cubic lattice, Sariban et al. reported the first molecular simulation study on the critical properties of symmetric blends at a polymer volume fraction of $\phi = 0.8$ and found that the critical exponents of short-chain ($N = 4 \sim 32$) systems belong to the 3D Ising universality class, instead of the mean-field behavior predicted by FH theory.¹¹ Subsequently, using MC simulations of the 3D bond-fluctuation model¹² with the multiple-histogram reweighting technique,¹³ Deutsch and Binder studied the cross-over phenomenon from the Ising critical behavior to the mean-field behavior for symmetric blends of much longer chain lengths ($N = 8 \sim 512$) at $\phi = 0.5$.¹⁴ These simulations were performed in a semi-grand-canonical ensemble

and the results were analyzed using the finite-size scaling theory¹⁵ to obtain the system phase behavior in the thermodynamic limit. On the other hand, Cifra et al. performed MC simulations of SMAW chains ($N = 20$) at $\phi = 10/11$ on both the square¹⁶ and the simple cubic¹⁷ lattices in a canonical ensemble. To test the nonrandom-mixing theory for compressible binary blends based on the quasi-chemical approximation of Guggenheim, they also performed MC simulations of SMAW chains ($N = 30$) on the simple cubic lattice in an isothermal-isobaric ensemble for miscible blends, and in an isothermal-isobaric semi-grand-canonical ensemble for immiscible blends.¹⁸ Off-lattice MC or molecular dynamics simulations of the phase behavior of symmetric blends in 3D have also been reported by de Pablo and co-workers^{19,20} and by Kremer and co-workers.²¹ The phase behavior of symmetric blends in 3D is therefore well understood.

In contrast, only Cavallo et al. reported MC simulations in a semi-grand-canonical ensemble to study the phase behavior of symmetric blends in 2D²² (in addition to the aforementioned work by Cifra et al.¹⁶). They used the 2D limit of the 3D bond-fluctuation model (i.e., ultrathin film confined in two lattice layers, $N = 16 \sim 256$ at $\phi \leq 0.5$) and found that the system belongs to the 2D Ising universality class.²² They also found that the critical temperature $T_c \sim N^{5/8}$,^{22,23} different from $T_c \sim N$ found in 3D simulations;^{11,14,20,21} this highlights the effects of dimensionality on the system fluctuations/correlations for SMAW chains.

As the standard and most studied model of binary polymer blends in polymer field theories,²⁴ incompressible symmetric blends are probably the simplest case for FH theory.²⁵ In all of the above lattice MC simulations, however, vacancies representing

small molecules of a neutral and good solvent were introduced as required by their MC trial moves (i.e., hopping, crank-shaft, end-rotation, and reptation); their systems under investigation are therefore not incompressible binary blends, but incompressible ternary blends (or equivalently compressible binary blends). The presence of such vacancies dilutes the system and makes the two polymer species more miscible. More significantly, this, together with the use of a nearest-neighbor interaction parameter, prevents unambiguous quantification of the fluctuation/correlation effects on the critical properties of symmetric blends, due to the complication of determining the χ parameter used in FH theory from the simulations.

In this work, we study the critical properties of incompressible symmetric blends in 2D using FLMC simulations⁶ with the generalized CMA⁵ in a semi-grand-canonical ensemble and the finite-size scaling theory.¹⁵ We also use the replica-exchange scheme²⁶ to greatly improve our sampling, and the multiple histogram reweighting technique¹³ to accurately locate the critical point and to estimate the thermodynamic quantities. To the best of our knowledge, this is the first MC study of incompressible symmetric blends.²⁷ Furthermore, instead of the SMAW chain model and the nearest-neighbor interaction used in conventional lattice simulations, here we adopt the model system with MOLS and the Kronecker δ -function interaction, which is the lattice counterpart of the standard model of incompressible binary homopolymer blends used in continuum polymer field theories (i.e., Model C in Ref. [24]). This enables direct comparisons between our FLMC results and FH predictions without any parameter-fitting (e.g., to determine the χ -parameter). The effects of system fluctuations/correlations on the critical point and phase diagram of incompressible symmetric blends are therefore unambiguously

and quantitatively revealed in this work. We finally note that, while this study is for incompressible symmetric blends on the hexagonal lattice, our method (i.e., FLMC simulations⁶ with the generalized CMA⁵ in a semi-grand-canonical ensemble) is quite general and not limited to either incompressible systems or the hexagonal lattice.

2 Model and Methods

2.1 Model system

We consider a model system of incompressible symmetric binary homopolymer blends consisting of n_A chains of type A and $n_B = n - n_A$ chains of type B, each having N segments, on the hexagonal lattice of $V = L^2$ sites with the periodic boundary conditions applied in all directions. Each segment occupies one lattice site, and each lattice site is occupied by a total of $\rho_0 = nN/V$ segments. In this work, we take the lattice spacing and $k_B T$ as the unit of length and energy, respectively, with k_B being the Boltzmann constant and T the thermodynamic temperature. The system Hamiltonian has two parts,

$$\mathcal{H} = \sum_{k=1}^n h_k^C + \mathcal{H}^E, \quad (1)$$

where h_k^C is the Hamiltonian due to the connectivity of the k^{th} chain; $h_k^C = 0$ if its connectivity is maintained and ∞ otherwise. $\mathcal{H}^E$ is the Hamiltonian due to the non-bonded interaction and given by

$$\mathcal{H}^E = \frac{\chi}{\rho_0} \sum_{\mathbf{r}} \hat{\rho}_A(\mathbf{r}) \hat{\rho}_B(\mathbf{r}), \quad (2)$$

where $\hat{\rho}_A(\mathbf{r}) \equiv \sum_{k=1}^{n_A} \sum_{s=1}^N \delta_{\mathbf{r}, \mathbf{R}_{k,s}}$ and $\hat{\rho}_B(\mathbf{r}) \equiv \sum_{k=n_A+1}^n \sum_{s=1}^N \delta_{\mathbf{r}, \mathbf{R}_{k,s}}$ are the microscopic density of segments of type A and B, respectively, at lattice site $\mathbf{r}$, with $\delta_{\mathbf{r}, \mathbf{R}_{k,s}}$ denoting

the Kronecker δ -function and $\mathbf{R}_{k,s}$ the spatial position of the s^{th} segment on the k^{th} chain. Finally, χ is the Flory-Huggins parameter characterizing the repulsion between an A and a B segment at the same lattice site.

