Theory of infinite dilution chemical potential

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ABSTRACT

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Exact expressions for the infinite dilution chemical potential in terms of the pair correlation function are derived. Appropriate approximations are introduced in these expressions to derive simple equations for the infinite dilution chemical potential in terms of molecular size and energy, and the solvent thermodynamic properties. The predictions of these simple equations are compared with computer simulation data and are found to be accurate for small solute molecules and within the uncertainties of the simulation data for large solute molecules. The new equations perform better than the van der Waals solution theory for small solute molecules, but no definite conclusion was possible for large solute molecules because of the large uncertainties in the simulation data for these molecules.

INTRODUCTION

Chemical potential calculations have attracted considerable interest in recent years both because the chemical potential provides a sensitive test of mixture theories and because of its importance in solubility studies (Shing, 1986; Shing and Gubbins, 1982, 1983; Shing et al., 1988; Lotfi and Fischer, 1989). Computer simulations of chemical potential are very useful in evaluating and comparing mixture theories because they allow errors arising from an inaccurate potential energy function to be distinguished from errors arising from approximations introduced into statistical mechanical equations. The most widely used mixture theory is the van der Waals one-fluid theory (vdW1) which is simple and reasonably accurate for mixtures of similar molecules. However, this theory is known to be inaccurate for molecules which differ greatly in size and energy (Hoheisel et al., 1983).

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This work concentrates on the chemical potential at infinite dilution of molecules interacting by conformal intermolecular potentials. Exact relationships between the infinite dilution chemical potential and the pair correlation function are derived. Then by introducing suitable approximations, simple equations for the chemical potential, which are more accurate than the vdW1 equations, are obtained. The new equations overcome the deficiency of the van der Waals theory for small values of the energy and size ratios.

DERIVATION OF THE CHEMICAL POTENTIAL EQUATIONS

Consider a binary system of N_1 molecules of type one, and N_2 molecules of type two confined to a volume V and at a temperature T. The molecules in the system interact via pairwise additive potentials u_{ij}. The potential functions contain parameters s_{ij}, such as energy and size parameters. Hamad (1988) and Hamad and Mansoori (1989) have derived the following expression for the derivative of the partition function of this system with respect to a parameter s_{11}:

$$(\partial \ln Q_c / \partial s_{11})_{V,T} = -\beta/V \left[N_1^2/2 \int \partial u_{11}/\partial s_{11} g_{11} \, \mathrm{d}\vec{r} + N_1 N_2 \int \partial u_{12}/\partial s_{11} g_{12} \, \mathrm{d}\vec{r} \right]$$

(1)

where Q_c is the configurational canonical partition function and g_{ij} is the pair correlation function for molecules i and j:

$$g_{ij} = F_{ij}(\vec{r})/Q_c \tag{2}$$

$$F_{ij}(\vec{r}) = V^2(1 - 1/\delta_{ij}) \int \cdots \int \exp(-U\beta) \, \mathrm{d}\vec{r}_3 \cdots \mathrm{d}\vec{r}_n \tag{3}$$

β is $1/kT$, k is the Boltzmann constant, δ_{ij} is the Kronecker delta and $\vec{r}$ is the position vector. The differentials in eqn. (1) are taken with all parameters constant except s_{11}. (For the multicomponent version of eqn. (1) see Hamad and Mansoori (1989).)

To obtain the chemical potential of component 1, we differentiate eqn. (1) with respect to N_1 at constant V, T and N_2, and then interchange the order of differentiation on the left-hand side. Using $\beta\mu_{ir} = -\partial \ln Q_c / \partial N_i$ we arrive at

$$\partial \mu_{1r}/\partial s_{11} = N_1/V \int \partial u_{11}/\partial s_{11}(g_{11} + N_1 \, \partial g_{11}/\partial N_1) \, \mathrm{d}\vec{r}$$

$$+ N_2/V \int \partial u_{12}/\partial s_{11}(g_{12} + N_1 \, \partial g_{12}/\partial N_1) \, \mathrm{d}\vec{r} \tag{4}$$

