Predicting Flory-Huggins χ from Simulations

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Predicting Flory-Huggins χ from simulations

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We introduce a method, based on a novel thermodynamic integration scheme, to extract the Flory-Huggins χ parameter as small as 10^{-3} kT for polymer blends from molecular dynamics (MD) simulations. We obtain χ for the archetypical coarse-grained model of nonpolar polymer blends: flexible bead-spring chains with different Lennard-Jones interactions between A and B monomers. Using these χ values and a lattice version of self-consistent field theory (SCFT), we predict the shape of planar interfaces for phase-separated binary blends. Our SCFT results agree with MD simulations, validating both the predicted χ values and our thermodynamic integration method. Combined with atomistic simulations, our method can be applied to predict χ for new polymers from their chemical structures.

The Flory-Huggins χ parameter is undoubtedly important for inhomogeneous polymers. The value of χ quantifies the free energy to mix different species, and governs phase behavior and mesoscale structures of polymer blends and block copolymers, which are critical in many applications, including lithography and photovoltaics [1, 2]. Predicting χ from molecular structures would accelerate development of new materials.

Although χ can be measured experimentally, for example by using X-ray or neutron scattering and the random phase approximation (RPA) [3], predicting χ is very challenging. The free energy of mixing depends on many factors, including mismatch in enthalpic interactions and local packing of different monomers. Accurate prediction of χ can only be obtained from the proper liquidlike structures of polymers. As a consequence, the effect of the chemical structure on χ is difficult to parameterize.

In principle, χ can be predicted using molecular simulations, by imitating an experiment from which χ can be determined. For example, miscible binary blends can be simulated, the structure factor $S(q)$ measured, and RPA applied to fit χ [4]. Nevertheless, this approach is limited to polymers with relatively large χ values. To observe enough variation in $S(q)$ to fit χ, the blend must be not too far from phase separation, which for small χ implies long chains, hence large simulation systems and long equilibration times.

Values of χ have also been obtained from vapor-liquid equilibria densities for oligomer blends using Gibbs ensemble Monte Carlo (GEMC)[5]. However, χ values obtained this way are reported with rather large uncertainties, as a result of the uncertainties in the phase equilibria densities. For blends of olefin oligomers, the uncertainty in χ is as big as the experimental value.

Finally, χ has been obtained from analyzing the coexistence volume fractions or interfacial concentration profiles between demixed chains in simulations [6, 7]. However, this approach is again limited to systems with large χ, because of the large systems and long times required to equilibrate a demixed configuration with long chains.

In this work, we introduce a general method to accurately extract χ from molecular dynamics (MD) simulations. Using a novel thermodynamic integration, we compute the excess Helmholtz free energy of mixing ΔF_{ex} per monomer, from which χ can be extracted:

$$\beta \Delta F_{ex} = \beta F_{blend} - \phi_A \beta F^A_{pure} - \phi_B \beta F^B_{pure} = \chi \phi_A \phi_B \quad (1)$$

Here $\beta = 1/kT$, ϕ_A and ϕ_B are the volume fractions of polymer A and B, and F_{blend}, F^A_{pure} and F^B_{pure} are the free energy of the binary blend, homopolymer A and homopolymer B, respectively.

We perform a thermodynamic integration on a path along which polymer A continuously transforms ("morphs") into polymer B. The path variable λ represents the degree of similarity between two kinds of polymers. We obtain the free energy F_{blend} and F^B_{pure}, with respect to the free energy of homopolymer A, as the thermodynamic work of morphing either some of the chains (for the blend) or all the chains (for pure B). The homopolymer A melt serves as the reference state. In this way, we avoid awkward reference states of polymer gases, which appear in conventional thermodynamic integration with respect to temperature. We also avoid trying to extract the mixing free energy as a small difference between large free energies (i.e., we avoid comparing the free energy required to "boil" a blend versus pure components).

The χ parameter we obtain in eqn 1 is the "apparent" χ, that one can extract by fitting the structure factor $S(q)$ of a miscible blend in the long wavelength limit, or by fitting the peak intensity of $S(q)$ for a disordered diblock copolymer melt to the renormalized one-loop (ROL) theory [8–10]. This value of χ depends weakly on chain length, and can be regarded as the sum of an "effective" χ_e for chains of infinite length, plus a one-loop renormalized correction term of order $O(N^{-1/2})$. One can therefore obtain χ_e by extrapolating the apparent $\chi(N)$ to the infinite chain length limit ($N^{-1/2} = 0$). Thus, the apparent χ is the relevant parameter for modeling mesostructures and phase behaviors using self-consistent field theory (SCFT) for chains with finite length N. The apparent χ may also depend on chain concentration ϕ, in whatever way is necessary to reconcile the actual dependence of the mixing free energy on ϕ with the assumed form of eqn 1 [10].

