First-Order Corrections to Infinite Dilution Fugacity Coefficients Using Computer Simulation

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The relative merits of various approaches using computer simulation methods for estimating first-order correction terms to Henry's law in dilute supercritical mixtures are investigated. Three thermodynamic formulations are provided for the calculation of these properties. One method, termed the fluctuation integral approach, requires the explicit calculation of solute–solvent pair correlation functions at the infinite dilution limit, which is a difficult task for simulations given the conflicting demands of both small numbers of solute species (for approximating the infinite dilution limit) as well as the need for large numbers of solute species to improve simulation statistics. A second approach, called the pressure gradient method, does not require the explicit determination of these solute–solute functions and, as a result, is not as sensitive to the choice of system size and other difficulties associated with establishing an adequate ensemble size and/or number of solute species to be used in the simulations. The third approach uses the exact formulation for the property of interest using Kirkwood–Buff theory. This approach, however, requires all the solute pair correlation functions to be established, making it the most sensitive to issues concerning number of solute species used in the simulations, and so on. An example is given showing simulation results for these approaches, illustrating their respective strengths and drawbacks.

Introduction

The use of computer simulation techniques to study the thermodynamic behavior of dilute supercritical fluid solutions has become an important problem in the simulation field (Shing and Gubbins, 1981; Shing and Chung, 1987; Wu et al., 1990; Petsche and Debenedetti, 1991; Chialvo and Debenedetti, 1992; Li et al., 1993; Munoz and Chimowitz, 1993a,b; Munoz et al., 1995). These solutions are invariably extremely dilute, with solute mole fractions typically of the order 10^{-4}, and the infinite dilution limit of solute properties are often the target quantities of the simulation results. These simulations usually approximate the solute's infinite dilution limit by using one solute species immersed in an ensemble where the balance of the molecules are solvent. However, in many situations the use of a single solute molecule is not sufficient to calculate the property of interest accurately. A good example of this concerns the calculation of correction factors to the Henry's law approximation (which is based upon the solute's infinite dilution limit) for estimating solubilities in these systems. This subject has drawn the interest of several researchers (Debenedetti and Kumar, 1986; Shing and Chung, 1988; Brennecke et al., 1990; Munoz and Chimowitz, 1992; Jonah and Cochran, 1993; Munoz et al., 1995) concerned with the general applicability of properties based upon the solute's infinite dilution limit in supercritical solutions. For example, Munoz and Chimowitz (1993b) and Munoz et al. (1995), using integral equation calculations in model fluids, showed that in the solvent's near-critical region these correction terms are of a very significant magnitude. The central property for evaluating the first-order asymptotic corrections to the Henry's law result is the quantity given by $K_{11} = -(\partial \ln \hat{\phi}_1/\partial x_1)^{\infty}_{T,P}$. Here $\hat{\phi}_1$ is the solute's fugacity coefficient, ∞ denotes infinite dilution, and x_1 is the mole fraction of solute species 1. The main goal of this article is to discuss shortcomings and potential remedies for the use of computer simulation in calculating K_{11} in dilute solutions. The most difficult part of this calculation is finding an accurate value for the solute–solute fluctuation integral defined by G^{∞}_{11}, where $G^{\infty}_{11} \equiv \int_v (g_{11} - 1)\, dV$. There are several reasons why the calculation of G^{∞}_{11} is not straightforward in near-critical mixtures. Recent results have shown that these solute–solute pair correlation functions have high first peaks, representative of solute clustering in the solution (Wu et al., 1990; Chialvo and Debenedetti, 1992; Munoz et al., 1995) and in addition, the correlation length for g_{11} becomes very large in the solvent's near-critical region. This implies that its determination at long range is especially difficult given the conflicting need to maintain small numbers of solute molecules to approximate the infinite dilution limit accurately and the concomitant requirement for large numbers of solute species to promote better statistics for the simulations. The resolution of this dilemma is important, given the need to keep reasonable ensemble sizes for these simulations with finite and often expensive computational resources available.

These issues were addressed recently (Chialvo and Debenedetti, 1992; Munoz et al., 1995); however, how these objectives can be accomplished without using extraordinarily large sample sizes remains an open question. In this article, we discuss two new methods for approaching this problem using computer simulation in dilute supercritical mixtures.

