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# Role of the Barker–Henderson diameter in thermodynamics

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Sensitivity of thermodynamics to the Barker–Henderson (BH) diameter for the Lennard-Jones (LJ) potential is discussed, which covers both its approximation in calculation and improvement in rationality. With regarding to the approximation, pressure and internal energy for the LJ fluid, LJ chains and LJ chain mixtures are investigated. It is found that internal energy is much more sensitive to an approximation to the diameter than pressure for pure fluids, and both pressure and internal energy are very sensitive to the diameter for mixtures. It is also found that the approximating expression given by Cotterman *et al.* (1986) covers the widest range of temperatures. The rationality of the BH diameter itself at very high temperatures and densities is also analyzed. Through a functional expansion of Helmholtz free energy, we conclude that a density-dependent BH diameter is fundamentally more appropriate. The proposed diameter yields almost the same results as the original BH diameter at normal conditions and remedies its deficiencies at extreme ones. The density-dependent diameter provides a convenient way to study the LJ systems undergoing gas-solid phase transition or freezing. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1461360]

## I. INTRODUCTION

The Lennard-Jones (LJ) fluid is studied most extensively in modern liquid theories. There are a number of reasons for its publicity. First, the LJ potential was theoretically justified and the potential can satisfactorily represent the true interactions among simple molecules, like Ar and CH4. Second, its potential and radial distribution function (RDF) is smooth functions, which are more tractable than the square-well (SW) fluid. The SW potential and RDF exhibit some discontinuities, which is detrimental to some applications. Last, sophisticated information about this fluid can contribute lots to more complex molecules, such as LJ chains, through thermodynamics perturbation theory (TPT).[1] Therefore, this fluid has been treated by various thermodynamic methods in recent decades. Barker and Henderson (BH) presented[2] the first successful perturbation theory for this fluid by mapping the repulsive part with hard spheres and by introducing a second-order correction. Weeks, Chandler, and Anderson (WCA)[3] made a first-order perturbation expansion by introducing a different split between repulsive and attractive forces. There were also a number of studies based on integral equations,[4] but these methods are computationally much more costly.

Recently, Tang and Lu[5] proposed the method of the Hilbert transform to solve the OZ equation. The Hilbert transform yields an analytical solution for almost all the spherical intermolecular potentials, including the LJ potential. Tang *et al.*[6] have subsequently obtained an analytical RDF and developed a new second-order perturbation theory based on the mean spherical approximation (MSA). The MSA theory has been further extended to LJ mixtures,[7] associating LJ chains,[8,9] and very recently associating LJ chain mixtures.[10] The fully predictive theory has been proven to perform very satisfactory across these complex fluids. The achievement is attributed to the underlying RDF, which is well defined, refined, and formulated. For instance, we have recently derived a simple analytical expression of RDF around the molecular size for both the LJ fluid and mixtures,[8,10] greatly facilitating the study of associating LJ chains through the TPT theory.

The common ground for the above-mentioned theories is their perturbation expansion about a reference—usually hard spheres or making use of hard spheres. Unlike the SW fluid with a reference clearly defined, that of the LJ fluid is somehow arbitrary. Only requirement is that the repulsive portion of the LJ fluid is simulated effectively by a hard-sphere system, which is in turn characterized by a diameter. Two different types of diameters, BH and WCA, have been developed according to their treatment of the range and depth of the repulsive force. Our MSA theory[6] makes use of the BH diameter

$$d=\int_0^\sigma (1-e^{-\beta u(r)})dr, \tag{1}$$

due to its simplicity in splitting the repulsive and attractive parts of the LJ potential

$$u(r)=4\varepsilon\left(\frac{\sigma^{12}}{r^{12}}-\frac{\sigma^6}{r^6}\right). \tag{2}$$

To facilitate computation in the MSA theory, we have substituted the integral (1) by the empirical expression of Souza and Ben-Amotz (SB)[11] in several papers.[6–8] The formulated theory performs very well over a wide rang of conditions. However, when carrying out extensive investigations, some subtle details emerge unexpectedly: The resulting internal energy is worse than pressure, even in the valid region of the adopted empirical expression. Such an uneven performance is well demonstrated in Figs. 1 and 2: The prediction of internal energy deteriorates severely at $T^*>4.0$ while that

