Analytical Description of the Lennard-Jones Fluid and Its Application

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A simplified exponential (SEXP) approximation, combining the exponential approximation and the first-order mean spherical approximation, is proposed to improve the equation of state for the Lennard-Jones (LJ) fluid. The SEXP approximation, which can be implemented in an analytical manner, yields better radial distribution functions of the LJ fluid. Extensive comparisons with two typical perturbation theories show that the SEXP approximation is more appropriate to describe the behaviors of the LJ fluid. The latest 33-parameter modified Benedict-Webb-Rubin equation, also calculated, is inadequate in the region of phase coexistence. The SEXP approximation is applied to the calculation of methane properties with much better results than the Peng-Robinson equation of state for saturated liquid densities and second virial coefficients.

Introduction

An accurate equation of state is essential for describing fluid behaviors in chemical engineering applications. The (6,12) Lennard-Jones (LJ) fluid is very basic in statistical thermodynamics consideration. The repulsive- and attractive-force parts of the LJ potential

$$u(r) = 4\epsilon\left(\frac{\sigma^{12}}{r^{12}} - \frac{\sigma^6}{r^6}\right) \tag{1}$$

closely account for the repulsion and dispersion forces between a pair of real molecules. The LJ potential itself is adequate to explore the behaviors of simple fluids like argon and methane (Lee, 1988). For anisotropic molecules, the LJ fluid may serve as a reference for studying complex fluids (Shulka, 1994). The knowledge about the LJ fluid is essential to develop an equation of state for the LJ chain fluid in a perturbation theory (Wertheim, 1987). Since the LJ potential represents the basic molecular interaction, any equation capable of describing real fluid behaviors should, in principle, describe correctly those of the LJ fluid. In reality, there is still a lack of such an equation. The cubic equations of state such as the Soave-Redlich-Kwong (SRK) (1972) and the Peng-Robinson (PR) (1976) equations are widely utilized in engineering calculations. A recent study (Harismiadis et al., 1994) suggests that these cubic equations are inappropriate to describe phase coexistence and other properties of the simple LJ fluid. Even with additional adjustable parameters, a simultaneous description of these behaviors remains in doubt. The situation further deteriorates for calculating the properties of LJ mixtures due to the introduction of mixing rules. Thus, there is a fundamental limitation on the application of simple empirical equations of state. There is a need to develop a new equation of state which, as a first step, describes the LJ fluid correctly. Intuitively, the success of such a development should have recourse to statistical thermodynamics.

The theoretical studies of the LJ fluid have progressed considerably in recent decades. Two well-known perturbation theories, the Barker-Henderson (BH) (1967) and the Weeks-Chandler-Anderson (WCA) (1971) theories, have described the LJ fluid fairly well beyond low densities. In addition, a number of integral-equation theories such as the Percus-Yevick (PY), the hypernetted chain (HNC) and other recently developed approximations toward solving the Ornstein-Zernike (OZ) equation are adopted to study the LJ fluid (e.g., Madden and Fitts, 1975; Sarkisov et al., 1993; Lomba and Lee, 1996). An integral-equation theory has an advantage over the BH and WCA theories by providing structure and properties simultaneously. However, the involved computation is very time-consuming because of tedious numerical iterations in solving the integral equation. The BH and WCA theories appear to be computationally simpler, but they are less satisfactory due to the shortage of direct structure information and inaccuracy at some state conditions. Even for the computation itself, the two perturbation theories are not so simple as to be acceptable to engineers. Then, some fully empirical equations, such as the 33-parameter modified Benedict–Webb–Rubin (MBWR) equation, were utilized to describe the LJ fluid (Nicolas et al., 1979). The MBWR equation was further improved by Adachi et al. (1988) and Johnson et al. (1993). In its latest version (Johnson et al., 1993), the MBWR equation was fitted by new extensive Monte-Carlo simulation data. The simplicity of the MBWR equation makes it easily accessible to engineering calculations, and its large number of adjustable parameters enable the equation to describe the LJ fluid very accurately at the fitted conditions. Like many other empirical equations, the MBWR equation is of interest only for studying the properties of the LJ fluid itself. It is impossible for the equation to yield the structural information needed by perturbation theories to explore more complex fluids. In the future development of the equation of state for LJ mixtures, the MBWR equation will only be useful after a certain mixing rule is introduced, and its high accuracy is unlikely to be maintained (Fotouh and Shukla, 1997).

We recently proposed a new mathematical method to solve the OZ equation (Tang and Lu, 1993). The new solution, based on the mean spherical approximation (MSA), provides analytically a radial distribution function (RDF) of the LJ fluid. The first-order analytical solution, or the first-order MSA, has been proven to yield a good prediction of the structure and properties of the LJ fluid (Tang and Lu, 1994a). The achievement is, however, not completely satisfactory, as the computation work is as time-consuming as the BH and WCA theories. The developed RDF also shows nonnegligible deviation from the MC data at $r \sim \sigma$. Recently, the first deficiency was eliminated by introducing a two-Yukawa (TY) function (Tang et al., 1997)

$$u^{TY}(r) = \begin{cases} \infty, & r < R \\ -k_0\epsilon\dfrac{e^{-z_1(r-\sigma)}}{r} + k_0\epsilon\dfrac{e^{-z_2(r-\sigma)}}{r}, & r > R \end{cases} \tag{2}$$

to represent the LJ potential, with $k_0 = 2.1714\sigma$, $z_1 = 2.9637/\sigma$, $z_2 = 14.0167/\sigma$. The TY function was found to reproduce the LJ function (Eq. 1), the LJ RDF, and the LJ properties very well. The resulting difference between Eqs. 1 and 2 is graphically invisible. Very simple algebraic expressions for the Helmholtz free energy, compressibility factor, and internal energy were developed. The present work is devoted to resolving the second deficiency of the first-order MSA. A simplified exponential (SEXP) approximation is proposed, based on a combination of the first-order MSA with the available exponential (EXP) approximation (Anderson et al., 1976; Stell, 1976). The SEXP approximation can improve substantially the prediction of the LJ RDF at $r \sim \sigma$ and subsequently the LJ properties. The SEXP approximation retains the simplicity of the first-order MSA, and so can be easily implemented for engineering purposes. We feel that simple and reliable expressions of the LJ RDF and properties could greatly expedite the studies of both the LJ fluid itself and the relevant complex fluids using the LJ fluid as the reference system. Finally, the developed expressions are used to study the behaviors of a simple real fluid, methane. Comparison with the PR equation indicates that the present equation provides a fundamental improvement over the empirical equation.

First-Order MSA Results

In an earlier paper (Tang and Lu, 1994a), we reported an analytical RDF $g_1^{LJ}(r)$ expression for the LJ fluid by implementing the first-order MSA solution:

$$\int_0^\infty r g_1^{LJ}(r) e^{-sr} dr = \frac{4\beta\epsilon e^{-sR}}{Q^2(sR)} \int_0^\infty \frac{\dfrac{\sigma^6}{4!}t^4 - \dfrac{\sigma^{12}}{10!}t^{10}}{(t+s)Q^2(tR)} e^{-tR}\, dt, \tag{3}$$

where R is the BH diameter of the reference system of hard spheres. This is given by De Souza and Ben-Amotz (1993):

$$R = 2^{1/6}\left[1 + \left(1 + \frac{T^* + C_2 T^{*2} + C_3 T^{*4}}{C_1}\right)^{1/2}\right]^{-1/6} \sigma, \tag{4}$$

where $c_1 = 1.1287$, $c_2 = -0.05536$, and $c_3 = 0.0007278$; $T^* = 1/\beta\epsilon = kT/\epsilon$ is the reduced temperature; and $Q(t)$ is the factorization function of hard spheres with density ρ, and is given by

$$Q(t) = \frac{S(t) + 12\eta L(t) e^{-t}}{(1-\eta)^2 t^3} \tag{5}$$

$$S(t) = (1-\eta)^2 t^3 + 6\eta(1-\eta)t^2 + 18\eta^2 t - 12\eta(1+2\eta) \tag{6}$$

$$L(t) = \left(1 + \frac{\eta}{2}\right)t + 1 + 2\eta; \qquad \eta = \frac{1}{6}\pi\rho R^3. \tag{7}$$

To avoid the troublesome integration appearing in Eq. 3, we adopted the TY function (Eq. 2) to study the LJ fluid (Tang et al., 1997), which led to the following new LJ RDF expression:

$$\int_R^\infty r g_1(r) e^{-sr} dr = \frac{\beta\epsilon k_1 e^{-sR}}{(s+z_1)Q^2(sR)Q^2(z_1R)} - \frac{\beta\epsilon k_2 e^{-sR}}{(s+z_2)Q^2(sR)Q^2(z_2R)}, \tag{8}$$

where

$$k_1 = k_0 e^{z_1(\sigma - R)}, \qquad k_2 = k_0 e^{z_2(\sigma - R)}. \tag{9}$$

The inverse Laplace transform of Eq. 8 was carried out (Tang and Lu, 1997; Tang et al., 1997), giving

$$r g_1(r) = \beta\epsilon k_1 \frac{(1-\eta)^4}{Q^2(z_1R)} \sum_{n=0}^{\infty} (1+n) \times (-12\eta)^n D(6, n, n+2, z_1R, r-n-1)$$