To obtain ΔF_{ex}, we define two coupling functions $f(\lambda)$ and $g(\lambda)$. As λ varies downward from unity, $f(\lambda)$ and $g(\lambda)$ morph polymer A ($\lambda = 1$) into polymer B. The function $f(\lambda)$ transforms the the intra-species bonded and non-bonded interactions of polymer A (E_{AA}) to those of polymer B so that $E_{BB} = f(\lambda)E_{AA}$. Likewise, $g(\lambda)$ morphs the non-bonded intra-species interactions of polymer A (E^{nb}_{AA}) into the cross-interactions between A and B (E^{nb}_{AB}).

Our method relies on the fact that the partial derivative of the excess Helmholtz free energy of mixing with respect to λ is an energy-like quantity, measurable in simulations. By differentiating the log of the partition functions for mixed and pure systems with respect to λ, we show that the free energy integrand is an explicit function of the interactions for polymer B:

$$\begin{aligned}\frac{\partial \Delta F_{ex}(\lambda)}{\partial \lambda} &= \frac{\partial F_{blend}(\lambda)}{\partial \lambda} - \phi_B \frac{\partial F^{B}_{pure}(\lambda)}{\partial \lambda} \\ &= \langle \frac{\partial f(\lambda)}{\partial \lambda} \sum_{i=1}^{N_B} \sum_{j=i}^{N_B} E_{AA} + \frac{\partial g(\lambda)}{\partial \lambda} \sum_{i=1}^{N_A} \sum_{j=1}^{N_B} E^{nb}_{AA} \rangle_{blend} - \phi_B \langle \frac{\partial f(\lambda)}{\partial \lambda} \sum_{i=1}^{N_B} \sum_{j=i}^{N_B} E_{AA} \rangle_{pure}\end{aligned} \tag{2}$$

Here $\langle \_ \rangle_{blend}$ and $\langle \_ \rangle_{pure}$ denote the ensemble average for the blend and homopolymer B, and N_A and N_B are the total numbers of monomer A and B. Because the volume change upon mixing and the resulting PV work are negligible, we approximate the Gibbs free energy of mixing ΔG_{ex} from which the Flory-Huggins $\chi(\lambda)$ is more properly obtained as equal to the excess Helmholtz free energy of mixing ΔF_{ex}.

At each λ_i, we perform two simulations: one for a randomly mixed binary blend, where a volume fraction ϕ of the chains are morphed; and one for a homopolymer melt, where all chains are morphed. The free energy integrand can be then obtained by measuring the inter-species and intra-species potential energy of the morphing molecules from the simulations. By measuring the excess free energy integrand (eqn 2) at discrete points $\{\lambda_i\}$ from simulations, we can compute the excess free energy by numerical integration, $\Delta F_{ex} = \int_{\lambda_0}^{\lambda_1} d\lambda \frac{\partial \Delta F_{ex}(\lambda)}{\partial \lambda}$. In our method, the excess free energy of mixing is not only averaged over simulation trajectories, but also over many morphing chains, which leads to statistically robust results even for systems with small χ.

In previous work, we have obtained χ for the special and simple case of bead-spring chains that differ only in backbone stiffness, but otherwise have identical interactions between monomers [11]. It was predicted long ago using polymer field theory that even this simple difference between chains would give rise to "entropic" repulsive interactions, arising only from non-ideal local packing [12]. Our results are in excellent agreement with those predictions, and consistent with experimental data [13]. This work, however, cannot incorporate enthalpic interactions between monomers.

In real polymers, mismatches in enthalpic interactions between monomers can arise from differences in molecular polarizability, presence of dipolar groups of different magnitude, or differences in hydrogen bonding propensity. The simplest model with different enthalpic interactions between monomers, which is a coarse-grained idealization of real nonpolar polymers with different molecular polarizability, is the ubiquitous example of a structurally symmetric polymer blend of flexible bead-spring chains with different interactions between A and B monomers. In this work, we develop and apply a new morphing strategy (eq 2) to obtain χ from simulations of this important and widely studied system. We then confirm our results by using our χ values together with lattice self-consistent field theory (SCFT) to predict the density profiles of planar interfaces for phase separated binary mixtures, which we can compare to simulation results for immiscible blends.

