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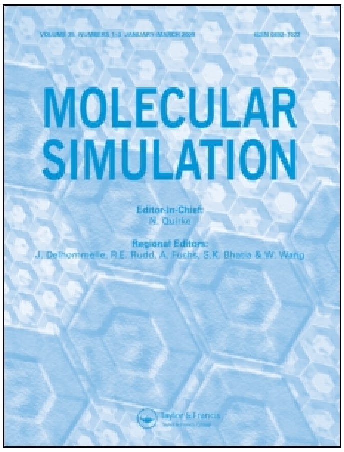

Molecular Simulation

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713644482

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To cite this Article Chialvo, Ariel A. and Debenedetti, Pablo G.(1991) 'A Study of Solute-Solvent Interactions at Infinite Dilution via the Coupling Parameter Approach', Molecular Simulation, 7: 5, 265 — 283

To link to this Article: DOI: 10.1080/08927029108022457

URL: http://dx.doi.org/10.1080/08927029108022457

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Molecular Simulation, 1991, Vol. 7, pp. 265–283
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A STUDY OF SOLUTE–SOLVENT INTERACTIONS AT INFINITE DILUTION VIA THE COUPLING PARAMETER APPROACH

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(*Received November 1990, accepted January 1991*)

The dependence of chemical potential at infinite dilution on size and energy parameters as well as on arbitrary combining rules is studied using a novel version of Kirkwood's coupling parameter method. This method enjoys several advantages over the test particle approach (it does not fail at high density or increasing size ratio) and the literal interpretation of Kirkwood's coupling parameter approach (the simulation quantities are well-behaved, and the simulation requirement is at least an order of magnitude smaller).

The simulations predict a monotonic size–ratio dependence for the chemical potential of Lennard-Jones mixtures at infinite dilution, for which earlier calculations showed a minimum about a size ratio of unity.

A simulation method is also proposed to calculate the isochoric rate of change of pressure upon solute addition at infinite dilution. This quantity plays a key role in the thermodynamics of dilute supercritical mixtures and determines their classification into attractive or repulsive.

KEY WORDS: Chemical potential, infinite dilution, coupling parameter method.

INTRODUCTION

Accurate infinite dilution properties obtained via computer simulation provide a direct link between the nature of solute–solvent interactions and its effect upon mixture properties, because of the absence of solute–solute interactions. Since infinite dilution properties are sensitive to the strength of the solute–solvent interactions [1,2], these quantities provide stringent tests of theories of mixtures [2–4]. Unfortunately, the accurate calculation of infinite dilution quantities via computer simulation is not a trivial task [5–12].

Considerable attention has been devoted to the calculation of the chemical potential at infinite dilution, both computationally as well as theoretically. Until recently, the preferred simulation routes to the chemical potential at infinite dilution have been Widom's test particle method in its different implementations [6–12], and the literal interpretation of Kirkwood's coupling parameter approach [5,10–12]. Simulation results have been used to test theoretical predictions for Henry's constant [6,7,11], mixing rules [10], and the validity of hypotheses underlying theories of mixtures [13–16], such as the postulated linear dependence of the unlike direct correlation function on the corresponding like correlation functions [13].

Much of the simulation work on chemical potentials has been done applying the test particle approach, a technique that invariably fails either at high density [10–12] or, in the case of mixtures, for increasing size asymmetries [7,11]. In this paper we illustrate how a convenient definition of the coupling parameter allows the development of more accurate and flexible methods to study the effect of molecular asymmetry (differences in size and energy between solute and solvent) upon mixture behavior. These methods are applied to the study of the dependence of the infinite dilution chemical potential (and its related quantities: activity coefficient or Henry's constant) on the strength of the solute–solvent interactions (including asymmetries on size and energy parameters, as well as combining rules). We also propose a coupling parameter approach to the calculation of the isochoric and isothermal rate of change of pressure upon solute addition at infinite dilution, a quantity which plays a key role in the thermodynamics of supercritical mixtures [27,30].

In Section 1 we describe the application of the single charging integral approach [5,17] to the calculation of the chemical potential at infinite dilution and its related quantities. In Section 2 we propose a simulation method for the calculation of the isochoric rate of change of pressure upon solute addition in a mixture at infinite dilution. In Section 3 we study the dependence of the chemical potential at infinite dilution on size and energy parameters, via isobaric–isothermal molecular dynamics simulation of Lennard-Jones mixtures. Simulation results are then used to test the accuracy of current theories of mixtures. Finally, we discuss the advantages of the present method (which allows for the introduction of different coupling parameters to study individual molecular asymmetries) with respect to alternative simulation routes to infinite dilution thermal properties.

DETERMINATION OF THE CHEMICAL POTENTIAL AT INFINITE DILUTION: A COUPLING PARAMETER APPROACH

Consider a binary mixture of N_A rigid molecules of component A and N_B rigid molecules of component B ($N = N_A + N_B$) at fixed temperature T and pressure P. The total potential energy $U(\mathbf{r}^N, \omega^N, \lambda)$ can be written as a function of molecular positions $\mathbf{r}^N$, molecular orientations ω^N, and interaction potential parameters λ (coupling parameters). These coupling parameters describe the mixture's asymmetries, including size and/or energy parameters [18–20], molecular elongation [21], and deviation from the Lorentz-Berthelot combining rules [22–23].

The difference of residual chemical potentials between species A and B in the above system can be written as [24]

$$\begin{aligned}(\mu_A - \mu_B)^{\text{res}} &= \left[\frac{G^{\text{res}}(N_A + 1, N_B - 1) - G^{\text{res}}(N_A, N_B - 1)}{1}\right]_{PT} \\ &\quad - \left[\frac{G^{\text{res}}(N_A, N_B - 1) - G^{\text{res}}(N_A, N_B)}{-1}\right]_{PT} \\ &= \Big[G^{\text{res}}(N_A + 1, N_B - 1) - G^{\text{res}}(N_A, N_B)\Big]_{PT} \qquad (1)\end{aligned}$$

where G^{res} and μ^{res} indicate residual contributions to the Gibbs free energy and chemical potential, respectively. For the special case of $N_A = 0$, infinitely dilute A in B, Equation (1) gives the change of residual Gibbs free energy associated with the conversion of one solvent particle (B) into a solute particle (A). For this situation the total potential energy $U(\mathbf{r}^N, \omega^N, \lambda)$ after the conversion can be written explicitly as the sum of two contributions [5]

$$U(\mathbf{r}^N, \omega^N, \lambda) = U_{N-1}(\mathbf{r}^{N-1}, \omega^{N-1}) + \sum_{j=1}^{N-1} \phi_{Aj}(\mathbf{r}_{Aj}, \omega_{Aj}, \lambda) \qquad (2)$$

where U_{N-1} denotes the intermolecular potential energy of the $(N - 1)$ unchanged solvent molecules, and ϕ_{Aj} corresponds to the interactions of the coupled A-particle (up to the extent λ) with a B-molecule. Then, invoking the definition of an isobaric-isothermal ensemble average, we can recast Equation (1) as follows [5]

$$(\mu_A^\infty - \mu_B^0)^{\mathrm{res}} = \sum_{i=1}^{k_A} \int_{\lambda_B^i}^{\lambda_A^i} \left\langle \frac{\partial U_{AB}}{\partial \lambda_i} \right\rangle_{NPT\lambda_{j\neq i}} d\lambda_i \qquad (3)$$

where angle brackets represent isobaric–isothermal ensemble (time) averages at the current λ-value, with

$$U_{AB} = \sum_{j=1}^{N-1} \phi_{Aj}(\mathbf{r}_{Aj}, \omega_{Aj}, \lambda) \qquad (4)$$

and k_A indicates the number of coupling parameters involved (molecular asymmetries). The process described by Equation (3) is the "creation" of an infinitely dilute mixture of A in B, starting from the pure solvent B. In particular,

i) For $\lambda = \lambda_B$ the system is an "ideal solution" (pure component B). All molecules have identical potential parameters, but one of them is labelled A.

ii) For $\lambda = \lambda_A$ the system has one molecule of type A (with potential parameters corresponding to component A) immersed in $(N - 1)$ molecules of type B (with potential parameters corresponding to component B).