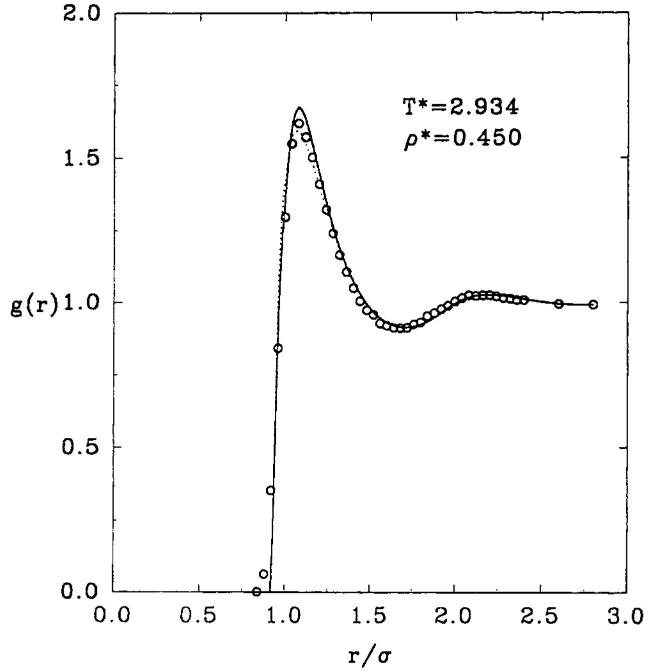

Figure 1. RDF predicted by the SEXP approximation (solid line) and the first-order MSA (dotted line); circles are computer-simulation data (Verlet, 1968).

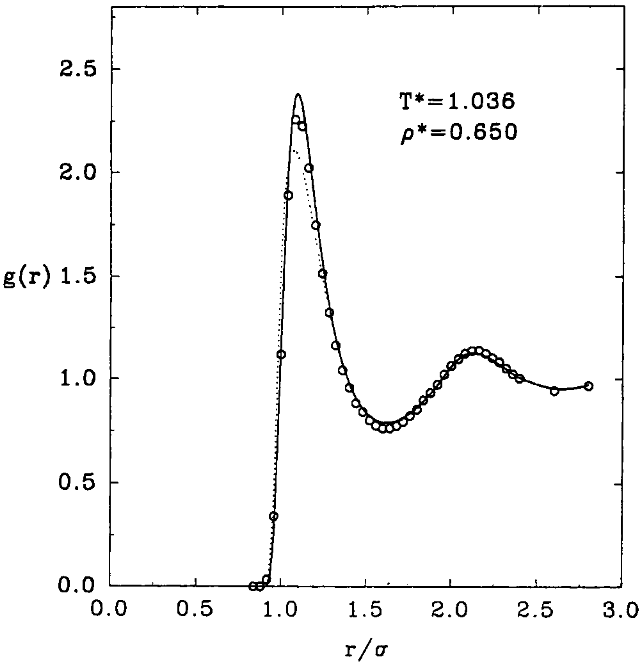

Figure 2. RDF predicted by the SEXP approximation (solid line) and the first-order MSA (dotted line); circles are computer-simulation data (Verlet, 1968).

$$-\beta\epsilon k_2 \frac{(1-\eta)^4}{Q^2(z_2R)} \sum_{n=0}^{\infty}(1+n) \times(-12\eta)^n D(6,n,n+2,z_2R,r-n-1), \quad (10)$$

where $D(n_1,n_2,n_3,z,r)$ is given in Appendix A. We have verified that the RDF from Eq. 8 is practically indistinguishable from Eq. 3. The computation in Eq. 8 or 10 is much faster than Eq. 3.

The TY potential has enabled us to obtain explicit analytical expressions for Helmholtz free energy, compressibility factor, and internal energy (Tang et al., 1997). Because of the lengthy appearance of these expressions, they are left in Appendix B. The expressions of the LJ RDF and its properties have been tested extensively by comparing them with the MC data. We find that the first-order MSA RDF is fairly good at $r \gg \sigma$, but deviates noticeably from the computer simulation data at $r \sim \sigma$. Mostly, the first-order MSA, which may be extended to the full MSA, underestimates the first peak of the LJ RDF and overpredicts the RDF value at $r = R$. These defects inevitably cause some errors in predicting the LJ properties.

Simplified Exponential Approximation

The original EXP approximation was proposed some years ago by Anderson et al. (1976) and independently by Stell (1976). From the cluster expansion of the attractive force around the repulsive one, Anderson concluded that the following EXP approximation

$$g(r)=g_0(r)e^{g^{\mathrm{MSA}}(r)-g_0(r)} \quad (11)$$

is inherently more accurate than the MSA result $g(r)=g^{\mathrm{MSA}}(r)$, although in the EXP approximation a certain number of terms in the cluster expansion of $g(r)$ are neglected. The subscript 0 in Eq. 11 and throughout this article refers to

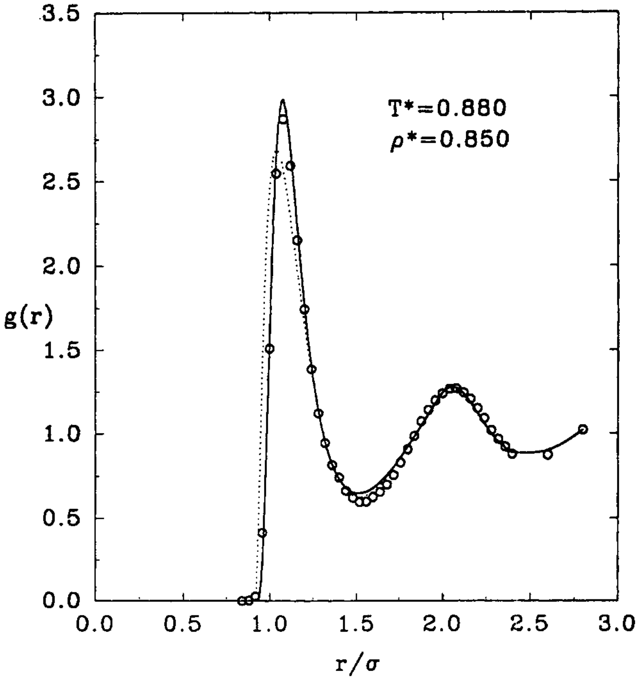

Figure 3. RDF predicted by the SEXP approximation (solid line) and the first-order MSA (dotted line); circles are computer-simulation data (Verlet, 1968).

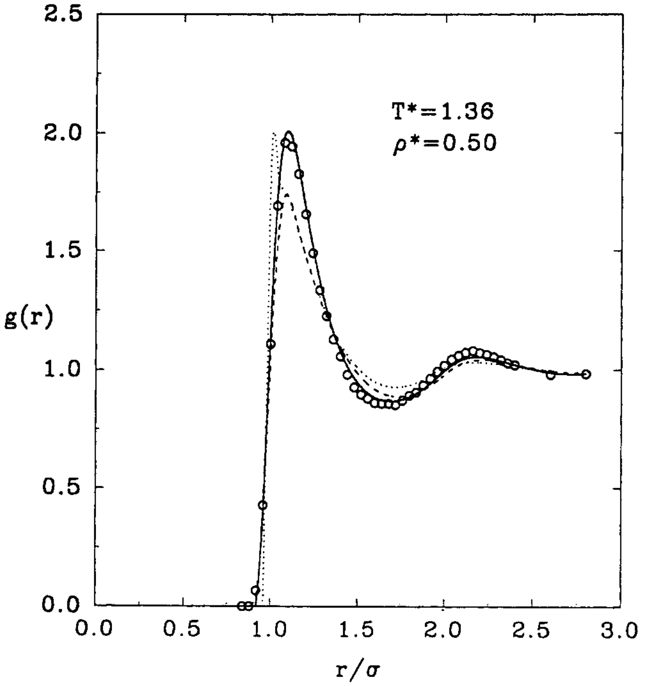

Figure 4. RDF predicted by the SEXP approximation (solid line), the BH theory (dotted line), and the WCA theory (dashed line); circles are computer-simulation data (Verlet, 1968).