To obtain the chemical potential at infinite dilution we set N_1 equal to one molecule. In this limit g_{11} is zero from eqns. (2) and (3) and $N_1 \partial g_{ij} / \partial N_1 = x_1 x_2 \partial g_{ij} / \partial x_1$ is of the order $1/N$ and can be neglected for macroscopic systems in comparison with g_{12}. Equation (4) thus reduces to

$$\partial \mu_{1r}^{\infty} / \partial s_{12} = \rho \int \partial u_{12} / \partial s_{12} g_{12} \, d\vec{r} \tag{5}$$

where ρ is the density (N_2/V), and s_{11} has been replaced by s_{12} which is permissible because s_{22} is kept constant. This relationship is exact for pairwise additive potentials.

Now let us express eqn. (5) in terms of specific parameters, namely energy ϵ_{12} and size σ_{12}. First we assume that molecules one and two interact via a conformal potential

$$u_{ij} = \epsilon_{ij} \phi(r/\sigma_{ij}) \tag{6}$$

where ϕ is a known function of r/σ_{ij}. Combining eqns. (5) and (6) we obtain

$$\partial \mu_{1r}^{\infty} / \partial \epsilon_{12} = \rho / \epsilon_{12} \int_0^{\infty} u_{12} g_{12} 4\pi r^2 \, dr \tag{7}$$

$$\partial \mu_{1r}^{\infty} / \partial \sigma_{12} = -\rho / \sigma_{12} \int_0^{\infty} r \, \partial u_{12} / \partial r g_{12} 4\pi r^2 \, dr \tag{8}$$

where r is the radial distance from the center of mass of molecule 1. Next we introduce some approximations in the above equations to derive the expression for the chemical potential.

APPROXIMATIONS AND DISCUSSION

Equations (5), (7) and (8) can be integrated to obtain μ_{1r}^{∞} if the dependence of g_{12} on ϵ_{12} and σ_{12} is known. This dependence can be obtained from computer simulation, but this makes the calculation of the chemical potential extremely lengthy. However, a suitable approximation for the dependence of g_{12} on potential parameters can be made and an analytical expression for μ_{1r}^{∞} is obtained. For example, the conformal solution approximation of the pair correlation function (Leland et al., 1968)

$$g_{12}(r/\sigma_{12}) = g_{22}(r/\sigma_{22}) \tag{9}$$

yields the one-fluid van der Waals solution theory expression for the chemical potential

$$\beta \mu_{1r}^{\infty} = \beta \mu_{2r} + 2h(f - 1)E_{2r}/NkT + 2(h - 1)(Z_2 - 1) \tag{10}$$