2.2 Fast Lattice Monte Carlo Simulations

To investigate the critical point and phase diagram of our model system, we perform fast lattice Monte Carlo (FLMC) simulations in a semi-grand-canonical ensemble, where the total number of chains n and the chemical potential difference between A and B chains $\Delta\mu \equiv \mu_A - \mu_B = 0$ are fixed.¹¹ The semi-grand-canonical partition function is given by

$$\mathcal{Z}(\Delta\mu, n) = \sum_{n_A=0}^n \frac{\exp[\Delta\mu(n_A - n/2)]}{n_A!(n - n_A)!} \prod_{k=1}^n \prod_{s=1}^N \sum_{\mathbf{R}_{k,s}} \cdot \exp(-\mathcal{H}) \cdot \prod_{\mathbf{r}} \delta_{\hat{\rho}_A(\mathbf{r}) + \hat{\rho}_B(\mathbf{r}), \rho_0}, \quad (3)$$

where $n_A!$ and $(n - n_A)!$ are due to the indistinguishability of A and B chains, respectively, and the last term enforces the incompressibility constraint at all lattice sites.

We use three types of trial moves to efficiently sample the configuration space in our FLMC simulations. The cooperative motion algorithm (CMA) is the only way to update chain configurations in monodisperse and incompressible polymer melts; it was first proposed by Pakula for the self- and mutual-avoiding walk (i.e., at $\rho_0 = 1$)⁷ and was recently generalized by us to the case of $\rho_0 > 1$.⁵ Its acceptance criterion is

$$\mathcal{P}_{acc}^{\text{CMA}} = \min [1, \exp(-\Delta\mathcal{H}^E)], \quad (4)$$

where $\Delta\mathcal{H}^E$ is the difference in the non-bonded Hamiltonian $\mathcal{H}^E$ between the trial and the current configurations. On the other hand, the chain relabeling (RL) trial move (i.e., $A \rightarrow B$ or $B \rightarrow A$), where the type of a randomly chosen chain is changed while its

configuration is kept, is used to update n_A . If an A chain is chosen, the relabeling makes $n_A \rightarrow n_A - 1$ and the trial configuration is accepted according to

$$\mathcal{P}_{acc}^{RL}(n_A \rightarrow n_A - 1) = \min [1, \exp (-n_A \Delta\mu - \Delta\mathcal{H}^E)] . \quad (5)$$

Similarly, if a B chain is chosen, the relabeling makes $n_A \rightarrow n_A + 1$ and the trial configuration is accepted according to

$$\mathcal{P}_{acc}^{RL}(n_A \rightarrow n_A + 1) = \min [1, \exp (n_A \Delta\mu - \Delta\mathcal{H}^E)] . \quad (6)$$

About $(5 \sim 10) \times 10^6$ Monte Carlo steps (MCS) are performed in each simulation, where one MCS is defined as on average one segment trial move (due to CMA) for each segment in the system.⁵ One RL trial move is attempted every 5 MCS. We also use the replica-exchange (RE) technique to improve our sampling efficiency. The acceptance criterion for swapping two replicas at χ_i and χ_j having E_i and E_j , respectively, is

$$\mathcal{P}_{acc}^{RE} = \min \left\{ 1, \exp \left[\frac{(\chi_i - \chi_j)(E_i - E_j)}{\rho_0} \right] \right\} , \quad (7)$$

where $E \equiv \sum_{\mathbf{r}} \hat{\rho}_A(\mathbf{r}) \hat{\rho}_B(\mathbf{r})$. The odd-even RE²⁸ scheme is adopted here, which is attempted every 10 MCS. We choose the χ -range to be broad enough to cover the critical point, and use $R = 8 \sim 40$ replicas (depending on the system) such that the average acceptance rate of RE trial moves is $\geq 20\%$.

We further use the self-consistent multiple histogram reweighting technique¹³ (which is nicely combined with RE) to analyze our simulation results, so that the critical point can be accurately located. With $H_i(n_A, E)$ denoting the total number of sampled configurations at χ_i having n_A and E , we have

$$\mathcal{Z}_j = \sum_{n_A} \sum_E \frac{\sum_{i=1}^R H_i(n_A, E)/g_i}{\sum_{i=1}^R \exp [(\chi_j - \chi_i) E/\rho_0] M_i/g_i \mathcal{Z}_i} , \quad (8)$$

where $\mathcal{Z}_j$ ($j = 1, \dots, R$) is proportional to the semi-grand-canonical partition function at χ_j with $\mathcal{Z}_1 = 1$, $M_i \equiv \sum_{n_A} \sum_E H_i(n_A, E)$, and $g_i \equiv 1 + 2\tau_i$ with τ_i being the correlation length of E for the samples collected at χ_i and estimated using the correlation-function method.²⁹ Once these $R - 1$ equations are solved using the globally convergent Newton-Raphson method³⁰ with the convergence criterion of their maximum absolute residual error being less than 10^{-12} , we estimate the probability of the system having n_A and E at any $\chi \in [\chi_1, \chi_R]$ (we order the χ -values in RE such that $\chi_i < \chi_{i+1}$), $p_\chi(n_A, E)$ with $\sum_{n_A} \sum_E p_\chi(n_A, E) = 1$, as

