Monte Carlo Simulation of Coarse Grain Polymeric Systems

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We introduce a particle-based Monte Carlo formalism for the study of polymeric melts, where the interaction energy is given by a local density functional, as is done in traditional field-theoretic models. The method enables Monte Carlo simulations in arbitrary ensembles and direct calculation of free energies. We present results for the phase diagram and the critical point of a binary homopolymer blend. For a symmetric diblock copolymer, we compute the distribution of local stress in lamellae and locate the order-disorder transition.

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The self-assembly of block copolymers into ordered morphologies [1] continues to pose formidable challenges: questions of fundamental interest, such as the temperature for the order-disorder transition (ODT), are still under investigation [2]; meanwhile, a new host of issues has been raised by the rapidly increasing number of applications using block copolymer thin films to create nanoscale devices, including high-density magnetic storage media [3].

Given the length scale of the ordered morphologies (5 to 500 nm), a fully atomistic description is beyond the reach of currently available computational resources. Coarse-grained descriptions are necessary, and it is desirable to identify approaches that are amenable to analytical treatments in limiting cases. Existing mesoscopic models can be classified into two categories: particle-based or field-based. In the latter, the fundamental degrees of freedom are the continuous fields of the local densities, and the interaction free energy is written as a functional of those fields. Prominent among them is the ‘‘standard model’’ of block copolymers [4,5], which is one of the cornerstones of polymer physics and has served as the starting point for subsequent analytical and numerical treatments. With the exception of recent field-theoretic methods [6], field-based approaches, including the self-consistent field theory (SCFT) [7], invoke a mean-field assumption and neglect fluctuation effects. In contrast, particle-based approaches do not introduce fields but work directly at the level of the particles or molecules that constitute the system, which facilitate description of complex molecular architectures [8,9]. Field-based and particle-based approaches have generally been pursued in the context of drastically different models; mapping the results of one model onto another is not straightforward [10], and has often hindered direct comparisons between results of distinct approaches.

Recent efforts have sought to introduce particle-based simulations of the same coarse-grained models or Hamiltonians that are used in theoretical treatments, including SCFT. Zuckermann and co-workers, for example, employed a coarse-grained Hamiltonian to study polymer brushes [11] and, more recently, similar approaches have been applied to investigate polymer blends and copolymer nanocomposites [12–14]. Similar to numerical field-theoretic schemes, particle-based implementations of coarse-grained models have often resorted to discretization procedures, in which space is subdivided into discrete ‘‘cells.’’ Unfortunately, their use is restricted to constant-volume applications. Approaches that allow for fluctuating domain shape and size would be particularly useful because they would enable direct calculation of stresses, phase boundaries, and free energies.

In this work we introduce a new particle-based Monte Carlo (MC) formalism in which the interaction between chains is taken into account with a functional of the densities, as is done in traditional field-theoretic approaches [5,7]. However, the discretization of space is circumvented by introducing off-grid, continuous interactions. We show how, by doing so, MC simulations can be carried out in a variety of ensembles and used to compute directly thermodynamic and structural properties, including free energies, phase diagrams, and local stresses. Specifically, we determine the coexistence curves for a binary blend of homopolymers in the presence of fluctuations and provide a precise estimate of the critical solution temperature by direct mapping onto the critical point order parameter distribution of the 3D Ising model. For a lamellae-forming block copolymer, we compute the local stresses and locate the ODT.

We consider n chains of an AB diblock copolymer, in a volume V at temperature T. Each chain is represented by a collection of N beads, connected by harmonic springs. The position of the sth bead in the ith chain is denoted by $\mathbf{r}_i(s)$. Consistent with the standard model, the bonded energy is given by $\beta\mathcal{H}_b = \frac{3}{2}\sum_{i=1}^{n}\sum_{s=1}^{N-1}[\mathbf{r}_i(s+1) - \mathbf{r}_i(s)]^2/b^2$, where $\beta^{-1} = k_BT$, k_B is Boltzmann's constant, and b^2 is the mean squared bond length for an ideal chain. The nonbonded free energy is given by

$$\frac{\beta\mathcal{H}_{\text{nb}}}{\sqrt{\mathcal{N}}} = \int_V \frac{d\mathbf{r}}{R_{eo}^3}\left[\chi_o N\phi_A\phi_B + \frac{\kappa_o N}{2}(\phi_A+\phi_B)^2\right], \quad (1)$$

where $R_{eo}^2 = (N-1)b^2$ is the mean squared end-to-end distance of an ideal chain, $\phi_A(\mathbf{r})$ denotes the local, dimensionless density of block A, and $\overline{\mathcal{N}} = (\rho_o R_{eo}^3/N)^2$, where ρ_o is the bead number density. The first term of the functional describes the incompatibility between unlike beads while the second, akin to the Helfand quadratic approximation [5], gives the melt a finite compressibility. The assumption of strict incompressibility, often introduced in field-theoretic models, need not be made in a particle-based description.