where $\beta \mu_{2r}$ is the residual chemical potential of the solvent, $h = (\sigma_{12}/\sigma_{22})^3$, $f = \epsilon_{12}/\epsilon_{22}$, and E_{2r} and Z_2 are the residual internal energy and the com-
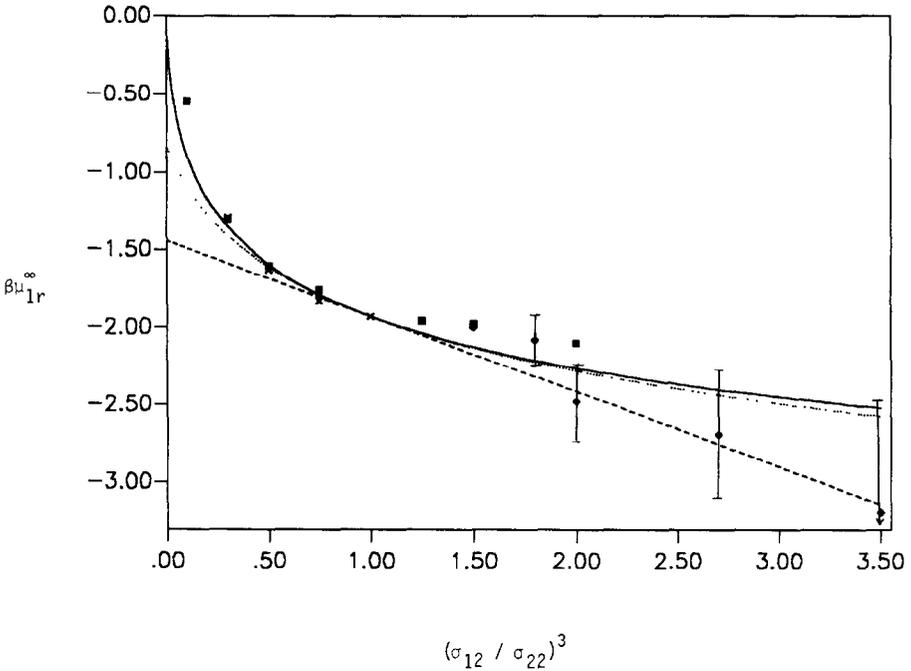
Fig. 1. Infinite dilution chemical potential vs. size ratio at $T^* = 1.2$ and $\rho^* = 0.7$. The points are simulation data of Lotfi and Fischer (1989) (■), Shing et al. (1988) (◆), and Shing and Gubbins, (1982) (×). The curves are predictions made using eqn. 22 (———), eqn. 21 (······) and vdW1 (-----).

pressibility factor of the solvent respectively. The vdW1 equation is known to be deficient for small values of energy and size parameters and this can be seen in Figs. 1 and 2 where comparison is made with computer simulation data of Lennard-Jones molecules. To derive more accurate expressions for the chemical potential at infinite dilution, we start by deriving another exact equation for the chemical potential in terms of integrals of $F_{12}(r)$, rather than g_{12}, and then treat the size dependence and energy dependence separately.

We start by defining $y = \beta\mu_{1r}^{\infty}$, $s = s_{12}/s_{22}$ and differentiating eqn. (5) with respect to:

$$\partial^2 y/\partial s^2 = \beta\rho \; \partial(I/Q_c)/\partial s = (\partial \ln I/\partial s - \partial \ln Q_c/\partial s) \; \partial y/\partial s \qquad (11)$$

where

$$I = \int \partial u_{12}/\partial s F_{12}(\vec{r}) \; d\vec{r} \qquad (12)$$

To evaluate $\partial \ln Q_c/\partial s$ we put $N_1 = 1$ in eqn. (1) and compare with eqn. (5) which yields

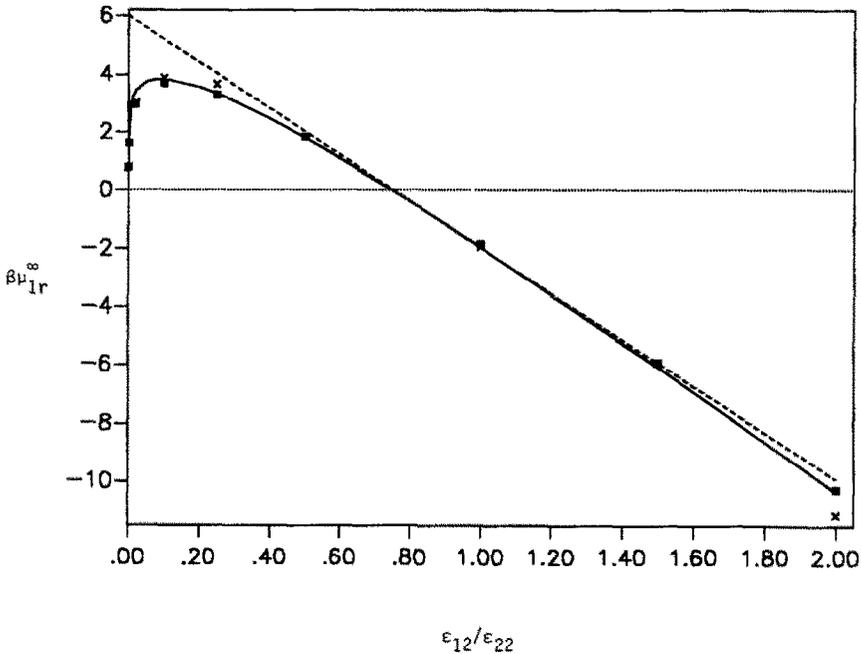$$\partial \ln Q_c/\partial s = -\partial y/\partial s \qquad (13)$$