the hard-sphere reference system with its diameter given by Eq. 4. In the past, the accuracy of the EXP approximation was tested for a number of potentials. Anderson et al. (1976) and Stell and Weis (1980) applied Eq. 11 for the LJ fluid and found that the EXP approximation is indeed in better agreement with the computer-simulation data than is the MSA. When applying the EXP approximation to the studies of Yukawa fluid, Henderson et al. (1978) and Konior and Jedrzejek (1985) found that the EXP approximation improves the prediction of the Yukawa RDF remarkably over the MSA. In inspecting the thermodynamics of the MSA, Høye and Stell (1977) concluded that the EXP approximation can enhance the thermodynamic consistency between two routines: the internal energy and the virial pressure. Here we give more arguments to justify the EXP approximation. It is known that the exact relation between the direct correlation function $c(r)$ and the total correlation function $h(r)$ is

$$c(r) = -\beta u(r) + h(r) - \ln g(r) + B(r) \tag{12}$$

where $B(r)$ is the bridge function. Similarly, for the reference system of hard spheres,

$$c_0(r) = h_0(r) - \ln g_0(r) + B_0(r), \qquad r > R. \tag{13}$$

Subtracting Eq. 13 from Eq. 12 yields

$$g(r) = g_0(r) e^{\Delta g(r) - \Delta c(r) - \beta u(r) + \Delta B(r)}, \qquad r > R, \tag{14}$$

where the symbol Δ represents the difference of a quantity from its reference one. The bridge function has been found to be of a certain universality (Rosenfeld and Ashcroft, 1979). Therefore, we can assume that $\Delta B(r) = 0$ and Eq. 14 can be reduced to

$$g(r) = g_0(r) e^{\Delta g(r) - \Delta c(r) - \beta u(r)}, \qquad r > R, \tag{15}$$

which, when supplemented by the OZ equation,

$$h(r) = c(r) + \rho \int h(r') c(r - r')\, dr', \tag{16}$$

can in principle determine an approximate RDF. In order to obtain the RDF, we can design the following iteration procedure to solve Eqs. 15 and 16. Initially, it is assumed that $g(r) = g_0(r)$ or $\Delta g^{(0)}(r) = 0$. Applying the relation 15 yields

$$\Delta c(r) = -\beta u(r), \qquad r > R, \tag{17}$$

which is essentially equivalent to the MSA relation

$$c(r) = -\beta u(r), \qquad r > R, \tag{18}$$

since $c_0(r)$ vanishes rapidly outside of the hard core. The solution of Eq. 18 and the OZ equation (Eq. 16) yields a new relation, $\Delta g^{(1)}(r) = g^{\mathrm{MSA}}(r) - g_0(r)$. Substituting $\Delta g^{(1)}(r)$ into Eq. 15 gives

$$g(r) = g_0(r) e^{g^{\mathrm{MSA}}(r) - g_0(r)}, \tag{19}$$

which is precisely the EXP approximation. Thus, the EXP approximation is an intermediate result in an iteration solu-

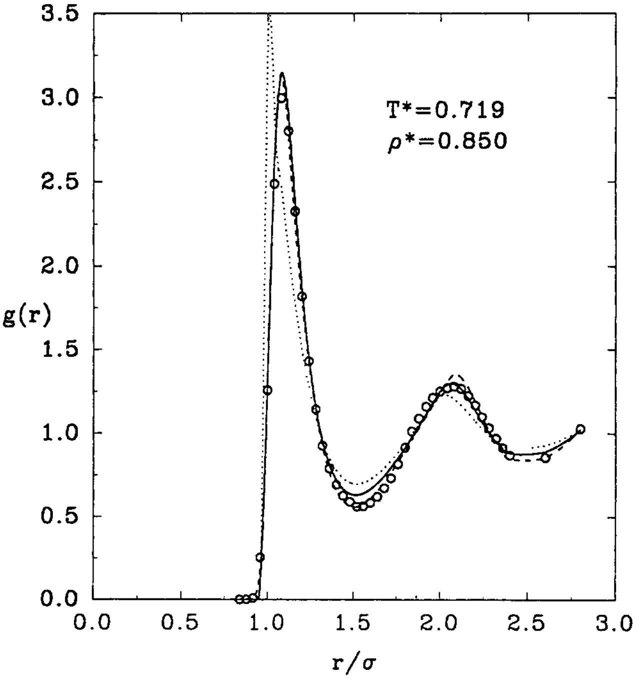

Figure 5. RDF predicted by the SEXP approximation (solid line), the BH theory (dotted line), and the WCA theory (dashed line); circles are computer-simulation data (Verlet, 1968).

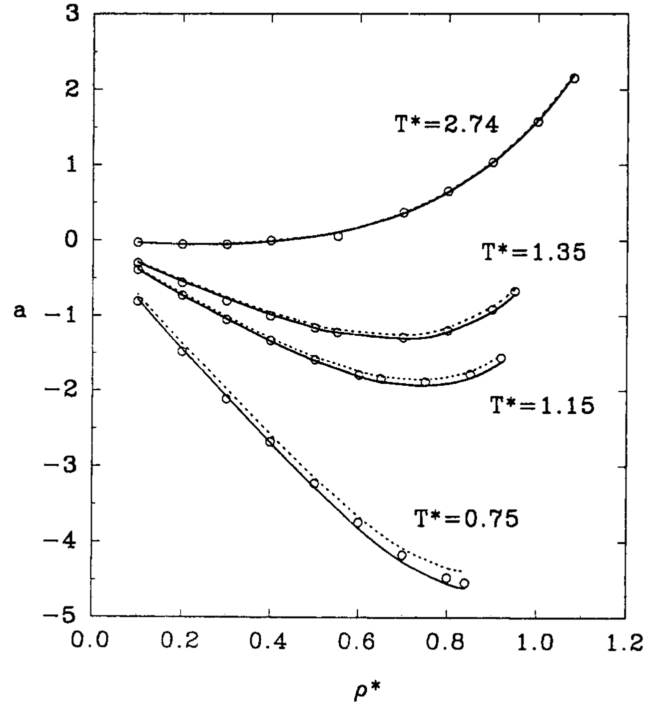

Figure 6. Helmholtz free energy predicted by the SEXP approximation (solid line) and the first-order MSA (dotted line); circles are computer-simulation data (Hansen, 1970).

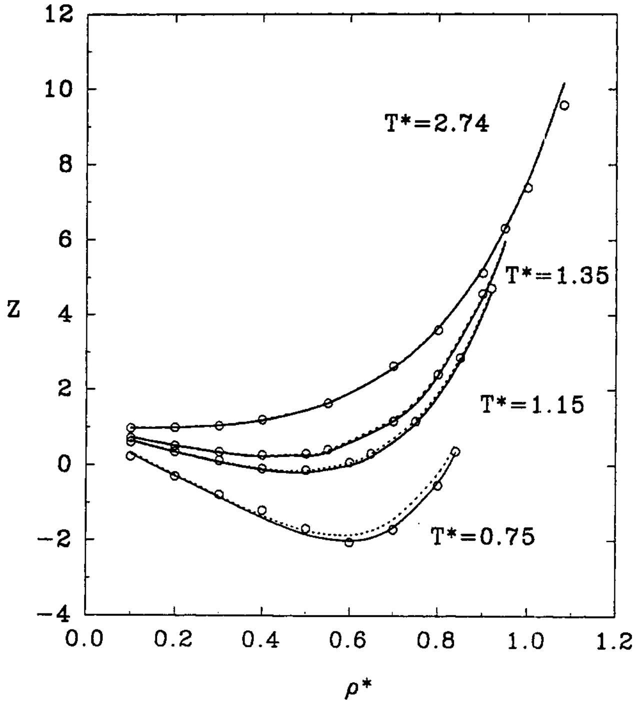

Figure 7. Compressibility factor predicted by the SEXP approximation (solid line) and the first-order MSA (dotted line); circles are computer-simulation data (Hansen, 1970).

tion of Eqs. 15 and 16. Since Eq. 15 is generally considered a better approximation, the EXP approximation is naturally more accurate than the MSA. An algebraic analysis indicates that relation 15 can be equally derived by the HNC approximation (Eq. 12) after dropping $B(r)$. Since in the HNC approximation the energy routine gives strictly the same results as that of the virial pressure, it is not surprising to see that the EXP approximation based on Eq. 15 yields better thermodynamic consistency. These arguments strongly suggest that the EXP approximation is inherently better than the MSA. We expect that proper utilization of the EXP approximation may overcome some deficiencies of the first-order MSA just reported.

In order to incorporate the first-order MSA RDF into the EXP approximation, we propose the following simplified EXP (SEXP) approximation

$$g(r) = g_0(r)e^{g_1(r)}, \tag{20}$$

where, in other words, the full MSA RDF is approximately substituted by the sum of the first-order RDF and the reference one. Our previous experience with the Yukawa and the square-well fluids (Tang and Lu, 1993, 1994b) shows that a full MSA RDF is dominated by its first-order RDF. For the LJ fluid, such a domination may still be valid since the first-order MSA RDF was previously found satisfactory (Tang and Lu, 1994a). More significantly, the SEXP approximation makes the resulting RDF $g(r)$ as easily attainable as does the first-order MSA RDF. In the EXP approximation, one has to predetermine the full MSA RDF by a tedious numerical solution, while in the SEXP approximation, we can obtain the RDF $g(r)$ in a very straightforward manner by using Eq. 10.