According to Equation (3), the charging process yields the chemical potential of component A at infinite dilution relative to the chemical potential of pure component B. In more familiar terms, we can write [5,17]

$$[\mu_A^\infty(P,T) - \mu_B^0(P,T)]^{\mathrm{res}} = kT \ln\left(\frac{H_A(P,T)}{f_B(P,T)}\right) \qquad (5)$$

where H_A and f_B are Henry's constant for component A and the fugacity of pure component B, respectively. We can also obtain the ratio of Henry's constant to fugacity for the same component, as [5,17]

$$\begin{aligned}(\mu_A^\infty - \mu_A^0)^{\mathrm{res}} &= (\mu_A^\infty - \mu_B^0)^{\mathrm{res}} + (\mu_B^0 - \mu_A^0)^{\mathrm{res}} \\ kT\ln(H_A/f_A) &= (\mu_A^\infty - \mu_B^0)^{\mathrm{res}} + C_{AB}(T,P)\end{aligned} \qquad (6)$$

where $H_A/f_A = \gamma_A^\infty$ is the infinite dilution activity coefficient for component A, and $C_{AB}(T,P) = kT\ln(f_B/f_A)$ can be obtained from simulation, either after the following coupling parameter charging process [5,17],

$$C_{AB}(PT) = N^{-1} \sum_{i=1}^{k_B} \int_{\lambda_{\mathrm{pure}\,A}^i}^{\lambda_{\mathrm{pure}\,B}^i} \left\langle \frac{\partial U}{\partial \lambda_i} \right\rangle_{NPT\lambda_{i\neq j}} d\lambda_i \qquad (7)$$

or as the difference between the two possible charging integrals (for binaries) at any arbitrary composition, i.e.,

$$C_{AB}(P,T) = I_A(P,T,x_A = 0) = [I_A(P,T,x_A) - I_B(P,T,x_A)]_{\mathrm{any}\,x_A} \qquad (8)$$

where $I_A\ (P,T,\ x_A)$ is the A-charging integral [5,17],

$$I_A\ (P,T,\ x_A)\ \equiv\ (g^{\text{res}}_{\text{mix}} - g^{\text{res}}_{\text{pure}\,A})_{TPx_A}\ =\ (1/N)\sum_{l=1}^{k_B}\int_{\lambda_A^l}^{\lambda_B^l}\left\langle\frac{\partial U}{\partial\lambda_l}\right\rangle_{NPT\lambda_{j\neq l}} d\lambda_l \tag{9}$$

and $I_B\ (P,T,\ x_A)$ is the symmetric counterpart.

The λ-derivatives in the integrands of Equation (3) are usually related to the unlike pair potential ϕ_{Aj} in very simple ways. For example, the Lennard-Jones potential generates the following expressions

$$\frac{\partial\phi_{Aj}}{\partial\lambda}\ =\ \frac{\phi_{Aj}}{2\lambda},\ \lambda\ =\ \frac{\varepsilon_{AA}}{\varepsilon_{BB}} \tag{10}$$

with $\varepsilon_{AB}\ =\ (\varepsilon_{AA}\ \varepsilon_{BB})^{0.5}$,

$$\frac{\partial\phi_{Aj}}{\partial\lambda}\ =\ -\ \frac{\Psi_{Aj}}{1\ +\ \lambda},\ \lambda\ =\ \frac{\sigma_{AA}}{\sigma_{BB}} \tag{11}$$

with $\sigma_{AB}\ =\ 0.5\ (\sigma_{AA}\ +\ \sigma_{BB})$ and $\Psi_{Aj}\ =\ \mathbf{r}_A\cdot\partial\phi_{Aj}/\partial\mathbf{r}_A$,

$$\frac{\partial\phi_{Aj}}{\partial\lambda}\ =\ \frac{\phi_{Aj}}{\lambda},\ \lambda\ =\ \frac{\varepsilon_{AB}}{\sqrt{\varepsilon_{AA}\ \varepsilon_{BB}}} \tag{12}$$

$$\frac{\partial\phi_{Aj}}{\partial\lambda}\ =\ -\ \frac{\Psi_{Aj}}{\lambda},\ \lambda\ =\ \frac{2\sigma_{AB}}{(\sigma_{AA}\ +\ \sigma_{BB})} \tag{13}$$

which pertain to asymmetries in energy parameters, asymmetries in size parameters, deviations from the Berthelot combining rule, and deviations from the Lorentz combining rule, respectively. Consequently, the integrands of Equation (3) are not only well-behaved, but can be otained accurately and straightforwardly from simulation.

Note that the energy and size asymmetry dependencies ($C\ \equiv\ (\varepsilon_{AB}/\varepsilon_{BB})$, $D\ \equiv\ (\sigma_{AB}/\sigma_{BB})^3$) of the chemical potential at infinite dilution can be obtained using two alternative routes. The first route is the straightforward generation of the integrand of Equation (3), using either Equation (10) or (11), and subsequent numerical integration. The second route takes advantage of an already calculated value of μ_A^∞ for a particular value of C and/or D, used as a reference [a particularly convenient choice is $\mu_A^\infty\ (\eta\ =\ 1,\ \xi\ =\ 1)$] [25], so that

$$C_{\text{new}}\ =\ \xi\ C_{\text{ref}},\ D_{\text{new}}\ =\ \eta^3\ D_{\text{ref}} \tag{14}$$

where ξ and η are the coupling parameters defined in Equations (12) and (13) respectively. Then, we calculate the change $\Delta\mu_A^\infty\ (\eta,\xi)\ \equiv\ \mu_A^\infty\ (\eta,\xi)\ -\ \mu_A^\infty\ (1,1)$ by means of Equation (3). This procedure is particularly advantageous for the prediction of the C-dependence of μ_A^∞ because $d\mu_A^\infty/d\xi\ =\ \langle U_{AB}\ \ (\xi)\rangle/\xi\ \cong$ constant for $0.6\ \leqslant\ \xi\ \leqslant\ 1.4$ (see Figure 1). This behavior can be understood by writing

$$\langle U_{AB}\rangle\ =\ 4\pi\ x_A\ x_B\ \rho\ \varepsilon_{AB}\int f(r/\sigma_{AB})\ g_{AB}\ (r/\sigma_{AB})\ r^2\ dr \tag{15}$$

While the solute–solvent pair correlation function (g_{AB}) shows a pronounced dependence on ε_{AB} [10] we have found that the mixture's density, in contrast, is virtually insensitive to ε_{AB}. This behavior translates into an insensitivity of the integral over the solute–solvent pair correlation function to changes in ε_{AB}, Equation (15), and consequently allows us to write

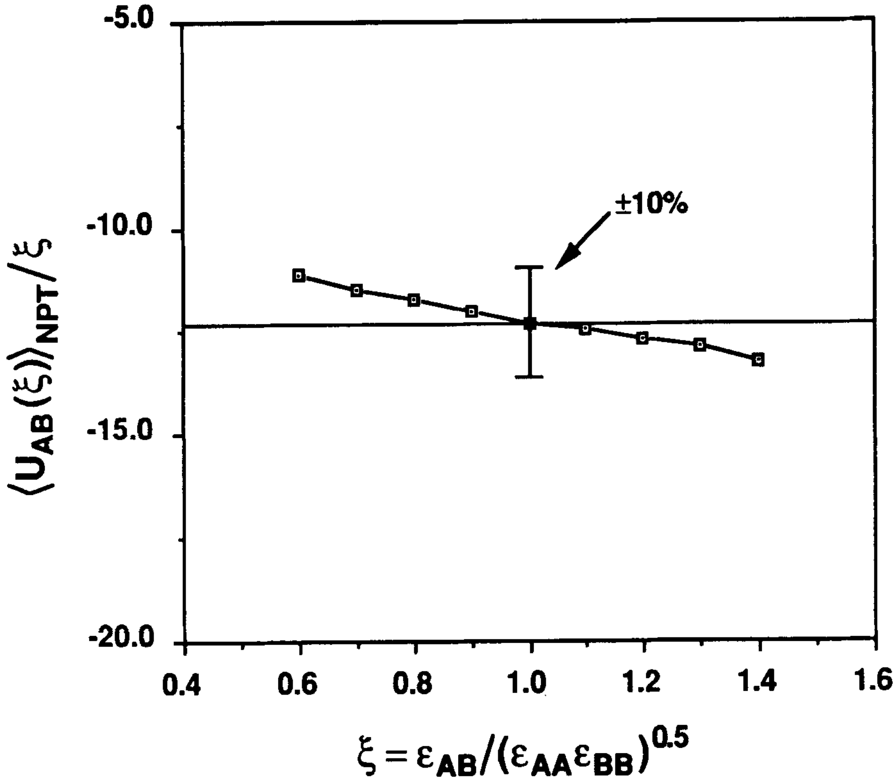

Figure 1 Test of the approximation given by Equation (16) for Lennard-Jones mixtures of atoms at infinite dilution with $C = 1.25$ and $D = 1.0$. The state condition is $kT/\varepsilon_{BB} = 1.2$ and $P\sigma_{BB}^3/\varepsilon_{BB} = 0.654$.