$$\mathcal{Z}(\chi)p_\chi(n_A, E) = \frac{\sum_{i=1}^R H_i(n_A, E)/g_i}{\sum_{i=1}^R \exp[-(\chi_i - \chi)E/\rho_0] M_i/g_i \mathcal{Z}_i}, \quad (9)$$

where $\mathcal{Z}(\chi)$ is proportional to the semi-grand-canonical partition function at χ and estimated as $\mathcal{Z}(\chi) = \sum_{n_A} \sum_E \mathcal{Z}(\chi)p_\chi(n_A, E)$. Finally, the ensemble average of any physical quantity A at χ is given by

$$\langle A \rangle (\chi) = \sum_{n_A} \sum_E A p_\chi(n_A, E). \quad (10)$$

In our FLMC simulations, we calculate the internal energy per chain as

$$u_c = \chi N \frac{\langle E \rangle}{\rho_0^2 V} \quad (11)$$

and the specific heat as

$$\frac{C_v}{k_B} \equiv \frac{1}{n} \left[\langle (\mathcal{H}^E)^2 \rangle - \langle \mathcal{H}^E \rangle^2 \right] = \frac{\chi^2}{n \rho_0^2} \left[\langle E^2 \rangle - \langle E \rangle^2 \right]. \quad (12)$$

To characterize the phase behavior of symmetric blends, we define the order parameter $\psi \equiv |n_A - n_B|/n = |2n_A/n - 1|$, and calculate $\langle \psi \rangle$ via Eq. (10) and its fluctuation σ_ψ^2 , also

known as the susceptibility,¹⁴ as

$$\sigma_\psi^2 = n \left(\langle \psi^2 \rangle - \langle \psi \rangle^2 \right). \quad (13)$$

In the thermodynamic limit, both C_v and σ_ψ^2 diverge at the critical point $(\chi N)_c$. For finite systems used in simulations, however, the location of the critical point is shifted and the divergence is rounded due to the finite-size effects.¹⁵ We therefore use the Binder's second- and fourth-order cumulants³¹ B_2 and B_4 defined, respectively, as

$$B_2(\chi) \equiv \frac{\langle \psi^2 \rangle}{\langle \psi \rangle^2} \quad (14)$$

and

$$B_4(\chi) \equiv \frac{\langle \psi^4 \rangle}{\langle \psi^2 \rangle^2} \quad (15)$$

to estimate $(\chi N)_c$, which for different L intersect closely around $(\chi N)_c$ and exhibit negligible finite-size effects. With χ_c estimated, we then determine the critical exponent β and the critical amplitude B given by

$$\langle \psi \rangle(\chi) = B t^\beta, \quad (16)$$

where $t \equiv (\chi - \chi_c)/\chi_c$.

2.3 The Flory-Huggins Predictions

For our model system given in Sec. 2.1, one can easily derive the corresponding self-consistent field theory under the mean-field approximation,²⁴ which is identical to the Flory-Huggins (FH) theory.²⁵ It gives the system Helmholtz free energy of mixing ΔF_{mix} as

$$\frac{\Delta F_{\text{mix}}}{\rho_0 V} = \frac{\phi}{N} \ln \phi + \frac{1-\phi}{N} \ln(1-\phi) + \chi \phi(1-\phi), \quad (17)$$

where ϕ is the volume fraction of A chains and is related to the order parameter according to $\langle\psi\rangle = |2\phi - 1|$. The binodal curve is then given by $[\partial(\Delta F_{\text{mix}}/\rho_0 V)/\partial\phi]_\chi = 0$, i.e.,

$$\ln \frac{\phi}{1-\phi} + \chi N(1-2\phi) = 0, \quad (18)$$

which is symmetric about $\phi = 1/2$. On the other hand, the critical point is given by $[\partial^2(\Delta F_{\text{mix}}/\rho_0 V)/\partial\phi^2]_\chi = 0$ and $[\partial^3(\Delta F_{\text{mix}}/\rho_0 V)/\partial\phi^3]_\chi = 0$, i.e.,

$$\phi_{c,\text{FH}} = 1/2, \quad (19)$$

and

$$(\chi N)_{c,\text{FH}} = 2. \quad (20)$$

Finally, Taylor-expanding Eq. (18) with respect to ϕ around $\phi = \phi_{c,\text{FH}}$ and retaining only the leading order of $\phi - \phi_{c,\text{FH}}$, one obtains

$$|\phi - \phi_{c,\text{FH}}| = \sqrt{\frac{3}{8}} [\chi N - (\chi N)_{c,\text{FH}}]^{1/2}. \quad (21)$$

Comparing the above with Eq. (16), one then finds the critical exponent β and critical amplitude B given by FH theory as

$$\beta_{\text{FH}} = 1/2, \quad B_{\text{FH}} = \sqrt{3}/2. \quad (22)$$

3 Results and Discussion

Our model system of incompressible symmetric binary homopolymer blends on the hexagonal lattice is specified by four parameters: the chain length N , the Flory-Huggins (FH) interaction parameter χ characterizing the repulsion between an A and a B segment at the same lattice site, the box size L controlling the finite-size effects in our fast lattice