In our MD simulations, we describe pairwise interactions of polymer A using a Lennard-Jones (LJ) potential:

$$U_{AA}(r) = \begin{cases} 4\epsilon \left[(\frac{r}{\sigma})^{-12} - (\frac{r}{\sigma})^{-6} \right] & \text{if } r \le 2\sigma \\ 0 & \text{if } r > 2\sigma \end{cases} \tag{3}$$

in which $\epsilon = kT$. We morph polymer A into polymer B along a simple path: the intra-species interactions of polymer B vary linearly away from $U_{AA}(r)$, so $f(\lambda) = \lambda$ and $U_{BB}(\lambda, r) = \lambda U_{AA}(r)$. A-B interactions are controlled by $g(\lambda) = \lambda^{1/2}$, so that $U_{AB}(\lambda, r) = \lambda^{1/2} U_{AA}(r)$. This choice for $g(\lambda)$ satisfies the Berthelot mixing rule for dispersive interactions, so any value of λ corresponds to a coarse-grained model of a nonpolar blend with A and B monomers of different polarizability. Tuning λ away from unity creates mismatch in enthalpic interactions between different polymers. For this structurally symmetric blend, bonded interactions remain the same during morphing, described by a harmonic potential $U_b(l) = \frac{1}{2} k_b \left(l/\sigma - 1 \right)^2$, with bond length l and $k_b = 400\ kT$.

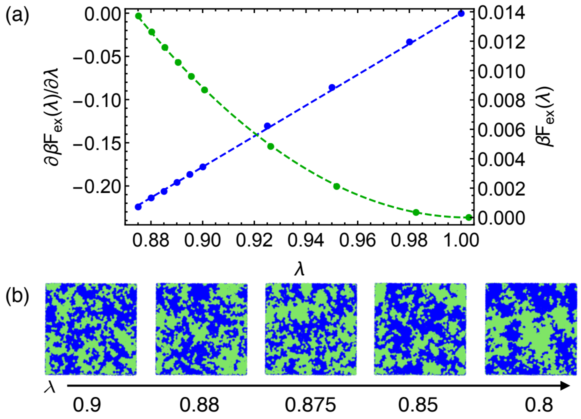

FIG. 1. (a) Excess free energy integrand $\partial\beta F_{ex}/\partial\lambda$ (blue, left axis) and free energy βF_{ex} (green, right axis) vs. morphing parameter λ. Points are simulation results, error bars smaller than symbols; dashed curves are linear and quadratic fits. (b) Simulation snapshots of binary blends for various λ. The critical point $\chi N = 2$ is at about $\lambda = 0.88$.

We perform MD simulations using the GROMACS simulation platform [14]. For each λ, we perform NPT simulations at $T = 1$ and $P = 0.1\ kT/\sigma^3$ for a melt of homopolymer B and a symmetric binary blend ($\phi = 0.5$). Each simulation box contains 2196 chains of bead-spring 40-mers (N=40). The randomly mixed initial configurations for the blend simulations are generated by randomly labeling chains in an equilibrated homopolymer melt. To ensure sufficient sampling, our simulations last about 10τ, where τ is the time for chains to diffuse by their radius of gyration R_g.

It turns out the free energy integrand varies quite linearly with respect to λ, resulting in a parabolic function for the excess free energy of mixing (Figure 1a). The free energy cost is positive, indicating the mismatch in enthalpic interactions results in a penalty for mixing.

When the free energy cost of mixing is large enough, the binary blends demix. Our morphing method for obtaining the excess free energy assumes a one-phase system. To stay away from demixing, we only compute $\frac{\partial \Delta F_{ex}(\lambda)}{\partial\lambda}$ for $\lambda \geq 0.875$. For systems with $\lambda < 0.875$, our chains tend to form large clusters (Figure 1b), indicating these systems may demix. For $\lambda > 0.875$, we observe weakly inhomogeneous, miscible blends. We will show later that we can accurately infer χ for demixed chains by extrapolating to smaller λ.

The value of χ is positive, increasing quadratically when λ decreases from unity (Figure 2). The location of the critical point ($\chi N = 2$ for $\phi = 0.5$) is estimated at about $\lambda = 0.88$. Recall that we see indications of phase separation at $\lambda = 0.875$ (Figure 1b), although not fully resolved to two demixed phases because of slow equilibration, consistent with a critical point at $\lambda = 0.88$.