Theory

First-order corrections to the infinite dilution limit of solute fugacity coefficients

In a binary solute–solvent system, for example, the solute's fugacity coefficient to first order in composition is given by (Debenedetti and Kumar, 1986; Chialvo, 1993; Jonah and Cochran, 1993; Munoz et al., 1995):

$$\hat{\phi}_1 = \hat{\phi}_1^\infty \exp(-K_{11}x_1), \tag{1}$$

where

$$K_{11} \equiv -\left(\frac{\partial \ln \hat{\phi}_1}{\partial x_1}\right)^\infty_{T,P} = \frac{1}{x_1} - \frac{1}{kT}\left(\frac{\partial \mu_1}{\partial x_1}\right)^\infty_{T,P}. \tag{2}$$

The solubility of the solute corrected to first order from Henry's law result is given by

$$\frac{x_1}{x_{1,HL}} = \exp(K_{11}x_1). \tag{3}$$

The term K_{11} is positive in near-critical solutions diverging only at the critical point itself (Munoz et al., 1995). It can be related to correlation function integrals in the Kirkwood–Buff theory (1951), which provides that

$$\begin{aligned} K_{11} &= \lim_{x_1 \to 0}\left[\frac{\rho_2(G_{11}+G_{22}-2G_{12})}{1+x_1\,\rho_2(G_{11}+G_{22}-2G_{12})}\right] \\ &= \rho(G_{11}+G_{22}-2G_{12})^\infty, \end{aligned} \tag{4}$$

where ρ is the number density of the system and the correlation fluctuation integrals G_{ij} are defined by

$$G_{ij} \equiv \int_v (g_{ij}-1)\,dV. \tag{5}$$

Here g_{ij} is the pair correlation function of molecule species i and j. Although Eq. 4 provides a simple expression for K_{11}, it is not useful as stated for computer simulation techniques owing to the inherent difficulty of calculating G_{11}^∞ in extremely dilute systems as shown in subsequent results. Good statistics of this calculation requires a reasonably large number of solute species, which implies the need for large ensemble sizes to maintain a close approximation to the infinite dilution limit. Choosing an adequate number of solute species and the concomitant ensemble size for these calculations is therefore not straightforward but involves artful judgment as well as trial-and-error. As a result we reformulate this problem to sidestep these issues.

Alternative formulations for simulations of K_{11} at supercritical conditions

In their treatment of synergistic effects in supercritical solutions, Munoz and Chimowitz (1993b) defined K_{11} as:

$$K_{11} = \tilde{G}_{11} + \tilde{F}_{11}. \tag{6}$$

Note that $\tilde{G}_{11}$ is different from G_{11} in the Kirkwood–Buff theory. In the infinite dilution limit, $x_1 \to 0$ and $x_2 \to 1$, the functions $\tilde{G}_{11}$ and $\tilde{F}_{11}$ are given by

$$\tilde{G}_{11} = \frac{1}{\rho kT}\left[\left(\frac{\partial P}{\partial x_1}\right)^\infty_{T,\rho}\right]^2 K_T^\infty \tag{7}$$

and

$$\tilde{F}_{11} = (C_{11}+C_{22}-2C_{12})^\infty, \tag{8}$$

where K_T^∞ is the isothermal compressibility in the infinite dilution and C_{ij} are integrals of the direct correlation functions $c_{ij}(r)$ defined as (O'Connell, 1971):

$$C_{ij} \equiv \rho \int c_{ij}(r)\,dV = \frac{-N}{kT}\left(\frac{\partial \mu_i^r}{\partial N_j}\right)_{T,V,N_{K\neq j}}. \tag{9}$$

In their integral equation study of dilute near-critical solutions Munoz and Chimowitz (1993a,b) showed that $\tilde{F}_{11}$ is likely to be extremely small compared to $\tilde{G}_{11}$, especially in the near-critical region where the compressibility dominates other terms in Eq. 7. A typical set of these results from the prior study is shown in Figure 1 for solvation in a binary mixed solvent at its azeotropic composition along its critical isotherm. The critical azeotrope in a binary mixed solvent system shares many features with the pure fluid critical point, including a diverging isothermal compressibility that is central to the results given below. These considerations imply that in the near-critical regime Eq. 6 can be simplified to

$$K_{11} \cong \frac{1}{\rho kT}\left[\left(\frac{\partial P}{\partial x_1}\right)^\infty_{T,\rho}\right]^2 K_T^\infty. \tag{10}$$