Monte Carlo (FLMC) simulations, and the total number of segments at each lattice site ρ_0 controlling the system fluctuations/correlations in the simulations; note that the mean-field (FH) theory is exact in the limit of $\rho_0 \rightarrow \infty$, where the product χN is the only parameter controlling the system properties. At given ρ_0 and N , we perform FLMC simulations at different L , and estimate the critical point $(\chi N)_c$ and the binodal curve in the thermodynamic limit (i.e., $L \rightarrow \infty$) using the finite-size scaling theory.¹⁵ Due to our use of the Kronecker δ -function interaction instead of the nearest-neighbor interaction, phase separation does not occur at $N = 1$ ³² or $\rho_0 = 1$. For $N = 2$, we find that the phase separation occurs at $\rho_0 \geq 3$. We therefore first fix $N = 2$ and investigate the effects of ρ_0 on the critical point and binodal curve, then perform FLMC simulations at $N = 40$ to investigate the effects of N . In Sec. 3.1 below, we take the system with $N = 2$ and $\rho_0 = 3$ as an example and show how to accurately determine in FLMC simulations the critical point and the binodal curve in the thermodynamic limit. We then present in Sec. 3.2 their dependence on ρ_0 and N .

3.1 The example case of $N = 2$ and $\rho_0 = 3$

3.1.1 Binder's cumulants and critical point

According to the finite-size scaling theory,^{15,31} the Binder's second- and fourth-order cumulants B_2 and B_4 , respectively, calculated in simulation boxes of different length L intersect closely around the critical point in the thermodynamic limit $(\chi N)_c$; this is shown in Fig. 1. Using the intersections of B_2 and B_4 at the three largest L ($= 40, 60$, and 80), we estimate $(\chi N)_c = 7.50 \pm 0.01$, which is much larger than the mean-field prediction of $(\chi N)_{c,\text{FH}} = 2$.

Figure 1: Binder's (a) second-order cumulant B_2 and (b) fourth-order cumulant B_4 obtained from our FLMC simulations in boxes of various length L . The inset in each part shows results near the estimated critical point $(\chi N)_c \approx 7.50$ in the thermodynamic limit, which is marked by a vertical line. $N = 2$ and $\rho_0 = 3$.

We also note that, at small χN , the system is in the miscible region and the probability distribution of $\psi' \equiv 2n_A/n - 1$ can be approximated by a Gaussian function, i.e., $P(\psi') = A_1 \exp(-\psi'^2/C_1)$, which gives $B_2 = \pi/2$ and $B_4 = 3$.³³ On the other hand, at large χ , the system is in the phase-separated region, and the probability distribution of ψ' can be approximated by the superposition of two well-separated Gaussian functions, i.e., $P(\psi') = A_2 \{\exp[-(\psi' - \psi'_0)^2/C_2] + \exp[-(\psi' + \psi'_0)^2/C_2]\}$, which gives $B_2 = B_4 = 1$.³³

3.1.2 Order parameter and its fluctuation

In the thermodynamic limit (i.e., $L \rightarrow \infty$), the ensemble-averaged order parameter $\langle \psi \rangle$ is 0 for $\chi N < (\chi N)_c$ and increases monotonically from 0 to 1 with increasing χ for

Figure 2: Ensemble-averaged order parameter $\langle\psi\rangle$ obtained from our FLMC simulations in boxes of various L as a function of (a) χN and (b) the reduced distance t above $(\chi N)_c$. The solid curve in part (a) is our constructed binodal curve in the thermodynamic limit as explained in the main text. The vertical line in part (a) marks the estimated $(\chi N)_c \approx 7.50$, and those in part (b) mark the boundaries between regimes I, II, and III in the case of $L = 80$; see main text for details. $N = 2$ and $\rho_0 = 3$.

$\chi N > (\chi N)_c$. Fig. 2(a) shows $\langle\psi\rangle$ as a function of χN obtained from our simulations at different L , we see that at small χN , $\langle\psi\rangle$ is not 0 due to the finite-size effects and decreases monotonically towards 0 with increasing L . At large χN , however, $\langle\psi\rangle$ at different L collapse, indicating that the finite-size effects are negligible here.

Fig. 2(b) shows $\langle\psi\rangle$ as a function of the reduced distance from the critical point $t \equiv \chi N / (\chi N)_c - 1$. In the thermodynamic limit, the power-law relation $\langle\psi\rangle = Bt^\beta$ is expected for small $t > 0$ with β being the critical exponent and B the critical amplitude. In finite-size systems, however, three different regimes are observed, as shown in Fig. 2(b)

for $L = 80$. Here the two vertical lines at $t_1 \approx 0.015$ and $t_2 \approx 0.049$ are determined by maximizing the t -range $t_1 < t < t_2$ under the constraint that the relative variation of $k \equiv d \ln \langle \psi \rangle / d \ln t$ within this range is smaller than 3%. In regime I (i.e., very close to the critical point), the correlation length of the composition fluctuations is limited by L and $\langle \psi \rangle$ becomes flat; also note that the finite-size effects here decrease with increasing L . The expected power-law behavior is found in regime II, where the correlation length is smaller than L and the system is still in the critical region; here we estimate $\beta = \int_{t_1}^{t_2} k dt / (t_2 - t_1) = 0.111 \pm 0.007$ and $B = \int_{t_1}^{t_2} (\langle \psi \rangle / t^k) dt / (t_2 - t_1) = 1.15 \pm 0.02$ using our largest simulation box of $L = 80$. Finally, regime III is out of the critical region and the power-law relation does not hold.

To construct the binodal curve in the thermodynamic limit, we use the power-law relation $\langle \psi \rangle = B t^\beta$ with B and β estimated above to generate the binodal curve in both regimes I (where the finite-size effects are significant) and II (where the finite-size effects are negligible), and use the simulation data in regime III (where the finite-size effects are negligible). The so-obtained binodal curve in the thermodynamic limit is shown in Fig. 2(a), which can be compared with our simulation results obtained at finite L .