Fig. 2. Infinite dilution chemical potential vs. energy ratio at $T^* = 1.2$ and $\rho^* = 0.7$. The points are simulation data of Lotfi and Fischer (1989) (■), and Shing and Gubbins (1982) (×). The curves are predictions made using eqn. 24 (——) and vdW1 (- - - - - -).

Equation (11) finally becomes

$$\partial^2 y / \partial s^2 = (\partial y / \partial s)(\partial \ln I / \partial s) + (\partial y / \partial s)^2 \tag{14}$$

Equation (14) is a differential equation for y which can be integrated using standard methods to give

$$y = C_2 - \ln(C_1 - I \, ds) \tag{15}$$

where C_1 and C_2 are integration constants which, in this case, can depend on all state variables in addition to potential parameters except s_{12}. To evaluate these constants we need to know the value of y at two points. If y $(s = 0) = 0$, and $y \, (s = 1) = y_0$, then

$$y = y_0 - \ln(1 - aR) \tag{16}$$

where $a = \exp y_0 - 1$ and

$$R = \left(\int_0^s I \, ds \Big/ \int_0^1 I \, ds \right) - 1 \tag{17}$$

The boundary condition $y \, (s = 0) = 0$ is true for both energy and size parameters because the mixture behaves ideally when either parameter approaches zero for conformal potential functions. At $s = 1$, two boundary

conditions can be derived. As h and f simultaneously approach unity, y approaches $\beta\mu_{2r}$. The second boundary condition is obtained by setting $\epsilon_{12} = \epsilon_{22}$ in eqn. (7) and $\sigma_{12} = \sigma_{22}$ in eqn. (8):

$$\epsilon_{12}\,\partial\mu_{1r}^{\infty}/\partial\epsilon_{12} = 2E_{2r} \qquad (f = 1) \tag{18}$$

$$\beta\sigma_{12}\,\partial\mu_{1r}^{\infty}/\partial\sigma_{12} = 6(Z_2 - 1) \qquad (h = 1) \tag{19}$$

Other boundary conditions can also be derived.

Equation (15) is an *exact* relationship for calculating μ_{1r}^{∞} for pairwise additive potentials. Now we are faced with the problem of evaluating the quantity I as a function of s_{12}. However, if approximations are made in this equation, then there is the advantage that the Q_c part of the pair correlation function is treated exactly, unlike in eqn. (5) where approximations must be introduced for the full pair correlation function which include both $F_{12}(r)$ and Q_c. Thus, eqn. (15) is expected to yield more accurate expressions for the infinite dilution chemical potential than eqn. (5) if equivalent approximations are made in the two equations. To see the result of this treatment, let us consider the variation of μ_{1r}^{∞} with the size parameter σ_{12}. The use of the conformal solution pair correlation function in eqn. (8) implies that the integral on the right-hand side of this equation is proportional to σ_{12}^{3}. Introducing the equivalent approximation

$$F_{12}(r/\sigma_{12}) = F_{22}(r/\sigma_{22}) \tag{20}$$

in eqns. (12) and (15), and restricting the equation for $\epsilon_{12} = \epsilon_{22}$ we arrive at

$$\beta\mu_{1r}^{\infty} = \beta\mu_{2r} - z\,\ln[1 - a(1 - h)] \qquad (\epsilon_{12} = \epsilon_{22}) \tag{21}$$