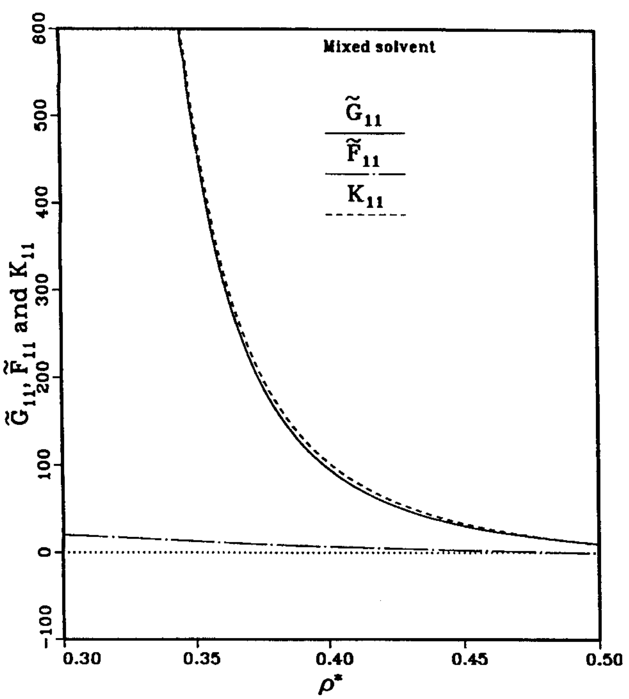

Figure 1. $\tilde{F}_{11}$, $\tilde{G}_{11}$, and K_{11} as a function of reduced density ρ^*, along the isotherm of the critical azeotrope of the mixed solvent.

From Munoz and Chimowitz (1993b).

This approximation was given by Debenedetti and Chialvo (1992) in their molecular dynamics study of dilute supercritical solutions. Equation 10 can be recast using a thermodynamic identity for $(\partial p/\partial x_1)_{T,\rho}^\infty$ given by

$$\left(\frac{\partial P}{\partial x_1}\right)_{T,\rho}^\infty = \frac{1}{K_T^\infty}(\rho\bar{V}_1^\infty - 1). \tag{11}$$

Therefore Eq. 10 can be rewritten as

$$K_{11} \cong \frac{1}{\rho kT}\frac{1}{K_T^\infty}(\rho\bar{V}_1^\infty - 1)^2. \tag{12}$$

The terms K_T^∞ and $\rho\bar{V}_1^\infty - 1$ at $x_1 \to 0$ can be expressed using the Kirkwood-Buff theory

$$\begin{aligned} K_T^\infty &= \frac{1}{\rho kT}\lim_{x_1\to 0}\frac{1 + x_1\rho G_{11} + x_2\rho G_{22} + x_1x_2\rho^2(G_{11}G_{22} - G_{12}^2)}{1 + x_1x_2\rho(G_{11} + G_{22} - 2G_{12})} \\ &= \frac{1}{\rho kT}(1 + \rho G_{22}^\infty) \end{aligned} \tag{13}$$

and

$$\begin{aligned} \rho\bar{V}_1^\infty - 1 &= \lim_{x_1\to 0}\left\{\frac{\rho[1 + x_2\rho(G_{22} - G_{12})]}{\rho[x_1 + x_2 + x_1x_2\rho(G_{11} + G_{22} - 2G_{12})]} - 1\right\} \\ &= \rho(G_{22}^\infty - G_{12}^\infty) \end{aligned} \tag{14}$$

leading to two formulations for K_{11} in supercritical solutions.

Pressure Gradient Representation of K_{11}. Using Eqs. 10 and 13, K_{11} can be expressed as

$$K_{11} \cong \left(\frac{1}{\rho kT}\right)^2\left[\left(\frac{\partial P}{\partial x_1}\right)_{T,\rho}^\infty\right]^2(1 + \rho G_{22}^\infty). \tag{15}$$

Correlation Fluctuation Integral Representation of K_{11}. Using Eqs. 12, 13 and 14, K_{11} can simply be expressed as

$$K_{11} \cong \frac{[\rho(G_{22}^\infty - G_{12}^\infty)]^2}{1 + \rho G_{22}^\infty}. \tag{16}$$

