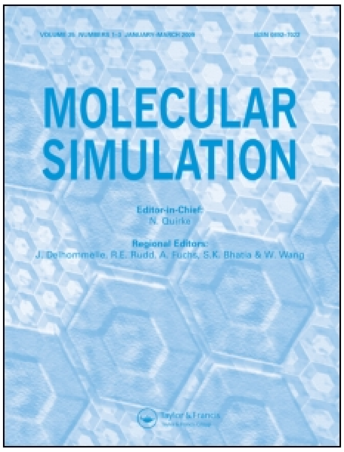

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Phase Coexistence Curves for Off-lattice Polymer-Solvent Mixtures: Gibbs-Duhem Integration Simulations

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Phase Coexistence Curves for Off-lattice Polymer–Solvent Mixtures: Gibbs–Duhem Integration Simulations

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The Gibbs–Duhem integration scheme is combined with the osmotic Gibbs-ensemble simulation method presented in previous work [Brennan, J.K. and Madden, W.G. "Phase coexistence curves for off-lattice polymer–solvent mixtures: Gibbs-ensemble simulations." ***Macromolecules*****, 2002, 35, 2827.] to calculate the phase coexistence of a polymer–solvent mixture. Gibbs–Duhem integration simulations are carried out at temperatures for which the osmotic Gibbs-ensemble method is not valid because the solvent-rich phase contains a significant amount of polymer. This combined strategy allows for the calculation of the full coexistence curve for polymer–solvent systems in the continuum. An alternative formulation of the Gibbs–Duhem integration algorithm is also presented. A major strength of the technique is that neither chain insertions nor deletions are required. The method allows for the calculation of the phase behavior of polymer–solvent mixtures containing long chains or branched and networked chains not previously possible.**

Keywords: Gibbs–Duhem integration; Osmotic Gibbs ensemble; Polymer–solvent mixture; Phase coexistence curves

INTRODUCTION

In previous work by Brennan and Madden [1], the lower-temperature portion of the coexistence curve of a polymer–solvent mixture was determined by using the Gibbs-ensemble method in an unusual osmotic formulation. This was possible because, at low temperatures, virtually no polymer is dissolved in the solvent-rich phase and the osmotic pressure is essentially zero. Under these conditions, only the smaller solvent particles need to be exchanged between the simulation cells representing the coexisting phases. For chains of finite length, as the solution temperature approaches the solution critical temperature, the solvent-rich phase will eventually contain substantial amounts of polymer. Some other method must then be used to determine the conditions of coexistence. A more conventional Gibbs-ensemble calculation could be implemented but would require exchanges of both the polymer and solvent molecules between the coexisting phases. For chains of reasonable length, such a simulation is not feasible without computationally expensive configurational bias-sampling methods. Indeed, Gromov *et al.* have performed such simulations using recently developed configurational-bias techniques [6]. However, even with these bias-sampling techniques, the length of the chain as well as the complexity of the chain architecture (e.g. chain branching and crosslinking) becomes limited to highly coarse-grained model potentials.

Several alternatives to the Gibbs-ensemble method exist that overcome some general phase equilibrium difficulties as well as certain polymer-specific problems. One such alternative is an identity switch method, where the identity of two different species are interchanged while their positions in the simulation box remain the same. The method has been applied by Kofke and Glandt [2] to

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small-molecule mixtures and by Sariban and Binder [3] to lattice polymer solutions. This *semi-grand ensemble* method can only be used when the two components that are being exchanged are quite similar in size and shape. For polymeric systems, application of the method is limited to blends in which the polymer chains have nearly identical lengths and architecture.

A classic, albeit laborious alternative to the Gibbs-ensemble method is a direct search of the conditions of the equality of chemical potentials from a series of isothermal–isobaric simulations. The chemical potentials are usually calculated during the simulations using the Widom particle-insertion method [4]. Initially, this method was not applicable to polymer systems because direct insertion of a polymer chain into a dense fluid mixture is impractical. However, it is now possible to make accurate estimates of the full-chain chemical potential by incremental addition of the monomer chemical potential [5].

Recently, a simulation method was devised, termed the *Gibbs–Duhem integration technique*, which embodies much of the simplicity and elegance of the Gibbs-ensemble method [7–9]. The method is based on a thermodynamic integration scheme along a saturation line. Similar to the Gibbs-ensemble method, the Gibbs–Duhem integration technique determines a pair of coexistence points from a single dual-cell simulation, with each cell representing one of the coexisting phases. For a pure fluid simulation [7,8], no particle insertions are needed to enforce the equality of the chemical potential. For a binary mixture simulation [9], the method requires particle insertions of one species only. When applied to a mixture of polymer and solvent, the choice of that species will (of necessity) be the solvent molecule. Mehta and Kofke demonstrated that several different ensembles could be incorporated in the Gibbs–Duhem integration scheme [9]. In the present paper, we introduce still another ensemble that involves parallel (μ_s, N_p, P, T) simulations, where μ_s is the solvent chemical potential, N_p is a fixed number of polymer molecules, P, is the pressure and T is the absolute temperature.

Despite the flexibility of the Gibbs–Duhem integration method, the method does have a few drawbacks. First, it requires *a priori* knowledge of a pair of coexistence points from which the thermodynamic integrations are initiated. Furthermore, to keep the numerical integration sufficiently accurate, a fairly large number of simulations may be required to move from the known point on the coexistence curve to the phase point of interest. Mehta and Kofke addressed both these issues by noting that for some mixtures the starting point can be taken from the unmixed pure fluids, and furthermore the entire coexistence curve is often needed anyway [9]. Moreover, Mehta and Kofke showed that the Gibbs–Duhem integration method is competitive with the Gibbs-ensemble method whenever a large portion of the coexistence curve is to be examined.

The advantage of applying the Gibbs–Duhem integration method to binary mixtures with species of widely disparate sizes was recognized early [7–9]. Only the smaller molecule needs to be inserted or deleted, a completely plausible undertaking even for polymer solutions. Nevertheless, several difficulties must be addressed before the Gibbs–Duhem integration method can be applied to polymer–solvent systems. First, the coexistence curve of a polymer–solvent mixture is highly asymmetric, so that for long or even moderately long chains, the solvent-rich phase is exceedingly dilute at low temperatures (i.e. at poor solvent conditions). Furthermore, the corresponding polymer-rich phase incorporates substantial solvent, especially when the solvent is itself a supercritical fluid. Therefore, a Gibbs–Duhem integration simulation well below the solution critical point is so dilute in polymer in the solvent-rich phase that the required number of solvent molecules becomes exceedingly large—the simulation of which is impractical.