where $z = 2(Z_2 - 1)/a$ and the integration constants are evaluated from the boundary conditions $y(h = 1) = \beta\mu_{2r}$ and eqn. (19). Equation (21) is compared with the simulation data of Lennard–Jones molecules in Fig. 1. It is clear that there is an improvement in the prediction of the infinite dilution chemical potential for $\sigma_{12} < \sigma_{22}$. Equation (21), however, does not go to zero at $\sigma_{12} = 0$ as it should. While this is not expected to be significant for real systems, we can correct this by slightly modifying the expression for the quantity I. Approximation (20) implies that I is proportional to σ_{12}^{3}, which is only exact in the limit when the density approaches zero, i.e. for the second virial coefficient. If one includes the third virial coefficient, then a term proportional to σ_{12}^{2} appears. On the basis of this observation we suggest that $I = I_0(\sigma_{12}^{3} + b\sigma_{12}^{2})$. Deiters (1987) also used a σ exponent less than three. Using the above expression for I in eqns. (12), (16) and (17) and evaluating b from the boundary condition (19), we obtain

$$\beta\mu_{1r}^{\infty} = \beta\mu_{2r} - \ln\{1 - a[(3z - 2)h - 3(z - 1)h^{2/3} - 1\} \qquad (\epsilon_{12} = \epsilon_{22}) \tag{22}$$

This equation is also compared with the computer simulation of Lennard-Jones molecules in Fig. 1. This figure clearly shows the improvement in the

predictions for small values of σ_{12}. Predictions made using eqns. (21) and (22) for large molecules are almost identical, but the figure suggests that the vdW1 mixture theory is more accurate in this range. This conclusion is not definite at this stage because of the large uncertainties in the simulation results at large size ratios. Simulation data with uncertainties in the range 1–2% are needed before any definite conclusions can be made about this region. For small size ratios, the conclusions are definite because of the small uncertainties in the simulation data in this region.

The dependence of the chemical potential on the energy parameter ϵ_{12} is not accurately represented by vdW1 mixture theory for small values of ϵ_{12}, as shown in Fig. 2. To correct for this deficiency we use the mean density approximation (Leland et al., 1962; Mansoori and Leland, 1972) of the pair correlation function which is known to be accurate in representing the dependence of the pair correlation function on the energy parameter (Hoheisel and Lucas, 1984). The mean density approximation assumes the following:

$$g_{12}(r/\sigma_{12}, kT/\epsilon_{12}) = g_{22}(r/\sigma_{22}, kT/\epsilon_{22}) \tag{23}$$

Substituting this approximation in eqn. (7), and integrating over ϵ_{12} gives

$$\mu_{1r}^{\infty} = \mu_{1r}^{\infty}(f=1) + 2h[A_r(\epsilon_{12}/kT, \rho\sigma_{22}^3) - A_r(\epsilon_{22}/kT, \rho\sigma_{22}^3)] \tag{24}$$

where A_r is the solvent residual Helmholtz free energy function per mole, $\epsilon_{12}/kT = f/T^*$ and $T^* = kT/\epsilon_{22}$. Equation (24) is compared with the simulation data and the vdW1 theory in Fig. 2 for molecules of equal size. The improvement in representing the chemical potential at small energy values is clear. However, at $\epsilon_{12} = 0$, eqn. (24) does not predict a zero value as it should (at the conditions of Fig. 2 it predicts a value of $\beta(\mu_{2r} - 2A_{2r}) = 1.55$). Since this inaccuracy is in a very small region close to $\epsilon_{12} = 0$ it does not seem to be significant, but it can be corrected for by a procedure similar to that used to derive eqn. (22). For systems containing molecules which differ in both energy and size, either eqn. (21) or eqn. (22) can be substituted for the first term on the right-hand side of eqn. (24). Figure 3 compares the combination of eqns. (22) and (24) with Lennard-Jones simulation data. The predictions are accurate except for the point at $h = 2.7$ and $f = 2$. However, with such a large size difference the uncertainty in the simulation data is as stated earlier.