Furthermore, using Eqs. 4 and 16, G_{11}^∞ can be recovered by the identity:

$$\begin{aligned} G_{11}^\infty &\cong 2G_{12}^\infty - G_{22}^\infty \\ &+ \frac{[\rho(G_{22}^\infty - G_{12}^\infty)]^2}{1 + \rho G_{22}^\infty} = \frac{2G_{12}^\infty - G_{22}^\infty + \rho(G_{12}^\infty)^2}{1 + \rho G_{22}^\infty}. \end{aligned} \tag{17}$$

We proceed to analyze both of these equations for finding K_{11} using simulations in dilute near-critical solutions. Prior to presenting computational results, however, let us look at the qualitative differences between Eqs. 15 and 16. Neither equation involves the solute–solute correlation fluctuation integral, which is the most difficult of the three integrals to calculate accurately. Equation 16, however, still requires that G_{12}^∞ be found, while this is not the case with Eq. 15. Since G_{12}^∞ involves solute–solvent correlations, it is likely to be more difficult to establish accurately than G_{22}^∞, for example, which involves solvent species that are present in significant numbers in the dilute system. Hence Eq. 15 is likely to be the more accurate one for finding K_{11} in a given ensemble using similar sampling steps for the simulation. Note that establishing the number of solute species to evaluate G_{12}^∞ for the fluctuation integral approach is not straightforward, while no such ambiguity exists for the pressure gradient method, since the derivative $(\partial P/\partial x_1)_{T,\rho}^\infty$ is evaluated from calculations done at conditions of 0, 1, and 2 solute species.

Computational Procedures and Other Simulation Details

We chose to study a model system similar to that used by Munoz et al. (1995) in their integral equation study of the near-critical behavior of G_{11}^∞, G_{12}^∞, and G_{22}^∞. The intermolecular potential functions, reduced temperature, and density conditions studied are shown in Table 1. These potential parameters represent a large solute solvated in a solvent descriptive of so-called "attractive solutions" (Debenedetti and Mohamed, 1989) which are of most interest in supercritical

Table 1. Lennard-Jones Parameters of Solute and Solvent Species at Reduced Conditions

	Solute–Solute	Solute–Solvent	Solvent–Solvent
σ_{ij}(Å)	5.37	4.60	3.83
ϵ_{ij}(K)	378.21	278.23	204.68

$T^* = kT/\epsilon_{22} = 1.5$ and $\rho^* = N\sigma_{22}^3/V = 0.35$.

fluid technology. The cutoff distance used for these simulations was $4\sigma_{22}$ (four solvent diameters), which was more conservative than that used in our recent simulation work involving solvation free-energy calculations in near-critical mixtures (Li et al., 1993), where a cutoff range of three solvent diameters was shown to be sufficient for providing good agreement between integral equation theory (which implicitly accesses long-range structure) and simulation results. Two sampling systems were used, a large one where the total number of molecules included 980 solvent species and 20 solute molecules, as well as a smaller system involving 216 total molecules of which 4 were solute species. This choice of solute mole fraction was guided by integral equation results that under these conditions the pair correlation functions for this 2% solution were virtually identical to that of the infinite dilution result, which can be established from the theory in a straightforward manner (Munoz et al., 1995). Hence an ensemble size maintaining 2% solute should in principle provide a good approximation to the infinite dilution limit and computer simulation results using the 1,000-particle ensemble in comparison to theory at the *limit of infinite dilution* (Figure 2). Both sets of results agree well except for the solute–solute pair correlation function, which is the most difficult of the solution correlation functions to establish accurately.

