Determination of the Chemical Potentials of Polymeric Systems from Monte Carlo Simulations

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We propose a new computer-simulation technique, based on the Widom test-particle method, to calculate the chemical potentials of components in a polymeric system. The technique is based on the insertion of test segments onto a polymer and is applicable for any chain length at gas and liquidlike densities. We perform sample calculations on homopolymers and show that the proposed technique allows for the enumeration of their thermodynamic behavior in the subcritical and supercritical temperature ranges.

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Exact calculations of the thermodynamic properties of truly macromolecular systems, to date, have been mostly restricted to the determination of the PVT equation of state for idealized systems where the polymer chains have been modeled as necklaces of connected hard spheres.¹⁻³ Such computations, though useful in delineating the equation of state (and chemical potentials) for strings of hard spheres, are of limited value in determining the phase equilibrium behavior for "real" polymers since they do not incorporate the attractive part of the potential that characterizes the energetic interactions between the segments in the chains. Lattice-based calculations have also been performed using finite-size scaling⁴ or simulations of systems with an interface present.⁵ The direct calculation of chemical potentials in dense, real chain systems has only been feasible for very short lengths (i.e., $v \le 5$), although a recently proposed technique by Siepmann^{6,7} appears promising in dealing with chains of longer length. The current understanding of the phase equilibria of macromolecular systems has thus largely been obtained through the use of the classic Flory-Huggins mean-field lattice model (or its improvements),⁸ which include one adjustable parameter, χ , per binary pair in the system. This model is not of value in quantitative predictions of polymer phase equilibrium since, for example, it has been shown recently through neutron scattering⁹ that the χ parameter, which is assumed to be a constant in the original theory, is actually a complicated function of the chain lengths of the constituent polymers as well as composition. Recent work in this area has involved the application of integral equation techniques¹⁰ on reference interaction-site models to enumerate the thermodynamic properties of macromolecular systems.

In this paper we present a technique to calculate the

chemical potentials of polymer chains from Monte Carlo simulations. The proposed technique is based on the Widom test-particle method which has been utilized successfully in the past to calculate the chemical potentials of small, nearly spherical molecules.¹¹⁻¹³ Mathematically, one obtains an equation for the residual chemical potential ($\mu_r = \mu - \mu^{0i}$, where μ^{0i} is the chemical potential of the molecule in the ideal-gas state at the same density and temperature as the fluid) for a molecule in a fluid which can be expressed as¹¹

$$-\beta\mu_r = \ln\langle \exp(-\beta U_t) \rangle_N, \qquad (1)$$

where $\beta = 1/k_B T$, k_B is Boltzmann's constant, T is the temperature, U_t is the energy of interaction experienced by a test particle that is inserted at random into a fluid containing N particles in the canonical ensemble at equilibrium, and $\langle \cdots \rangle_N$ denotes an ensemble average. The average in Eq. (1) is performed in an ensemble where the particles in the system are not affected by the test (ghost) molecule. In a similar fashion, the chemical potential of a molecular system can be obtained through the inverse Widom equation,¹²

$$\beta \mu_r = \ln \langle \exp(\beta U_t) \rangle_{N+1}, \qquad (2)$$

where $\langle \cdots \rangle_{N+1}$ is an average in the canonical ensemble containing N+1 real particles, and U_t is the interaction energy lost by the system if one molecule out of the N+1 in the simulated system were to be removed. Equations (1) and (2) are not very accurate at low temperatures or at high densities since the terms that contribute most to the ensemble averages cannot be sampled correctly under these conditions.^{12,13} The difficulties are especially severe for the inverse Widom equation [Eq. (2)].¹⁴ To partially overcome these problems one can use an alternative expression that relates the distribution functions $f(U_t)$ and $g(U_t)$, for the test- and real-particle energies, respectively, to the residual chemical potential, ¹²

$$\ln[f(U_t)/g(U_t)] = -\beta U_t + \beta \mu_r.$$
(3)

Equation (3) can sometimes be applied in the region of overlap of the two distribution functions to obtain estimates of μ_r even in ranges of thermodynamic space where Eqs. (1) and (2) by themselves do not yield reliable results.

The extension of this scheme to polymeric systems would involve the insertion of a test polymer chain at random into the melt and determining its chemical potential through Eqs. (1)-(3). Although such a technique has been applied successfully to dense systems comprised of short lattice chains $(v \le 5)$, ¹⁻³ when one deals with longer chains the distribution function $f(U_t)$ cannot be determined accurately over all ranges of U_t (especially negative values), since the insertion of a test chain will almost always result in the situation where it overlaps one or more of the chains in the system. Also, there is expected to be almost no overlap between the two distribution functions, making the use of Eq. (3) also practically impossible in this context. Obtaining an accurate value of μ_r will thus not be possible through the insertion of a test polymer chain. A promising alternative to testparticle insertions is provided by the technique recently introduced by Siepmann⁶ for chain molecules on a lattice and its generalization for continuous space.⁷ However, these methods are still of limited use when one deals with long chains (i.e., for $v \ge 20$) and high densities ($\rho^* \ge 0.6$).⁷

