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Chemical Potential Prediction in Realistic Fluid Models with Scaled Particle Theory[1]

D. M. Pfund,[2] L. L. Lee,[2] and H. D. Cochran[3]

A procedure frequently proposed in the literature for calculating chemical potentials relies on the Kirkwood charging process. Numerical problems associated with coupling large repulsive forces can be avoided by estimating the contribution to the chemical potential due to these forces with scaled particle theory. The contribution due to soft repulsive forces and attractive forces can be calculated with the Kirkwood charging process using distribution functions for a test particle obtained from integral equation theories. We have used the accurate HMSA theory of Zerah and Hansen to provide distribution functions in mixtures of Lennard–Jones molecules, and we have used the PYP theory of Lee to scale the distribution functions over the charging process. The theory provides accurate estimates of chemical potentials over a range of densities from gas-like to liquid-like when the reduced temperature kT/ε is greater than 2. Accurate results for excess free energy changes of mixing are also obtained at these conditions. At lower temperatures accurate results are obtained for low to moderate reduced densities ($\rho\sigma^3 \leqslant 0.5$).

KEY WORDS: chemical potential; Kirkwood charging process; Lennard–Jones fluid; scaled particle theory.

1. INTRODUCTION

Scaled particle theory (SPT) provides an expression for the chemical potential of a hard sphere solute in a fluid mixture. The theory was originally applied to the calculation of the chemical potential of a hard sphere in a pure fluid of hard spheres [1]. Central to the theory is the dis-

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[2] School of Chemical Engineering and Materials Science, University of Oklahoma, Norman, Oklahoma 73019, U.S.A.

[3] Chemical Technology Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, U.S.A.

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tribution function $G(r+R)$, which is defined to be the local concentration of molecular centers adjacent to a spherical cavity of radius r from which all molecular centers have been excluded [2]. Thus $G(r+R)$ is equal to the contact value of the radial distribution function for the hard sphere bath molecules about the test particle. SPT postulates a particular functional form for the G and a procedure for evaluating the constants in the function. With the G function specified the work of forming a cavity of any radius can be calculated. When the cavity formed has radius $2R$, then the work of cavity formation is equal to the work of inserting a new bath molecule into the fluid, which in turn, is equal to the configurational part of the chemical potential [3]. The SPT theory has been extended to mixtures [4]. SPT has also been extended to give the work of inserting a hard sphere into a bath of molecules which have hard cores and soft repulsive and attractive forces [5]. SPT provides exact results for the work of cavity formation in two extremes of core or cavity size:

when the test particle has a radius of zero and

when the cavity has effectively an infinite radius.

For intermediate cavity sizes SPT provided a reliable interpolation formula for the work of cavity formation.

The work of cavity formation obtained from SPT can be used in the computation of the chemical potentials of species which are not hard spheres. Solvation has been considered as a process in which a molecule of solute is moved from a fixed location in an ideal gas phase to a fixed location in the fluid of interest [6]. The solute molecule is then liberated to move freely within the fluid. Workers interested in solvation have considered that the free energy change associated with the interphase transfer step consists of two parts [7]. The first part is the work of creating a cavity in the fluid big enough to hold the solute; the free energy change for this part is positive. The second part arises when the solute is placed within the cavity and is allowed to interact with the surrounding molecules. The free energy change associated with this second part is usually negative. The inventors of SPT recognized that the work of forming a cavity just big enough to contain the solute (which is presumed to have a hard core) was given approximately by their theory [5]. They proposed that the work which results from the action of forces which reach outside of the cavity, work which is due to soft repulsive and attractive forces between the solute and its surroundings, be calculated by using a Kirkwood charging process. In this paper we first review the equations from SPT which can be used to estimate the work needed to form a cavity in the fluid. Then we will describe the application of a Kirkwood charging process [8] to the calculation of the contribution to the chemical potential associated with the soft forces. Then we describe a procedure for estimating the distribution functions about the test particle. Finally, we give the results of a procedure which combines the work of cavity formation from SPT with the contribution associated with soft forces determined from Kirkwood charging. The model fluid used combines a Lennard–Jones (LJ) pair potential with a hard core cutoff. The results are compared to simulation data for residual Gibbs free energies in pure LJ fluids and for excess Gibbs free energies in LJ mixtures. The combination of scaled particle theory and the Kirkwood charging process promises to yield a fast, accurate method for estimating chemical potentials.