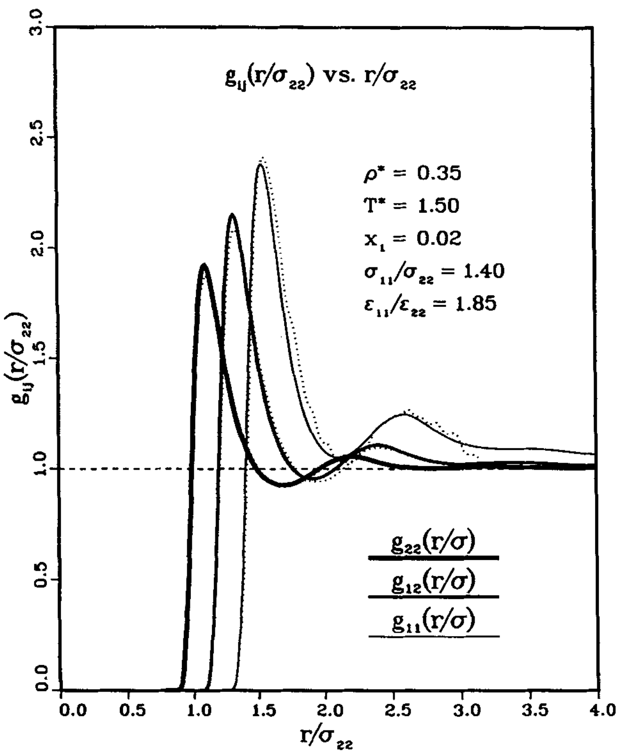

Figure 2. Pair correlation functions for the Lennard-Jones system in Table 1, with solute mole fraction $x_1 = 0.02$.

Solid line calculated with the Percus–Yevick equation and dotted lines calculated with Monte Carlo simulations using 5×10^7 sampling steps for the averaging phase and 1,000 sampling molecules. 1 denotes solute species and 2 denotes solvent species. $T^* = kT/\epsilon_{22}$ and $\rho^* = N\sigma_{22}^3/V$.

Large system simulations for the correlation fluctuation integral approach (Eq. 16) included an equilibration phase of 5×10^6 configurations followed by an additional averaging phase of 5×10^7 configurations. Small system simulations for both approaches included an equilibration phase of 4.32×10^5 configurations followed by an additional computational averaging phase consisting of 4.32×10^6 configurations. The algorithm for the pressure calculations required in Eq. 15 was based on that described by Allen and Tildesley (1987). For the derivative $(\partial P/\partial x_1)^\infty_{T,\rho}$ three conditions were chosen corresponding to 0, 1, and 2 solute species, respectively. In addition, after the simulations were completed the radial distance for establishing various integrals was found by evaluating the distance beyond which the various pair correlation functions assumed a value of unity. This was found to be $r > 4.5\ \sigma_{22}$ for g^∞_{11} and $r > 4\ \sigma_{22}$ for g^∞_{12} and g^∞_{22}.

Results

The first set of results in Figure 3 are meant to demonstrate differences between large and small system simulations for the solute–solute pair correlation function at conditions similar to those in Figure 2. The fluctuations in the solute–solute pair correlation function, especially beyond the first solvation shell, are in evidence, even when using the large system for the simulations. This is not the case for the solvent–solvent pair correlation function, as shown in Figure 4 where the system size dependence appears to be much weaker. However, the same is not true for the solute–solvent function results in Figure 5, where the more pronounced fluctuations in the small system results are clearly shown. Figure 6 shows simulation results for the quantity $(\partial P/\partial x_1)^\infty_{T,\rho}$,

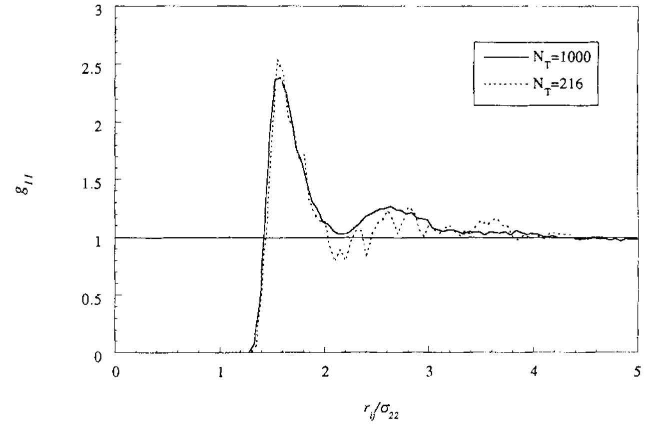

Figure 3. Solute–solute correlation functions calculated by Monte Carlo simulations.

Solid line denotes the calculation results done with 1,000 sampling molecules, including 980 solvents and 20 solutes, where the averaging phase consists of 5×10^7 sampling steps, and dotted line denotes the calculation results done with 216 molecules where the averaging phase consists of 4,320,000 sampling steps. $T^* = 1.50$ and $\rho^* = 0.35$.