The superiority of the SEXP approximation is indicated immediately by its limiting value at the zero density. When $\rho = 0$, one can easily find from Eqs. 16 and 18 that

$$g_1(r) = -\beta u(r) \tag{21}$$

for the first-order MSA, and the SEXP approximation then yields

$$g(r) = e^{-\beta u(r)}, \tag{22}$$

which is exact at $\rho = 0$, while the first-order MSA result is only a linear approximation of Eq. 22. This observation suggests that the SEXP approximation is more reliable at low densities. The performance of the SEXP approximation at moderate and high densities can be demonstrated by comparison with the computer-simulation data (Verlet, 1968). Figures 1 to 3 show RDFs predicted by the SEXP approximation as well as by the first-order MSA at three sets of densities and temperatures [the $g(r)$ of the SEXP approximation at $r < R$ in all the figures is extrapolated using values at $r > R$]. These graphical comparisons show that the SEXP approximation is an appreciable improvement over the first-order MSA. The improvement is very pronounced in the vicinity of the first peak of the RDF. Both the peak position and height are correctly shifted by the SEXP approximation. The RDF value at $r \sim \sigma$ is brought down close to the MC data. While away from the first peak, the SEXP RDF is practically indistinguishable from the first-order MSA RDF, since $g_1(r)$ approaches zero and $g_0(r)$ approaches unity rapidly. It appears that the performance of the SEXP approximation for the LJ

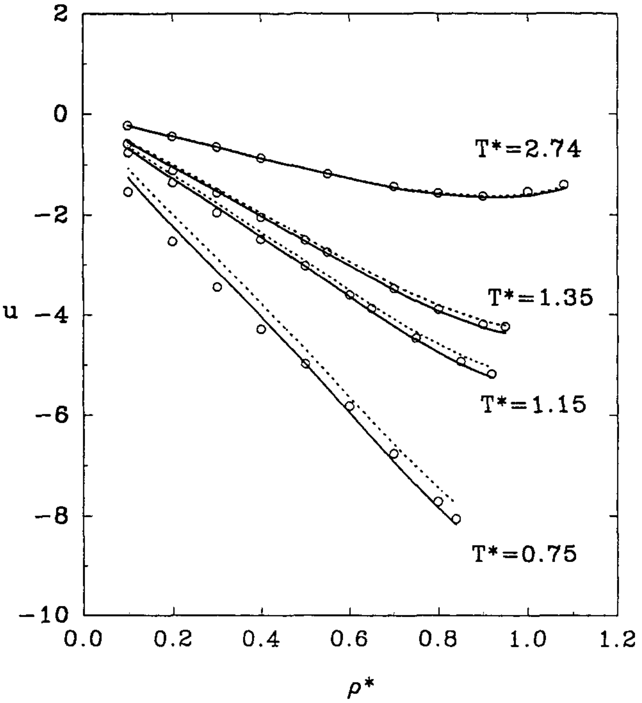

Figure 8. Internal energy predicted by the SEXP approximation (solid line) and the first-order MSA (dotted line); circles are computer simulation data (Hansen, 1970).

fluid is basically the same as that found by Anderson et al. (1976) and Stell and Weis (1980) for the EXP approximation, and the overall accuracy of the approximation is excellent even though the excellent results may not be kept at all states. A more subtle inspection shows that the SEXP approximation somewhat overcorrects the first-order MSA at higher temperatures, a characteristic perhaps inherited from the original EXP approximation. Nevertheless, the EXP approximation, hence possibly the SEXP approximation, remains one of the best liquid theories, and any attempts to improve it systematically is extremely difficult (Stell and Weis, 1980).

In addition to the SEXP approximation, the BH and WCA theories can also be implemented simply. The two theories were not originally developed for the fluid structure. Nevertheless, we can extract the structural information by the functional derivative of the Helmholtz free energy with respect to the potential function $u(r)$:

$$\frac{\partial A}{\partial u(r)}=\frac{1}{2}N\rho g(r). \qquad (23)$$

Because $g(r)$ is more fundamental than the quantity A, it will shed more light on a liquid theory. Intuitively, a reliable theory for thermodynamics should yield the equally reliable RDF.

In the BH theory,

$$\frac{A-A_0}{NkT}=\frac{1}{2}\rho\beta\int g_0(r)u(r)\,dr-\frac{1}{4}\rho\beta\left(\frac{\partial\rho}{\partial P}\right)_0\int g_0(r)u^2(r)\,dr \qquad (24)$$

and in the WCA theory,

$$\frac{A-A_0}{NkT}=\frac{1}{2}\rho\beta\int g_0^{\mathrm{WCA}}(r)u^{\mathrm{WCA}}(r)\,dr. \qquad (25)$$

A straightforward application of Eq. 23 to Eqs. 24 and 25 yields

$$g^{\mathrm{BH}}(r)=g_0(r)\left(1-\left(\frac{\partial\rho}{\partial P}\right)_0 u(r)\right) \qquad (26)$$

$$g^{\mathrm{WCA}}(r)=g_0^{\mathrm{WCA}}(r). \qquad (27)$$

The reference system of the BH theory is the same as ours, and no further introduction is needed. For the WCA theory, the reference potential $u_0^{\mathrm{WCA}}(r)$ and the perturbation potential $u^{\mathrm{WCA}}(r)$ are defined by

$$u_0^{\mathrm{WCA}}(r)=\begin{cases}u(r)+\epsilon, & r<2^{1/6}\sigma\\ 0, & r>2^{1/6}\sigma,\end{cases}$$
$$u^{\mathrm{WCA}}(r)=\begin{cases}-\epsilon, & r<2^{1/6}\sigma\\ u(r), & r>2^{1/6}\sigma,\end{cases} \qquad (28)$$

respectively. The reference RDF $g_0^{\mathrm{WCA}}(r)$ is technically determined through the cavity function $y_0(r,d)$ of hard spheres with the diameter d:

$$g_0^{\mathrm{WCA}}(r)=e^{\beta u_0^{\mathrm{WCA}}(r)}y_0(r,d). \qquad (29)$$

The quantity d is somewhat more complicated than the R of the BH theory, and the analytical expression of De Souza and Ben-Amotz (1993)

$$d=2^{1/6}\left[1+\left(\frac{T^*+C_2T^{*2}+c_3T^{*4}}{c_1(1+c_4\rho^*+c_5\rho^{*2}+c_6\rho^{*3})}\right)^{1/2}\right]^{-1/6}\sigma \qquad (30)$$

is adopted here. In Eq. 30, $c_1=1.5001$, $c_2=-0.03367$, $c_3=0.0003935$, $c_4=-0.09835$, $c_5=0.04937$, $c_6=-0.1415$. For convenience, we use the PY cavity function in the calculation of Eq. 29.

Figures 4 and 5 show two RDFs predicted by the SEXP approximation, the BH and the WCA theories. In both figures, the BH theory does not yield reasonably the structure of the LJ fluid. The BH RDF is out of phase, and values at $r=R$ are overpredicted. The worst deficiency of the BH theory is that it is incapable of drawing the first peak of the LJ RDF. The WCA theory was previously found (Weeks et al., 1971) to be accurate at high densities but poor at other densities. Our calculations confirm these observations. The theory gives a very good prediction of the RDF in Figure 5, but the prediction deteriorates at a moderate density, as shown in Figure 4. Such a deterioration may become more severe at low densities. The deterioration indicates that one key assumption, that the cavity function of the reference system can be approximated by that of a hard-sphere system, is no longer valid except at high densities. Therefore, the application of the WCA theory to the LJ RDF and even thermodynamics is

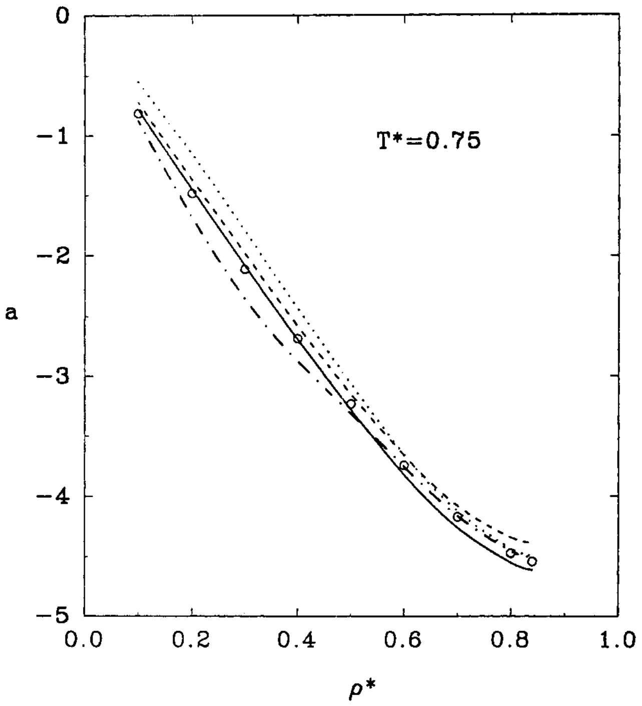

Figure 9. Comparison among the SEXP approximation (solid line), the BH theory (dashed line), the WCA theory (dotted line), and the MBWR equation (dash-dotted line) for the Helmholtz free energy; circles are computer-simulation data (Hansen, 1970).

dynamics is limited. Contrary to the two preceding theories, the SEXP approximation yields a very reliable RDF at both moderate densities and high densities. The SEXP RDF shown in Figure 4 is much better than both the BH RDF and the WCA RDF. As shown in Figure 5, the SEXP RDF is better at a high density than the BH RDF and globally comparable to the WCA RDF. Overall, the SEXP theory is fundamentally more sophisticated. The LJ RDF have been extensively investigated by other integral-equation theories, typically the PY theory and the HNC theory. A comparison with the results reported in the literature (Madden and Fitts, 1975) indicates that the SEXP RDF is better than the PY RDF and is somewhat similar to that of the HNC theory, while the computation work involved in the PY and HNC theories is much more tedious than in the present work.