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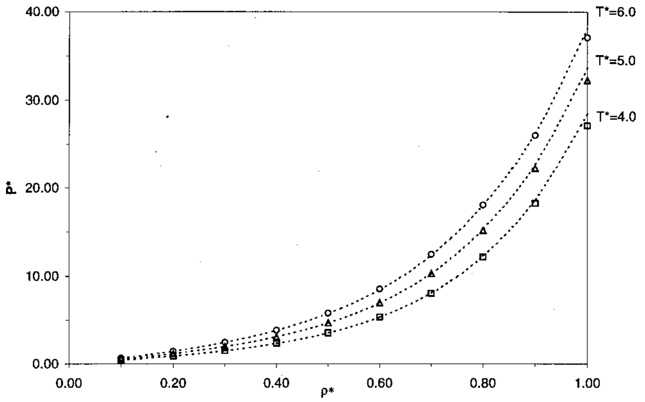

FIG. 1. Pressure of the LJ fluid obtained from computer simulation (symbols) (Ref. 12) and from the MSA theory (Ref. 6) using the SB diameter (dashed lines).

for pressure remains reliable. A first thought is that the problem is caused by the inverse temperature expansion adopted in our MSA theory,[6] since the temperature-dependence is not always well represented in a perturbation theory. However, such an explanation is directly contrary to the known fact that a perturbation theory is only worsening at lower temperatures, instead of higher temperatures observed in Fig. 2. Moreover, when the theory is extended to LJ chain mixtures, we come up with poor results for both pressure and internal energy. These abnormal observations force us to review the MSA theory and its formulation. Section II reports how a diameter approximation can affect substantially thermodynamic calculations and possibly yields misleading results. As a comparison, we include another approximating expression given by Cotterman, Schwarz, and Prausnitz (CSP)[13] in this investigation.

Motivated by the sensitivity of thermodynamics to the BH diameter found above, we extend the scope of the present MSA theory to extreme conditions—very high temperatures and densities in Sec. III. The applicability of a theory to this region is crucial to study gas–solid transition or freezing. It has been long known that perturbation theories are of serious problems at these conditions. For instance, the BH theory yields so much higher values of compressibility factor that its validity has been harshly doubted.[14] The applicability of the WCA theory is even worse: The resulting packing factor is beyond the limit of hard-sphere systems and the theory is totally invalid. Some remedies to the WCA theory were proposed,[15–17] which however brought substantial more computations. The present MSA theory is believed to inherit the inadequacies of the BH theory, because the hard-sphere term, which is the same in the two theories, plays the leading role in thermodynamic calculations at these conditions. The sensitivity found in Sec. II prompts that it may be exactly the original BH diameter, not perturbation theory, to be blamed for those inadequacies. Section III is devoted to explore this possibility. Subsequently, a density-dependent BH diameter is proposed, which remedies some problems at extreme conditions. This work shows that thermodynamic calculations are very sensitive to the hard-sphere diameter and one should treat it cautiously.

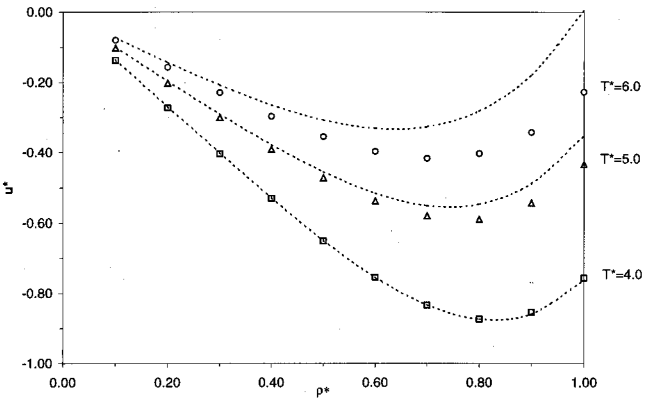

FIG. 2. Same as in Fig. 1 except for internal energy.