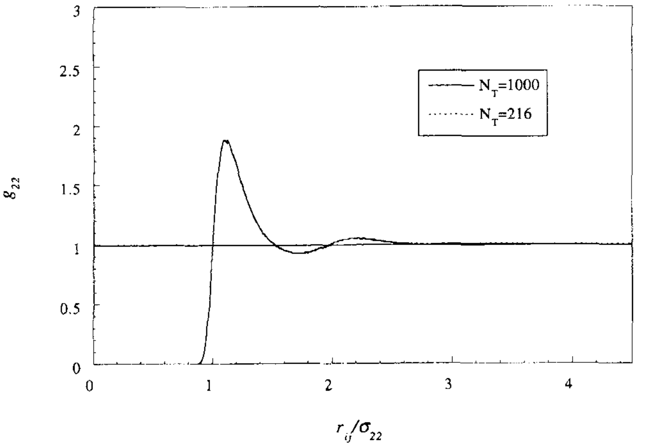

Figure 4. Solvent-solvent correlation functions calculated by Monte Carlo simulations.

Solid line denotes the calculation results done with 1,000 sampling molecules where the averaging phase consists of 5×10^7 sampling steps, and dotted line denotes the calculation results done with 216 molecules where the averaging phase consists of 4,320,000 sampling steps. $T^* = 1.50$ and $\rho^* = 0.35$.

where the simulation results have been fit to a straight line using least squares. This quantity is required for finding K_{11} using Eq. 15, and derivatives of this nature (at constant density) are well-behaved, even in the vicinity of a critical point, as discussed by Munoz et al. (1995).

The numerical counterpart to the graphical results in Figures 3-6 are provided in Table 2 with standard deviations reported for all results. We have also included results for K_{11}, using the exact formulation provided by the Kirkwood-Buff theory as given in Eq. 4. Table 2 illustrates a number of important aspects relevant to the ideas described in previous sections. The values for K_{11}, Henry's law correction term, are shown calculated using three different approaches described earlier, with both system sizes used for all the respective simulations. The extreme system size dependency of the method using the exact prescription for K_{11} provided by the Kirkwood-Buff theory (see Eq. 4) is clearly in evidence. In the large sampling system ($N_T = 1{,}000$), the value of K_{11} provided by the Kirkwood-Buff method is almost a factor of 2 different from the small system result, a result we attribute mainly to the large variations in G_{11}^{∞} with system size that cannot be accurately established even in the large system (Figure 2). The Kirkwood-Buff approach unfortunately has the disadvantage of explicitly requiring G_{11}^{∞} and G_{12}^{∞} to be established accurately. The correlation fluctuation integral approach (Eq. 16) also shows a reasonably strong system size dependency, although it is much less pronounced than the Kirkwood-Buff result. The result with the fluctuation integral approach (Eq. 16) using the large system is considered to be accurate given that the required pair correlation functions appear to be found quite accurately (Figure 2). The pressure gradient method (Eq. 15), which does not require the explicit evaluation of any of the solute pair correlation functions, shows the weakest size dependency of all three approaches with a decrease in standard deviation in the larger system. The results, with this method with *both* the large and

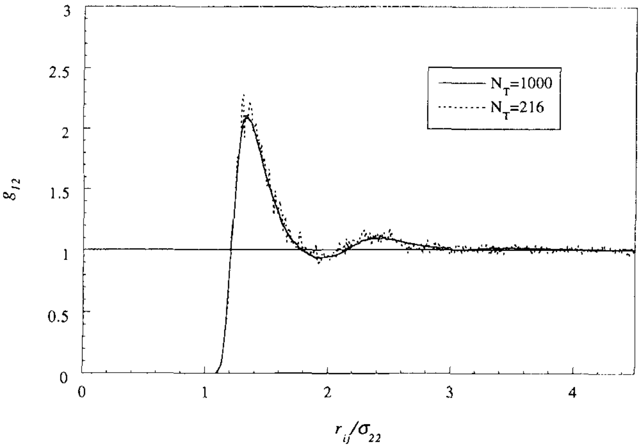

Figure 5. Solute-solvent correlation functions calculated by Monte Carlo simulations.

Solid line denotes the calculation results done with 1,000 sampling molecules, including 980 solvents and 20 solutes, where the averaging phase consists of 5×10^7 sampling steps, and dotted line denotes the calculation results done with 216 molecules where the averaging phase consists of 4,320,000 sampling steps. $T^* = 1.50$ and $\rho^* = 0.35$.