$$\phi_{Aj} = \varepsilon_{Aj} f(r/\sigma_{Aj}) \Rightarrow \sum_{j=1}^{N} \phi'_{Aj} \cong \varepsilon'_{AB} \sum_{j=1}^{N} f(r/\sigma_{Aj}) = \varepsilon'_{AB} \sum_{j=1}^{N} \left(\phi_{Aj}/\varepsilon_{Aj}\right) = \xi \sum_{j=1}^{N} \phi_{Aj}$$

$$\Rightarrow \langle U_{AB}(\xi)\rangle_{\xi}/\xi \cong \langle U_{AB}(\xi = 1)\rangle_{\xi=1} \qquad \xi = \varepsilon'_{AB}/\varepsilon_{AB} \quad (16)$$

Thus, the value of $\langle U_{AB}(\xi = 1)\rangle_{\xi=1}$ from the reference mixture suffices to predict μ_A^{∞} over a wide range of C. The bigger the C-value chosen for the reference, the wider the C-range which can be predicted (see Equation (14)).

The combined effect of the k_A asymmetries on the charging integrands of Equation (3) or of the k_B asymmetries on the integrands of Equation (7) can be computed following either a stepwise or a simultaneous multiple parameter charging process since we are dealing with state functions [18,19].

DETERMINATION OF $\delta = \lim_{N_A \to 0} N(\partial P/\partial N_A)_{TVN_B}$ FROM COMPUTER SIMULATION

It has been shown recently [27,30] that all infinitely dilute binary mixtures in which the solvent is near its critical point fall into one of three categories, according to the sign of the solute's diverging partial molar properties, and of the excess number of solvent molecules surrounding the infinitely dilute solute with respect to a uniform distribution at bulk conditions, a quantity which also diverges at the solvent's critical point. In attractive mixtures, the solute's partial molar volume and enthalpy diverge to $-\infty$, and the excess number of solvent molecules, to $+\infty$; in repulsive mixtures, these quantities diverge to $+\infty$ and $-\infty$, and, in weakly attractive mixtures, to $+\infty$ and $+\infty$, respectively. Attractive behavior is a necessary condition for solubility enhancement in supercritical solvents; repulsive behavior near the critical point of the less volatile component is closely related to gas-gas immiscibility [30].

The key thermodynamic quantity that determines the attractive or repulsive character of a particular dilute supercritical system is the rate of change of pressure upon isochoric and isothermal solute addition. Specifically, with

$$\delta = \lim_{N_A \to 0} N \left(\frac{\partial P}{\partial N_A} \right)_{TVN_B} \tag{17}$$

it can be shown [27,30] that

$$\begin{gathered} \delta < 0 \Rightarrow \text{attractive behavior} \Rightarrow \bar{V}_A^\infty \to -\infty \, ; \, \Gamma \to +\infty \\ \rho kT > \delta > 0 \Rightarrow \text{weakly attractive behavior} \Rightarrow \bar{V}_A^\infty \to +\infty \, ; \, \Gamma \to +\infty \\ \delta > \rho kT \Rightarrow \text{repulsive behavior} \Rightarrow \bar{V}_A^\infty \to +\infty \, ; \, \Gamma \to -\infty \end{gathered} \tag{18}$$

where

$$\Gamma = \rho \int (g_{AB}^\infty - 1) \, d^3 r \tag{19}$$

and g_{AB}^∞ is the unlike pair correlation function at infinite dilution. In the above equations, ρ is the pure solvent number density. It follows from Equation (19) that Γ represents the statistical excess of solvent molecules surrounding solute molecules at infinite dilution with respect to a uniform distribution at bulk conditions.

Given the importance of δ in influencing the global phase behavior of a given system in a broad region including the solvent's critical point [30] it is of considerable interest to develop computational techniques that would allow its efficient calculation. This would permit the study of the effects of size, energy, and shape asymmetries on mixture behavior, and a comparison with theoretical predictions [30]. As a first step in that direction, we propose below a computational method for the calculation of δ based on the coupling parameter approach.

Consider the same system as before, now held at constant temperature and volume V. Imagine a process consisting of converting a particle labelled A (but otherwise identical to the other N-1 particles labelled B, and having potential parameters characteristic of species B) into a different species (a solute particle), by gradually changing its potential parameters. The thought experiment can be easily achieved by an appropriate isochoric-isothermal coupling parameter charging process. The configurational contribution to the reversibe work involved in such a process can be expressed as

$$\begin{aligned} F^c(N-1,1) - F^c(N,0) &= F^c\,(\text{infinite dilution}) - F^c\,(\text{ideal solution}) \\ &= \sum_{i=1}^{k_A} \int_{\lambda_B^i}^{\lambda_A^i} \left\langle \frac{\partial U_{AB}}{\partial \lambda_i} \right\rangle_{NVT\lambda_{j \neq i}} d\lambda_i \end{aligned} \tag{20}$$

where F^c denotes configurational Helmholtz free energy. Note also that F^c(ideal solution) is just F^c(pure solvent), since the A-labelled particle is initially identical to the solvent particles. The non-configurational contributions to P are due to translational and rotational degrees of freedom. These quantities can be trivially calculated. For Lennard-Jones spheres (with no rotational degrees of freedom) these contributions cancel upon subtraction. Now, recalling that $P = -(\partial F/\partial V)_{\beta N}$, with $\beta = (kT)^{-1}$, we have

$$\begin{aligned} P(N-1,1) - P(N,0) &= P(\text{infinite dilution}) - P(\text{ideal solution}) \\ &= \sum_{i=1}^{k_A} \frac{\partial}{\partial V}\left[\int_{\lambda_B^i}^{\lambda_A^i} \left\langle \frac{\partial U_{AB}}{\partial \lambda_i} \right\rangle_{NVT\lambda j \neq i} d\lambda_i\right]_{\beta N} \end{aligned} \tag{21}$$

Before solving the volume derivative in the rhs of Equation (21), we recast the lhs, as follows

$$\begin{aligned} P(N-1,1) - P(N,0) &= \lim_{N_A \to 0}\left[\frac{P(N_B-1,N_A+1) - P(N_B-1,N_A)}{1}\right. \\ &\quad \left. - \frac{P(N_B-1,N_A) - P(N_B,N_A)}{-1}\right] \\ &= \lim_{N_A \to 0}\left[\left(\frac{\partial P}{\partial N_A}\right)_{TVN_B} - \left(\frac{\partial P}{\partial N_B}\right)_{TVN_A}\right] \end{aligned} \tag{22}$$

where we can immediately identify [27]

$$\delta = \lim_{N_A \to 0} N\left(\frac{\partial P}{\partial N_A}\right)_{TVN_B} \tag{17}$$

and

$$(\kappa_T)^{-1} = \lim_{N_A \to 0} N\left(\frac{\partial P}{\partial N_B}\right)_{TVN_A} \tag{23}$$

with κ_T, the solvent's isothermal compressibility.