2. FORMAL DEVELOPMENT

The chemical potential of a solute consists of two contributions. One contribution is the work needed to make a cavity in the fluid large enough to contain a test solute particle. This contribution is equivalent to the work needed to insert the hard core of a test particle into the fluid. The other contribution is the work done by the test particle against the soft repulsive and attractive forces in the fluid. Calculation of both contributions requires knowledge of the pair correlation functions for molecules about the test particle. We show (in Section 3) that the work needed to insert the core of a test particle can be estimated accurately by scaled particle theory—provided that these correlation functions are known accurately. The accuracy of the estimated soft contribution depends only on the accuracy of these correlation functions. We demonstrate a procedure for estimating pair correlation functions about a test particle using an integral equation theory. Therefore, the principle approximation in the chemical potential calculation is the approximate closure to the system of integral equations.

SPT gives the work required to insert the hard core of a molecule into a fluid. Therefore, in applications of SPT, the pair potential between molecules of species i and j must have an infinitely repulsive core,

$$u_{ij}(r) = \begin{cases} +\infty & r \leqslant R_{ij} = (R_i + R_j) \\ \phi_{ij}(r) & R_{ij} < r, \end{cases} \tag{1}$$

where ϕ_{ij} is assumed in this work to have the form of a Lennard–Jones potential. In this case R_i is the radius of the hard core of molecules of species i. Given a pair potential of the above form, the chemical potential of species i can be divided into hard core and soft contributions

$$\mu_i = \mu_i^{\mathrm{H}} + \mu_i^{\mathrm{S}} \tag{2}$$

The hard core contribution equals the ideal gas chemical potential of species i plus the work needed to insert the core of a molecule into the fluid at a fixed point:

$$\frac{\mu_i^{\mathrm{H}}}{kT} = \ln[\rho_i h^3/(2\pi m_i kT)^{3/2}] + \frac{W(R_i)}{kT} \tag{3}$$

The first term in Eq. (3) is the ideal gas chemical potential for a species with molecular mass m_i; the second term is the work of insertion.

Scaled particle theory provides a cubic formula for the work of insertion. The theory gives an expression for the work of forming a cavity in the fluid of radius r. When the cavity radius equals the core radius, then the work of cavity formation equals the work of inserting the molecular core. The SPT formula for the work cavity formation is

$$\beta W(r) = \beta W(0) + Ar + Br^2 + \frac{4\pi P r^3}{3kT} \tag{4}$$

where $\beta = 1/kT$. The pressure-dependent term is necessary to ensure that the work consists only of pressure–volume work when the cavity radius is large. The $\beta W(0)$ term is the exact expression provided by SPT for the work of forming a cavity of zero radius [4]

$$\beta W(0) = -\ln(1 - \xi_3) \tag{5}$$

The density-dependent functions ξ_{L} are defined by

$$\xi_{\mathrm{L}} = \frac{\pi}{6} \sum_{i=1}^{m} \rho_i (2R_i)^{\mathrm{L}} \tag{6}$$

where m is the number of different species in the mixture. In SPT the coefficient A is determined by imposing continuity on the derivative of the work when the cavity size is zero. The result is [4]

$$\beta \left.\frac{dW}{dr}\right|_{r=0} = \frac{6\xi_2}{1 - \xi_3} = A \tag{7}$$

SPT gives an exact expression for the derivative of the work when the cavity radius equals the radius of a molecule of spcies j:

$$\begin{aligned}\beta \left.\frac{dW}{dr}\right|_{r=R_j} &= 4\pi(R_j + R_1)^2 \rho_1 g_{1c}(R_j + R_1, \lambda = 0) \\ &\quad + 4\pi(R_j + R_2)^2 \rho_2 g_{2c}(R_j + R_2, \lambda = 0)\end{aligned} \tag{8}$$