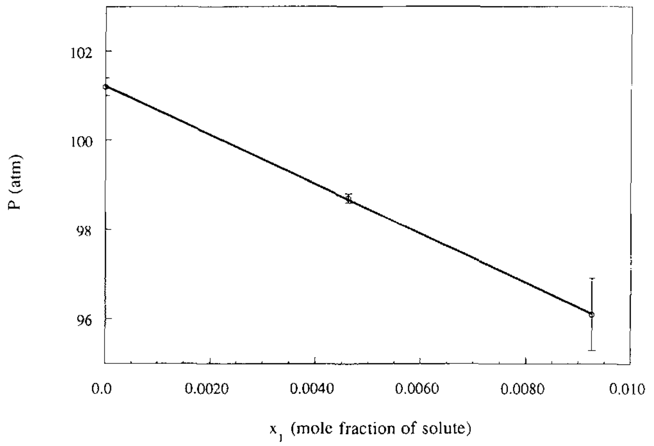

Figure 6. $(\partial P/\partial x_1)^{\infty}_{T,\rho}$ calculated by least squares linear fitting of three pressure data corresponding to three different sampling compositions including 0, 1, and 2 solute species, respectively, with the same total sample size—216.

$T^* = 1.50$ and $\rho^* = 0.35$.

Table 2. G_{11}^{∞}, G_{12}^{∞}, G_{22}^{∞} and K_{11} at Various Sampling Sizes $N_T = 1{,}000$ and 216 at $T^* = 1.50$ and $\rho^* = 0.35$

	$N_T = 1{,}000$	$N_T = 216$
G_{11}^{∞} (Å^3)	$1{,}280 \pm 20$	$1{,}700 \pm 300$
G_{12}^{∞} (Å^3)	370 ± 2	320 ± 20
G_{22}^{∞} (Å^3)	22.7 ± 0.6	18.9 ± 0.7
$\left(\frac{\partial P}{\partial x_1}\right)^{\infty}_{T,\rho}$ (atm)	-500 ± 30	-510 ± 40
K_{11}	3.5 ± 0.2^1 4.10 ± 0.08^2 4.3 ± 0.4^3	7 ± 2^1 3.2 ± 0.7^2 4.6 ± 0.8^3

*Here, the superscript 1 denotes the simulation results of the Kirkwood-Buff method (Eq. 4), 2 denotes the integral equation method (Eq. 16) and 3 denotes the pressure gradient method (Eq. 15).

small system sizes, are in reasonable accord with that provided by the correlation fluctuation integral method in the large system.

Conclusions

The results of this study clearly show the effects of the choice of a number of solute molecules, and by extension system size, in establishing accurate simulation results for the infinite dilution correlation fluctuation integrals in dilute binary mixtures. This is especially true for the pair correlation functions involving the dilute solute species, that is, G_{11}^{∞} and G_{12}^{∞}, where very large systems and concomitantly large computational times are required to promote accuracy in these calculations. These results also have important implications for establishing simulation methods aimed at providing corrections to thermodynamic properties that have been evaluated based on the use of the infinite dilution limit like the Henry's law approach, a main focus of this study. Various approaches for calculating K_{11}, the basis for the first-order correction term to the Henry's law approximation for solubility predictions in supercritical mixtures, have been discussed. The first uses the Kirkwood-Buff result for K_{11} and explicitly requires both G_{11}^{∞} and G_{12}^{∞} for its use. The results here have shown that these functions are very sensitive to system size and cannot accurately be found even in the largest system used. This is a major drawback for this particular approach. The correlation fluctuation integral approach studied is less system size dependent, since it only requires the evaluation of G_{12}^{∞}, with the least size dependent approach the pressure gradient method, which does not explicitly require the evaluation of any of the solute pair correlation functions. As a result, it is probably the best method if small system sizes are used that greatly reduce the computational times for these calculations. Perhaps its biggest advantage revolves around the issue of choosing the number of solute species and system size for the calculations. This specification for both the Kirkwood-Buff and fluctuation integral methods is not straightforward without extensive trial and error to determine these values. This is not the case for the pressure equation approach as described earlier. In general the use of integral equation results as a guide to system size specification, as was done in this study, will not be easily available, especially if simulations using more complicated site-site potentials are of interest.

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Notation

k = Boltzmann's constant
K_T = isothermal compressibility
P = pressure
T = temperature
T^* = reduced temperature with respect to energy well depth of LJ parameter $(=Kt/\epsilon_{22})$
$\bar{V}_i$ = partial molar volume of species i
V = volume
$x_{1,HL}$ = mole fraction of solute obtained using Henry's law
2 = solvent molecule

Greek letters

ϵ = well-depth parameter of Lennard-Jones energy function
σ = collision diameter of Lennard-Jones energy function
μ_1^r = solute's residual chemical potential
ρ^* = reduced density with respect to collision diameter $(=N\sigma_{22}^3/V)$

Literature Cited

Allen, M. P., and D. J. Tildesley, *Computer Simulation of Liquids*, Oxford Science Publications, Oxford (1987).