Suitably, previous work has shown [1] that the osmotic Gibbs-ensemble method can be used in precisely the circumstances that frustrate a direct application of the Gibbs–Duhem integration method. The osmotic Gibbs-ensemble results provide the necessary point of departure—a pair of coexisting points—for the Gibbs–Duhem integration simulations. There is no precise location on the phase envelope at which one need make the transition from the osmotic Gibbs-ensemble method to the Gibbs–Duhem integration scheme. The only requirement is that the solvent-rich phase be dilute, but not so dilute that the simulation cell becomes excessively large. Mehta and Kofke used second virial coefficients to assist them in making a graceful departure from the pure phase conditions used in the initiation of the integration scheme [8,9]. Such coefficients are difficult to calculate for chain molecules in solution so this is not a practical approach to the problem at hand.

Instead, the Gibbs–Duhem integration technique will be initiated from a pair of coexisting points determined previously by an osmotic Gibbs-ensemble simulation. This pair of coexisting points should lie below another pair of points on the coexistence curve that have also been determined from an osmotic Gibbs-ensemble simulation. The polymer concentration predicted from the Gibbs–Duhem integration simulation initiated at the lower coexisting points should be coincident with the osmotic Gibbs-ensemble result at the next pair of points along the coexistence curve. Quantitative agreement between the Gibbs–Duhem integration and the Gibbs-ensemble results for at least one pair of points along the coexistence curve ensures that the Gibbs–Duhem scheme has been initiated accurately. This first

Gibbs–Duhem integration simulation may be computationally costly due to the size of the simulation cell required for the highly dilute solvent-rich phase. However, as the integration scheme is continued towards the solution critical point, the solvent-rich phase will become more concentrated in polymer, resulting in simulations that are manageable. Achieving a balance between Gibbs–Duhem integration simulations that are computationally reasonable yet still accurate may require performing additional osmotic Gibbs-ensemble simulations in the region of departure.

The same polymer–solvent model used in previous work will be simulated [1]. A collection of 20-bead polymer chains (p) is immersed in a monomeric solution of solvent particles (s). Solvent molecules and the polymer beads not covalently bonded to one another interact through a standard Lennard-Jones potential. The relative sizes of the particles are identical ($\sigma_{\mathrm{ss}} = \sigma_{\mathrm{sp}} = \sigma_{\mathrm{pp}}$) as are the energy parameters for like species ($\varepsilon_{\mathrm{ss}} = \varepsilon_{\mathrm{pp}}$). The polymer–solvent bead interaction is $\varepsilon_{\mathrm{sp}} = 0.75\varepsilon_{\mathrm{ss}}$. The interactions between the covalently-bonded beads of the chain are represented by a harmonic spring with equilibrium length, $r_{\mathrm{b}} = \sigma_{\mathrm{ss}}$ and spring constant $k_{\mathrm{b}} = 200\varepsilon_{\mathrm{ss}}\sigma_{\mathrm{ss}}^{-2}$. A potential spherical cutoff of $2.5\sigma_{\mathrm{ss}}$ was used with standard long-range corrections accounting for interactions outside this cutoff [10]. Further details of the model can be found in the previous paper [1].

GIBBS–DUHEM INTEGRATION METHOD

The original derivation of the Gibbs–Duhem integration technique for binary mixtures was cast in terms of the species fugacity [9]. An alternative formulation in terms of the species chemical potential is presented in the Appendix. The strategy of the Gibbs–Duhem integration technique is fully described in the original work of Kofke and Mehta [7–9]. A brief outline of the method based on the formulation presented in the Appendix is given here.

(1) The chemical potential of the inserted species (here designated 1) and the coexisting concentrations at one or more suitable values of T and P must be known.

(2) During the course of simultaneous simulations of the two phase points, the thermodynamic quantities needed to evaluate $\Delta\mu_1/\Delta P$ (Eq. (A5)) or $\Delta\mu_1/\Delta T$ (Eq. (A11)) are accumulated.

(3) Some polynomial form is assumed and known values of $\Delta\mu_1/\Delta P$ or $\Delta\mu_1/\Delta T$ are used to extrapolate to the next pair of phase points. For example, a quadratic polynomial leads to the trapezoid formula: $y_{i+1} = y_i + hf_i$; where y_{i+1} is the predicted value of some quantity (here, μ_1), y_i is its initial value, f_i is the value of either $\Delta\mu_1/\Delta P$ or $\Delta\mu_1/\Delta T$ calculated in step (2) at the current point in the integration, and h is the integration step size (ΔP or ΔT).

(4) Dual simulations are performed in a (μ_1, N_2, P, T) ensemble. These simulations are carried out in both cells at the value of μ_1 predicted in step (3). The simulations are used to evaluate f_{i+1}, the integrand at the predicted point. These data are then used to correct the estimate of y_{i+1}. If the trapezoid formula is used in step (3), the corresponding corrector formula is $y_{i+1} = y_i + h(f_{i+1} + f_i)$. In practice, the corrector quantity f_{i+1} is refined during the course of the simulations by accumulating *running* averages. The predicted chemical potential can fluctuate during the initial stages of calculating f_{i+1} but eventually stabilizes, after which equilibrium averages can be taken.

(5) Once satisfactory averages are achieved, the process is repeated starting from step (2) to determine the next pair of coexisting phase points.

For Gibbs–Duhem integration simulations of polymer–solvent mixtures, the inserted/deleted species is always the solvent. Parallel simulations in (μ_{s}, N_{p}, P, T) ensembles are performed in cycles of three moves: particle displacements, coupled volume rearrangements, and insertion or deletion of solvent particles at constant-density. In each cycle, a total of N particle displacements are attempted where the acceptance probability is given by the standard criteria [10].