Thermodynamic Properties

It appears that the most straightforward way to obtain the LJ properties with the LJ RDF is through the functional relation between the RDF and the Helmholtz free energy, as shown by Eq. 23. Assigning a perturbation coupling parameter ξ to the perturbation potential $u(r)$, we obtain

$$\frac{\partial\left(\frac{A}{NkT}\right)}{\partial \xi} = \int \frac{\partial(A/NkT)}{\partial[\xi u(r)]}\frac{\partial[\xi u(r)]}{\partial \xi}dr$$

$$= 2\pi\rho\beta\int_\sigma^\infty g(r,\xi)u(r)r^2\,dr, \quad (31)$$

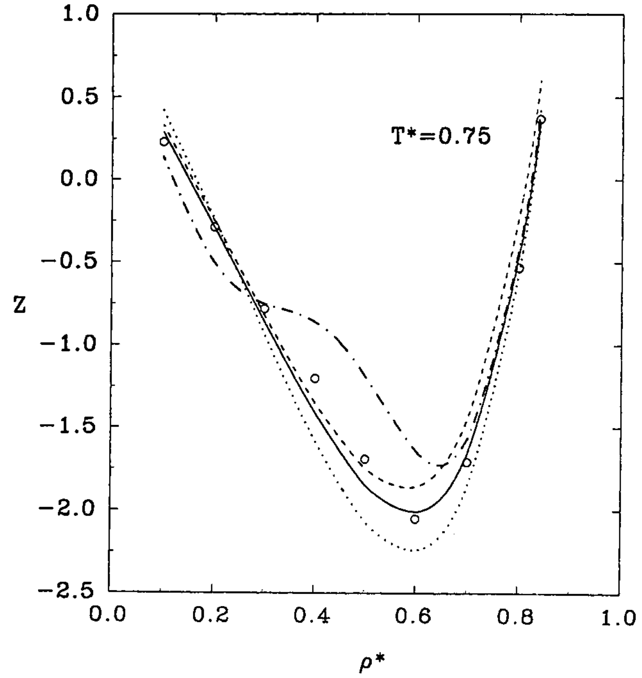

Figure 10. Comparison among the SEXP approximation (solid line), the BH theory (dashed line), the WCA theory (dotted line), and the MBWR equation (dash-dotted line) for the compressibility factor; circles are computer-simulation data (Hansen, 1970).

where $g(r,\xi)$ is the RDF of the system with the perturbation potential $\xi u(r)$. Integrating Eq. 31 with respect to ξ and utilizing the SEXP approximation (Eq. 20) yields

$$a - a_0 = \frac{A - A_0}{NkT} = 2\pi\rho\beta\int_0^1 d\xi\int_\sigma^\infty g(r,\xi)u(r)r^2\,dr$$

$$= 2\pi\rho\beta\int_\sigma^\infty g_0(r)\frac{e^{g_1(r)}-1}{g_1(r)}u(r)r^2\,dr = a_1 + a_2 + a_r, \quad (32)$$

where a_0, a_1, and a_2 are given explicitly in Appendix B, and a_r is the revised part brought by the SEXP approximation:

$$a_r = \frac{48\eta\beta\epsilon}{R^3}\int_\sigma^\infty g_0(r) \times \frac{e^{g_1(r)} - 1 - g_1(r) - g_1^2(r)/[2g_0(r)]}{g_1(r)}\left(\frac{\sigma^{12}}{r^{10}} - \frac{\sigma^6}{r^4}\right)dr. \quad (33)$$

Accordingly, the compressibility factor and the internal energy can be obtained through the following thermodynamic relations:

$$Z = Z_0 + Z_1 + Z_2 + Z_r \quad (34)$$

$$u = u_0 + u_1 + u_2 + u_r \quad (35)$$

with

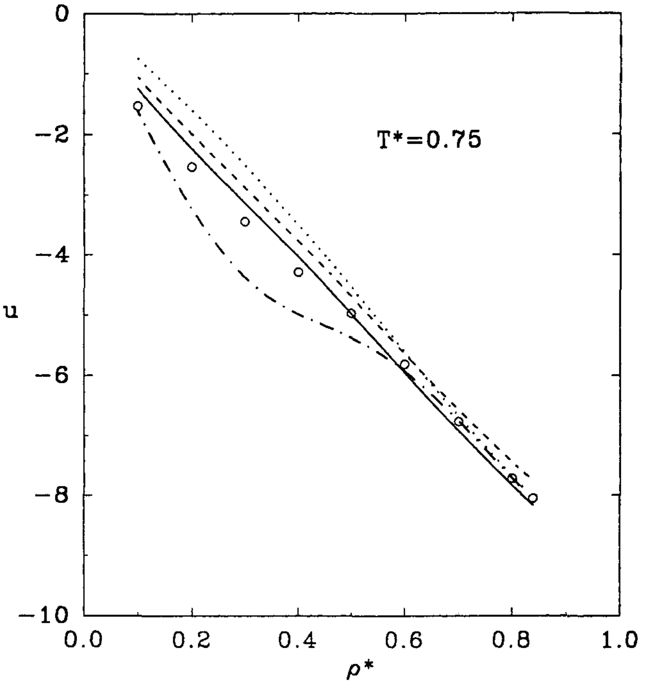

Figure 11. Comparison among the SEXP approximation (solid line), the BH theory (dashed line), the WCA theory (dotted line), and the MBWR equation (dash-dotted line) for the internal energy; circles are computer-simulation data (Hansen, 1970).

$$Z_r = \rho \frac{\partial a_r}{\partial \rho}, \qquad u_r = \beta \frac{\partial a_r}{\partial \beta}, \tag{36}$$

where Z_i and u_i ($i = 0, 1, 2$) are shown in Appendix B.

Figures 6 to 8 exhibit the Helmholtz free energy, the compressibility factor, and the internal energy calculated by Eqs. 32, 34 and 35, respectively. In addition, the MSA results are indicated in these figures by dashed lines. The agreement between the SEXP approximation and the MC data (Hansen, 1970) is excellent throughout four temperature sets. At moderate and high temperatures, the performance of the SEXP approximation is expectedly very close to that of the first-order MSA, since the first-order MSA was found to be very accurate at these states (Tang et al., 1997). At low temperatures, the SEXP approximation shows a visible improvement over the first-order MSA for all the three quantities. Obviously, the improvement is attributed to the better RDF provided by the SEXP approximation, as discussed in the previous section. Figures 9 to 11 give comparisons among the SEXP approximation, the BH theory, the WCA theory, and the 33-parameter MBWR equation for predicting the three just-mentioned properties at a low temperature, $T^* = 0.75$, where the theoretical prediction is more sensitive than that at a high temperature. One can easily see that the SEXP approximation is overall the best in each of the figures. The WCA theory is a little more accurate at very high densities, but shows large errors at both low densities or moderate densities. Such a performance is parallel to that of the prediction of the WCA RDF. It is somewhat unexpected to see that the BH theory yields better predictions of the Helmholtz free energy and the internal energy than does the WCA theory, although its RDF prediction is very poor. It appears that such a performance is due to error cancellations in obtaining these thermodynamic quantities from the LJ RDF. In spite of the good results for the Helmholtz free energy and the internal energy, the BH theory predicts poorly the compressibility factor, as shown in Figure 10. In addition, all the properties calculated by the BH theory systematically deviate from the MC data at high densities. It is surprising to see that the MBWR equation, although it contains so many adjustable empirical parameters, gives distorted profiles of u and Z vs. density at $T^* = 0.75$. Only the Helmholtz free energy is predicted to be relatively consistent with the other three theories. An investigation of the work of Johnson et al. (1993) indicates that their MBWR equation is not actually defined in the region of phase coexistence, which covers most states at $T^* = 0.75$. The missing definition may not cause any inconvenience to the studies of the LJ fluid itself, but it could be troublesome when the LJ fluid is used as a reference to study more complex fluids, since the region of phase coexistence of these complex fluids is not certain to cover that of the LJ fluid. In this situation, we feel that using a theoretical equation of state provides more confidence in the determination of the LJ properties.