We now seek an explicit expression for the volume derivative in Equation (21), in terms of canonical ensemble averages available from simulation. To that end we recall the following identity, which follows upon application of Green-Bogoliubov's method [28]

$$\begin{aligned} \frac{\partial}{\partial V}[Q\,\langle B\rangle_{NV\beta}]_{\beta N} &= \langle B\rangle_{NV\beta}\left[\frac{\partial Q}{\partial V}\right]_{\beta N} + Q\,\frac{\partial}{\partial V}\langle B\rangle_{NV\beta} \\ &= \beta\, Q\left\langle B\left(\frac{\rho}{\beta} - \frac{\partial U}{\partial V}\right)\right\rangle_{NV\beta} + Q\left\langle\frac{\partial B}{\partial V}\right\rangle_{NV_\beta} \end{aligned} \tag{24}$$

where Q is the canonical partition function. Therefore, rearranging the rhs of Equation (24), and recalling the definition of a canonical ensemble average, we can write

$$\frac{\partial}{\partial V}\langle B\rangle_{NV\beta} = \beta\,[\langle BP\rangle - \langle B\rangle\langle P\rangle]_{NV\beta} + \left\langle\frac{\partial B}{\partial V}\right\rangle_{NV\beta} \tag{25}$$

where $B \equiv \partial U_{AB}/\partial\lambda$, and $P \equiv \rho/\beta - \partial U/\partial V$. In addition, we can recast the last term of Equation (25) by reversing the order of differentiation i.e.,

$$\left\langle\frac{\partial B}{\partial V}\right\rangle_{NV\beta} = \left\langle\frac{\partial}{\partial V}\left(\frac{\partial U_{AB}}{\partial\lambda}\right)\right\rangle_{NV\beta} = \left\langle\sum_{i=1}^{N}\mathbf{r}_i\cdot\frac{\partial}{\partial\mathbf{r}_i}\left(\frac{\partial U_{AB}}{\partial\lambda}\right)\right\rangle_{NV\beta}(3V)^{-1}$$

$$= \left\langle\frac{\partial\Psi_{AB}}{\partial\lambda}\right\rangle_{NV_\beta}(3V)^{-1} \tag{26}$$

Finally, from Equations (21)–(26), we have

$$\delta = (\kappa_T^{-1}) - N\sum_{i=1}^{k_A}\int_{\lambda^i_B}^{\lambda^i_A}\left\{\beta\left[\langle B_iP\rangle - \langle P\rangle\langle B_i\rangle\right] - \left\langle\frac{\partial\Psi_{AB}}{\partial\lambda_i}\right\rangle(3V)^{-1}\right\}_{NVT\lambda_{j\neq i}} d\lambda_i \tag{27}$$

with $B_i = (\partial U_{AB}/\partial\lambda_i)$. U_{AB} and Ψ_{AB} are the solute–solvent contributions to the configurational internal energy and virial, respectively.

According to Equation (27), δ can be determined by numerical integration of the second term provided κ_T is available for the pure solvent. In fact we have two different alternatives: we can either evaluate the isobaric-isothermal average of the volume fluctuation ($\langle V\rangle = N/\rho$), so that

$$\kappa_T = \beta\frac{\langle(\langle V\rangle - V)^2\rangle_{NPT}}{\langle V\rangle_{NPT}} \tag{28}$$

or we can perform a coupling parameter charging process similar to that in the second term of Equation (27), in which the initial state is a system with (N − 1) solvent particles, and the final state is the ideal solution of N solvent particles. Then, the process is just one in which we introduce an initially ideal gas solvent particle, and couple it to the system by "switching on" progressively its potential parameters. The isochoric-isothermal change of pressure due to the introduction of a new particle to the system is then given by

$$(\kappa_T)^{-1} = \lim_{N_A\to 0} N(\partial P/\partial N_B)_{TVN_A}$$

$$= -N\sum_{i=1}^{k_A}\int_0^{\lambda^i_B}\left\{\beta\left[\langle B_iP\rangle - \langle P\rangle\langle B_i\rangle\right] - \left\langle\frac{\partial\Psi_{AB}}{\partial\lambda_i}\right\rangle(3V)^{-1}\right\}_{NVT\lambda_{j\neq i}} d\lambda_i \tag{29}$$

where $\lambda^i_B = 0$ represents zero interaction strength (ideal gas solvent particle). Note that the averages involved in the integrands of Equation (27) are well-behaved quantities. In fact, for systems whose asymmetries are due to size, energy, or elongation effects, the λ-derivatives are either proportional to, or linear combinations of, U_{AB} and Ψ_{AB}. Specifically,

$$\frac{\partial U_{AB}}{\partial\lambda} = \frac{U_{AB}}{\lambda} \quad \text{if } \lambda = \frac{\varepsilon_{AB}}{\varepsilon_{BB}} \tag{30}$$

$$\frac{\partial U_{AB}}{\partial\lambda} = -\frac{\Psi_{AB}}{\lambda} \quad \text{if } \lambda = \frac{\sigma_{AB}}{\sigma_{BB}} \tag{31}$$

$$\frac{\partial\Psi_{AB}}{\partial\lambda} = \frac{\Psi_{AB}}{\lambda} \quad \text{if } \lambda = \frac{\varepsilon_{AB}}{\varepsilon_{BB}} \tag{32}$$

$$\frac{\partial \Psi_{AB}}{\partial \lambda} = \frac{18\Psi_{AB} - 72U_{AB}}{\lambda} \quad \text{if } \lambda = \frac{\sigma_{AB}}{\sigma_{BB}} \tag{33}$$

The above methodology enables, in principle, the calculation of δ via simulation. It is anticipated that the computational effort involved will be considerable due to the influence of density fluctuations associated with criticality, which can be important even in the supercritical (as opposed to near-critical) region where the behavior of δ is of interest [30]. Simulation work is in progress on this topic.

CHEMICAL POTENTIAL AND ACTIVITY COEFFICIENT AT INFINITE DILUTION: SIMULATION RESULTS

We have studied the independent effects of the size ratio $D \equiv (\sigma_{AB}/\sigma_{BB})^3$ $(0 < D \leqslant 5)$, energy ratio $C \equiv (\varepsilon_{AB}/\varepsilon_{BB})$ $(0.125 \leqslant C \leqslant 2)$, and deviation from the Lorentz-Berthelot combining rules, on the chemical potentials of Lennard-Jones mixtures of atoms at infinite dilution. The state condition we chose is $kT/\varepsilon_{BB} = 1.2$

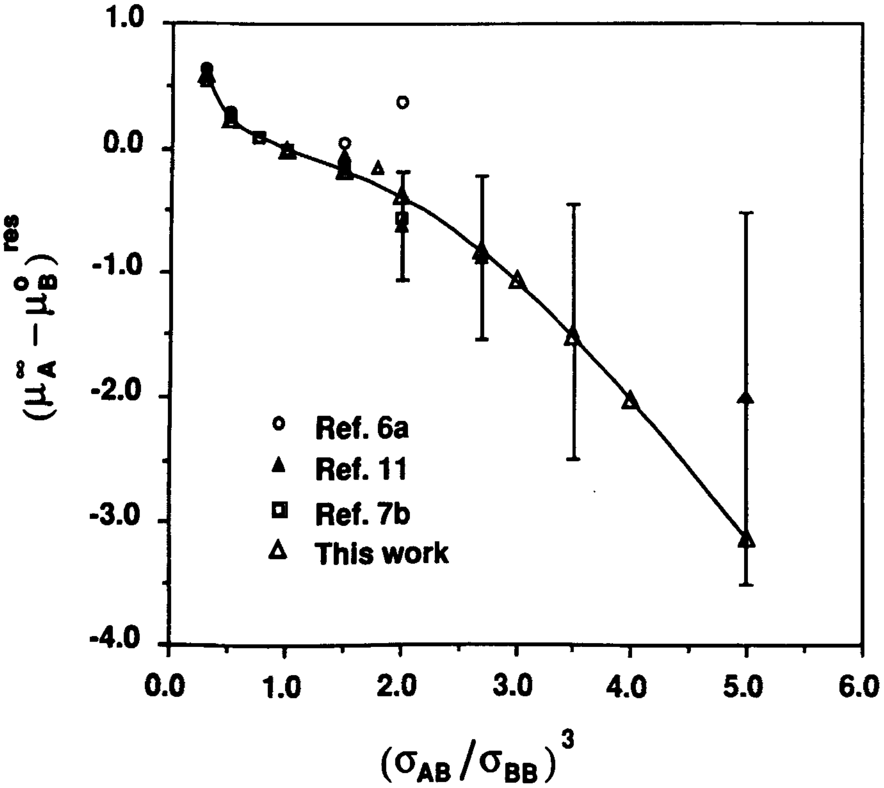

Figure 2 Dependence of $(\mu_A^\infty - \mu_B^0)^{res}$ (in ε_{BB} units) on size ratio D for Lennard-Jones mixtures of atoms at infinite dilution with $C = 1.0$. The state condition is $kT/\varepsilon_{BB} = 1.2$ and $P\sigma_{BB}^3/\varepsilon_{BB} = 0.654$. Comparison of results from our NPT-MD method and other reported simulation approaches: NPT-MD test particle [7], NVT-MC test particle [6], and NPT-MC Kirkwood coupling parameter [11].

and $P\sigma_{BB}^3/\varepsilon_{BB} = 0.654$, corresponding to a density $\langle\rho\rangle\,\sigma_{BB}^3 = 0.7$ (where B denotes the solvent's potential parameters). Since this condition has been used in numerous computational and theoretical studies [3–7, 11, 13–16], it allows a direct comparison between our results and both simulation and theoretical calculations.