In the above equation g_{ic} is the pair correlation function for molecules of species i about a molecule of species c evaluated at the core-to-core contact distance $R_j + R_i$. These contact values for the hard core–bath molecule distribution functions can obtained from the integral equation theories. Applying the constraint given by Eq. (8) to Eq. (4) yields an expression for the coefficient B:

$$B_j = \frac{2\pi}{R_j} \sum_{i=1}^{m} \rho_i (R_i + R_j)^2 \, g_{ic}(R_i + R_j, \lambda = 0) - \frac{2\pi}{kT} P R_j - [3\xi_2/(1 - \xi_3)]/R_j \tag{9}$$

where the test particle is considered to be the core of a molecule of species j. The resulting expression for the work of insertion is

$$\frac{W(R)}{kT} = -\ln(1 - \xi_3) + [6\xi_2/(1 - \xi_3)] \, R_i + B_i R_i^2 + \frac{4}{3kT} \pi P R_i^3 \tag{10}$$

The soft contribution μ_i^{S} is the change in the Helmholtz free energy (at constant temperature, volume, and number of molecules of each species) which results when the interaction potential between the inserted hard core (or test particle) and the surrounding molecules is turned on. Specifically, the pair potential between the test particle (denoted by subscript c) and molecules of species i is given by

$$\mathrm{u}_{ic}(r) = \mathrm{u}_{ic}^{\mathrm{HS}}(r) + \lambda \phi_{ic}(r) \tag{11}$$

Computation of μ_i^{S} requires knowledge of the pair correlation functions for molecules about the test particle when the coupling parameter λ is between zero and one. When $\lambda = 0$, the test particle consists of the hard core of a molecule of species j. When $\lambda = 1$, the test particle is identical to any other molecule of species j. If the chemical potential of a molecule of species i is desired, then

$$\frac{\mu_i^{\mathrm{S}}}{kT} = \frac{1}{kT} \int_0^1 \int_0^{+\infty} [\rho_1 \phi_{1i}(r) \, g_{1c}(r, \lambda) + \rho_2 \phi_{2i}(r) \, g_{2c}(r, \lambda)] \, 4\pi r^2 dr \, d\lambda \tag{12}$$

where $g_{ic}(r; \lambda)$ is the radial dstribution function for molecules of species i about the test particle. Once these distribution functions have been determined for a range of λ, the above integration can be performed numerically to obtain the soft contribution to the chemical potential.

Integral equation theories can be used to obtain the distribution functions for molecules about the test particle. Consider a ternary mixture of molecules of species 1, molecules of species 2, and one test particle. The test particle interacts with the other molecules in the mixture with pair potentials given by Eq. (4). The system of two Ornstein–Zernike (OZ) equations for the ternary mixture with one species (the test particle) at infinite dilution are

$$h_{ic}(\lambda) - c_{ic}(\lambda) = \rho_1 \int ds\, c_{i1} h_{1c}(\lambda) + \rho_2 \int ds\, c_{i2} h_{2c}(\lambda) \tag{13}$$

where the species index i equals 1 or 2.

The h_{ic} are the total correlation functions for molecules of species i about the test particle. The total correlation functions are dependent on the value of the coupling parameter. The test particle OZ equations are exact and can be considered to be the definitions of the direct correlation functions c_{ic}. The c_{ij} are the direct correlation functions for molecules of species 1 and 2 with each other. The c_{ij} are independent of the coupling parameter λ and obey the system of three OZ equations for species 1 and 2:

$$h_{ij} - c_{ij} = \rho_1 \int ds\, c_{i1} h_{1j} + \rho_2 \int ds\, c_{i2} h_{2j} \tag{14}$$

The bath molecule correlation functions can be calculated using accurate, modern integral equation theories. One such theory is the HMSA theory of Zerah and Hansen [9].