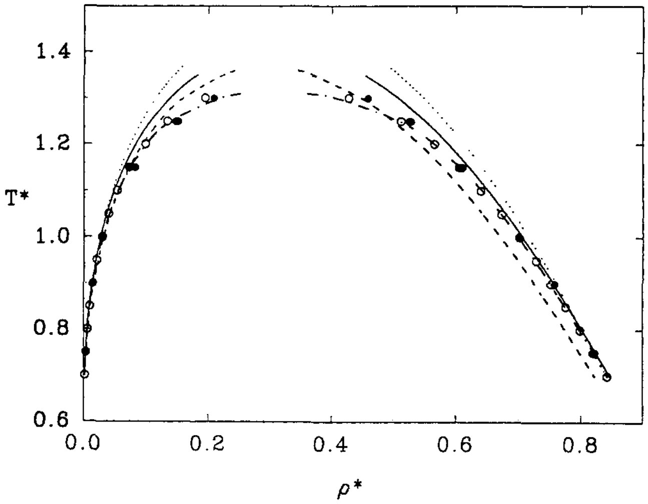

Figure 12. Phase diagram for the LJ fluid.

Open circles are MC data reported by Panagiotopoulos (1987); solid circles are MC data of Lotif et al. (1992). The legends are the same as in Figure 9.

In order to further illustrate the performance of the SEXP approximation, phase diagrams obtained from the preceding theories are plotted in Figure 12. It appears that a phase-diagram prediction is very sensitive to the theory's accuracy. In Figure 12, the BH theory underestimates saturated liquid densities, while the WCA theory overestimates these densities even away from the critical point. As in other thermodynamic calculations discussed previously, the SEXP approximation yields better results than the two perturbation theories. Both saturated vapor and liquid densities are well predicted by the SEXP approximation, provided that the state is away from the critical point. It is also noted that the MBWR equation yields a very good phase diagram of the LJ fluid. The good performance is associated with the large number of adjustable parameters in the equation and with the fact that

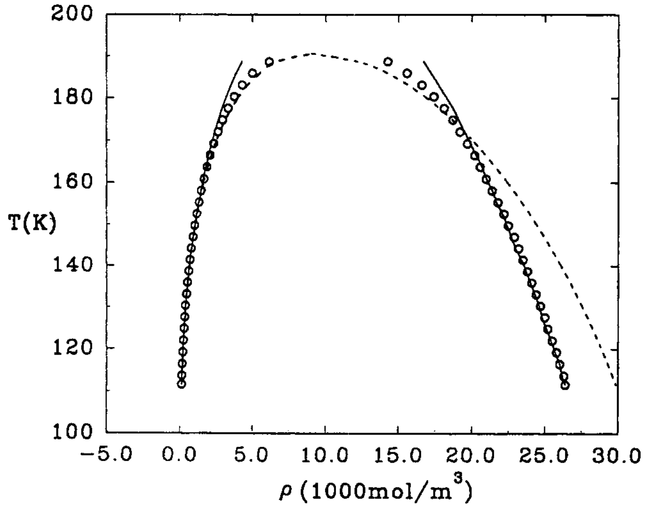

Figure 13. Phase diagram for methane.

Circles are the literature data (Canjar and Manning, 1967); solid line is calculated by the proposed EOS; dashed line is given by the PR EOS.

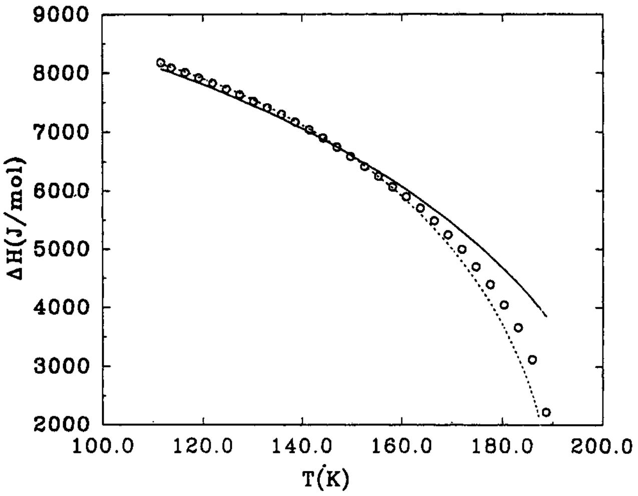

Figure 15. Heat of vaporization for methane.

The legends are the same as in Figure 13.

these parameters were so determined to reproduce the critical point exactly.

Engineers are always interested in knowing the performance of a theory for real fluids, that is, how well a success theory can be applied to real systems. Answering such a question is rather intricate because of uncertainties brought by both adjustable parameters and deficiencies of the theory itself. The success of the SEXP approximation for different thermodynamic properties and over a wide range of conditions reduces considerably these uncertainties. In this work, methane, whose intermolecular potential can be well treated as the LJ function, is selected for examination. We utilized saturated vapor and liquid densities of methane to locate two parameters of the LJ potential, yielding $\epsilon/k = 146.11$ K and $\sigma = 3.7177$ Å. The resulting regression is shown in Figure 13. With the two determined parameters, some typical thermodynamic properties, including vapor pressure, heat of vaporization, and second virial coefficient, were predicted. These are shown in Figures 14 to 16. To provide comparison with empirical equations, the results of the Peng–Robinson (PR) equation are also plotted in these figures. It is evident that except in the critical region the SEXP approximation yields much better results for saturated liquid densities and second virial coefficients, and gives a similar performance for vapor pressures. Only the prediction of heat of vaporization is somewhat worse, primarily due to the failure around the critical point. It should be mentioned that the better performance of the PR equation around the critical point is artificially ensured by fitting its parameters to reproduce the critical point exactly. Overall, the SEXP approximation is much more consistent in describing various behaviors of methane than is an empirical equation. This calculation suggests that only those equations of state based on sophisticated theories promise to give an accurate description of real fluids.

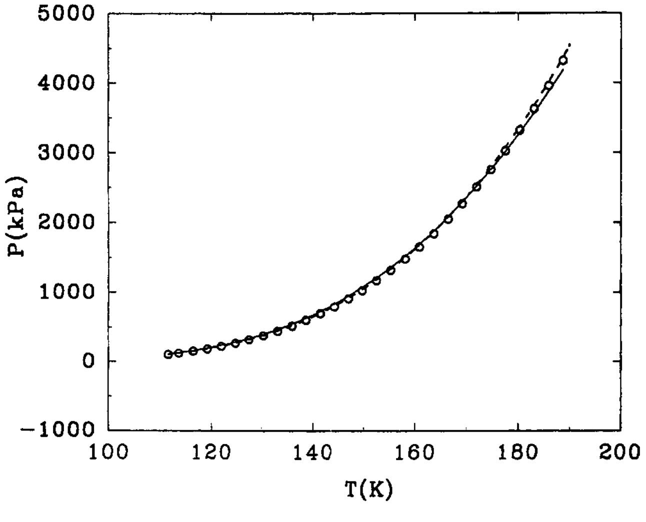

Figure 14. Vapor pressure for methane.

The legends are the same as in Figure 13.

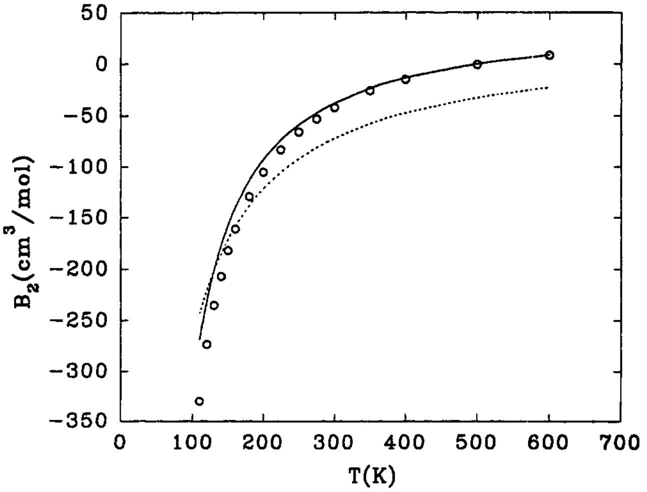

Figure 16. Second virial coefficient for methane.

Circles are the literature data (Dymond and Smith, 1980); the legends are the same as in Figure 13.

Conclusion

In this work, we suggest that the SEXP approximation, a combination of the EXP approximation with the first-order MSA, obtains a better RDF for the LJ fluid. The remaining deficiency of the first-order MSA is successfully corrected by the proposed approximation. Subsequently, thermodynamic properties, including the Helmholtz free energy, the compressibility factor, and the internal energy are more accurately obtained. Extensive comparisons among the SEXP approximation, the BH theory, and the WCA theory for both the structure and properties of the LJ fluid, show that the SEXP approximation performs the best. The latest MBWR equation is also compared in the thermodynamic calculations and is found somewhat inadequate in the region of phase coexistence. An application of the SEXP approximation to methane indicates that the present equation of state is more consistent in calculating the thermodynamic properties of simple fluids than is the empirical PR equation.