Following the trial particle displacements, a *coupled* volume change is attempted, which entails independent but simultaneous volume changes for each simulation cell. However, the acceptance of both volume changes is coupled into a single acceptance expression. The effect of such coupling is to force the densities of the two simulation cells (here labeled I and II) to remain on opposite sides of an arbitrary density value (typically chosen to be the mean density of the two phases at the previous pair of coexisting phase points). This constraint prevents either phase from unilaterally transforming into the other. The coupled volume change is accepted from the min(1, P_{vol}) where P_{vol} is

$$\begin{aligned}\ln P_{vol} = {} & -\beta\Delta E - \beta P\Delta V + N^{I}\ln\left(\frac{V^{I}_{new}}{V^{I}_{old}}\right) \\ & + N^{II}\ln\left(\frac{V^{II}_{new}}{V^{II}_{old}}\right) + \ln\left(\frac{\rho^{I}_{old}\rho^{II}_{old}}{\rho^{I}_{new}\rho^{II}_{new}}\right) \\ & + \ln\left(\frac{\rho^{I}_{old} - \rho^{II}_{old}}{\rho^{I}_{new} - \rho^{II}_{new}}\right) + \ln\left(\frac{(\rho^{II}_{new} - \rho)(\rho - \rho^{I}_{new})}{(\rho^{II}_{old} - \rho)(\rho - \rho^{I}_{old})}\right)\end{aligned} \tag{1}$$

where the subscripts "old" and "new" refer to the values before and after the trial volume change, and the arbitrarily chosen density, $\rho = (\rho^{\mathrm{I}} + \rho^{\mathrm{II}})/2$ is taken from the final averages of the phase points determined in the previous integration step.

After a trial coupled volume change, a predetermined number of insertions and deletions of the solvent particle are attempted. An accepted insertion or deletion of a particle affects the density of the system. This induces fluctuations that could undermine the role of the volume coupling scheme outlined above by causing both cells to search for the same phase point. Therefore, during an attempted insertion or deletion, the cell volume is adjusted in such a way that the density of the phase remains unchanged. An attempted insertion into cell I is accepted with the probability given by min (1, P_{ins}) where

$$\begin{aligned} \ln P_{ins} = {} & -\beta\Delta E - \beta P\Delta V + \ln\left(\frac{N^I + 1}{N^I}\right) \\ & + \left[(N^I + 1)\ln V^I_{new} - N^I \ln V^I_{old}\right] \\ & + \ln\left(\frac{z}{N^I_{solvent} + 1}\right) \end{aligned} \tag{2}$$

and where the activity $z = \sigma_{\mathrm{ss}}^3 \lambda^3 \exp(\beta\mu_{\mathrm{s}})$, λ is the thermal de Broglie wavelength of the solvent particle, μ_{s} is the solvent chemical potential, and $\Delta V = V_{\mathrm{new}} - V_{\mathrm{old}}$ for cell I. Similarly, an attempted deletion is accepted with a probability given by min (1, P_{del}) where

$$\begin{aligned} \ln P_{del} = {} & -\beta\Delta E - \beta P\Delta V + \ln\left(\frac{N^I - 1}{N^I}\right) \\ & + \left[(N^I - 1)\ln V^I_{new} - N^I \ln V^I_{old}\right] \\ & + \ln\left(\frac{N^I_{solvent}}{z}\right) \end{aligned} \tag{3}$$

VALIDATION OF METHODOLOGY

To verify that our chemical potential-based (μ_{s}-based) version of the Gibbs–Duhem integration scheme is appropriate for polymer solutions, we calculated the phase diagram for a polymer–solvent mixture using the Flory–Huggins lattice model for an incompressible solution by two approaches [11,12]. First, by a search algorithm that explicitly matched the chemical potentials of both the polymer and the solvent (thus satisfying the requirements of phase coexistence). And second, by using our μ_{s}-based formulation of the Gibbs–Duhem integration scheme. This exercise eliminates the simulation component entirely and is analogous to Kofke's illustration of the Gibbs–Duhem integration scheme applied to the calculation of the phase coexistence curve of a pure fluid using the van der Waal equation of state [7]. Results for the model system, which was comprised of 20-bead polymer chains in a monomeric solvent, are shown in Fig. 1. The solid line in Fig. 1 indicates the "exact" results obtained by simultaneously matching the chemical potentials of each species using the Flory–Huggins model. The Gibbs–Duhem integration scheme was performed by using the trapezoid formula with an integration step size of 0.01, except near the critical point where the step size was reduced to 0.005. Excellent agreement is found for both phases at all temperatures indicating that the μ_{s}-based formulation is thermodynamically stable and consistent.

As further validation of the method, a comparison of the coexistence points generated by the original formulation [9] and the μ_{s}-based formulation of the Gibbs–Duhem integration scheme for a small-molecule (Lennard-Jones) fluid mixture is shown in Fig. 2. The phase behavior of a mixture of Lennard-Jones particles (single bead) at $T^* = 1.15$ is simulated, where $\varepsilon_{11} = \varepsilon_{22} = \varepsilon_{12} = 1.0$ and $\sigma_{11} = 1.0$, $\sigma_{22} = 0.769$, $\sigma_{12} = 0.885$. A pair of coexisting points from the original work was chosen as the "known" starting point for our calculations. The trapezoid formula applied to Eq. (A5) was used for the integration routine with a step size of $h = \Delta P^* = 0.003$. The phase points that were calculated from the alternative formulation are coincident with the results of the earlier work. This exercise demonstrates that our version of the Gibbs–Duhem integration method is entirely equivalent to the original formulation.

RESULTS

The vapor–liquid phase behavior of a polymer–solvent mixture was determined by using the constant-pressure version of the Gibbs–Duhem integration scheme. The trapezoid formula (applied to Eq. (A11)) was used with an integration step size, $h = \Delta T^* = 0.005$–0.05, depending on the proximity to the critical point. (Step sizes were reduced as T_{critical} was approached). Quantities required in Eq. (A11) for the first integration step were taken from the osmotic Gibbs-ensemble simulation results performed in previous work [1]. The initial value of the solvent chemical potential (also taken from previous osmotic Gibbs-ensemble simulations) was calculated using the Widom particle-insertion method [4]. The Gibbs–Duhem integration simulations were carried out for a minimum of 1×10^6 cycles during equilibration, while 1×10^6–5×10^6 production cycles were generated for the prediction of each phase point.