To calculate the total energy $\mathcal{H}_b + \mathcal{H}_{\mathrm{nb}}$, the local densities must be inferred from the beads' positions. As alluded to earlier, resorting to a grid [12,14], as was done in past works, introduces a number of drawbacks. The interaction between beads depends on the grid position and one cannot easily implement calculations at constant stress. Here we associate a density cloud $w(\mathbf{r})$ to each bead [11,15], thereby allowing us to define a continuous density field of the form $\phi_A(\mathbf{r}) = \sum_i \delta_{AK_i} w(\mathbf{r} - \mathbf{r}_i)$, where the sum is taken over all beads i, δ is the Kronecker delta and K_i is A or B, the type of bead i. Considering for simplicity a single term $H = \int_V d\mathbf{r}\phi_A(\mathbf{r})\phi_B(\mathbf{r})$ of the functional, one can then write

$$H = \sum_{i,j} \delta_{AK_i}\delta_{BK_j} \int_V d\mathbf{r} w(\mathbf{r} - \mathbf{r}_i) w(\mathbf{r} - \mathbf{r}_j), \qquad (2)$$

where the integral on the right-hand side is now denoted by $I(\mathbf{r}_{ij})$ with $\mathbf{r}_{ij} = \mathbf{r}_j - \mathbf{r}_i$. The nonbonded contribution defined in Eq. (1) is thus rewritten as $\mathcal{H}_{\mathrm{nb}} = \sum_{j>i} U_{ij,\mathrm{nb}}$, the potential energy of a system of interacting particles, with the interbead potential given by [13]

$$\beta U_{ij,\mathrm{nb}} = \frac{\sqrt{\overline{\mathcal{N}}}}{R_{eo}^3}[\chi_o N(1 - \delta_{K_iK_j}) + \kappa_o N] I(\mathbf{r}_{ij}). \qquad (3)$$

Note that the procedure outlined above is applicable whenever $\mathcal{H}_{\mathrm{nb}}$ is a polynomial functional of the local densities, with terms of order p yielding p-body potentials.

It is apparent from Eq. (1) that the behavior of the copolymer model is governed by four physical invariants—the mean squared end-to-end distance, the Flory-Huggins parameter, the melt compressibility and the invariant degree of polymerization—related to the bare parameters of the model, R_{eo}^2, $\chi_o N$, $\kappa_o N$, and $\overline{\mathcal{N}}$, respectively. The values of $\chi_o N$ and $\overline{\mathcal{N}}$ adopt typical experimental values. Here, we do not attempt to match $\kappa_o N$ to its experimental counterpart, the isothermal compressibility. The contour discretization N and the cloud function $w(\mathbf{r})$ are discretization parameters whose influence on the results can be made minimal through judicious choices, as discussed below.

From interbead forces $\mathbf{f}_{ij} = -\nabla U_{ij}$, the local stress tensor $\sigma(\mathbf{r})$ can be determined from $\beta\sigma_{ab}(\mathbf{r}) = \sum_i \delta(\mathbf{r} - \mathbf{r}_i)\delta_{ab} + \beta\sigma'_{ab}(\mathbf{r})$, with

$$\beta\sigma'_{ab}(\mathbf{r}) = \sum_{i,j>i} r_{ij,a} f_{ij,b} \int_0^1 ds\, \delta(\mathbf{r} - \mathbf{r}_i - s\mathbf{r}_{ij}), \qquad (4)$$

where $a, b \in \{x, y, z\}$ [16]. The global stress is given by $\sigma_{ab} = \int_V d\mathbf{r}\sigma_{ab}(\mathbf{r})/V$ and the pressure is $P = \mathrm{Tr}(\sigma)/3$.