The simulation procedure is summarized in Appendix A. Since usually the chemical potential at infinite dilution is written as a perturbation about the chemical potential of the pure solvent [13–16], we can make more stringent tests of the accuracy of a theory by comparing $\Delta\mu_A^\infty \equiv \mu_A^\infty - \mu_B^0$ values instead of μ_A^∞ values, thereby eliminating uncertainties in μ_B^0. Although our method is also suitable for the evaluation of μ_B^0 (Equation (3) with $\lambda_A^i = 0, i = 1, \ldots, k_A$), in this paper we focus on the computation of $\mu_i^\infty - \mu_j^0$ and $\mu_i^\infty - \mu_i^0$.

In Figure 2 we display the dependence of $\Delta\mu_A^\infty$ on the size asymmetry $D \equiv (\sigma_{AB}/\sigma_{BB})^3$ obtained via simulation (Equation 3 and 10), and compare our calculations with three other sources of simulation results: the NVT-MC version of Widom's test particle method [6], the NVT-MD version of Widom's test particle method [7], and the NPT-MC version of Kirkwood's coupling parameter interpretation of the chemical potential [11]. In Figure 3 we compare the predictions of different theories of

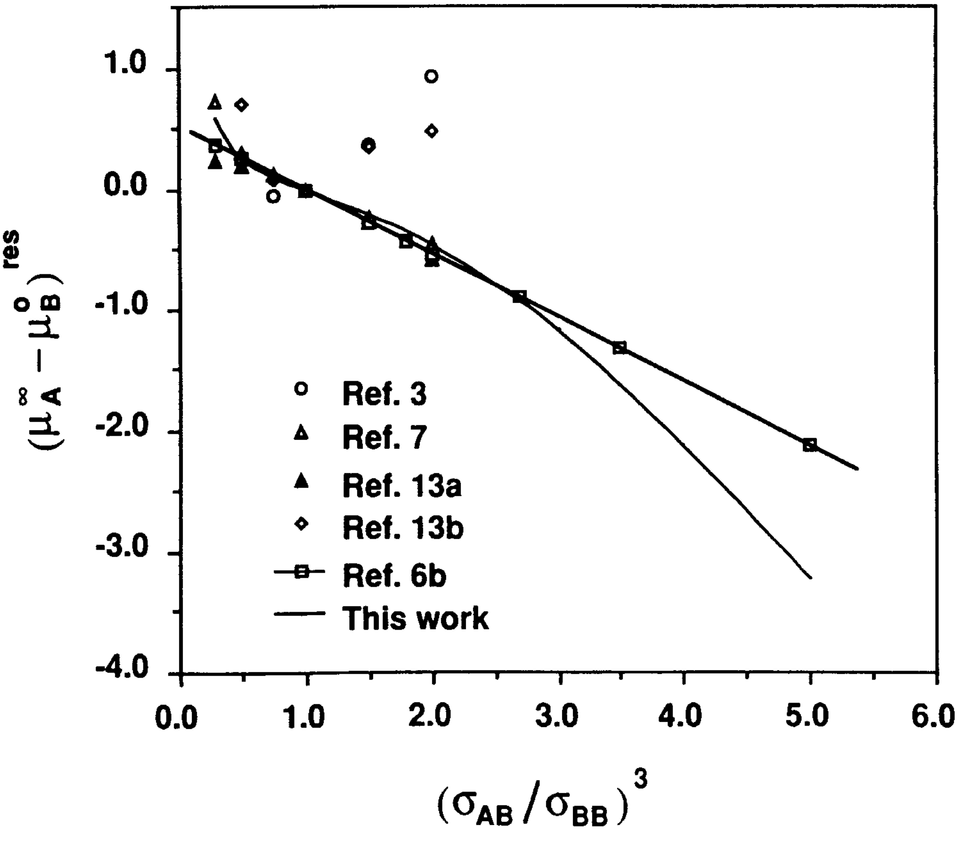

Figure 3 Dependence of $(\mu_A^\infty - \mu_B^0)^{res}$ (in ε_{BB} units) on size ratio D for Lennard-Jones mixtures of atoms at infinite dilution with $C = 1.0$. The state condition is $kT/\varepsilon_{BB} = 1.2$ and $P\sigma_{BB}^3/\varepsilon_{BB} = 0.654$. Comparison of results from the present NPT-MD method and theoretical results.

mixtures as to the D-dependence of $\Delta\mu_A^\infty$. Similar comparisons are displayed in Figures 4 and 5 for the dependence of $\Delta\mu_A^\infty$ on energy asymmetry $C \equiv (\varepsilon_{AB}/\varepsilon_{BB})$. The complete tabulation of our simulation results for the dependence of $\Delta\mu_A^\infty$ on C and D is given in Table 1, in conjunction with the corresponding results from Fischer-Lago-Bohn's perturbation theory of fluid mixtures (FLBPT) [7].

Results from the alternative method given by Equations. (11)–(13), as well as the corresponding approximation for the C-dependence (see Equation (14)) are displayed in Table 2. Tables 3 and 4 give the resulting activity coefficients at infinite dilution as functions of asymmetries C and D respectively. These tables also include the values of C_{AB} (TP), Equation (7), for each mixture.

Finally, in Tables 5 and 6, we present the thermodynamic properties for the pure component systems involved in the calculation of C_{AB} (TP), calculated via simulation and with an equation of state [29].

4 DISCUSSION AND CONCLUSIONS

In this paper we have applied a new implementation of Kirkwood's coupling parameter method [5,17] to study the behavior of model mixtures at infinite dilution. The

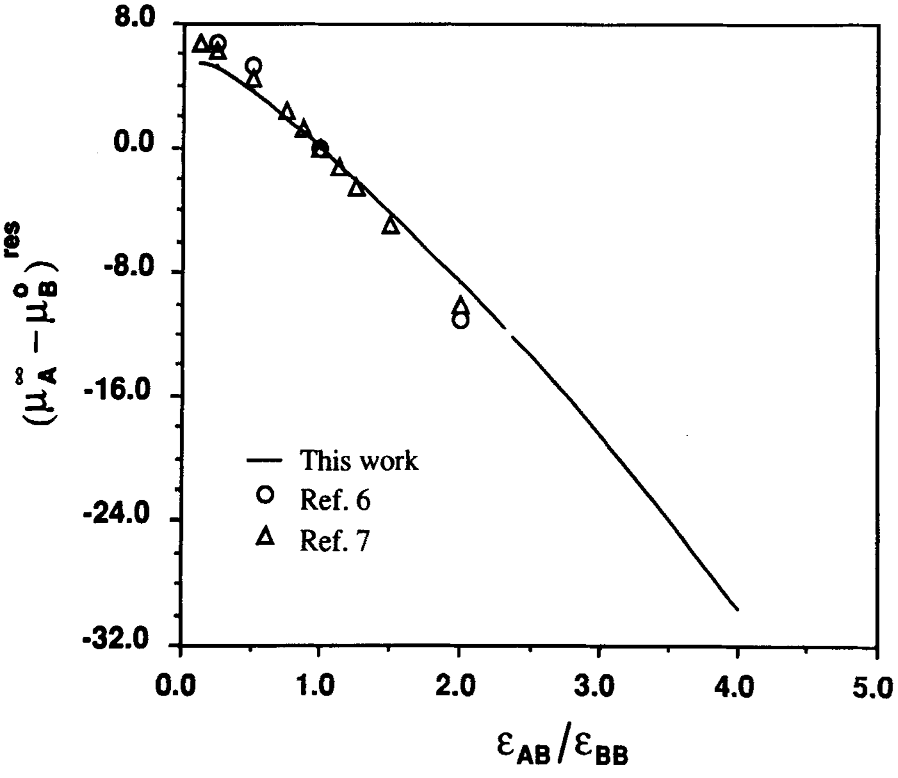

Figure 4 Dependence of $(\mu_A^\infty - \mu_B^0)^{res}$ (in ε_{BB} units) on energy ratio C for Lennard-Jones mixtures of atoms at infinite dilution with $D = 1.0$. The state condition is $kT/\varepsilon_{BB} = 1.2$ and $P\sigma_{BB}^3/\varepsilon_{BB} = 0.654$. Comparison of results from the present NPT-MD method and other simulation approaches: NPT-MD test particle [7] and NVT-MC test particle [6].

method does not require a linear parametrization of the system's Hamiltonian [5,17]. This approach allows the accurate calculation of thermodynamic excess properties and the corresponding infinite dilution quantities from NPT simulations, it does not require the knowledge of pure component properties, it allows the study of the individual contributions of any asymmetry to the system's nonideality, and involves well-behaved simulation quantities. The aim is to develop a microscopically-based understanding of important mixture properties which are determined by solute–solvent interactions, such as Henry's constant, activity coefficients at infinite dilution, patterns of nonideality, and the rate of change of pressure upon solute addition at infinite dilution, the later of fundamental importance in the thermodynamics of supercritical mixtures.