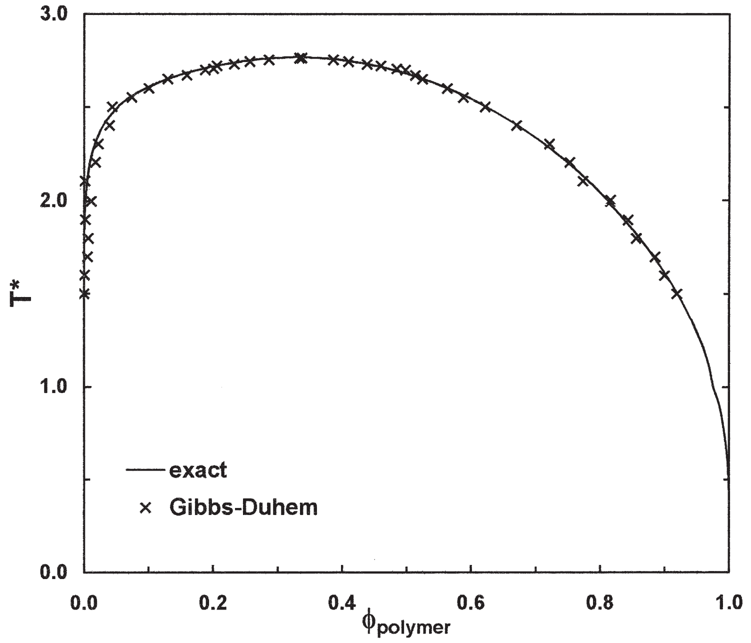

FIGURE 1 Verification of the Gibbs–Duhem integration scheme as applied to a polymer–solvent mixture (20-bead chains in a monomeric solvent). The solid line is the coexistence curve obtained by explicit matching of the chemical potentials for both species using the Flory–Huggins theory. Data points (×) are the results obtained using the Gibbs–Duhem integration method as formulated in the Appendix. T^* is the reduced temperature $T^* = kT/\varepsilon_{ss}$, where T is the system temperature, k is the Boltzmann constant, ε_{ss} is the Lennard-Jones energy parameter for the solvent and $\phi_{polymer}$ is the volume fraction of the polymer in the mixture.

To generate the starting configuration in the solvent-rich phase for the initial integration, a single 20-bead chain was randomly inserted into the simulation cell along with 20,000 solvent beads. This corresponds to an initial estimate of a polymer bead fraction $\phi_p = 0.001$. (Of course, this initial estimate only alters the time of convergence since the integration scheme is designed to predict

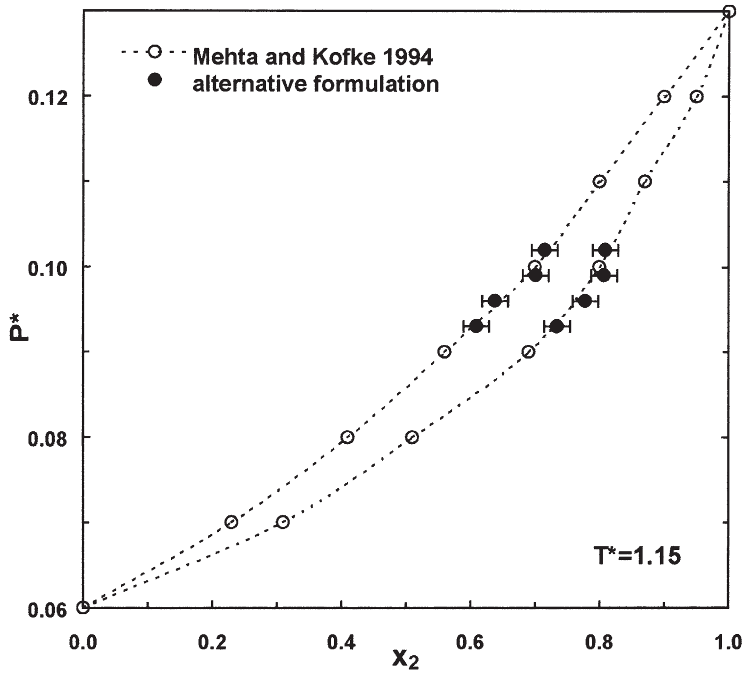

FIGURE 2 Phase coexistence curve of a binary mixture of Lennard-Jones particles (single bead) with $\varepsilon_{11} = \varepsilon_{22} = \varepsilon_{12} = 1.0$, $\sigma_{11} = 1.0$, $\sigma_{22} = 0.769$, and $\sigma_{12} = 0.885$ at $T^* = 1.15$. The reduced pressure $P^* = P\sigma_{11}^3/\varepsilon_{11}$ is plotted versus the number fraction of species 2, $x_2 = N_2/(N_1 + N_2)$ where N_i is the # of particles of species i. Open circles (○) were determined using the original formulation of the Gibbs–Duhem integration method [9]. The filled circles (●) are the results obtained from simulations using the formulation described in the Appendix. The dashed line is a visual guide only.

the coexisting chemical potential along with the true ϕ_{p}). The starting configuration for the polymer-rich phase consisted of 20 chains along with the requisite number of solvent beads determined from the osmotic Gibbs-ensemble simulation results. The initial configurations in subsequent integration steps along the coexistence curve were typically taken from the configuration of the previous pair of phase points. However, as the phase envelope is traced out towards the solution critical point, the number of solvent molecules decreases in the solvent-rich phase. Additionally, the polymer concentration in the solvent-rich phase increases as does the number of interactions between polymer chains. To mimic this behavior without producing an artificially small solvent-rich simulation cell, single chains were periodically added to the initial configuration of the solvent-rich phase at the start of an integration step.

The phase envelopes for two different pressures ($P^* = 0.3$ and 1.0) obtained from the Gibbs–Duhem integration simulations are shown in Figs. 3 and 4, along with the results of the osmotic Gibbs-ensemble simulations from previous work [1]. For both phase diagrams, the predictions of the Gibbs–Duhem integration simulations and the osmotic Gibbs-ensemble simulations are in excellent quantitative agreement over the entire temperature range. In Figs. 5 and 6, the corresponding temperature–density (T^*–ρ^*) phase diagrams are shown for the polymer–solvent mixtures. Again, excellent quantitative agreement is found between the osmotic Gibbs-ensemble and Gibbs–Duhem integration predictions along the entire coexistence curve.