Acknowledgments

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Literature Cited

Adachi, Y., T. Fijhara, M. Takamiya, and K. Nakanishi, "Generalized Equation of State for Lennard-Jones Fluids: I. Pure Fluids and Simple Mixtures," *Fluid Phase Equilib.*, **39**, 1 (1988).

Anderson, H. C., D. Chandler, and J. D. Weeks, "Roles of Repulsive and Attractive Forces in Liquids: The Equilibrium Theory of Classical Fluids," *Adv. Chem. Phys.*, **34**, 105 (1976).

Barker, J. A., and D. Henderson, "Perturbation Theory and Equation of State for Fluids: The Square-well Potential," and "II. A Successful Theory of Liquid," *J. Chem. Phys.*, **47**, 2856, 4714 (1967).

Canjar, L. N., and F. S. Manning, *Thermodynamic Properties and Reduced Correlations for Gases*, Gulf, Houston, TX (1967).

De Souza, L. E. S., and D. Ben-Amotz, "Optimized Perturbed Hard Sphere Expressions for the Structure and Thermodynamics of the Lennard-Jones Fluids," *Mol. Phys.*, **78**, 137 (1993).

Dymond, J. H., and E. B. Smith, *The Virial Coefficients of Pure Gases and Mixtures*, Clarendon Press, Oxford (1980).

Fotouh, K., and K. Shukla, "An Improved Perturbation Theory and van der Waals One-fluid Theory of Binary Fluid Mixtures: 1. Total and Excess Thermodynamic Properties," *Fluid Phase Equilib.*, **127**, 45 (1997).

Hansen, J. P., "Phase Transition of the Lennard-Jones System: II. High-Temperature Limits," *Phys. Rev. A*, **2**, 221 (1970).

Harismiadis, V. I., A. Z. Panagiotopoulos, and D. P. Tassios, "Phase Equilibria of Binary Lennard-Jones Mixtures with Cubic Equations of State," *Fluid Phase Equilib.*, **94**, 1 (1994).

Henderson, D., E. Waisman, J. L. Lebowitz, and L. Blum, "Equation of State of a Hard-Core Fluid with a Yukawa Tail," *Mol. Phys.*, **35**, 241 (1978).

Høye, J. S., and G. Stell, "Thermodynamics of the MSA for Simple Fluids," *J. Chem. Phys.*, **67**, 439 (1977).

Johnson, J. K., J. A. Zollweg, and K. E. Gubbins, "The Lennard-Jones Equation of State Revisited," *Mol. Phys.*, **78**, 591 (1993).

Konitor, J., and C. Jedrzejek, "Analytic Formulation of the WCA Type Perturbation Theory for a Hard-Core with One-Yukawa Tail Fluid," *Mol. Phys.*, **55**, 187 (1985).

Lee, L. L., *Molecular Thermodynamics of Nonideal Fluids*, Butterworths, Boston (1988).

Lomba, E., and L. L. Lee, "Consistency Conditions for the Integral Equations of Liquid Structures," *Intern. J. Thermophys.*, **17**, 663 (1996).

Lotif, A., J. Vrabec, and J. Fischer, "Vapour-Liquid Equilibria of the Lennard-Jones Fluid from the NPT Plus Test Particle Method," *Mol. Phys.*, **76**, 1319 (1992).

Madden, W. G., and D. D. Fitts, "Integral-Equation Perturbation Theory for the Radial Distribution Function of Simple Fluids," *Mol. Phys.*, **30**, 809 (1975).

Nicolas, J. J., K. E. Gubbins, W. B. Streett, and D. J. Tildesley, "Equation of State for the Lennard-Jones Fluid," *Mol. Phys.*, **37**, 1429 (1979).

Panagiotopoulos, A. Z., "Direct Determination of Phase Coexistence Properties of Fluids by Monte Carlo Simulation in a New Ensemble," *Mol. Phys.*, **61**, 813 (1987).

Peng, D.-Y., and D. B. Robinson, "A New Two-Constant Equation of State," *Ind. Eng. Chem. Fundam.*, **15**, 59 (1976).

Rosenfeld, Y., and N. W. Ashcroft, "Theory of Simple Classical Fluid: Universality in the Short-Range Structure," *Phys. Rev. A*, **20**, 1208 (1979).

Sarkisov, G., D. Tikhonov, J. Malinsky, and Yu. Magarshak, "Martynov-Sarkisov Integral Equation for the Simple Fluids," *J. Chem. Phys.*, **99**, 3926 (1993).

Shukla, K., "Phase Equilibria and Thermodynamic Properties of Molecular Fluids from Perturbation Theory," *Fluid Phase Equilib.*, **94**, 19 (1994).

Soave, G., "Equilibrium Constant from a Modified Redlich-Kwong Equation of State," *Chem. Eng. Sci.*, **37**, 1197 (1972).

Stell, G., "Fluids with Long-range Forces: Toward a Simple Analytic Theory," *Phase Transition and Critical Phenomena*, Vol. 5, C. Domb and M. S. Green, eds., Academic Press, London, p. 47 (1976).

Stell, G., and J. J. Weis, "Structure and Thermodynamics of a Simple Fluid," *Phys. Rev. A*, **21**, 645 (1980).

Tang, Y., and B. C.-Y. Lu, "A New Solution of the Ornstein-Zernike Equation from the Perturbation Theory," *J. Chem. Phys.*, **99**, 9828 (1993).

Tang, Y., and B. C.-Y. Lu, "First-Order Radial Distribution Functions Based on the Mean Spherical Approximation for Square-Well, Lennard-Jones, and Kihara Fluids," *J. Chem. Phys.*, **100**, 3079 (1994a).

Tang, Y., and B. C.-Y. Lu, "An Analytical Analysis of the Square-Well Fluid Behaviors," *J. Chem. Phys.*, **100**, 6665 (1994b).

Tang, Y., and B. C.-Y. Lu, "Analytical Representation of Radial Distribution Function for Classical Fluids," *Mol. Phys.*, **90**, 215 (1997).

Tang, Y., Z. Tong, and B. C.-Y. Lu, "An Analytical Equation of State Based on the Ornstein-Zernike Equation," *Fluid Phase Equilib.*, in press (1997).

Verlet, L., "Computer 'Experiments' on Classical Fluids: II. Equilibrium Correlation Functions," *Phys. Rev.*, **165**, 201 (1968).

Weeks, J. D., D. Chandler, and H. C. Anderson, "Roles of Repulsive Forces in Determining the Equilibrium Structure of Simple Liquids," *J. Chem. Phys.*, **54**, 5237 (1971).

Wertheim, M. S., "Thermodynamic Perturbation Theory of Polymerization," *J. Chem. Phys.*, **87**, 7323 (1987).

Appendix A

$D(n_1, n_2, n_3, z, r)$ in Eq. 12 is given by (Tang and Lu, 1997; Tang et al., 1997)

$$
D(n_1,n_2,n_3,z,r)
$$

$$
= \left\{ \begin{array}{l}
\displaystyle\sum_{\alpha=0}^{2}\sum_{i=1}^{n_3}\frac{(-1)^i B(n_1,n_2,n_3,i,\alpha)}{(t_\alpha+z)^i} \\
\displaystyle\quad\times\left(e^{-zr}-e^{t_\alpha r}\sum_{j=0}^{i-1}\frac{(-1)^j(t_\alpha+z)^j r^j}{j!}\right)H(r), \\
\qquad n_1+n_2<3n_3 \\
\displaystyle\frac{(1+\eta/2)^{n_2}}{(1-\eta)^{2n_3}}e^{-zr}H(r)+\sum_{\alpha=0}^{2}\sum_{i=1}^{n_3}\frac{(-1)^i B(n_1,n_2,n_3,i,\alpha)}{(t_\alpha+z)^i} \\
\displaystyle\quad\times\left(e^{-zr}-e^{t_\alpha r}\sum_{j=0}^{i-1}\frac{(-1)^j(t_\alpha+z)^j r^j}{j!}\right)H(r), \\
\qquad n_1+n_2=3n_3,
\end{array} \right.
$$

where

$$B(n_1,n_2,n_3,i,\alpha)=\frac{1}{(1-\eta)^{2n_3}}\sum_{k_1=0}^{n_3-i}\sum_{k_2=0}^{n_3-i-k_1}$$

$$\times\frac{(-1)^{n_3-i-k_1}(n_3-1+k_2)!(2n_3-1-i-k_1-k_2)!}{k_1!k_2!(n_3-1-k_1-k_2)![(n_3-1)!]^2}$$

$$\times\frac{A(n_1,n_2,k_1,t_\alpha)}{(t_\alpha-t_\beta)^{n_3+k_2}(t_\alpha-t_\gamma)^{2n_3-i-k_1-k_2}}$$

$$A(n_1,n_2,k_1,\alpha)=\sum_{i=\max(k_1-n_1,0)}^{n_2}$$

$$\times\frac{n_2!(i+n_1)!}{i!(n_2-i)!(i+n_1-k_1)!}(1+\eta/2)^i(1+2\eta)^{n_2-i}t_\alpha^{n_1+i-k_1},$$

in which $H(r)$ is the Heaviside function, which is 0 for $r<0$ and 1 for $r\geq 0$. $t_a(a=0,\ 1,\ 2)$ are the three zeros of $S(t)$ defined in Eq. 6 and are given more explicitly elsewhere (Tang and Lu, 1994a).