The method reduces the number of simulations required per data point by more than an order of magnitude when compared to the literal application of Kirkwood's coupling parameter method [5; see also Appendix]. In addition, a more convenient definition of the coupling parameters instead of the linear parametrization of the system's Hamiltonian used in the literal interpretation of Kirkwood's method [11,12] makes it possible to check the consistency of the simulation results (the consistency tests proposed by Lotfi and Fischer, Equation 15 and 21 in Reference [7] are just special cases of our charging integrands). As an example, we cite the case of earlier

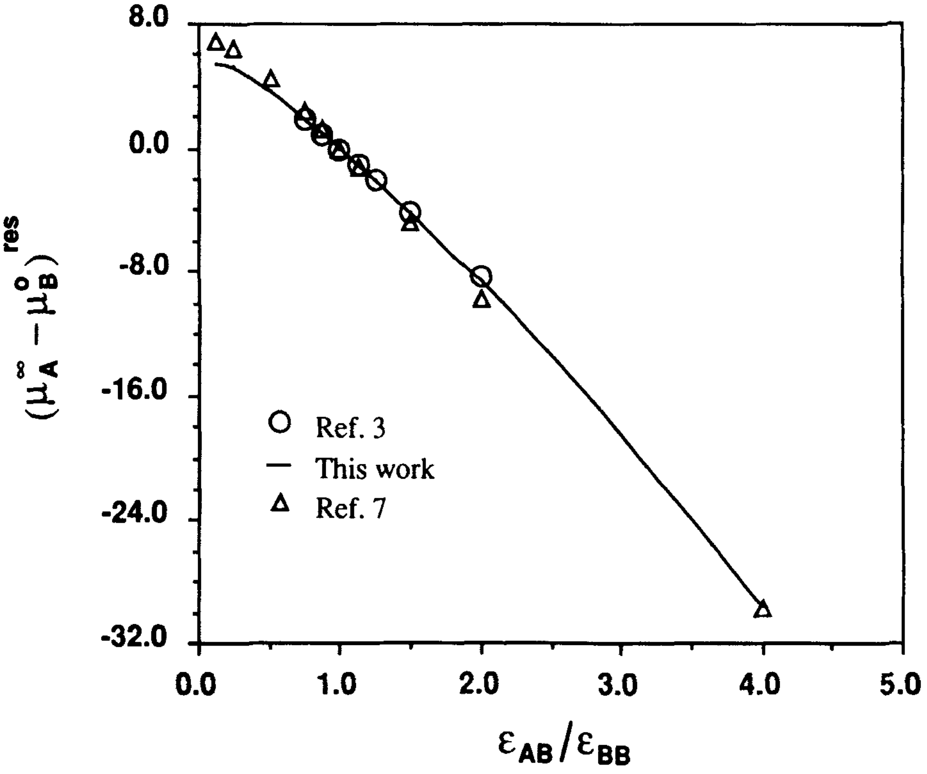

Figure 5 Dependence of $(\mu_A^\infty - \mu_B^0)^{res}$ (in ε_{BB} units) on energy ratio C for Lennard-Jones mixtures of atoms at infinite dilution with $D = 1.0$. The state condition is $kT/\varepsilon_{BB} = 1.2$ and $P\sigma_{BB}^3/\varepsilon_{BB} = 0.654$. Comparison of results from the present NPT-MD method and theoretical results.

Table 1 Chemical potentials of Lennard-Jones mixtures of spheres at infinite dilution with asymmetries in size and energy parameters. The state condition is $kT/\varepsilon_{BB} = 1.2$ and $P\sigma_{BB}^3/\varepsilon_{BB} = 0.654$, corresponding to $\langle\rho\rangle\,\sigma_{BB}^3 = 0.7$.

$(\sigma_{AB}/\sigma_{BB})^3$	$(\varepsilon_{AB}/\varepsilon_{BB})$	$(\mu_A^\infty - \mu_B^0)^{res}/kT$	
		This work	*FLBPT*$_{(a)}$
0.3	1.0	0.59	0.71
0.5	1.0	0.24	0.31
0.75	1.0	....	0.15
1.0	1.0	0.0	0.0
1.25	1.0	....	−0.12
1.5	1.0	−0.20	−0.22
2.0	1.0	−0.45	−0.45
2.7	1.0	−0.92	....
3.0	1.0	−1.16	....
3.5	1.0	−1.62	....
4.0	1.0	−2.12	....
5.0	1.0	−3.22	....
1.0	0.125	5.47	5.73
1.0	0.25	5.18	5.30
1.0	0.5	3.68	3.76
1.0	0.75	1.90	1.93
1.0	1.0	0.0	0.0
1.0	1.125	−1.02	−0.99
1.0	1.50	−4.16	−4.01
1.0	2.0	−8.61	−8.11
1.0	4.0	−29.6	−24.80

(a) See erratum in Ref. [7].

simulation results for the D-dependence of μ_A^∞ for Lennard-Jones mixtures of atoms at $kT/\varepsilon_{BB} = 1.2$ and $\rho\sigma_{BB}^3 = 0.7$ (i.e., $P\ \sigma_{BB}^3 \approx 0.654$), which showed a minimum about $D = 1$ [6]. This behavior is inconsistent with the predictions of accurate perturbation theories of mixtures [2]. According to Equation (11), the existence of such an extremum is subject to the following conditions

$$d\mu_A^\infty/dD \;=\; -\,(8/3)\,\langle\Psi_{AB}\rangle/(1+\lambda)^3 \;=\; 0$$

$$d^2\,\mu_A^\infty/dD^2 > 0$$

The first condition indicates that $\langle\Psi_{AB}\,(D)\rangle$ should vanish at the minimum. The

Table 2 Chemical potentials of Lennard-Jones mixtures of spheres at infinite dilution with asymmetries in energy parameters, and $D = 1.0$, treated as deviations from Berthelot rule about $C \equiv \varepsilon_{AB}/\varepsilon_{BB} = 1.25$.[(a)] The state condition is $kT/\varepsilon_{BB} = 1.2$ and $P\sigma_{BB}^3/\varepsilon_{BB} = 0.654$, corresponding to $\langle\rho\rangle\,\sigma_{BB}^3 = 0.7$.

ξ	$C' = \xi\, C$	*Equation (9)*	*Equation (11)*	*Equation (14)*
0.6	0.75	2.31	2.24	2.48
0.7	0.875	1.17	1.13	1.25
0.8	1.0	0.0	−0.04	0.02
0.9	1.125	−1.21	−1.22	−1.21
1.0	1.25	−2.44	−2.44	−2.44
1.1	1.375	−3.68	−3.68	−3.67
1.2	1.5	−4.97	−4.94	−4.90
1.3	1.625	...	−6.22	−6.13

(a) $(\mu_A^\infty\,(C') - \mu_B^0)^{\mathrm{res}} = (\mu_A^\infty\,(C') - \mu_A^\infty\,(C))^{\mathrm{res}} + (\mu_A^\infty\,(C) - \mu_B^0)^{\mathrm{res}}$

Table 3 Activity coefficients of Lennard-Jones mixtures of spheres at infinite dilution with asymmetries in energy parameters and $D = 1.0$. The state condition is $kT/\varepsilon_{BB} = 1.2$ and $P\sigma_{BB}^3/\varepsilon_{BB} = 0.654$, corresponding to $\langle\rho\rangle\ \sigma_{BB}^3 = 0.7$.

$C = \varepsilon_{AB}/\varepsilon_{BB}$	$\dfrac{(\mu_A^\infty(C) - \mu_B^0)^{res}}{\varepsilon_{BB}}$	$\dfrac{(\mu_B^0 - \mu_A^0)^{res}}{\varepsilon_{BB}}$	$\gamma_A^\infty = exp\ [(\mu_A^\infty(C) - \mu_A^0)^{res}/kT]$
0.5	4.44	−2.45	5.25
0.75	2.31	−1.69	1.67
0.875	1.17	−1.0	1.15
1.0	0.0	0.0	1.0
1.125	−1.21	1.36	1.13
1.25	−2.44	3.07	1.69
1.5	−4.97	7.46	7.96

Table 4 Activity coefficients of Lennard-Jones mixtures of spheres at infinite dilution with asymmetries in size parameters and $C = 1.0$. The state condition is $kT/\varepsilon_{BB} = 1.2$ and $P\ \sigma_{BB}^3/\varepsilon_{BB} = 0.654$, corresponding to $\langle\rho\rangle\ \sigma_{BB}^3 = 0.7$.