The test particle OZ equations make two equations in the four unknown functions h_{1c}, h_{2c}, c_{1c}, and c_{2c}. In order to solve the integral equations for all four functions, an additional pair of closure equations must be specified. The background correlation functions for the test particle–molecular interactions for a given value of the coupling parameter λ can be approximated using the following perturbative equation:

$$y_{ic}(\lambda) = y_{ij} \left\{ \frac{1 + [h_{ic}(\lambda) - c_{ic}(\lambda)]}{1 + (h_{ij} - c_{ij})} \right\} \tag{15}$$

where y_{ic} is the background correlation function for molecules of species i about the test particle. The test particle is considered to be identical to a molecule of species j when $\lambda = 1$. Thus

$$\begin{aligned} y_{ic}(\lambda = 1) &= y_{ij} \\ h_{ic}(\lambda = 1) &= h_{ij} \\ c_{ic}(\lambda = 1) &= c_{ij} \end{aligned} \tag{16}$$

This type of closure relation has been refered to as PYP or Percus–Yevick perturbed [10]. The basic assumptions embodied in this approximation are

(1) the fundamental Percus–Yevick assumption as stated in Ref. 10, and

(2) $|h_{ic} - c_{ic}| < 1$.

The system of two OZ equations and two closure equations can be solved numerically to obtain the distribution functions of the bath molecules about the test particle for any value of the coupling parameter, allowing numerical integration of the Kirkwood charging integral. This process also yields the contact values of the distribution functions for the bath molecules about the test particle when $\lambda = 0$. The contact values are then used in Eqs. (9) and (10) to estimate the work of insertion.

In the following section it is shown that Eq. (10) for the work of insertion is accurate provided that accurate contact values for the pair correlation functions are used in Eq. (9). Equation (12) for the soft contribution to the chemical potential is formally exact. Therefore, the principle sources of error in the chemical potential calculation are the closure equations used in obtaining the distribution functions for molecules about the test particle.

3. RESULTS

Results from the theory were compared to available simulation results for chemical potentials, residual Gibbs free energies, and excess free energies of mixing of Lennard–Jones fluids. The Lennard–Jones potential does not have the form of Eq. (1); however, the properties of a fluid with a hard core cutoff potential can be made to approach those of a Lennard–Jones fluid by choosing a core diameter which is sufficiently small. Core sizes were set to the smallest values which did not result in floating point overflow of the calculated Boltzmann factor. The maximum allowed logarithm of the Boltzmann factor was set at 21. Using smaller core sizes did not change the results significantly.

There are three main steps in the computation of the chemical potential. First, the direct, total and background correlation functions for the molecules in the bulk fluid are found. The accurate HMSA integral equation theory developed by Zerah and Hansen [9] is used to provide these functions. The HMSA solution for the distribution functions also yields a very accurate estimate of the pressure. In the second step the coupling parameter is varied between zero and one, and the distribution functions for the molecules about the test particle are obtained for each value of the coupling parameter. The integral over the coupling parameter, Eq. (12), which gives the soft contribution to the chemical potential is evaluated numerically. The distribution functions about the test particle are obtained by solving the test particle OZ equations (13) in Fourier transform space using fixed-point iteration. The distribution functions for zero coupling parameter are then extrapolated to the contact point of the cores with the test particle. These contact values of the distribution functions are used in the estimation of the work of inserting the core of the test particle. The third step is the calculation of the work of insertion using the SPT formula [Eq. (10]. The pressure used in the work formula is that obtained from the HMSA solution.