Appendix B

In a recent article (Tang et al.,1997), we obtained the following expressions for some major thermodynamic properties of LJ fluid.

1. Helmholtz free energy

$$a=\frac{A-A^{id}}{NkT}=a_0+a_1+a_2,$$

with

$$a_0=\frac{4\eta-3\eta^2}{(1-\eta)^2}$$

$$a_1=-\frac{12\eta\beta\epsilon}{R^3}\left[k_1\left(\frac{L(z_1R)}{z_1^2(1-\eta)^2Q(z_1R)}-\frac{1+z_1R}{z_1^2}\right)\right.$$

$$\left.-k_2\left(\frac{L(z_2R)}{z_2^2(1-\eta)^2Q(z_2R)}-\frac{1+z_2R}{z_2^2}\right)\right]$$

$$+48\eta\beta\epsilon\left[\frac{1}{9}\left(\frac{\sigma}{R}\right)^6-\frac{1}{3}\left(\frac{\sigma}{R}\right)^6\right]$$

$$-48\eta\beta\epsilon g_0(R)\left[\frac{1}{9}\left(\frac{\sigma}{R}\right)^{12}-\frac{1}{3}\left(\frac{\sigma}{R}\right)^6+\frac{2}{9}\left(\frac{\sigma}{R}\right)^3\right]$$

$$a_2=-\frac{6\eta\beta^2\epsilon^2}{R^3}\left[\frac{k_1^2}{2z_1Q^4(z_1R)}+\frac{k_2^2}{2z_2Q^4(z_2R)}\right.$$

$$\left.-\frac{2k_1k_2}{(z_1+z_2)Q^2(z_1R)Q^2(z_2R)}\right]$$

$$-24\eta\beta^2\epsilon^2\left[\frac{k_1/R}{Q^2(z_1R)}-\frac{k_2/R}{Q^2(z_2R)}\right]$$

$$\times\left[\frac{1}{9}\left(\frac{\sigma}{R}\right)^{12}-\frac{1}{3}\left(\frac{\sigma}{R}\right)^6+\frac{2}{9}\left(\frac{\sigma}{R}\right)^3\right],$$

where

$$g_0(R)=\frac{1+\eta/2}{(1-\eta)^2}.$$

2. Compressibility factor

$$Z=\frac{PV}{NkT}=Z_0+Z_1+Z_2,$$

with

$$Z_0=\frac{1+\eta+\eta^2-\eta^3}{(1-\eta)^3}$$

$$Z_1=a_1-\frac{12\eta^2\beta\epsilon}{R^3}\left[k_1\left(\frac{(5/2+\eta/2)z_1R+4+2\eta}{z_1^2(1-\eta)^3Q(z_1R)}\right.\right.$$

$$\left.-\frac{L(z_1R)Q'_\eta(z_1R)}{z_1^2(1-\eta)^2Q^2(z_1R)}\right)$$

$$\left.-k_2\left(\frac{(5/2+\eta/2)z_2R+4+2\eta}{z_2^2(1-\eta)^3Q(z_2R)}-\frac{L(z_2R)Q'_\eta(z_2R)}{z_2^2(1-\eta)^2Q^2(z_2R)}\right)\right]$$

$$-16\eta\beta\epsilon R\frac{\partial g_0(R)}{\partial R}\left[\frac{1}{9}\left(\frac{\sigma}{R}\right)^{12}-\frac{1}{3}\left(\frac{\sigma}{R}\right)^6+\frac{2}{9}\left(\frac{\sigma}{R}\right)^3\right]$$

$$Z_2=a_2+\frac{12\eta^2\beta^2\epsilon^2}{R^3}\left[\frac{k_1^2Q'_\eta(z_1R)}{z_1Q^5(z_1R)}+\frac{k_2^2Q'_\eta(z_2R)}{z_2Q^5(z_2R)}\right.$$

$$\left.-\frac{2k_1k_2[Q'_\eta(z_1R)Q(z_2R)+Q(z_1R)Q'_\eta(z_2R)]}{(z_1+z_2)Q^3(z_1R)Q^3(z_2R)}\right]$$

$$+48\eta^2\beta^2\epsilon^2\left[\frac{k_1/R}{Q^3(z_1R)}Q'_\eta(z_1R)-\frac{k_2/R}{Q^3(z_2R)}Q'_\eta(z_2R)\right]$$

$$\times\left[\frac{1}{9}\left(\frac{\sigma}{R}\right)^{12}-\frac{1}{3}\left(\frac{\sigma}{R}\right)^6+\frac{2}{9}\left(\frac{\sigma}{R}\right)^3\right],$$

where

$$R\frac{\partial g_0(R)}{\partial R}=\frac{3\eta(5+\eta)}{2(1-\eta)^3}$$

$Q'_\eta(t)$

$$=\frac{6(1-\eta)t^2+36\eta t-12(1+5\eta)+12[(1+2\eta)t+1+5\eta]e^{-t}}{(1-\eta)^3t^3}$$

3. Internal energy

$$u=\frac{U-U^{id}}{NkT}=u_0+u_1+u_2,$$

with

$$u_0 = 12\eta \frac{1-\eta/2}{(1-\eta)^3} \frac{d\ln R}{d\ln\beta}, \quad u_1 = a_1 + R\frac{\partial a_1}{\partial R}\frac{d\ln R}{d\ln\beta},$$

$$u_2 = 2a_2 + R\frac{\partial a_2}{\partial R}\frac{d\ln R}{d\ln\beta},$$

where

$$\frac{d\ln R}{d\ln\beta} = \frac{T^* + 2c_2T^{*2} + 4c_3T^{*4}}{12c_1\left(1 + \dfrac{T^* + c_2T^{*2} + c_3T^{*4}}{c_1} + \left(1 + \dfrac{T^* + c_2T^{*2} + c_3T^{*4}}{c_1}\right)^{1/2}\right)}$$

$$R\frac{\partial a_1}{\partial R} = \frac{12\eta\beta\epsilon}{R^3}\left[k_1\left(\frac{g_0(R)}{Q^2(z_1R)} - 1\right) - k_2\left(\frac{g_0(R)}{Q^2(z_2R)} - 1\right)\right]$$
$$+ 48\eta\beta\epsilon(g_0(R) - 1)\left[\left(\frac{\sigma}{R}\right)^{12} - \left(\frac{\sigma}{R}\right)^6\right]$$
$$- 48\eta\beta\epsilon R\frac{\partial g_0(R)}{\partial R}\left[\frac{1}{9}\left(\frac{\sigma}{R}\right)^{12} - \frac{1}{3}\left(\frac{\sigma}{R}\right)^6 + \frac{2}{9}\left(\frac{\sigma}{R}\right)^3\right]$$

$$R\frac{\partial a_2}{\partial R} = \frac{6\eta\beta^2\epsilon^2}{R^2}\left[\frac{f(z_1R)k_1^2}{Q^2(z_1R)} + \frac{f(z_2R)k_2^2}{Q^2(z_2R)}\right.$$
$$\left. - \frac{2k_1k_2[z_1f(z_1R)Q^2(z_1R) + z_2f(z_2R)Q^2(z_2R)]}{(z_1+z_2)Q^2(z_1R)Q^2(z_2R)}\right]$$
$$- 24\eta\beta^2\epsilon^2\left[\frac{k_1/R}{Q^2(z_1R)} - \frac{k_2/R}{Q^2(z_2R)}\right]$$
$$\times\left[-\frac{10}{9}\left(\frac{\sigma}{R}\right)^{12} + \frac{4}{3}\left(\frac{\sigma}{R}\right)^6 - \frac{2}{9}\left(\frac{\sigma}{R}\right)^3\right]$$
$$+ 24\eta\beta^2\epsilon^2[k_1z_1f(z_1R) - k_2z_2f(z_2R)]$$
$$\times\left[\frac{1}{9}\left(\frac{\sigma}{R}\right)^{12} - \frac{1}{3}\left(\frac{\sigma}{R}\right)^6 + \frac{2}{9}\left(\frac{\sigma}{R}\right)^3\right]$$

$$f(t) = \frac{1}{Q^2(t)} + 24g_0(R)\frac{Q(t) - Q(-t)e^{-t}}{t^2Q^3(t)}.$$

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