Fig. 3(a) shows the fluctuation of the order parameter (or the susceptibility), σ_ψ^2 , obtained from our FLMC simulations in boxes of various L as a function of χN . We see the well-known rounding and shifting of the peak of σ_ψ^2 ; the maximum value of σ_ψ^2 increases and its location approaches $(\chi N)_c$ monotonically with increasing L . Furthermore, Fig. 3(b) shows that the location of the maximum of σ_ψ^2 , denoted by $(\chi N)_1^*$, follows the linear relation $(\chi N)_1^* = 7.49 - 10.2/L$, obtained from the unweighted linear least-squares

Figure 3: (a) Semi-logarithmic plot of the fluctuation of the order parameter σ_ψ^2 obtained from our FLMC simulations in boxes of various L as a function of χN , where the vertical line marks the estimated $(\chi N)_c \approx 7.50$. (b) Dependence on L of the maximum of σ_ψ^2 , denoted by $(\sigma_\psi^2)^*$ (shown with the right and upper axes on logarithmic scales), and that of its location $(\chi N)_1^*$ (shown with the left and lower axes) obtained from our FLMC simulations; see main text for details. $N = 2$ and $\rho_0 = 3$.

fitting using our data from the three largest L , and that its value extrapolated to the thermodynamic limit (i.e., $L \rightarrow \infty$) is consistent with $(\chi N)_c = 7.50 \pm 0.01$ estimated using the Binder's cumulants. On the other hand, Fig. 3(b) also shows that the peak value of σ_ψ^2 follows the power-law relation $(\sigma_\psi^2)^* = 0.27L^{1.7}$, again obtained from the unweighted linear least-squares fitting using our data from the three largest L , and diverges in the thermodynamic limit.

3.1.3 Internal energy and specific heat

The internal energy per chain u_c is related to the ensemble average of the energy level $E \equiv \sum_{\mathbf{r}} \hat{\rho}_A(\mathbf{r}) \hat{\rho}_B(\mathbf{r})$ according to Eq. (11). Fig. 4(a) shows $\langle E \rangle / \rho_0^2 V$ obtained from our FLMC simulations in boxes of various L as a function of χN . At given L , $\langle E \rangle / \rho_0^2 V$ decreases monotonically with increasing χN . On the other hand, at both small and large χN far away from $(\chi N)_c$, the system exhibits negligible finite-size effects and $\langle E \rangle / \rho_0^2 V$ from different L collapse together. At χN close to $(\chi N)_c$, however, noticeable differences are found in $\langle E \rangle / \rho_0^2 V$, which increases with increasing L . We note that u_c exhibits similar behavior to $\langle E \rangle / \rho_0^2 V$ (data not shown).

The specific heat C_v/k_B is related to the fluctuations of E according to Eq. (12). Fig. 4(b) shows that C_v/k_B obtained from our FLMC simulations exhibits a maximum with varying χN at given L . The location of the maximum, denoted by $(\chi N)_2^*$, follows the relation $(\chi N)_2^* = 7.50 - 7.26/L$ for large L as shown in Fig. 4(c), which is obtained from the unweighted linear least-squares fitting using our data from the three largest L , and its value extrapolated to the thermodynamic limit (i.e., $L \rightarrow \infty$) is consistent with both $(\chi N)_c$ estimated using the Binder's cumulants and $(\chi N)_1^*(L \rightarrow \infty)$ given above. On the other hand, the maximum value of C_v , denoted by C_v^* , increases monotonically with increasing L . Finally, Fig. 4(b) also shows that the finite-size effects on C_v/k_B are negligible at χN far from $(\chi N)_c$, where our simulation results from different L collapse together.

Figure 4: Dependence on χN of (a) the ensemble-averaged energy level $\langle E \rangle$ and (b) the specific heat C_v/k_B obtained from our FLMC simulations in boxes of various L , where the vertical line in each part marks the estimated $(\chi N)_c \approx 7.50$. Part (c) shows the dependence on L of the maximum of the specific heat, denoted by C_v^* (shown with the right and upper axes on logarithmic scales), and that of its location $(\chi N)_2^*$ (shown with the left and lower axes) obtained from our FLMC simulations; see main text for details. $N = 2$ and $\rho_0 = 3$.

3.2 Critical points and binodal curves at various N and ρ_0

For $N = 2$ and 40, we perform FLMC simulations at various ρ_0 and estimate the critical point $(\chi N)_c$ and the binodal curve in the thermodynamic limit using the finite-size analysis technique described above. Fig. 5 shows the shift of the critical point $(\chi N)_c$ from the mean-field value, $(\chi N)_{c,\text{FH}} = 2$, as a function of ρ_0 for $N = 2$ and 40. This shift is due to the system fluctuations/correlations controlled by ρ_0 , which stabilize the homogeneous (mixed) phase. In both cases, the shift monotonically decreases with increasing ρ_0 , and exhibits a power-law relation with ρ_0 at large ρ_0 ; the unweighted linear least-squares fitting for the last three points at $N = 2$ gives $(\chi N)_c - 2 \propto \rho_0^k$ with $k = -0.98 \pm 0.03$. On the other hand, We see that the smallest ρ_0 where the phase separation can occur is 2 for $N = 40$, in contrast to 3 for $N = 2$. Note that the two curves for $N = 2$ and 40 cross at

Figure 5: Logarithmic plot of the shift of $(\chi N)_c$ from the mean-field prediction $(\chi N)_{c,\text{FH}} = 2$ as a function of the total number of segments at each lattice site ρ_0 . The straight line is obtained by the unweighted linear least-squares fitting using data for $N = 2$ at the three largest ρ_0 , with its slope k given in the legend; see main text for details.