The above tests of the new expressions for the chemical potential are all at one state point $\rho\sigma_{22}^3 = 0.7$ and $kT/\epsilon_{22} = 1.2$. To test the performance of the developed equations at other conditions we present in Fig. 4 the chemical potential at $kT/\epsilon_{22} = 1.5$ as a function of density. The size ratio is taken as 2.7 and the energy ratio as 2.0. These values were chosen because for real molecules large size and energy usually go together. Figure 4 indicates that eqn. (24) is slightly more accurate at small and intermediate densities and vdW1 theory is slightly more accurate for higher densities.
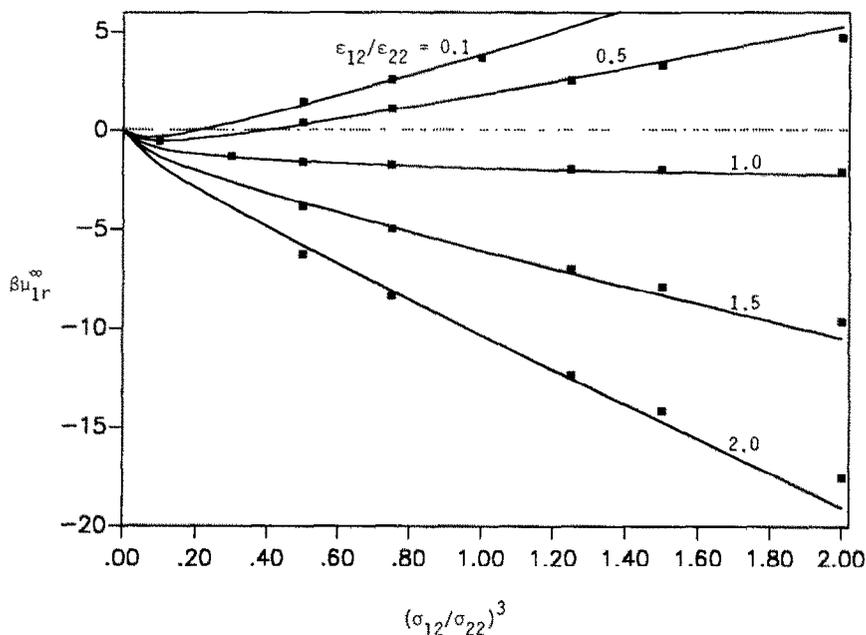
Fig. 3. Infinite dilution chemical potential at various energy and size ratios. The points are the simulation data of Lotfi and Fischer (1989) and the curves are predictions of eqn. (24) with eqn. (22).
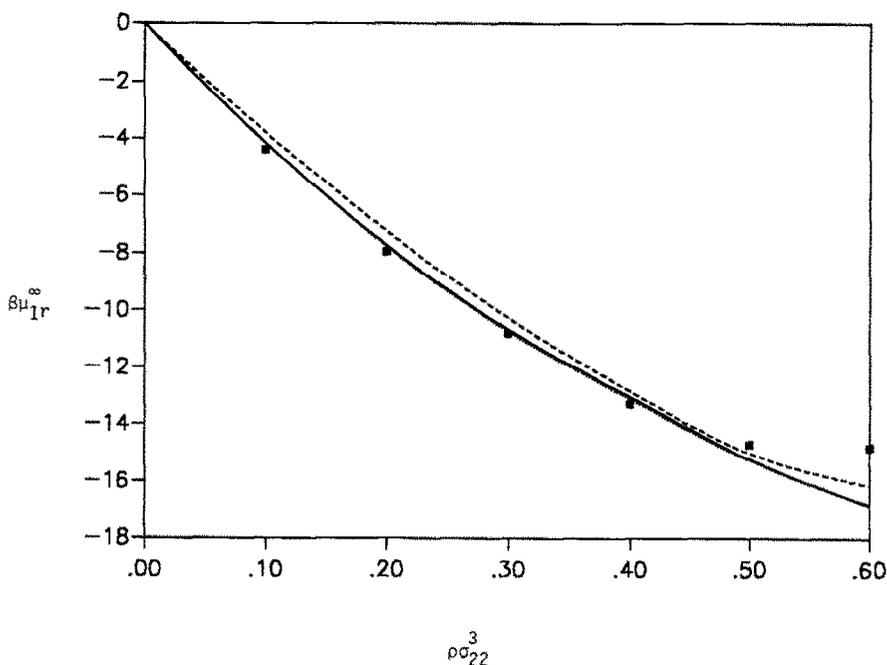