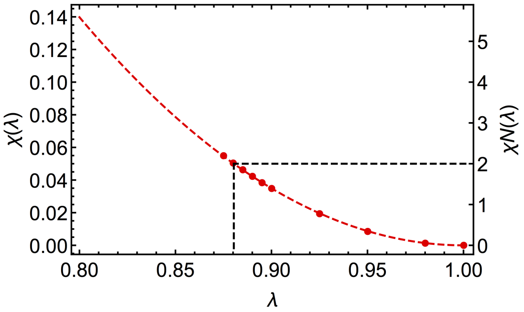

FIG. 2. Flory-Huggins χ vs. morphing parameter λ. Thermodynamic integration (disks), quadratic fitting function (dashed curve), location of mean field critical point $\chi N = 2$ (black dashed line). Error bars smaller than symbols.

To test our predicted χ, we compare the planar interfaces of phase separated binary blends obtained using a lattice version of SCFT, to the interfaces we observe in MD simulations. Lattice SCFT has been successfully applied to describe many interfacial phenomena, including chain adsorption on a surface and gradient copolymer self-assembly [15–18].

In the lattice SCFT model, we treat flexible chains of type A and B as random walks on a discretized pseudo one-dimensional lattice $\{r_i\}$, biased by a chemical potential field $W_{A/B}(r_i)$ and a hydrostatic pressure field $V(r_i)$. The chemical potential field governs the cost for monomer exchanging by $W_{A/B}(r_i) = \chi(1-2\phi_{A/B}(r_i))/2$, where ϕ_A and ϕ_B are the local volume fractions of polymer A and B, respectively. The hydrostatic pressure $V(r_i)$ ensures the incompressibility of the melt so that $\phi_A(r_i) + \phi_B(r_i) = 1$.

The lattice spacing of the pseudo one-dimensional lattice equals the statistical segment length b (1.23σ) of our bead-spring chains, so that random walks on the lattice have the proper mean-square end-to-end distance. Each lattice site represents a layer of polymer melt with thickness of b. The lattice model works well for describing phase-separated binary mixtures when the planar interface is wider than the statistical segment length b.

To complete the lattice SCFT model for a phase separated binary blend, we write the Boltzmann factor to place the first monomer A or B as $p_{A/B}(r_i, 1) = e^{-W_{A/B}(r_i)-V(r_i)}$. The propagation of this Boltzmann factor $p_{A/B}(r_i, n)$ is governed by a recursion relation, which is a discretized version of the SCFT propagator equation [17, 18]. We impose reflecting boundary layers to the two ends of the discretized lattice $\{r_i\}$, and take the total number of lattice layers L to be well in excess of the ultimate planar interface width.

For a given χ and chain length N, we can compute the interface of the binary blend by solving self-consistently for the density field $\phi(r_i)$ and the hydrostatic pressure $V(r_i)$. For a system with L layers, computing the binary interface requires solving $2L$ equations for $2L$ variables.

We predict the interfacial density profiles of symmetric blends for two different λ values, one with $\chi(0.85)$ and the other with $\chi(0.8)$. The two χ values are obtained by extrapolation along the quadratic fitting function (Figure 2). These χ values are convenient because they result in planar interfaces for bead-spring 40mers that are neither too wide to simulate nor too narrow compared with the statistical segment length b. We avoid systems too near the critical point ($\lambda = 0.88$ and 0.875), where the interfaces may be too wide to fit in a manageable simulation box, and the equilibration time is too long.

SCFT calculations give planar interfaces for immiscible blends of bead-spring 40-mers well described by a hyperbolic tangent function (Figure 3a):

$$\phi(x) = \frac{1}{2} + (\frac{1}{2} - \phi_{coex}) \tanh(x/\xi) \qquad (4)$$

Here x is the perpendicular distance from the center of the interface, ξ is the characteristic width of the interface, and ϕ_{coex} is the coexistence volume fraction in the bulk region. As expected, the width ξ decreases with increasing χ. A tanh shape for the planar interface is consistent with previous analytical SCFT results [19–21].

To compare with our SCFT interfacial profiles, we perform MD simulations of symmetric binary blends with $\lambda = 0.85$ and $\lambda = 0.8$. The initial configurations are constructed with sharp planar interfaces, built by gluing two slabs of bead-spring chains together. To help reach an equilibrated configuration more quickly, we also randomly swap chains between slab A and slab B so that the initial concentrations in the demixed slabs are as predicted by the SCFT coexistence volume fractions ϕ_{coex} far from the interface.