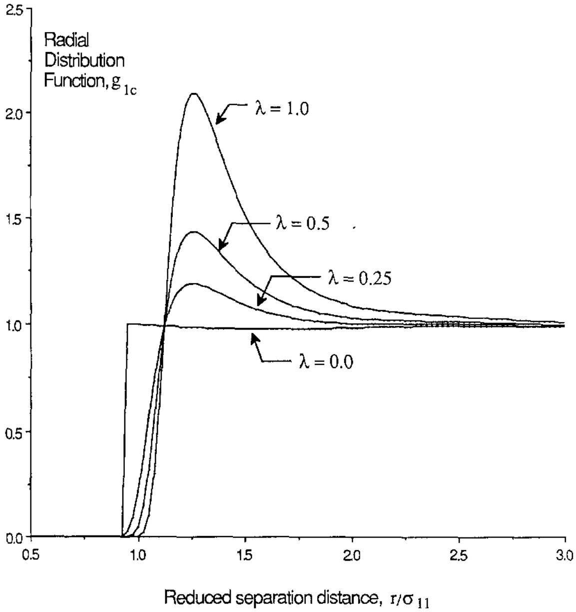

Fig. 1. Test particle distribution in low-density mixtures. Results are for a binary mixture with $\sigma_{11} = 3.405$ Å, $\sigma_{12} = 3.8305$ Å, $\sigma_{22} = 4.256$ Å, $d_{11} = 2.8091$ Å, $d_{12} = 3.2348$ Å, $d_{22} = 3.5752$ Å, and $\varepsilon_{11}/k = \varepsilon_{12}/k = \varepsilon_{22}/k = 119.8$ K. The mixture consisted of 75 % species 1 at $kT/\varepsilon = 1.35$ and $\rho\sigma_{11}^3 = 0.03$. Shown are distribution functions for molecules of species 1 about a test particle for several values of the coupling parameter λ. When $\lambda = 1$ the test particle is a member of species 2. At low densities the test particle distribution functions are equal to the Boltzmann factors of the species 1–test particle pair potentials.

The procedure was first tested at low densities where the SPT and integral equation closure approximations made in the theory are very accurate. The purpose of this test was to show that the mechanics of the coupling process were being carried out correctly. In the low-density case the test particle distribution functions match the Boltzmann factors for the interactions of the test particle with the molecules in the surrounding fluid. Plotted in Fig. 1 are the species 1–test particle distribution functions for an example case where the chemical potential of species 2 was being calculated. The Lennard–Jones (with a hard core cutoff in the pair potential) mixture used is described in the figure. The curve in Fig. 1 for coupling parameter equal to one is the species 1–species 2 distribution function. The curve for coupling parameter equal to zero shows that the test particle's only influence on the surrounding molecules at low density is to exclude them from a cavity with a radius equal to the radius of the test particle plus the radius of a molecular core. For the example mixture obeying the core-cutoff Lennard–Jones potential, the procedure reproduced the exact second virial results for the residual chemical potentials of each species to within 0.01. The core contributions to the chemical potentials matched the second virial core contributions to within 0.001. The soft contributions to the chemical potentials matched the second virial soft contributions to within 0.01.

The scaled particle theory Eq. (10) provides an accurate estimate for the work of inserting the hard core of the test particle into the fluid. Accurate results are obtained when the contact values of the correlation functions for the molecules about the test particle are accurate. Equation (10) was tested for two cases for which the contact values are known accurately: (1) a mixture of hard spheres and (2) a pure Lennard–Jones fluid at moderate density. For hard sphere mixtures the contact values of the correlation functions and the pressure are accurately estimated by the Carnahan–Starling (CS) equation [11]. Equation (10) was compared to the simulation results of Alder [12] for excess Gibbs free energies of mixing. CS contact values and pressures were used in the formula. The conditions used and the results obtained are given in Table I. The average absolute error in the excess Gibbs energy predicted by Eq. (10) was 1.62 %. The results obtained were nearly identical to those obtained by thermodynamically integrating the CS equation. For Lennard–Jones mixtures at moderate densities the work of insertion can be split into second and third virial contributions—each of which can be calculated by an integration of Mayer factors. The result can then be compared to Eq. (10). A representative calculation was made for the conditions: $\rho\sigma^3 = 0.15$, $kT/\varepsilon = 1.35$, $d/\sigma = 0.825$. The pressure was obtained from the HMSA calculation and the contact values of the correlation functions were obtained from PYP.

Table I. Excess Gibbs Free Energies from Scaled Particle Theory for a Hard Sphere Mixture[a]

Packing fraction	Predicted excess Gibbs energy g^E/kT	
	Exact[b]	Theory[c]
0.2333	−0.60	−0.591
0.2692	−0.81	−0.798
0.3106	−1.13	−1.107
0.3583	−1.63	−1.587
0.3808	−1.92	−1.875
0.4393	−2.91	−2.880
0.5068	−4.77	−4.759

[a] Excess Gibbs energies for mixing at constant packing fraction. The diameter ratio used was three to one. Each mixture was equimolar.

[b] Simulation results from Ref. 12.

[c] From Eqs. (9) and (10) with properties from Ref. 9.