For the $P^* = 0.3$ phase diagram shown in Fig. 3, the coexistence curve has more dome character than one usually observes for real polymer solutions. This behavior is attributed to the relatively short chains considered here which are oligomers, not long polymers. Furthermore, at the higher temperatures along the coexistence curve, these mixtures are supercritical with respect to the solvent temperatures and are rather compressible. For the $P^* = 1.0$ phase diagram shown in Fig. 4, the coexistence curve is substantially flatter. Some approximate lattice theories produce a flatter coexistence curve than we observe even for short chains, but these theories have been found to be weakest in their treatment of the solvent-rich phase. Simulation studies of both continuum and lattice systems have found the more dilute phase to be richer in polymer than the simple theories would suggest.

There is no obvious temperature at which one should depart from the osmotic Gibbs-ensemble simulation method and begin the Gibbs–Duhem integration simulations. If the departure temperature is too low, the solvent-rich cell will dilute itself until the simulation cell contains an unacceptably large number of solvent particles. When this is observed during the simulation, a slightly higher departure temperature should be chosen. However, a conservative choice of the departure point (no matter how computationally expensive the simulations are) will always be preferred since errors from the initial integration can accrue as the integration procedure is continued. Above all else, the critical criterion when choosing a departure point is that the resulting Gibbs–Duhem integration

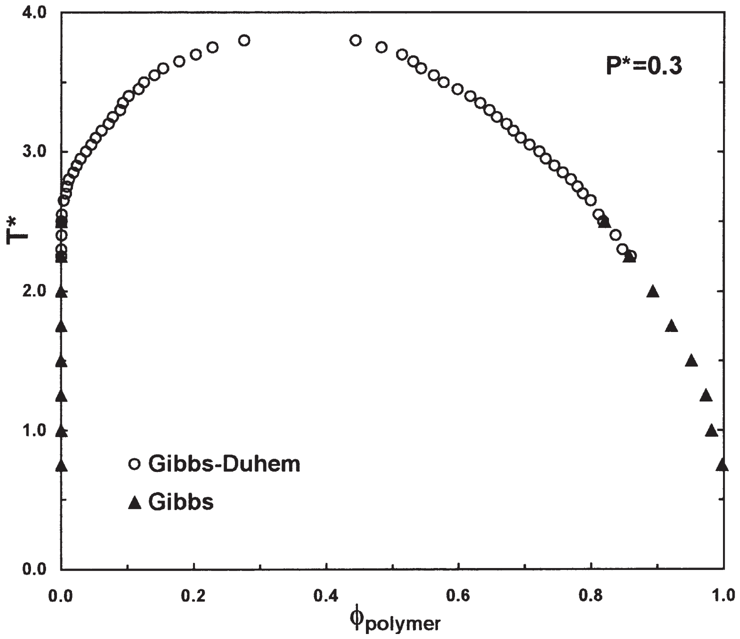

FIGURE 3 The full coexistence curve of a polymer–solvent system of 20-bead chains in monomeric solvent at $P^* = 0.3$. Both the osmotic Gibbs-ensemble simulations (▲) and the Gibbs–Duhem integration (○) results are shown.

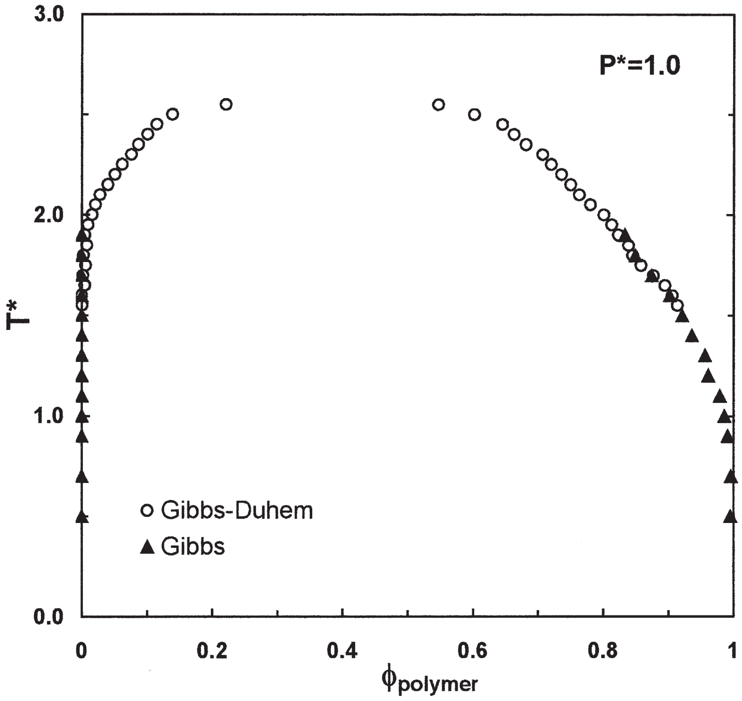

FIGURE 4 The full coexistence curve of a polymer–solvent system of 20-bead chains in monomeric solvent at $P^* = 1.0$. Both the osmotic Gibbs-ensemble simulations (▲) and the Gibbs–Duhem integration (○) results are shown.

predictions of the polymer-rich phase concentration are in agreement with the osmotic Gibbs-ensemble predictions. Finally, to verify convergence of the integration procedure Gibbs–Duhem simulations should be performed along the saturation curve in both directions, i.e. towards the solution critical point as well as away from the critical solution point. The predictions should be independent of the integration direction.