To overcome the disadvantages associated with the insertion of one test chain into the system, here we propose an alternative technique which involves the simulation of a system comprising N chains of length v, and inserting one bead on to an end of one of the chains in the system, and computing the analog of Eqs. (1)-(3) for this situation. U_t , the interaction energy experienced by the test particle would then correspond to the bonded and nonbonded potentials experienced by the new chain end and the chemical potential of this test bead could then be computed through Eq. (1). To apply the inverse Widom equation one removes a bead from the ends of one chain in the system. The energy loss associated with the removal of this chain end, U_t , can be calculated and the appropriate chemical potential computed through the application of Eq. (3).

It is important to emphasize that although the proposed scheme deals with the addition (or removal) of end beads of the chains, the chemical potential computed through this process corresponds to a thermodynamic property that is representative of the chains in the system. To offer a mathematical proof of this assertion we consider chains of length v. The chemical potential of a single chain, μ_{chain} , can then be written as

$$-\beta\mu_{\text{chain}}(v) = \ln Z(N, v; \beta, V) - \ln Z(N-1, v; \beta, V), \quad (4)$$

where

$$Z(N, v; \beta, V) = \int_{V} \cdots \int_{V} d\mathbf{r}_{1} \cdots d\mathbf{r}_{vN}$$
$$\times \exp[-\beta U(\mathbf{r}_{1}, \dots, \mathbf{r}_{vN})] \quad (5)$$

is the configurational part of the canonical partition function for a system of N chains of length v in a volume V at a temperature β . $U(\mathbf{r}_1, \ldots, \mathbf{r}_{vN})$ is the total interaction energy of the N-chain system including bonded and nonbonded contributions. Now consider a system comprised of N-1 chains of length v and 1 chain of length v+1. We can then write the chemical potential of the (v+1)th chain in a fashion similar to Eq. (4),

$$-\beta\mu_{chain}(\nu+1) = \ln Z(N-1,\nu,1,\nu+1;\beta,V) -\ln Z(N-1,\nu;\beta,V).$$
(6)

By subtracting Eq. (4) from Eq. (6) it follows that the difference in the residual chemical potentials, μ_r , is

$$-\beta[\mu_{\text{chain}}(\nu+1) - \mu_{\text{chain}}(\nu)] = -\beta\mu_r = \ln Z(N-1,\nu,1,\nu+1;\beta,V) - \ln Z(N,\nu;\beta,V).$$
(7)

To relate μ_r to the proposed test-bead insertion procedure one should note that

$$Z(N-1,\nu,1,\nu+1;\beta,V) = \int_{V} \cdots \int_{V} d\mathbf{r}_{1} \cdots d\mathbf{r}_{\nu N} d\mathbf{r}_{\nu+1} \exp[-\beta \{U(\mathbf{r}_{1},\ldots,\mathbf{r}_{\nu N}) + U_{\nu+1}(\mathbf{r}_{\nu+1})\}], \qquad (8)$$

where $U_{\nu+1}$ is the total interaction energy experienced by the $(\nu+1)$ th bead which is inserted onto an end of one of the chains in the system. From Eqs. (5)-(8) it follows that

$$\exp(-\beta\mu_r) = \frac{\int_V \cdots \int_V d\mathbf{r}_1 \cdots d\mathbf{r}_{vN} \exp[-\beta U(\mathbf{r}_1, \dots, \mathbf{r}_{vN})] \int_V d\mathbf{r}_{v+1} \exp[-\beta U_{v+1}(\mathbf{r}_{v+1})]}{Z(N, v; \beta, V)}.$$
(9)

Recognizing that $\exp[-\beta U(\mathbf{r}_1, \ldots, \mathbf{r}_{vN})]/Z(N, v; \beta, V)$ is the probability of the occurrence of a system of N molecules of length v in state $\mathbf{r}_1 \cdots \mathbf{r}_{vN}$ finally yields

$$-\beta\mu_r = \ln(\exp[-\beta U(r_{v+1})])_v.$$
⁽¹⁰⁾

Equation (10) proves that the quantity obtained from the test-bead insertion scheme is formally equal to the incremental, residual chemical potential between a chain of length v+1 and v at any density. In addition, this proof can be generalized to calculate the incremental chemical potential for any other desirable environment, e.g., for polymer molecules in a solvent.