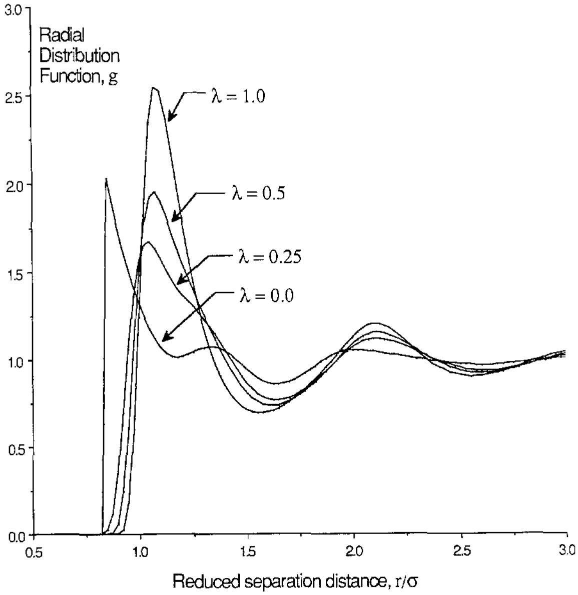

Fig. 2. Test particle distribution functions in a pure fluid at low temperature and high density. The reduced density is $\rho\sigma^3 = 0.75$ and the reduced temperature is $kT/\varepsilon = 0.928$. Shown are distribution functions for bath molecules about a test particle for several values of the coupling parameter λ. When $\lambda = 1$ the test particle is identical to a bath molecule. The calculated distribution functions show excessive overlap of the bath molecules with the test particle which corresponds to the appearance of a second coordination shell which is very close to the test particle.

Equation (10) reproduced the total of the second and third virial contributions to the work of insertion and was in error by only -0.4 %.

The theory has been used to predict residual (or configurational) Gibbs' free energies for pure Lennard–Jones fluids. It was found that accurate prediction are made at relatively high temperatures ($kT/\varepsilon \geqslant 2$). At lower temperatures residual Gibbs energies are underpredicted because of the too-close approach of molecules in the fluid to the test particle. Results from the theory were compared to results from the Lennard–Jones equation of state of Nicolas *et al.* [13] at $T^* = kT/\varepsilon = 2$. The theory and the equation of state agreed to an average absolute percentage difference of 7.5 % over a density range of $\rho^* = \rho\sigma^3$ from 0.1 to 0.8. The largest error occurred at a reduced density of 0.6. Near this density the residual Gibbs energy changes sign and has small absolute value so that small absolute errors become large percentage errors. Outside of this region the average absolute error was 4.7 %. At $T^* = 2$ good results were obtained at high densities: at $\rho^* = 0.8$ the error in the calculated residual free energy was only -7.2 %. The test particle distribution functions at $T^* = 2$, $\rho^* = 0.8$, reveal that the second coordination shell about the test particle is at a distance of about 2σ away from the test particle, moving inward slightly as the particle is decoupled. At $T^* = 0.928$, $\rho^* = 0.75$, the test particle distribution functions are qualitatively different. At this low temperature and high density the second coordination shell for the completely decoupled test particle moved inward to about 1.4σ, reflecting a clustering of the molecules about the test particle. The distribution functions for these conditions are plotted in Fig. 2. The very close approach of molecules to the test particle made the integrand of Eq. (12) too negative, resulting in underprediction of the residual Gibbs energy. At $T^* = 0.928$ the theory underpredicted the Gibbs energies of Lennard–Jones fluids over the range of reduced densities from 0.025 to 0.8, as compared to the simulation results of Panagiotopoulos *et al.* [14]. At $T^* = 0.928$ the error increased with density, going from 11.7 % at $\rho^* = 0.6$ to 61.8 % at $\rho^* = 0.8$.