Fig. 4. Infinite dilution chemical potential vs. density for $f = 2.0$ and $h = 2.7$ at $T^* = 1.5$. The points are the simulation data of Shing et al. (1988) and the curves are predictions of eqn. (24) with eqn. (22) (——), eqn. (24) with eqn. (21) (······), and vdW1 (--------).
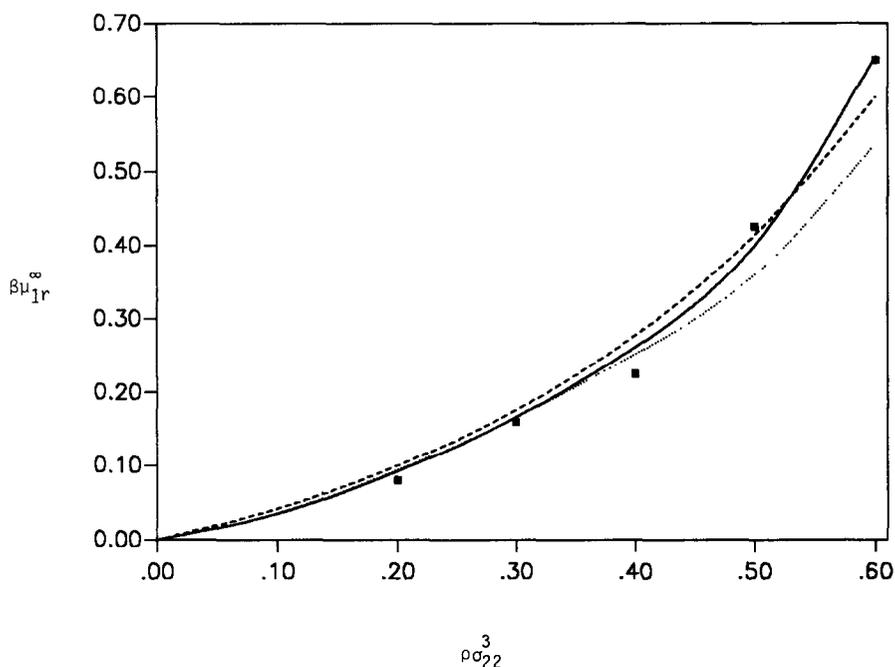
Fig. 5. Infinite dilution chemical potential vs. density for $f = 0.5$ and $h = 0.5$ at $T^* = 2.0$. The points are simulation data of Shing et al. (1988) and the curves are predictions of eqn. (24) with eqn. (22) (——), eqn. (24) with eqn. (21) (·····), and vdW1 (--------).

However, this conclusion is preliminary because it is based on molecular simulation data which contain large uncertainties at such large size ratios. The vdW1 solution theory prediction is compared with eqn. (24) and computer simulation at $kT/\epsilon_{22} = 2$ for small solvent molecules in Fig. 5. The combination of eqns. (22) and (24) gives the best overall prediction.

CONCLUSIONS

Exact relationships between the chemical potential at infinite dilution and the pair correlation function have been derived. Accurate representation of the chemical potential at infinite dilution was obtained by making approximations only when necessary, and by careful consideration of the known boundary conditions. The expressions for the chemical potential are simple and only solvent thermodynamic properties are needed in these expressions for conformal potentials. More accurate computer simulation data are needed at large size ratios in order to reach a definite conclusion on the performance of the various solution theories in this range.