It is worth noting that the Gibbs–Duhem expressions given in the Appendix reveal why the osmotic Gibbs-ensemble simulations work so well at

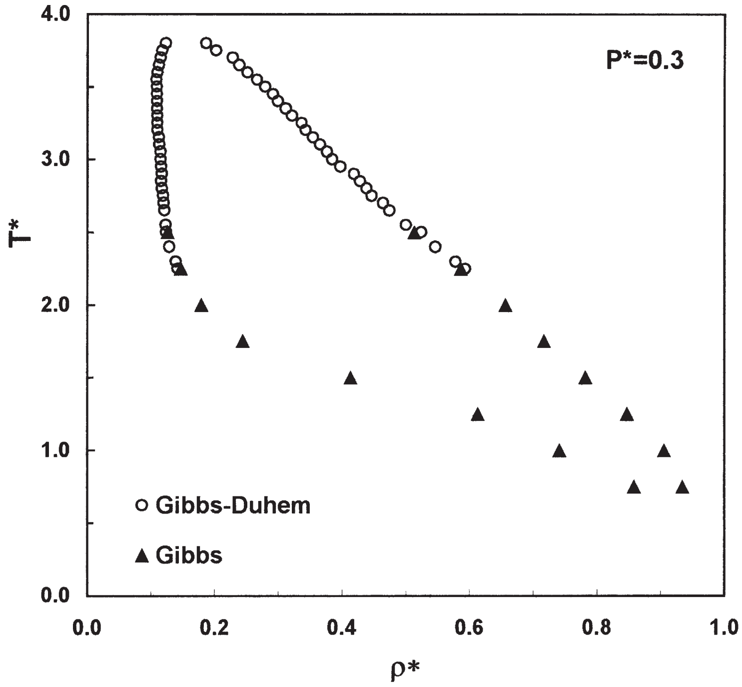

FIGURE 5 Temperature–density phase diagram corresponding to the coexistence curve shown in Fig. 3 for $P^* = 0.3$. Both the osmotic Gibbs-ensemble simulations (▲) and the Gibbs–Duhem integration (○) results are shown. The reduced density is defined as $\rho^* = \rho\sigma_{ss}^3$.

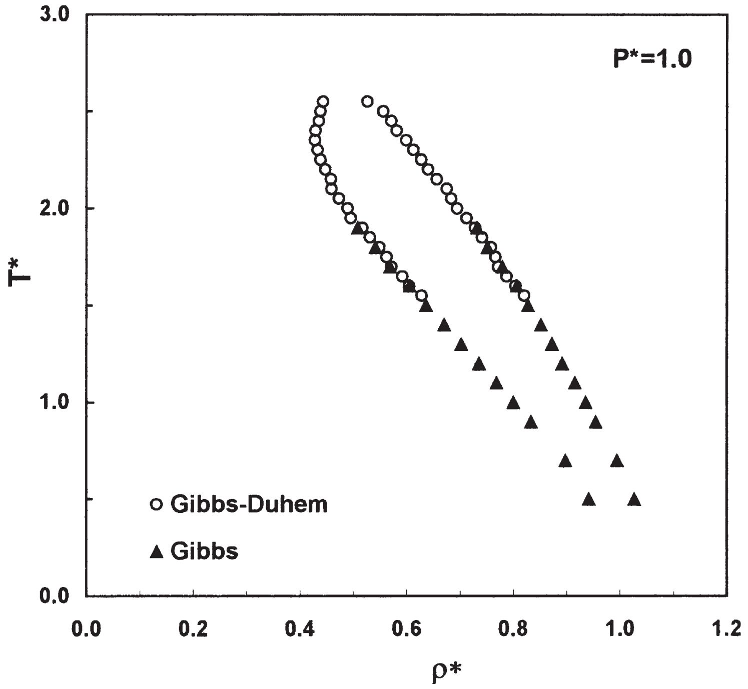

FIGURE 6 Temperature–density phase diagram corresponding to the coexistence curve shown in Fig. 4 for $P^* = 1.0$. Both the osmotic Gibbs-ensemble simulations (▲) and the Gibbs–Duhem integration (○) results are shown. The reduced density is defined as $\rho^* = \rho\sigma_{ss}^3$.

lower temperatures. The $\tilde{\Delta}$ operator weights some property in each phase by the mole fraction of species 2 (the species that is not inserted or deleted) in the opposite phase. For polymer solutions at low temperature, the polymer concentration in the solvent-rich phase is extremely low, which virtually eliminates the polymer-rich phase from the expressions (A5), (A6) and (A10). Only the properties of the nearly pure solvent phase contribute to the evolution of the chemical potential as the pressure or temperature is varied.

A final note concerning a technical aspect of performing the Gibbs–Duhem integration method. The constant-density insertion and deletion scheme suggested by Mehta and Kofke requires that computationally expensive simulation cell volume arrangements accompany each particle insertion and deletion [9]. The standard scaling tricks that enabled Mehta and Kofke to address small molecule mixtures will not, in general, be applicable to more complex systems. An energy algorithm recently suggested by Brennan and Madden [13] improves the computational efficiency of constant-density insertions and deletions by several orders of magnitude when compared with direct evaluation of the energy at every insertion or deletion. The method is applicable to potential models such as polymer chains and rigid molecules that are not amenable to the scaling techniques typically employed [10]. The application of the time-saving technique of Brennan and Madden [13] facilitated the equilibration of the simulations carried out in this work [14].

DISCUSSION

The feasibility of the Gibbs–Duhem integration method for calculating the phase behavior of polymer–solvent mixtures has been demonstrated here. The Gibbs–Duhem integration method appears to be the simplest and most efficient procedure for exploring the coexistence curve at the higher temperature and pressures, provided that the transition from the intractably dilute solvent-rich phase can be properly managed. Alternatives to the Gibbs–Duhem integration method for tracing out the coexistence curve towards the critical point are possible. The standard Gibbs-ensemble simulation method can be supplemented with an enhanced insertion scheme, such as configurational-bias Monte Carlo. This method has been the most widely used and successful approach for studying polymer blends and solutions [6,15–19]. However as indicated earlier, the configurational-bias methods become inefficient for long chains as well as branched and networked chain systems. Another possible approach for calculating the upper portion of the coexistence curve near the critical point is a direct search of the coexisting phases by explicitly matching the chemical potentials [20]. Finally, the histogram reweighting method could also be applied to the simulation of polymer–solvent phase coexistence [21–23]. However, both of these methods require multiple-simulation searches for equality of chemical potentials. Simulations using these methods would be an enormous endeavor limiting investigative studies to sporadic systems. Nevertheless, these other methods are useful as isolated tests to verify that no integration errors have crept into the Gibbs–Duhem integration calculations.