ρ_0 between 3 and 4; that is, the $N = 40$ case has smaller shift at $\rho_0 = 3$ but larger shift at larger ρ_0 . Finally, these two curves merge together at large ρ_0 as expected.

We also note that the difference in $(\chi N)_c$ between $N = 2$ and 40 is small for all ρ_0 as shown in Fig. 5; our results therefore approximately give $\chi_c \sim N^{-1}$ (or equivalently the critical temperature $T_c \sim N$), in agreement with both simulation results in 3D^{11, 14, 20, 21} and the FH prediction. This does not contradict the finding of $T_c \sim N^{5/8}$ by Cavallo et al.,^{22, 23} which is due to the fact that in 2D their chains obeying the self- and mutual-avoiding walk have the number of contacts between segments of different chains $z_c \sim N^{-3/8}$.³⁴ This can be seen from $k_B(T/\epsilon)_c = Nz_c$ (i.e., Eq. (6) of Ref. [23]), obtained by combining the FH prediction, Eq. (20), with the mapping of $\chi = 2z_c\epsilon/k_BT$, where ϵ is the interaction parameter (independent of N) between segments used in the lattice MC simulations of Cavallo et al.^{22, 23} For our model with multiple occupancy of lattice sites, chains in 2D are still interpenetrating and z_c is thus independent of N .

To construct the binodal curve in the thermodynamic limit at each set of N and ρ_0 , we use the relation $\langle\psi\rangle = Bt^\beta$ with β and B estimated using the procedure explained in Sec. 3.1.2. Fig. 6 shows the critical exponent β as a function of $1/\rho_0$ for $N = 2$ and 40. With increasing ρ_0 , β increases monotonically towards the mean-field value of $\beta_{\text{FH}} = 1/2$. On the other hand, at small ρ_0 , β is smaller than the value of $1/8$ given by the 2D Ising model.³⁵ This is probably because we use the Kronecker δ -function interaction instead of the nearest-neighbor interaction.³² Finally, at given ρ_0 , β for $N = 40$ is larger than that for $N = 2$.

Figure 6: Semi-logarithmic plot of the critical exponent β obtained from our FLMC simulations as a function of $1/\rho_0$. The horizontal dashed and solid lines mark, respectively, the mean-field (FH) and the 2D Ising values.

With $(\chi N)_c$, β and B obtained above, we then construct the binodal curves in the thermodynamic limit following the procedure explained in Sec. 3.1.2. Figs. 7(a) and 7(b) show the binodal curves at various ρ_0 for $N = 2$ and 40, respectively. We see that, with increasing ρ_0 , the binodal curve monotonically approaches the mean-field (FH) prediction given by Eq. (18). In addition, the binodal curve in the neighborhood of the critical point is flatter at smaller ρ_0 . Finally, for given ρ_0 , the binodal curve at $N = 2$ is flatter than that at $N = 40$; the former therefore lies below the latter except in the case of $\rho_0 = 3$. These results are in accordance with Figs. 5 and 6.

Figure 7: Binodal curves in the thermodynamic limit at various ρ_0 for (a) $N = 2$ and (b) $N = 40$. The mean-field (FH) prediction is given by Eq. (18), and the critical points are marked by open circles.

4 Conclusions

Using fast lattice Monte Carlo (FLMC) simulations⁶ in a semi-grand-canonical ensemble with the cooperative motion algorithm⁷ generalized in our previous work⁵ and the finite-size scaling theory,¹⁵ we have studied the critical properties of incompressible symmetric binary homopolymer blends on the hexagonal lattice. We have also used the replica-exchange scheme²⁶ to greatly improve our sampling, and the multiple histogram reweighting technique¹³ to accurately locate the critical point. Instead of the self- and mutual-avoiding walk chain model and the nearest-neighbor interaction used in conventional lattice simulations, here we adopt the model system with multiple occupancy of lattice sites and the Kronecker δ -function interaction, which is the lattice counterpart of the standard model of incompressible binary homopolymer blends used in continuum

polymer field theories (i.e., Model C in Ref. [24]). This enables direct comparisons between our FLMC results and mean-field (Flory-Huggins, FH) predictions without any parameter-fitting (e.g., to determine the FH χ -parameter). The effects of system fluctuations/correlations on the critical point and phase diagram of incompressible symmetric blends are therefore quantitatively and unambiguously revealed in this work.

Our model system is specified by four parameters: the chain length N , the χ parameter characterizing the repulsion between an A and a B segment at the same lattice site, the box size L controlling the finite-size effects in our FLMC simulations, and the total number of segments at each lattice site ρ_0 controlling the system fluctuations/correlations in the simulations; note that the mean-field theory is exact in the limit of $\rho_0 \rightarrow \infty$, where the product χN is the only parameter controlling the system properties. At given ρ_0 and N , we perform FLMC simulations at different L , and estimate the critical point $(\chi N)_c$ and the binodal curve in the thermodynamic limit (i.e., $L \rightarrow \infty$) using the finite-size scaling theory.¹⁵

Our $(\chi N)_c$ estimated using the Binder's second- and fourth-order cumulants³¹ is consistent with those obtained by extrapolating to the thermodynamic limit the peak position of either the fluctuations of the order parameter ψ (known as the susceptibility¹⁴) or the specific heat; due to the finite-size effects, both peaks are rounded and shifted in our simulations. The shift of $(\chi N)_c$ from the mean-field value of $(\chi N)_{c,\text{FH}} = 2$ as a function of ρ_0 is shown in Fig. 5 for $N = 2$ and 40. In both cases, the shift monotonically decreases with increasing ρ_0 , and we find $(\chi N)_c - 2 \propto \rho_0^k$ with $k = -0.98 \pm 0.03$ at large ρ_0 .