The planar interfaces are sharp initially, broaden during our simulations, and become stable when the systems reach equilibrium. The SCFT results agree nicely with our MD simulations, providing evidence that our predicted χ values are accurate, and our thermodynamic integration method is valid (Figure 3).

The consistency between our SCFT calculations and MD simulations also suggests that χ depends at most weakly on blend composition ϕ for our bead-spring chains. We have only extracted χ for $\phi = 0.5$, but ϕ varies significantly through the interface. If χ depended strongly on ϕ, the shape of the interface predicted by SCFT would be affected (e.g., if χ were smaller away from $\phi = 0.5$, the tails of the interface would be wider). In future work, we will investigate directly the dependence of χ on ϕ, by applying our method to systems with asymmetric compositions.

The total computational cost for predicting χ using our method is significant but manageable. Using parallel CPU computing (with typically about 1000 beads per CPU), we generate data for Figure 1 and 2 using about 120,000 CPU hours. Considering how small the errors are, one can decrease the simulation size and duration, and still obtain χ accurately.

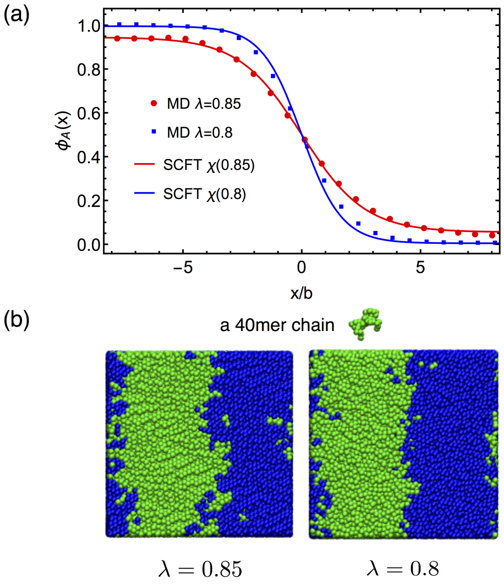

FIG. 3. (a) Volume fraction profile for polymer A near the interface. MD simulations (symbols), lattice SCFT (curves). (b) Snapshots of planar interfaces for $\lambda = 0.85$ and $\lambda = 0.8$. A single chain demonstrates length scale.

One way of describing our method is that it effectively combines the strength of MD simulations in performing proper thermodynamic averages of many interacting flexible molecules of irregular shape, with a well-defined analytical path to morph a one-component reference system into a two-component blend. As such, it resembles the insertion free energy method, in which the thermodynamic work is computed as a single molecule in solution is transformed from invisible to visible; this method has been successfully used to compute solvation energies of dissolved species, including biomolecules [22, 23].

Alternative analytical approaches to estimate χ have a hard time with averaging over the liquidlike structure, or do not perform a proper thermodynamic integral. Simple time-honored estimates for χ inevitably make uncontrolled assumptions regarding the relative positions of interacting species. For example, we may approximate a melt of bead-spring chains as a mixture of LJ monomers on a cubic lattice with a spacing of $2^{1/6}\sigma$, from which we can we can approximate $\chi_H(\lambda)$ analytically. The resulting values of $\chi_H(\lambda)$ scale correctly, but differ by more than a factor of two from our results, and provide no systematic way to introduce chain structure. More sophisticated calculations have been performed, using the self-consistent polymer reference interaction site model (PRISM) to introduce structural correlations [4]. Nevertheless, formulating such calculations is not easy, especially for systems with complicated interactions, and the results are of unknown accuracy.

Although we have developed our morphing method for the mixing free energy of bead-spring polymer blends, it can be applied more generally to any liquid mixtures, as long as a suitable morphing path can be found. For complex systems, we can obtain χ by morphing multiple types of interactions with different coupling functions along a single reaction coordinate λ. Alternatively, we may also perform "multi-stage" morphing, in which different interactions are handled in series. Indeed, designing the morphing paths and functions can be challenging for complex molecules. Still, as long as well-averaged free energy integrands are obtained during morphing, the thermal dynamic integration can lead to a unique value of χ regardless of the choices of morphing paths and functions. By relating the excess free energy integrand to energy-like quantities that can be measured in simulation, our method provides a general route to mixing free energies for real molecules.

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