The Gibbs–Duhem integration method will not be applicable to polymer blends with or without solvent. In its present form, only a single species can be eliminated from the insertion and deletion process. For ternary systems involving two or more polymer species, the direct search method may be required to ensure equality of chemical potentials for at least one of the polymer species (though it may be possible to combine the Gibbs–Duhem integration method with semi-grand methods [2] for certain applications). In more general cases, it may be possible to use a variant of the Gibbs–Duhem integration method to reduce a three-parameter search field to two. In summary, combining the techniques of the osmotic Gibbs-ensemble method and the Gibbs–Duhem integration scheme allows the entire phase coexistence curve to be calculated for polymer–solvent mixtures. Both methods are well-established small-molecule techniques that maintain their robust character when applied to polymer–solvent systems. A unique feature of the method is that chain insertions and deletions are not required, and thus avoids the key challenge of simulating the phase behavior of polymer–solvent mixtures. Additionally, no new simulation techniques or tools are required to implement the methods. Such a method is essential in the development and improvement of predictive models and theory. Furthermore, as more realistic and accurate model potentials are developed, the method could provide predictive capabilities for real systems.

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References

[1] Brennan, J.K. and Madden, W.G. (2002) "Phase coexistence curves for off-lattice polymer-solvent mixtures: Gibbs-ensemble simulations", *Macromolecules* **35**, 2827.

[2] Kofke, D.A. and Glandt, E.D. (1988) "Monte Carlo simulation of multicomponent equilibria in a semigrand canonical ensemble", *Mol. Phys.* **64**, 1105.

[3] Sariban, A. and Binder, K. (1987) "Critical properties of the Flory–Huggins lattice model of polymer mixtures", *J. Chem. Phys.* **86**, 5859.

[4] Widom, B. (1963) "Some topics in theory of fluids", *J. Chem. Phys.* **39**, 2808.

[5] Sheng, Y.J., Panagiotopoulos, A.Z., Kumar, S.K. and Szleifer, I. (1994) "Monte Carlo calculation of phase equilibria for a bead-spring polymeric model", *Macromolecules* **27**, 400.

[6] Gromov, D.G., de Pablo, J.J., Luna-Barcenas, G., Sanchez, I.C. and Johnston, K.P. (1998) "Simulation of phase equilibria for polymer-supercritical solvent mixtures", *J. Chem. Phys.* **108**, 4647.

[7] Kofke, D.A. (1993) "Direct evaluation of phase coexistence by molecular simulation via integration along the saturation line", *J. Chem. Phys.* **98**, 4149.

[8] Kofke, D.A. (1993) "Gibbs–Duhem integration: a new method for direct evaluation of phase coexistence by molecular simulation", *Mol. Phys.* **78**, 1331.

[9] Mehta, M. and Kofke, D.A. (1994) "Coexistence diagrams of mixtures by molecular simulation", *Chem. Eng. Sci.* **49**, 2633.

[10] Frenkel, D. and Smit, B. (1996) Understanding Molecular Simulation (Academic Press, New York).

[11] Flory, P.J. (1941) "Thermodynamics of high polymer solutions", *J. Chem. Phys.* **9**, 66.

[12] Flory, P.J. (1942) "Thermodynamics of high polymer solutions", *J. Chem. Phys.* **10**, 51.

[13] Brennan, J.K. and Madden, W.G. (1998) "Efficient volume changes in constant-pressure Monte Carlo simulations", *Mol. Simul.* **20**, 139.

[14] Brennan, J.K., "Molecular simulation of polymer–solvent phase behavior" Doctoral thesis, Wayne State University (Detroit, MI).

[15] de Pablo, J.J., Laso, M. and Suter, U.W. (1992) "Estimation of the chemical-potential of chain molecules by simulation", *J. Chem. Phys.* **96**, 6157.

[16] Laso, M., de Pablo, J.J. and Suter, U.W. (1992) "Simulation of phase equilibria for chain molecules", *J. Chem. Phys.* **97**, 2817.

[17] de Pablo, J.J. (1995) "Simulation of phase equilibria for chain molecules", *Fluid Phase Equilibria* **104**, 195.

[18] Escobedo, F.A. and de Pablo, J.J. (1995) "Extended continuum configurational bias Monte Carlo methods for simulation of flexible molecules", *J. Chem. Phys.* **102**, 2636.

[19] Frenkel, D., Mooij, G.C.A.M. and Smit, B. (1992) "Novel scheme to study structural and thermal properties of continuously deformable molecules", *J. Phys. Condens. Matter* **4**, 3053.

[20] Sheng, Y.J., Panagiotopoulos, A.Z., Kumar, S.K. and Szleifer, I. (1994) "Monte Carlo calculation of phase equilibria for a bead-spring polymeric model", *Macromolecules* **27**, 400.

[21] Ferrenberg, A.M. and Swendsen, R.H. (1988) "New Monte Carlo technique for studying phase-transitions", *Phys. Rev. Lett.* **61**, 2635.

[22] Ferrenberg, A.M. and Swendsen, R.H. (1989) "Optimized Monte-Carlo data-analysis", *Phys. Rev. Lett.* **63**, 1195.

[23] Panagiotopoulos, A.Z., Wong, V. and Floriano, M.A. (1998) "Phase equilibria of lattice polymers from histogram reweighting Monte Carlo simulations", *Macromolecules* **31**, 912.

[24] Yao, J., Greenhorn, R.A. and Chao, K.C. (1982) "Monte-Carlo simulation of the grand canonical ensemble", *Mol. Phys.* **46**, 587.

[25] Shing, K.S. and Chung, S.T. (1987) "Computer simulation methods for the calculation of solubility in supercritical extraction systems", *J. Phys. Chem.* **91**, 1674.

APPENDIX

For generality, consider an arbitrary mixture of species 1, which will be added and deleted from the simulation cells, and species 2 that will not. The relevant coexisting phases are indicated by α and β (rather than I and II used in the main text). The Gibbs–Duhem equations for each phase are

$$x_1^\alpha \mathrm{d}\mu_1^\alpha + x_2^\alpha \mathrm{d}\mu_2^\alpha = -\bar{S}^\alpha \mathrm{d}T + \bar{V}^\alpha \mathrm{d}P \qquad \text{(A1)}$$

and

$$x_1^\beta \mathrm{d}\mu_1^\beta + x_2^\beta \mathrm{d}\mu_2^\beta = -\bar{S}^\beta \mathrm{d}T + \bar{V}^\beta \mathrm{d}P \qquad \text{(A2)}$$

where $\bar{S} = S/n$ is the molar entropy, $\bar{V} = V/n$ is the molar volume, $n = n_1 + n_2$ is the total number of moles, x_i is the mole fraction of species i and μ_i is its chemical potential. Although we phrase all quantities in terms of moles, the equations can be directly transcribed to the molecular level by merely redefining the chemical potential and the meaning of the notational overscore. A similar redefinition leads to the site fractions used in the application reported in the main text. The chemical potential is then defined on a per bead basis.