While using boxes of variable size or shape is problematic in simulations of grid-based models, and isobaric calculations are unusual in traditional field-theoretic approaches (see Ref. [17] for notable exceptions), working in the nPT ensemble is particularly convenient because the size of the simulation box can adjust spontaneously to the natural periodicity of the relevant block copolymer morphology, thereby minimizing finite-size effects. Moreover, the combination of an isobaric simulation ensemble and the ability to accurately calculate the chemical potential (due to the absence of harsh, short-ranged interactions) allow for efficient computation of the relevant thermodynamic potential.

The model and methods outlined above are examined in the context of two systems: a homopolymer blend and a symmetric block copolymer. Unless otherwise noted, $\overline{\mathcal{N}} = 128^2$, which represents a value typical of experimental systems, $\kappa_o N = 50$, and $N = 32$. For computational simplicity, the density cloud is a square function $w(\mathbf{r}) = Cw(x)w(y)w(z)$, where $w(u) = 1$ if $|u| < \Delta L/2$ and 0 otherwise; other forms could be used [11]. The normalization constant C is fixed by the condition that the average density be unity when chains are ideal, i.e. $N\sqrt{\overline{\mathcal{N}}} \int \frac{d\mathbf{r}}{R_{eo}^3} w(\mathbf{r}) = 1$. Note that C and $\overline{\mathcal{N}}$ are constant throughout the simulation and independent of the ensemble considered. In the following, the interaction range ΔL is chosen so that a given bead interacts on average with $\rho_o(2\Delta L)^3 \approx 14$ other beads.

As a first illustration of the proposed MC approach, we have computed the coexistence curve for a binary blend of homopolymers in an isobaric semi-grand-canonical ensemble and in the nPT Gibbs ensemble [18]. Figure 1 shows the binodal curves obtained with $\overline{\mathcal{N}} = 86^2$, 128^2, 185^2, and 265^2. The other parameters ($\kappa_o = 1.5625$ and $N = 16, 32, 64, 128$, respectively) are such that the bead interaction potentials are the same in all cases.

The Flory-Huggins parameter, χN, is related but not identical to the bare model parameter, $\chi_o N$, because of fluctuation effects [2,10,12,19], e.g., fluidlike packing of the soft beads. The χN parameter can be identified by comparing the results of the simulation with the predictions of the Flory-Huggins mean-field theory, for $\chi N \ll 2$, i.e., far away from the critical point of the blend, where composition fluctuations are negligible and the mean-field approximation is accurate. We assume that $\chi N/\chi_o N = \alpha$ and estimate the constant α from the two-body distribution functions [10] or from the semigrand canonical equation of state, namely $\beta\Delta\mu = \ln[\phi_A/(1 - \phi_A)] - \chi N(2\phi_A - 1)$, where $\Delta\mu$ is the exchange chemical potential for a chain [10,20]. Both methods yield the ratio $\alpha = 0.82$ and we use $\chi N \approx 0.82\chi_o N$ as the ordinate in Fig. 1.

The location $\chi_c N$ of the critical solution point has been estimated by the condition that the normalized probability distribution of the composition obtained from the MC