The systems simulated in this work corresponded to the collection of bead-spring chains of desired length v in a box of size $l_x \times l_y \times l_z$ units in the x, y, and z directions, respectively, and were simulated in the canonical ensemble. Periodic boundary conditions were assumed in all three directions, and the systems simulated contained 200 to 800 beads depending on the length of the chains employed. Nonbonded beads were assumed to interact through the standard Lennard-Jones potential, where ε and σ correspond to the potential and size parameters associated with the model.¹⁵ The potential was truncated at a distance of 2.5σ , and all calculations of thermodynamic quantities were corrected for long-range effects.¹⁵ Bonded beads were assumed to interact through a spring potential as has been utilized by Gao and Weiner,¹⁶

$$U_b(r) = \frac{1}{2} \kappa (r - \sigma)^2, \quad 0.5 < r/\sigma \le 1.5, \quad (11)$$

while the potential is infinity elsewhere. For these calculations we have chosen $\kappa \sigma^2 / \epsilon = 400$. The initial state of the system was generated by placing the molecules randomly in the box ensuring that the centers of no two beads were closer than 0.5σ . Subsequently, the chains were moved through the use of the reptation and crankshaft moves as have been described in detail elsewhere,¹⁷ with the exception that bond lengths are also allowed to vary, and the states sampled through the use of Metropolis importance sampling. Equilibrium properties were then obtained using standard techniques.¹⁷

We have conducted simulations for chains of length 20 at reduced temperatures $T^*(=k_BT/\varepsilon)$ of 2 and 8, respectively. Pressures were calculated using the virial equation as has been suggested by Gao and Weiner,¹⁶ and it was found that the pressure approached the value expected of a molecular fluid as the system density approached zero (i.e., $P = \rho_m k_B T$, where $\rho_m = N/V$, N is the number of chains in the systems, and V is the total volume). We have calculated chemical potentials following Eqs. (1)-(3) and find that μ_r values determined from Eq. (3) were always consistent with those calculated from the test-particle method [Eq. (1)]. Further, the slope of the line $\ln[f(U_t)/g(U_t)]$ vs βU_t was always found to be equal to -1 within simulation uncertainty. The results obtained from the inverse Widom relationship [Eq. (2)], however, were not in agreement with the reduced chemical potentials calculated according to Eq. (1), at reduced bead densities $(\rho^* = Nv/V)$ greater than 0.3 at $T^* = 8$. This result is not surprising since similar results have been found for molecular systems under similar conditions.¹⁴ In Fig. 1 we plot the pressure, represented as P^*/T^* (= $P\sigma^3/k_BT$), as a function of the density of the fluid, ρ^* , at the two different temperatures. In addition, we plot the chemical potential,





FIG. 1. The reduced chemical potential μ^*/T^* and reduced pressure P^*/T^* plotted as a function of reduced density ρ^* at reduced temperatures of $T^*=2$ (Δ) and 8 (O), respectively.

The second term in Eq. (12) represents an ideal-gas contribution and has been divided by v since the chemical potentials utilized in this equation refer to a property related to a single bead. Assuming that the chemical potential of the full chain can be approximated by the product of the residual chemical potential per bead times the chain length v (an assumption whose validity is discussed in the next paragraph), and utilizing the phase equilibrium conditions of equality of pressure and chemical potential, we found the existence of a liquid phase of $\rho^* \approx 0.68$, in equilibrium with an ideal gas at a pressure $P^* \approx 1.0 \times 10^{-5}$, at a temperature $T^* = 2$. No such equilibrium was found for $T^* = 8$, indicating that it is a supercritical isotherm.

We have proven earlier that the chemical potentials calculated by the particle insertion-removal scheme correspond to an incremental Helmholtz energy between a chain of length v+1 and one of length v at all densities [Eq. (10)]. To examine the dependence of the incremental chemical potential on chain length in the zero-density limit we have calculated this quantity for a single chain of v connected beads (1 < v < 10) using a "primitive Monte Carlo" method. The technique involves the random generation of an ensemble of chain conformations to delineate all the thermodynamic properties at any temperature. It was found that this technique produced overlap-free conformations with reasonable efficiency for short chains but became inefficient as one proceeded to longer chains. Up to 5×10^8 configurations were generated for the longer chains. The incremental Helmholtz energy as a function of the chain length of the polymers was then calculated from Eq. (7). The results of these calculations along with computations from the Widom



FIG. 2. Zero-density reduced residual chemical potential μ_r^*/T^* as a function of chain length v at $T^*=2$ and 8, respectively: \triangle, \bigcirc , Widom test-bead insertion; \blacktriangle , \bigcirc , primitive Monte Carlo.

test-particle scheme are shown in Fig. 2 where μ_r^*/T^* $(=\beta\mu_r)$ is plotted against v. It is clear that there is good agreement between the two techniques, within simulation uncertainty, although the Widom method is more efficient at longer chain lengths. This calculation thus verifies that we can perform efficient sampling of the incremental chemical potential based on Eq. (10). The residual chemical potentials assume nonzero values at zero density due to the contributions of intrachain interactions alone. We further note that the incremental Helmholtz energy becomes independent of chain length if one considers chains of length larger than ca. 5-10 repeat units at these temperatures. We can thus estimate the chemical potential of a chain of arbitrary length by multiplying the incremental chemical potential by the number of beads in the chain, and adding corrections from simulations of short chains for which the incremental chemical potential is a function of chain length.

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