$D = (\sigma_{AB}/\sigma_{BB})^3$	$\dfrac{(\mu_A^\infty\ (D) - \mu_B^0)^{res}}{\varepsilon_{BB}}$	$\dfrac{(\mu_B^0 - \mu_A^0)^{res}}{\varepsilon_{BB}}$	$\gamma_A^\infty = exp\ [(\mu_A^\infty\ (D) - \mu_A^0)^{res}/kT]$
0.5	0.36	−0.78	0.70
1.0	0.0	0.0	1.00
1.5	−0.25	−0.1	0.75
2.0	−0.54	−0.64	0.37
2.7	−1.01	−1.74	0.09
3.0	−1.39	−2.29	0.04
3.5	−1.94	−3.27	0.01
4.0	−2.54	−4.31	0.003
5.0	−3.87	−6.52	0.0002

second condition implies $72\ \langle U_{AB}(D)\rangle > 15\ \langle\Psi_{AB}(D)\rangle$. The simulation results of Figure 6 show that $\langle\Psi_{AB}(D)\rangle$ is positive throughout the entire range $0 < D \leqslant 5$ (see also Equation A1). Consequently, μ_A^∞ cannot show an extremum in that region.

In contrast to our method, the literal application of Kirkwood's coupling parameter interpretation of the chemical potential [11,12] (linear parametrization of the system's Hamiltonian) involves only one coupling parameter, $0 \leqslant \lambda \leqslant 1$, which

Table 5 Thermodynamic properties of the pure Lennard-Jones atomic fluids involved in Tables 2 and 3 at the nominal state condition $kT/\varepsilon_{BB} = 1.2$ and $P\sigma_{BB}^3/\varepsilon_{BB} = 0.654$, corresponding to $\langle\rho\rangle\ \sigma_{BB}^3 = 0.7$.

C	ε/k	$P\sigma^3/\varepsilon$	kT/ε	$\rho\sigma^3$		$U/N\varepsilon$		$\Delta\mu^{res}/\varepsilon_{BB}$ (b)	
				EOS (a)	MD	EOS	MD	EOS	MD
0.5	29.95	2.616	4.8	0.376	0.371	−1.83	−1.85	2.5	2.45
0.75	67.39	1.1626	2.133	0.493	0.481	−3.05	−2.98	1.737	1.69
0.875	91.72	0.8542	1.567	0.602	0.586	−3.93	−3.84	0.999	1.00
1.0	119.8	0.654	1.2	0.7	0.698	−4.78	−4.72	0.0	0.0
1.125	151.62	0.5167	0.9481	0.781	0.778	−5.47	−5.45	−1.351	−1.35
1.25	187.187	0.4185	0.768	0.84	0.834	−6.04	−5.99	−3.08	−3.07
1.5	269.55	0.2906	0.533	0.926	0.924	−6.81	−6.80	−7.53	−7.46

(a) Reference [29]
(b) $\Delta\mu^{res} \equiv \mu^{res}(\varepsilon) - \mu^{res}(\varepsilon_{BB})$

Table 6 Thermodynamic properties of the pure Lennard-Jones atomic fluids involved in Tables 2 and 3 at the nominal state condition $kT/\varepsilon_{BB} = 1.2$ and $P\sigma_{BB}^3/\varepsilon_{BB} = 0.654$, corresponding to $\langle\rho\rangle\, \sigma_{BB}^3 = 0.7$.

D	σ	$P\sigma^3/\varepsilon_{BB}$	$\rho\sigma^3$		$U/N\varepsilon_{BB}$		$\Delta\mu^{res}/\varepsilon_{BB}$ *(b)*	
			EOS (a)	*MD*	*EOS*	*MD*	*EOS*	*MD*
0.5	2.2813	0.1967	0.629	0.615	−4.31	−4.20	0.76	0.78
1.0	3.405	0.654	0.70	0.698	−4.78	−4.72	0.0	0.0
1.5	4.3924	1.404	0.767	0.763	−5.17	−5.14	0.10	0.10
2.0	5.1756	2.2967	0.818	0.816	−5.46	−5.44	0.64	0.63
2.7	6.078	3.719	0.875	0.872	−5.73	−5.71	1.73	1.74
3.0	6.4164	4.376	0.895	0.894	−5.81	−5.80	2.28	2.29
3.5	6.9346	5.524	0.926	0.924	−5.92	−5.90	3.26	3.27
4.0	7.4052	6.727	0.953	0.952	−5.99	−5.98	4.30	4.31
5.0	8.2401	9.268	1.000	1.00	−6.06	−6.04	6.52	6.52

(a) Reference [29]
(b) $\Delta\mu^{res} \equiv \mu^{res}(\varepsilon) - \mu^{res}(\varepsilon_{BB})$

includes all molecular asymmetries. The charging integrands invariably change sign in the interval of integration; this behavior then imposes the need for 10–20 simulation points to assure the accurate calculation of the integrals (see related discussion in Reference 11).

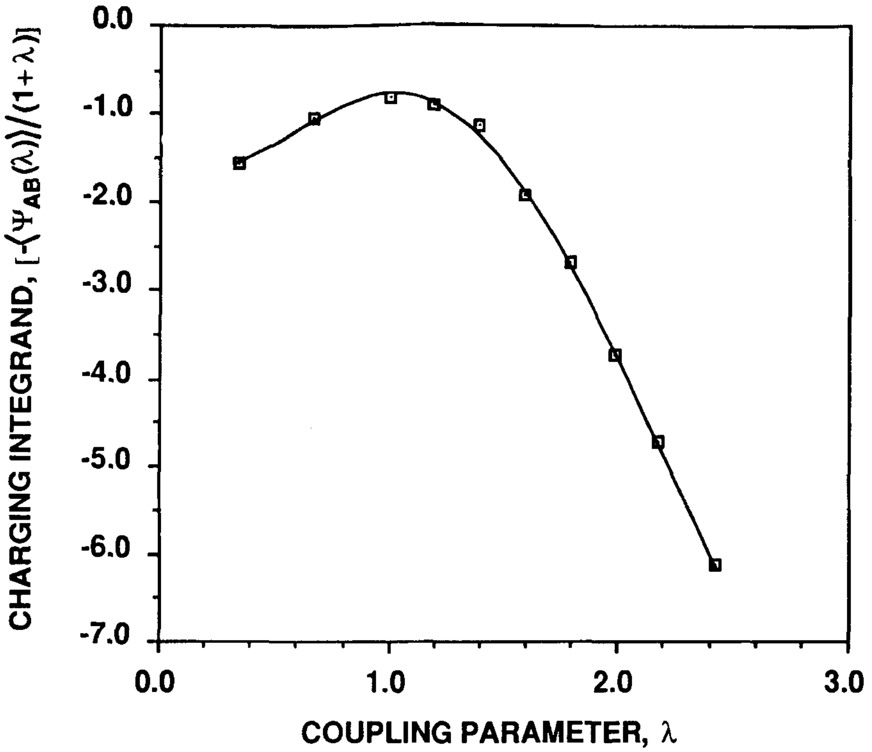

Figure 6 Coupling-parameter dependence of the charging integrand (in ε_{BB} units) for Lennard-Jones mixtures of atoms at infinite dilution with size asymmetries and $C = 1.0$. The state condition is $kT/\varepsilon_{BB} = 1.2$ and $P\sigma_{BB}^3/\varepsilon_{BB} = 0.654$.

A recent NPT-MD version of the test particle method [7] appears to be a more attractive approach to the calculation of chemical potentials of mixtures at infinite dilution, in that it requires one simulation per value of the chemical potential. However, the results show a strong dependence on simulation parameters such as the system size, the length of the run, and the test particle's cutoff [7]. For example in the case of a Lennard-Jones mixture of $N = 1372$ atoms with $D = 2.0$, the chemical potential at infinite dilution does not show convergence even after 2×10^5 time steps (ca. 2×10^3 psecs.). This simulation length is twice as long as that required with our method to obtain very accurate results for the charging integrands with $N = 256$. Although the present method requires more than one value for the integrand (at least two values, depending on the magnitude of the asymmetry), this requirement is still smaller than that corresponding to the test particle method for the same level of accuracy.