ACKNOWLEDGMENT

LIST OF SYMBOLS

a	quantity defined before eqn. (17)
A_r	molar Helmholtz energy of the solvent
b	parameter
C_i	integration constant
E_{2r}	solvent residual internal energy
f	energy parameter ratio, $\epsilon_{12}/\epsilon_{22}$
F_{ij}	quantity defined by eqn. (3)
g_{ij}	pair correlation function
h	size parameter ratio $(\sigma_{12}/\sigma_{22})^3$
I	quantity defined by eqn. (12)
k	Boltzmann constant
N	number of molecules
Q_c	configurational canonical partition function
r	radial distance
$\vec{r}$	position vector
R	quantity defined by eqn. (17)
s	parameter ratio, s_{12}/s_{22}
s_{ij}	parameter of the potential function
T	absolute temperature
T^*	kT/ϵ_{22}
u_{ij}	pair potential energy function
U	total potential energy function
V	volume
x_i	mole fraction of component i
y	dimensionless chemical potential, $\beta\mu_{1r}$
z	quantity defined after eqn. (21)
Z_2	solvent compressibility factor

Greek letters

β	$1/kT$
δ_{ij}	Kronecker delta
ϵ	energy parameter of potential function
μ_r	residual chemical potential
ρ	density
ρ^*	reduced density, $\rho\sigma_{22}^3$
σ	size parameter of potential function
ϕ	general function

REFERENCES

Deiters, U.K., 1987. Density-dependent mixing rules for the calculation of third phase equilibria at high pressures. Fluid Phase Equilibria, 33: 267–293.

Hamad, E.Z., 1988. Statistical mechanical modeling of complex mixtures: distribution function approach. Ph.D. Thesis, University of Illinois, Chicago, IL.

Hamad, E.Z. and Mansoori, G.A., 1989. Mixture radial distribution functions: are they all independent? Fluid Phase Equilibria, 51: 13–21.

Hoheisel, C. and Lucas, K., 1984. Pair correlation functions in binary mixtures from pure fluid data. Mol. Phys., 53: 51–67.

Hoheisel, C., Deiters, U. and Lucas, K., 1983. The extension of pure fluid thermodynamic properties to supercritical mixtures: a comparison of current theories with computer data over a large region of states. Mol. Phys., 49: 159–170.

Leland, T.W., Chappelear, P.S. and Gamson, B.W., 1962. Prediction of vapor–liquid equilibria from the corresponding state principle. AIChE J. 8: 482.

Leland, T.W., Rowlinson, J.S. and Sather, G.A., 1968. Statistical thermodynamics of mixtures of molecules of different sizes. Trans. Faraday Soc., 64: 1447–1460.

Lotfi, A. and Fischer, J., 1989. Chemical potentials of model and real dense fluid mixtures from perturbation theory and simulation. Mol. Phys., 66: 199–219.

Mansoori, G.A. and Leland, T.W., 1972. Statistical thermodynamics of mixtures. J. Chem. Soc., Faraday Trans., 68: 320–344.

Shing, K.S., 1986. Infinite-dilution activity coefficients of quadrupolar Lennard-Jones mixtures from computer simulation. J. Chem. Phys., 85: 4633–4637.

Shing, K.S. and Gubbins, K.E., 1982. The chemical potential in dense fluids and fluid mixtures via computer simulation. Mol. Phys., 46: 1109–1128.

Shing, K.S. and Gubbins, K.E., 1983. The chemical potential in nonideal liquid mixtures: computer simulation and theory. Mol. Phys., 49: 1121–1138.

Shing, K.S., Gubbins, K.E. and Lucas, K., 1988. Henry constants in non-ideal fluid mixtures: computer simulation and theory. Mol. Phys., 65: 1235–1252.