Brennecke, J. F., D. L. Tomasko, J. Peshkin, and C. A. Eckert, "Fluorescence Spectroscopy Studies in Dilute Supercritical Fluid Solutions," *Ind. Eng. Chem. Res.*, **29**, 1682 (1990).

Chialvo, A. A., and P. G. Debenedetti, "Molecular Dynamics Study of Solute-Solute Microstructure in Attractive and Repulsive Supercritical Mixtures," *Ind. Eng. Chem. Res.*, **31**, 1391 (1992).

Chialvo, A. A., "Solute-Solute and Solute-Solvent Correlation in Dilute Near-Critical Ternary Mixtures: Mixed-Solute and Entrainer Effects," *J. Phys. Chem.*, **97**, 2740 (1993).

Debenedetti, P. G., and S. K. Kumar, "Infinite Dilution Fugacity Coefficients and the General Behavior of Dilute Binary Systems," *AIChE J.*, **32**, 1253 (1986).

Debenedetti, P. G., and A. A. Chialvo, "Solute-Solute Correlations in Infinitely Dilute Supercritical Mixtures," *J. Chem. Phys.*, **97**, 504 (1992).

Debenedetti, P. G., and R. S. Mohamed, "Attractive, Weakly Attractive, and Repulsive Near-Critical Systems," *J. Chem. Phys.*, **90**, 4528 (1989).

Jonah, D., and H. D. Cochran, "Chemical Potential in Dilute, Multicomponent Solutions," *Fluid Phase Equilib.*, **92**, 107 (1994).

Kirkwood, J. G., and F. P. Buff, "The Statistical Mechanical Theory of Solutions. I," *J. Chem. Phys.*, **19**, 774 (1951).

Li, T. W., F. Munoz, and E. H. Chimowitz, "Computer Simulation and Theory for Free Energies in Dilute Near-Critical Solutions," *AIChE J.*, **39**, 1985 (1993).

Munoz, F., and E. H. Chimowitz, "Integral Equation Calculations of the Solute Chemical Potential in a Near-Critical Fluid Environment," *Fluid Phase Equilib.*, **71**, 237 (1992).

Munoz, F., and E. H. Chimowitz, "Critical Phenomena in Fluid Mixtures: I. Thermodynamic Theory for the Binary Critical Azeotrope," *J. Chem. Phys.*, **99**, 5438 (1993a).

Munoz, F., and E. H. Chimowitz, "Critical Phenomena in Fluid Mixtures: II. Synergistic and Other Effects Near Mixture Critical Points," *J. Chem. Phys.*, **99**, 5450 (1993b).

Munoz, F., T. W. Li, and E. H. Chimowitz, "Henry's Law and Synergism in Dilute Near-Critical Solutions: Theory and Simulation," *AIChE J.*, **41**, 389 (1995).

O'Connell, J. P., "Thermodynamic Properties of Solutions Based on Correlation Functions," *Mol. Phys.*, **20**, 27 (1971).

Petsche, I. B., and P. G. Debenedetti, "Influence of Solute-Solvent Asymmetry upon the Behavior of Dilute Supercritical Mixtures," *J. Phys. Chem.*, **95**, 356 (1991).

Shing, K. S., and S. T. Chung, "Computer Simulation Methods for the Calculation of Solubility in Supercritical Extraction Systems," *J. Phys. Chem.*, **91**, 1674 (1987).

Shing, K. S., and S. T. Chung, "Calculation of Infinite-Dilution Partial Molar Properties by Computer Simulation," *AIChE J.*, **34**, 1973 (1988).

Shing, K. S., and K. E. Gubbins, "The Chemical Potential from Computer Simulation Test Particle Method with Umbrella Sampling," *Mol. Phys.*, **43**, 717 (1981).

Wu, R.-S., L. L. Lee, and H. D. Cochran, "Structure of Dilute Supercritical Solutions: Clustering of Solvent and Solute Molecules and the Thermodynamic Effects," *Ind. Eng. Chem. Res.*, **29**, 977 (1990).

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