In finite-size systems, three different regimes are observed as $t \equiv \chi N / (\chi N)_c - 1 > 0$ varies: Both regimes I and II are in the critical region (i.e., at small t); the finite-size effects are significant in regime I, where the correlation length of the composition fluctuations is limited by L , but negligible in regime II, where the correlation length is smaller than L and the power-law relation $\langle \psi \rangle = Bt^\beta$ is found. The effects of ρ_0 on the critical exponent β are shown in Fig. 6 for $N = 2$ and 40. With increasing ρ_0 , β increases monotonically towards the mean-field value of $\beta_{\text{FH}} = 1/2$.

On the other hand, regime III (i.e., at large t) is out of the critical region and the power-law relation does not hold. To construct the binodal curve in the thermodynamic limit, we use the obtained power-law relation in both regimes I and II, and the simulation data in regime III (where the finite-size effects are negligible). The so-obtained binodal curves in the thermodynamic limit are shown in Fig. 7. With increasing ρ_0 , the binodal curve monotonically approaches the mean-field (FH) prediction given by Eq. (18). In addition, the binodal curve in the neighborhood of the critical point is flatter at smaller ρ_0 . For given ρ_0 , the binodal curve at $N = 2$ is flatter than that at $N = 40$; the former therefore lies below the latter except in the case of $\rho_0 = 3$.

To the best of our knowledge, this is the first MC study of incompressible symmetric blends.²⁷ Our work provides accurate simulation data for quantitative test of advanced theories capturing the fluctuation/correlation effects in multi-component polymeric systems and promotes the development of such theories. We finally note that, while this study is for incompressible symmetric blends on the hexagonal lattice, our method (i.e., FLMC simulations⁶ with the generalized cooperative motion algorithm⁵ in a

semi-grand-canonical ensemble) is quite general and not limited to either incompressible systems or the hexagonal lattice.

Acknowledgement

This work was supported by NSF CAREER Award CBET-0847016, which is gratefully acknowledged.

References

- [1] P. Zhang, X. Zhang, B. Li, Q. Wang, Quantitative Study of Fluctuation Effects by Fast Lattice Monte Carlo Simulations. I. Compressible Homopolymer Melts. *Soft Matter* 7 (2011) 4461-4471.
- [2] P. Zhang, B. Li, Q. Wang, Quantitative Study of Fluctuation Effects by Fast Lattice Monte Carlo Simulations. 2. Homopolymer Brushes in an Implicit, Good Solvent. *Macromolecules* 44 (2011) 7837-7852.
- [3] P. Zhang, B. Li, Q. Wang, Quantitative Study of Fluctuation Effects by Fast Lattice Monte Carlo Simulations. III. Homopolymer Brushes in an Explicit Solvent. *Macromolecules* 45 (2012) 2537-2550.
- [4] P. Zhang, Q. Wang, Quantitative Study of Fluctuation Effects by Fast Lattice Monte Carlo Simulations: Compression of Grafted Homopolymers. *J. Chem. Phys.* 140 (2014) 044904.
- [5] P. Zhang, D. Yang, Q. Wang, Quantitative Study of Fluctuation Effects by Fast Lattice Monte Carlo Simulations. V. Incompressible Homopolymer Melts. *J. Phys. Chem. B* 118 (2014) 12059-12067.
- [6] Q. Wang, Studying Soft Matter with “Soft” Potentials: Fast Lattice Monte Carlo Simulations and Corresponding Lattice Self-Consistent Field Calculations. *Soft Matter* 5 (2009) 4564-4567; *ibid.*, 6 (2010) 6206.
- [7] T. Pakula, Cooperative Relaxations in Condensed Macromolecular Systems. 1. A Model for Computer Simulation. *Macromolecules* 20 (1987) 679-682.

- [8] P. J. Flory, Principles of Polymer Chemistry, Cornell University Press, 1953.
- [9] See, for example, K. Binder, Phase Transitions in Polymer Blends and Block Copolymer Melts: Some Recent Developments. *Adv. Polym. Sci.* 112 (1994) 181-299; M. Müller, Miscibility Behavior and Single Chain Properties in Polymer Blends: a Bond Fluctuation Model Study. *Macromol. Theory Simul.* 8 (1999) 343-374; D. Schwahn, Critical to Mean Field Crossover in Polymer Blends. *Adv. Polym. Sci.* 183 (2005) 1-61; K. F. Freed, J. Dudowicz, Influence of Monomer Molecular Structure on the Miscibility of Polymer Blends. *Adv. Polym. Sci.* 183 (2005) 63-126; and references therein.
- [10] D. Frenkel, B. Smit, Understanding Molecular Simulation: From Algorithms to Applications, 2nd ed., Academic Press, New York, 2002.
- [11] A. Sariban, K. Binder, D. W. Heermann, Critical Phenomena in Polymer Mixtures: Monte Carlo Simulation of a Lattice Model. *Colloid Polym. Sci.* 265 (1987) 424-431; A. Sariban, K. Binder, Critical Properties of the Flory-Huggins Lattice Model of Polymer Mixtures. *J. Chem. Phys.* 86 (1987) 5859-5873; A. Sariban, K. Binder, D. W. Heermann, Monte Carlo Test of the Flory-Huggins Theory for Polymer Mixtures. *Phys. Rev. B* 35 (1987) 6873-6876.
- [12] H.-P. Deutsch, K. Binder, Interdiffusion and Self-Diffusion in Polymer Mixtures: a Monte Carlo Study. *J. Chem. Phys.* 94 (1991) 2294-2304.
- [13] A. Ferrenberg, R. Swendsen, Optimized Monte Carlo Data Analysis. *Phys. Rev. Lett.* 63 (1989) 1195-1198.