The theory gives good results for the chemical potentials in binary mixtures of Lennard–Jones molecules at high temperatures ($kT/\varepsilon \geqslant 2$). The isothermal, isobaric, excess Gibbs free energies of mixing predicted by the theory for three mixtures have been compared to the simulation results of Shukla and Haile [15]. The fluids examined were equimolar mixtures of species with equal characteristic energies and unequal characteristic sizes. Since the procedure gives good results for pure fluids at a reduced temperature $kT/\varepsilon = 2$, it was a natural next step to examine mixtures at the same reduced temperature. First, residual Gibbs free energies for the pure components were calculated under isobaric conditions. The results obtained compare favorably with those obtained from Nicolas' equation of

Table II. Isobaric Residual Gibbs Free Energies from Combined Scaled Particle Theory and Integral Equation Theory for Pure Lennard–Jones Fluids at High Temperature[a]

		Calculated density ($\rho\sigma^3$)			Predicted Gibbs energy $(g - g^*)/kT$	
σ (Å)	Required $P\sigma^3/\varepsilon$	Exact[b]	Nicolas[c]	HMSA	Nicolas[c]	Theory
3.405[d]	1.2	0.5219	0.5332	0.5276	−0.2406	−0.2603
4.256	2.3433	0.6523	0.6590	0.6559	0.4964	0.4035
5.108	4.0512	0.7530	0.7547	0.7545	1.5635	1.4625
5.959	6.4321	0.8355	0.8367	0.8388	2.9527	2.9897

[a] Calculations for reduced temperature $kT/\varepsilon = 2.0$.

[b] Simulation results from Ref. 15.

[c] Calculated from the approximate equation of state for the Lennard–Jones fluid given in Ref. 13.

[d] Diameters shown give $P/\varepsilon = 1.2/(3.405\ \text{Å})^3 = 3.03969 \times 10^{-2}\ \text{Å}^{-3}$.

Table III. Excess Gibbs Free Energies from Combined Scaled Particle Theory and Integral Equation Theory for Lennard–Jones Mixtures at High Temperature[a]

		Required density ($\rho\sigma_{11}^3$)		Predicted excess Gibbs energy g^E (J · mol^{-1})	
Mixture	σ_{22} (Å)	Exact[b]	HMSA	Exact[b]	Theory
1	4.256	0.4091	0.4120	−66	−68.3
2	5.108	0.3142	0.3155	−228	−249.4
3	5.959	0.2418	0.2422	−430	−457.5

[a] Excess Gibbs energies for isothermal, isobaric mixing at $kT/\varepsilon = 2.0$, $P\sigma_{11}^3/\varepsilon = 1.2$. Pure component free energies taken from column 7 in Table II. All mixtures are equimolar with $\varepsilon_{11}/k = \varepsilon_{12}/k = \varepsilon_{22}/k = 119.8$ K, $\sigma_{11} = 3.405$ Å, and $\sigma_{12} = (\sigma_{11} + \sigma_{22})/2$.

[b] Simulation results from Ref. 15.

state. Detailed information on the molecular sizes of each species, the densities at which isobaric conditions are reached, and the calculated residual Gibbs energies for the pure components are listed in Table II. Next, densities were determined for each of the three mixtures using the HMSA theory to give pressures equal to the simulation results. Finally, the chemical potentials of each species in Shukla and Haile's mixtures were estimated with the theory and the excess Gibbs free energies of mixing were calculated at constant temperature and pressure. Detailed information on the densities at which isobaric conditions were reached and the calculated excess Gibbs energies for the mixtures are listed in Table III. Results from the theory were 3 to 9 % low, the theory giving results that were 6.4 % low for the most asymmetric mixture.

4. CONCLUSIONS

Scaled particle theory can be combined with a Kirkwood charging process to obtain accurate estimates of the chemical potentials in fluids with realistic attractive and repulsive forces. Acceptable results were obtained from the current version of the theory only at high temperatures ($kT/\varepsilon \geqslant 2$). At lower temperatures accurate results were obtained only at low to moderate densities ($\rho\sigma^3 \leqslant 0.5$). Results at lower temperatures were compromised by the related consequences of assuming a particular core size for the test particle and of approximations made in the closure equation for the test particle distribution functions. An improved procedure is to replace the division of the test particle pair potential used [Eq. (1)] with the Andersen *et al.* [16] division. Then a perturbation theory similar to that of Lado [17] is used to estimate the contribution of the WCA repulsive force to the chemical potential with scaled particle theory. Such a division of the pair potential reduces the requirements for accuracy placed on the closure equations for the test particle distribution functions since the structure of the fluid is perturbed to a smaller extent as the particle is coupled. Our work in progress uses this approach.

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