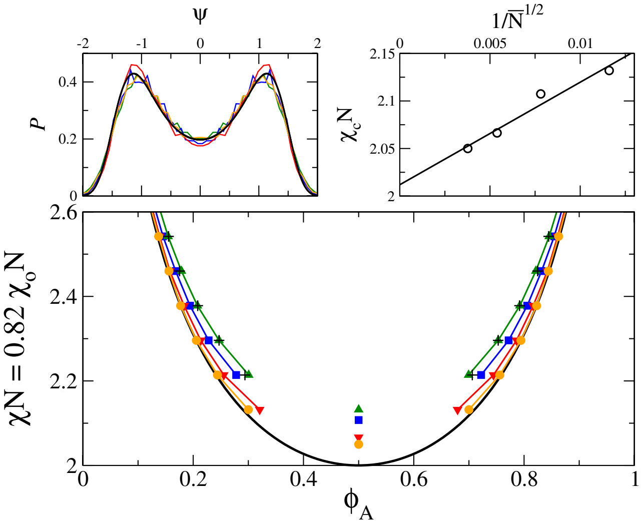

FIG. 1 (color online). Coexistence curves computed in the semigrandcanonical ensemble for binary blends of homopolymers with $\overline{\mathcal{N}} = 86^2$ (▲), 128^2 (■) 185^2 (▼) and 265^2 (●). The Gibbs ensemble curve for $\overline{\mathcal{N}} = 86^2$ is also shown (+). The pressure is $P = 18.8$, 18.0, 17.6, $17.4\beta^{-1}b^{-3}$ for $N = 16$, 32, 64, 128, respectively. At $\chi_o N = 0$, these pressures yield a bead density $\rho_o = 23.7b^{-3}$. The black line represents the mean-field prediction for an incompressible blend. The top left graph shows the probability distribution $\mathcal{P}$ of the order parameter $\psi = (\phi_A - 1/2)/\langle(\phi_A - 1/2)^2\rangle^{1/2}$; the black line is the result for the 3D Ising universality class, and the other curves are results for the different blends at our estimate of $\chi_c N$. The limiting value of $\chi_c N = 2$ as $1/\sqrt{\overline{\mathcal{N}}} \rightarrow 0$ is shown at the top right.

simulation matches the universal 3D Ising curve [21]. As expected, the critical point shifts towards lower χN upon increasing $\overline{\mathcal{N}}$ and reaches $\chi_c N = 2$ in the limit $\overline{\mathcal{N}} \rightarrow \infty$.

We now turn our attention to the lamellar morphology of a symmetric diblock copolymer. Figure 2 shows density profiles at $\chi_o N = 35$ from MC simulations and SCFT in the *nVT* ensemble. For the comparison of MC results with the predictions of field-theoretic calculations, we *assume* that the ratio $\chi N/\chi_o N \approx 0.82$ is identical to that of the blend system, i.e., $\chi N = 28.7$ [22]. The MC data computed with $N = 32$ ($\Delta L = 0.075 R_{eo}$) and $N = 64$ ($\Delta L \approx 0.06 R_{eo}$) are identical within the scale of the figure. The lamellar spacing L_0, reached when the global stress tensor is isotropic, is 1.78 and 1.79 R_{eo} for $N = 32$ and 64, respectively. Both numbers are slightly greater than the SCFT result, $L_0 = 1.75\ R_{eo}$.

The prediction of local mechanical properties in ordered morphologies is not trivial, and it is only recently that SCFT has been extended to determine the distribution of local stress [17]. A recent study has presented flat tangential stress profiles and a normal stress with a minimum at the interface and a maximum in its vicinity [24]. Our simulations yield the local stress profiles shown in Fig. 2. The normal stress is flat, as required by mechanical stability. The tangential stresses are not constant but exhibit a minimum at the interface and a maximum in its immediate vicinity.

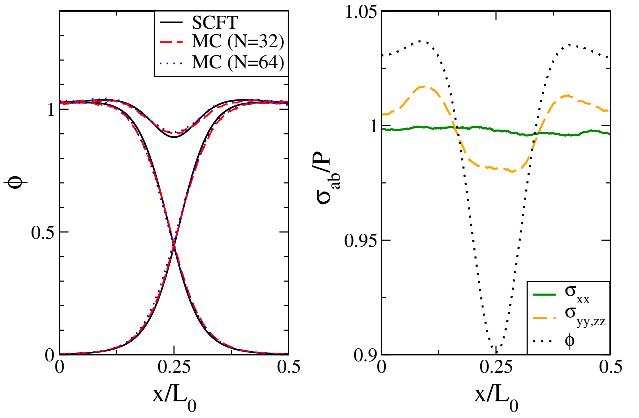

FIG. 2 (color online). (Left) Density profiles in a lamellar phase of a symmetric diblock, computed with MC simulations and SCFT, in the *nVT* ensemble, for $\chi N = 28.7$ ($\chi_o N = 35$). The x coordinates are normalized by the lamellar spacing L_0. The system size for the MC simulation is $2L_0 \times L_0 \times L_0$. (Right) Local stress for the MC simulation with $N = 32$; each component is divided by the pressure $P = 19.4\beta^{-1}b^{-3}$. The total density ϕ is also shown.