- [14] H.-P. Deutsch, K. Binder, Evidence Against the Integral Equation Theory of Polymer Blends. *Europhys. Lett.* 17 (1992) 697-702; H.-P. Deutsch, K. Binder, Critical Behavior and Crossover Scaling in Symmetric Polymer Mixtures: a Monte Carlo Investigation. *Macromolecules* 25 (1992) 6214-6230; K. Binder, H.-P. Deutsch, Crossover Phenomena and Finite-Size Scaling Analysis of Numerical Simulations. *Europhys. Lett.* 18 (1992) 667-672; H.-P. Deutsch, K. Binder, The Mean Field to Ising Crossover in the Critical Behavior of Polymer Mixtures: a Finite Size Scaling Analysis of Monte Carlo Simulations. *J. Phys. II France* 3 (1993) 1049-1073.
- [15] V. Privman, *Finite Size Scaling and Numerical Simulation of Statistical Systems*, World Scientific, Singapore, 1990.
- [16] P. Cifra, F. E. Karasz, W. J. MacKnight, Distribution of Interactions in Binary Polymer Mixtures: a Monte Carlo Simulation Study. *Macromolecules* 21 (1998) 446-451.
- [17] P. Cifra, F. E. Karasz, W. J. MacKnight, Computer Simulation of a Binary Polymer Mixture in Three Dimensions. *J. Polym. Sci. B* 26 (1998) 2379-2383.
- [18] P. Cifra, E. Nies, J. Broersma, Equation of State and Miscibility Behavior of Compressible Binary Lattice Polymers. a Monte Carlo Study and Comparison with Partition Function Theories. *Macromolecules* 29 (1996) 6634-6644.
- [19] D. G. Gromov, J. J. de Pablo, Structure of Binary Polymer Blends: Multiple Time Step Hybrid Monte Carlo Simulations and Self-Consistent Integral-Equation Theory. *J. Chem. Phys.* 103 (1995) 8247-8256; *ibid.* Phase Equilibria in Binary Polymer Blends: Integral Equation Approach. 109 (1998) 10042-10052.

- [20] F. A. Escobedo, J. J. de Pablo, On the Scaling of the Critical Solution Temperature of Binary Polymer Blends with Chain Length. *Macromolecules* 32 (1999) 900-910.
- [21] G. S. Grest, M.-D. Lacasse, K. Kremer, A. M. Gupta, Efficient Continuum Model for Simulating Polymer Blends and Copolymers. *J. Chem. Phys.* 105 (1996) 10583-10594.
- [22] A. Cavallo, M. Müller, K. Binder, Anomalous Scaling of the Critical Temperature of Unmixing with Chain Length for Two-Dimensional Polymer Blends. *Europhys. Lett.* 61 (2003) 214-220.
- [23] A. Cavallo, M. Müller, K. Binder, Unmixing of Polymer Blends Confined in Ultra-thin Films: Crossover between Two-Dimensional and Three-Dimensional Behavior. *J. Phys. Chem. B* 109 (2005) 6544-6552.
- [24] G. H. Fredrickson, *The Equilibrium Theory of Inhomogeneous Polymers*, Oxford University Press, 2006.
- [25] P. G. de Gennes, Qualitative Features of Polymer Demixtion. *J. Phys. Lett. (Paris)* 38 (1977) L441-L443.
- [26] R. Swendsen, J. Wang, Replica Monte Carlo Simulation of Spin-Glasses. *Phys. Rev. Lett.* 57 (1986) 2607-2609.
- [27] We note that incompressible binary homopolymer blends of SMAW chains with different stiffness on a face-centered cubic lattice were studied by Pakula and co-workers using CMA; see A. Gauger, A. Weyersberg, T. Pakula, Monte Carlo Studies of Static Properties of Interacting Lattice Polymers with the Cooperative-Motion Algorithm. *Makromol. Chem., Theory Simul.* 2 (1993) 531-560.

- [28] M. Lingenheil, R. Denschlag, G. Mathias, P. Tavan, Efficiency of Exchange Schemes in Replica Exchange. *Chem. Phys. Lett.* 478 (2009) 80-84.
- [29] G. Jacucci, A. Rahman, Comparing the Efficiency of Metropolis Monte Carlo and Molecular-Dynamics Methods for Configuration Space Sampling. *Il Nuovo Cimento* 4D (1984) 341-356.
- [30] Chap. 9.7 in W. H. Press, S. A. Teukolsky, W. T. Vetterling, B. P. Flannery, *Numerical Recipes in Fortran 77: the Art of Scientific Computing*, 2nd Ed., Cambridge University Press, 1992.
- [31] K. Binder, Finite Size Scaling Analysis of Ising Model Block Distribution Functions. *Z. Phys. B* 43 (1981) 119-140.
- [32] R. Finken, J.-P. Hansen, A. A. Louis, Phase Separation of a Multiple Occupancy Lattice Gas. *J. Phys. A: Math. Gen.* 37 (2004) 577-590.
- [33] H.-P. Deutsch, Optimized Analysis of the Critical Behavior in Polymer Mixtures from Monte Carlo Simulations. *J. Stat. Phys.* 67 (1992) 1039-1082.
- [34] A. N. Semenov, A. Johner, Theoretical Notes on Dense Polymers in Two Dimensions. *Eur. Phys. J. E.* 12 (2003) 469-480.
- [35] C. N. Yang, The Spontaneous Magnetization of a Two-Dimensional Ising Model. *Phys. Rev.* 85 (1952) 808-816.