Calculations of activity coefficients at infinite dilution have been recently reported [8,9]. In this approach, use is made of a version of the test particle method that avoids the separate calculation of $\mu_A^{\infty\text{res}}$ and $\mu_A^{0\text{res}}$ in the evaluation of $(\mu_A^{\infty} - \mu_A^0)^{\text{res}}$. In addition to the well-known problems with test particle techniques [6,7], the method is restricted to mixtures with $\phi_{AA} = \phi_{BB} \neq \phi_{AB}$. If such a restriction is relaxed, the method gives the difference $(\mu_A^{\infty} - \mu_B^0)^{\text{res}}$. This quantity is related to Henry's constant for component A and the fugacity of pure component B (see Equation (5)). However, the method does not allow the evaluation of $C_{AB}\ (PT)$ (Equation (6)). This quantity would make it possible to bypass the above restriction without performing two independent pure component simulations.

Although solute chemical potentials at infinite dilution show a very asymmetric functional dependence on both C and D (see Figures 1 and 2), the corresponding activity coefficients are remarkably symmetric about the ideal solution, $\gamma_A^{\infty} = 1$ (see Tables 3 and 4). These simple Lennard-Jones mixtures show positive deviations from ideal solution behavior (as defined in terms of the Lewis-Randall rule) [31] for energy asymmetries, and negative deviations for size asymmetries. Consequently, a mixture involving both asymmetries is expected to show behavior ranging from negative to positive deviations, depending on the relative strength of each asymmetry [32]. In both cases, however, the solute's activity coefficient is unity at two different limiting conditions: when the solute molecule is identical to the solvent molecule (solute–solvent interactions = solvent–solvent interactions), and when the solute becomes an ideal gas particle (strength of solute–solvent interactions = 0).

A remarkable feature that emerges from the analysis of Figures 2–5 is that something must be essentially wrong in the way in which most theories treat size asymmetries (size combining rules), even though they account properly for energy asymmetries. The majority of these theories predict chemical potentials at infinite dilution with an extremum in their D-dependence around $D = 1$ [3,13–16]. A notable exception is the FLBPT [40], which predicts accurate values of $\mu_A^{\infty\text{res}}$ for Lennard-Jones mixtures of atoms with $0 < D \leqslant 2.0$ (see Table 1). The present results support the already reported accuracy of that perturbation theory [5,7,17,22,23].

Acknowledgements

The authors gratefully acknowledge the financial support the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences (Grant DE-FG02-87ER13714). Calculations were performed on a CRAY Y-MP8/864 machine located at the San Diego Supercomputer Center through Grant PTN201. P.G.D. gratefully acknowledges the generous support of the Camille and Henry Dreyfus Foundation, through a 1989 Teacher-Scholar Award.

APPENDIX A

We performed isothermal-isobaric molecular dynamics simulations (NPT-MD) using 256 Lennard-Jones (L-J) spheres. The condition of infinite dilution, absence of solute–solute interactions, is created by performing simulations with one A-particle (solute) immersed in (N-1) B-particles (solvent). The temperature was controlled by momentum scaling [33], and the pressure was fixed by Andersen's method [34]. The NPT-equations of motion were solved using a fifth-order predictor-corrector algorithm [35] with a time step size $\Delta = 0.003\sigma_B\sqrt{m/\varepsilon_B}$, and a volume inertial parameter $M = 0.0005\,m/\sigma_B^4$. The Lennard-Jones potential was truncated at $r_c = 3.2\,(L/L_0)\sigma_B$ [21,36], where (L/L_0) denotes the isotropic change of system size due to volume fluctuations, and the corresponding long-range corrections were added to the configurational energy and virial at each time step according to the prescription developed elsewhere [21]. Each run was started from an FCC lattice structure, with initial velocity components randomly assigned and scaled to the desired temperature. Periodic boundary conditions and the minimum image criterion were employed [37]. An automated Verlet neighbor list with optimum skin size was used as described elsewhere [36,38]. When the mean squared displacement reached the value $0.4\,\sigma_B$, the simulation averages were evaluated in an equilibrium stage of (4–20) × 10^4 time steps depending on the property to be calculated (usually partial contributions to the virial relax slower than the corresponding configurational energies). These simulations are substantially longer than those required for finite composition, because the number of solute–solvent interactions is approximately N times smaller.

The ideal solution simulations were performed with $N_B = N\text{-}1$, $N_A = 1$, and $\varepsilon_A = \varepsilon_B$, $\sigma_A = \sigma_B$. This allows us to estimate the accuracy of the simulation results involved in the calculation of the charging integrands. In fact, for these trivial mixtures the solute–solvent contributions to the configurational energy and virial should be given by the following expressions (in units of the solvent's ε/k and σ)

$$\begin{aligned} \langle U_{AB}^{\infty}\rangle &= 2\,(N-1)\langle U_{\text{total}}\rangle/N \\ \langle \Psi_{AB}^{\infty}\rangle &= 6\,(N-1)[T - P/\langle\rho\rangle]/N \end{aligned} \tag{A1}$$

where angle brackets denote NPT averages. Thus we define the relative errors for the partial contributions as

$$\begin{aligned} \delta\langle U_{AB}^{\infty}\rangle &= [\langle U_{AB}^{\infty}\rangle - 2(N-1)\langle U_{\text{total}}\rangle/N]/[2(N-1)\langle U_{\text{total}}\rangle/N] \\ \delta\langle \Psi_{AB}^{\infty}\rangle &= [\langle \Psi_{AB}^{\infty}\rangle - 6(N-1)(T - P/\langle\rho\rangle)/N]/[6(N-1)(T - P/\langle\rho\rangle)/N] \end{aligned} \tag{A2}$$

After several test runs, we have found that $\delta\langle U_{AB}^{\infty}\rangle \approx 1.0\%$ and $\delta\langle \Psi_{AB}^{\infty}\rangle \approx 3.0\%$. To ascertain the size of the error in the charging integrals corresponding to these maximum uncertainties, we assume that the above uncertainties are uniformly distributed (conservative assumption) over the intervals $\pm\,\delta\langle U_{AB}^{\infty}\rangle$ and $\pm\,\delta\langle \Psi_{AB}^{\infty}\rangle$. Then, for the desired state condition, we run a Monte Carlo simulation [39] as follows:

(a) we generate random values of the charging integrands, e.g., Equation (9), for each value of the coupling parameter λ, i.e.,

$$\langle U_{AB}^{\infty}(\lambda)\rangle_{\text{rand}} = \langle U_{AB}^{\infty}(\lambda)\rangle_{\text{sim}} + \chi\,[\delta\langle U_{AB}^{\infty}\rangle \cdot \langle U_{AB}^{\infty}(\lambda)\rangle_{\text{sim}}] \tag{A3}$$

where $\langle U_{AB}^{\infty}(\lambda)\rangle_{\text{sim}}$ and χ are the simulation result and a random number uniformly distributed over the interval $[-1,1]$, respectively.

(b) we compute the charging integrals I_{rand}, up to the desired value of λ, using the integrands generated in step (a).

(c) we compute the relative error $= (I_{\text{rand}} - I_{\text{sim}})/I_{\text{sim}}$, where I_{sim} denotes the charging integral obtained from simulation.

This scheme is iterated about $(5\text{–}10)\cdot 10^3$ times to generate a representative sample. Finally, for a particular confidence level (say 95%) we obtain the desired maximum uncertainty (error) for the charging integral. Since the charging integrands (Equations 10 and 11) do not change sign over the entire interval of integration, the maximum uncertainties for the corresponding charging integrals are also about 1–3%.

The inconvenient coupling parameter-dependence of the charging integrands involved in the literal interpretation of Kirkwood's method (see for example Figure 1 in Reference 11), and the need for a different integrand for each value of molecular asymmetry make the number of simulations per data point high compared to the present approach. According to Reference 11, each integrand requires 10 to 20 simulations to cover the range of variation of the coupling parameter ($0 \leqslant \lambda \leqslant 1$); the stronger the asymmetry, the higher the number of simulations. Consequently, for **n** data points the requirement will be **n** × (10 to 20) simulations. In contrast, the present method (Equation 13) involves about 8 to 10 simulations to produce the only integrand needed to evaluate **n** data points covering the entire range of asymmetry. For example, if **n** = 5 the present method will require at least 5 to 10 times fewer simulations than the literal application of Kirkwood's method. This reduction becomes bigger as **n** increases.

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