At phase equilibrium, $\mu_1^\alpha = \mu_1^\beta \equiv \mu_1$ and $\mu_2^\alpha = \mu_2^\beta \equiv \mu_2$. To remain on the coexistence line, it must also be true that $\mathrm{d}\mu_1^\alpha = \mathrm{d}\mu_1^\beta \equiv \mathrm{d}\mu_1$ and $\mathrm{d}\mu_2^\alpha = \mathrm{d}\mu_2^\beta \equiv \mathrm{d}\mu_2$. Solving Eqs. (A1) and (A2) for $\mathrm{d}\mu_2^\alpha$ and $\mathrm{d}\mu_2^\beta$ and equating the resulting expressions gives:

$$\begin{aligned} &-\frac{\bar{S}^\alpha}{x_2^\alpha}\mathrm{d}T + \frac{\bar{V}^\alpha}{x_2^\alpha}\mathrm{d}P - \frac{x_1^\alpha}{x_2^\alpha}\mathrm{d}\mu_1 \\ &= -\frac{\bar{S}^\beta}{x_2^\beta}\mathrm{d}T + \frac{\bar{V}^\beta}{x_2^\beta}\mathrm{d}P - \frac{x_1^\beta}{x_2^\beta}\mathrm{d}\mu_1 \qquad \text{(A3)} \end{aligned}$$

which may be written compactly as

$$\tilde{\Delta}\bar{S}\mathrm{d}T - \tilde{\Delta}\bar{V}\mathrm{d}P + \tilde{\Delta}x_1\mathrm{d}\mu_1 = 0, \qquad \text{(A4)}$$

where $\tilde{\Delta}Y \equiv x_2^\alpha Y^\beta - x_2^\beta Y^\alpha$.

To calculate coexistence curves in the $P{-}x$ plane, we set $\mathrm{d}T = 0$ and obtain

$$\frac{\mathrm{d}\mu_1}{\mathrm{d}P} = \frac{\tilde{\Delta}\bar{V}}{\tilde{\Delta}x_1} = \frac{(x_2^\alpha \bar{V}^\beta - x_2^\beta \bar{V}^\alpha)}{(x_2^\alpha x_1^\beta - x_2^\beta x_1^\alpha)} \qquad \text{(A5)}$$

All quantities on the far right of Eq. (A5) can be evaluated during the course of simultaneous, but independent, simulations of the coexisting phases. The corresponding expression for the $T{-}x$ plane is

$$\frac{\mathrm{d}\mu_1}{\mathrm{d}T} = -\frac{\tilde{\Delta}\bar{S}}{\tilde{\Delta}x_1} = -\frac{(x_2^\alpha \bar{S}^\beta - x_2^\beta \bar{S}^\alpha)}{(x_2^\alpha x_1^\beta - x_2^\beta x_1^\alpha)} \qquad \text{(A6)}$$

This expression is less useful because there is no straightforward way to make a direct evaluation of $\bar{S}_\alpha$ and $\bar{S}_\beta$ during the simulation. However,

$$T\tilde{\Delta}\bar{S} = \tilde{\Delta}\bar{H} - \tilde{\Delta}\bar{G} = \tilde{\Delta}\bar{H} - (x_2^\alpha \bar{G}^\beta - x_2^\beta \bar{G}^\alpha) \qquad \text{(A7)}$$

Furthermore, for any single-phase, two-component system,

$$\bar{G} = \frac{n_1\mu_1 + n_2\mu_2}{n} = x_1\mu_1 + x_2\mu_2 \qquad \text{(A8)}$$

so

$$\begin{aligned} T\tilde{\Delta}\bar{S} &= \tilde{\Delta}\bar{H} - [x_2^\alpha(x_1^\beta\mu_1 + x_2^\beta\mu_2) - x_2^\beta(x_1^\alpha\mu_1 \\ &\quad + x_2^\alpha\mu_2)] \\ &= \tilde{\Delta}\bar{H} - \mu_1\tilde{\Delta}x_1 = \tilde{\Delta}\bar{E} + P\tilde{\Delta}\bar{V} - \mu_1\tilde{\Delta}x_1 \qquad \text{(A9)} \end{aligned}$$

since $\tilde{\Delta}\bar{H} = \tilde{\Delta}\bar{E} + P\tilde{\Delta}\bar{V}$. Combining Eqs. (A6) and (A9) gives

$$\frac{\mathrm{d}\mu_1}{\mathrm{d}T} = -\frac{\tilde{\Delta}\bar{E} + P\tilde{\Delta}\bar{V} - \mu_1\tilde{\Delta}x_1}{T\tilde{\Delta}x_1} \qquad \text{(A10)}$$

All of the quantities on the right side of Eq. (A10) are either specified in a set of paired (μ_1, N_2, P, T) simulations or are readily calculated as averages during the course of such simulations. In this work, μ_1 represents the full chemical potential of species 1 and E the total internal energy. The Widom insertion method produces a residual chemical potential, to which one must add the ideal gas contribution, $-kT\ln(N_1\lambda_1^3/V)$, where $\lambda_1 = [h^2/(2\pi m_1 kT)]^{1/2}$ is the thermal de Broglie wavelength of species 1. Setting $\lambda_1 = \sigma_{11}$ is equivalent to defining a reduced configurational chemical potential [24]. Defining μ_1^r as the excess chemical potential (over the ideal gas) and E^{c} as the configurational energy, one can rearrange Eq. (A10) as

$$\frac{\mathrm{d}\mu_1^r}{\mathrm{d}T} = -\frac{\tilde{\Delta}E^c + P\tilde{\Delta}V - \mu_1^r\tilde{\Delta}x_1}{T\tilde{\Delta}x_1} \qquad \text{(A11)}$$

In order to incorporate the proper fluctuations for an isothermal–isobaric ensemble, the chemical potential should be calculated according to the methods described by Shing and Chung [25].