To estimate the ODT of the symmetric copolymer, simulations are implemented in the *nPT* ensemble. The pressure is set to $P = 18\beta^{-1}b^{-3}$, the value obtained in an *nVT* ensemble for $\chi_o N = 0$ and the default parameters ($\overline{\mathcal{N}} = 128^2$, $\kappa_o N = 50$, and $N = 32$). The excess chemical potential μ^{ex} (or Gibbs free energy) can be determined directly from the configurations of the system using a configurational bias Widom insertion method [25]. Figure 3 plots μ^{ex} as a function of $\chi_o N$. Branches for the disordered and ordered phases are approximately linear in the vicinity of the ODT, with distinctly different slopes. Our results provide strong evidence for the fluctuation-induced first-order character of the ODT [13,26,27]. For $\overline{\mathcal{N}} = 128^2$ and $N = 32$ (case I), the transition takes place at $(\chi_o N)_{\mathrm{ODT}} = 16.8$. To assess the effect of discretization, the curve with $N = 64$ and all physical invariants being the same is also shown (case II); it gives $(\chi_o N)_{\mathrm{ODT}} = 16.3$. On the other hand, we also computed $\mu^{\mathrm{ex}}(\chi_o N)$ for $\overline{\mathcal{N}} = 185^2$, which corresponds to a molecular weight twice as large as that corresponding to case I. The other parameters ($\kappa_o N = 100$ and $N = 64$) are such that the bead interaction potentials for case III are the same as in case I. This system has an ODT at $\chi_o N = 16.5$.

In order to compare these simulation results to those of field-theoretic approaches, both the renormalization of the bare interactions by short-ranged correlations and discretization effects of the chain architecture must be considered [15]. We account for the former by the ratio $\chi N/\chi_o N = 0.82$, 0.86, 0.82 for cases I–III; i.e., the ODT occurs at $\chi_{\mathrm{ODT}} N = 13.8$, 14.0, and 13.5, respectively. The discretization effects of the chain architecture are accounted for by calculating the partial structure factors

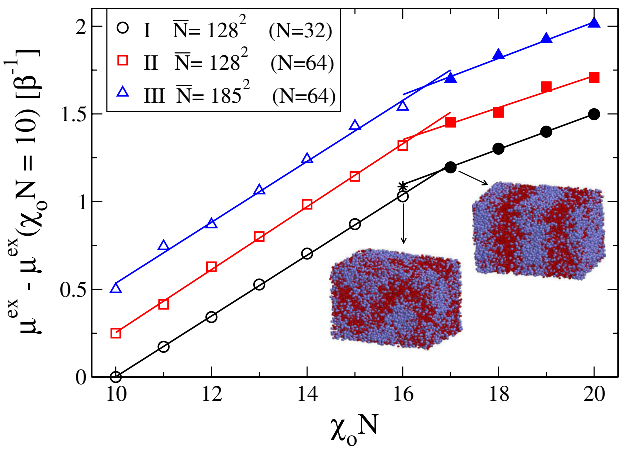

FIG. 3 (color online). Excess chemical potential as a function of $\chi_o N$. The curves have been shifted for clarity. Empty and filled symbols denote the disordered and lamellar phases, respectively. Lines are linear fits to the data. From case I to case III, $(\chi_o N)_{\rm ODT}$ is estimated as 16.8, 16.3, and 16.5. The error is comparable to the symbol size.

S_{AA} and S_{AB} of blocks of a single chain in the noninteracting melt with $\chi_o N = 0$; these structure factors are used to predict the ODT according to the random phase approximation, $\chi_{\rm ODT}^{\rm RPA} N = \min_{\mathbf{q}}[\frac{N}{S_{AA}(\mathbf{q}) - S_{AB}(\mathbf{q})}]$ [28]. This yields $\chi_{\rm ODT}^{\rm RPA} N = 10.1$ and 10.3 for chain discretizations $N = 32$ and 64. Thus, the ratio between the location of the observed first-order transition and the mean-field prediction is $\chi_{\rm ODT} N / \chi_{\rm ODT}^{\rm RPA} N = 1.36$, 1.36, and 1.31 for cases I-III, respectively. Our results are slightly larger than those obtained from a Hartree analysis of fluctuations [29] and than results of a similar lattice-based model [13], but the shift away from the mean-field prediction is consistent with the short-chain models of lattice chains with excluded volume [27] and field-theoretic simulations [6].

In conclusion, we have proposed a particle-based MC simulation method for coarse-grained polymer models where the interaction energy is a functional of the local density. The method enables direct simulations of phase behavior in arbitrary ensembles, with fluctuations and in a variable-shape simulation box, and permits calculation of local stresses, pressure, elastic moduli, chemical potentials, and free energies. We anticipate that the methods outlined in this work for simple systems will find widespread use in the study of multiblock copolymers and nanocomposites, where much less is known about their morphologies and mechanical properties.

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