## II. APPROXIMATIONS TO THE BH DIAMETER AND THEIR VALIDITY

The integral in the BH diameter (1) is rather inconvenient in practical applications, because it represents some extra numerical work and $u(r)\rightarrow\infty$ at the limit $r=0$. The diameter is used so often that it is very tempting to approximate the original BH diameter by a simple analytical expression. Such an approximation is also technically achievable since the diameter is only temperature-dependent. Two widely exploited expressions are cited here:

(a) Cotterman, Schwarz, and Prausnitz (CSP)[13]

$$d=\frac{1+0.2977T^*}{1+0.331\,63T^*+1.047\,710^{-3}T^{*2}}\,\sigma, \tag{3}$$

(b) Souza and Ben-Amotz (SB)[11]

$$d=2^{1/6}\left[1+\left(1+\frac{T^*-0.055\,36T^{*2}+0.000\,727\,8\,T^{*4}}{1.1287}\right)^{1/2}\right]^{-1/6}\sigma. \tag{4}$$

The CSP and SB expressions have been used widely in a number of perturbation theories[6,7,13,18] and apparently no abnormalities have been reported before. Other expressions, although claimed to approximate the BH diameter, are actually tied to some particular applications. A good collection of these diameters can be found in Silva *et al.* paper[19] for calculating self-diffusion coefficients. Most of these diameters, however, are incapable of reproducing the BH diameter reliably.

To illustrate the accuracy of the approximations, the CSP and SB profiles together with the exact BH diameter are depicted in Fig. 3. The figure shows that, at $T^*<5.0$—SB's valid range, the two expressions yield nearly identical results. They are extremely close to the exact BH diameter and in fact gives the exact limit $d=\sigma$ at $T^*=0.0$. At very high temperatures $(T^*>5.0)$, the differences between the SB approximation and the exact diameter emerges. The SB ap-

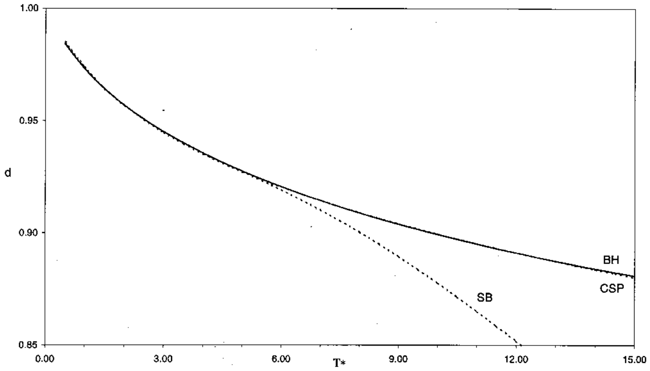

FIG. 3. Profiles of the BH, CSP, and SB diameters, in which the CSP diameter is very close to the BH diameter.

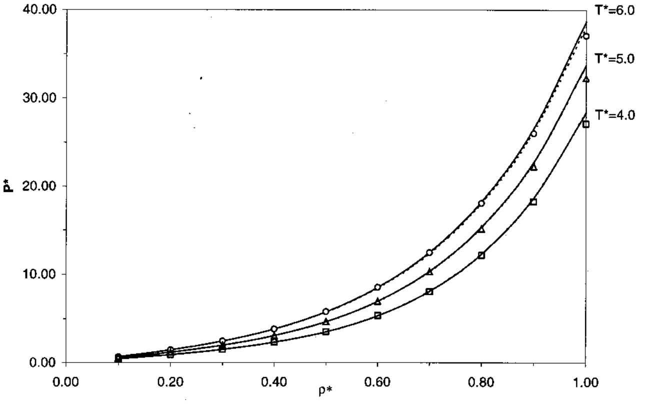

FIG. 5. Pressure of the LJ fluid obtained from computer simulation (symbols) (Ref. 12) and from the MSA theory (Ref. 6) using the SB (dashed lines) and BH (solid lines) diameter, respectively.

proximation underestimates the diameter substantially with increasing temperatures, while the CSP approximation is as good as at moderate temperatures and is almost indistinguishable from the exact. To further analyze the impact of these approximations, the derivatives of the two approximating expressions with respect to temperature are plotted in Fig. 4. The figure somehow repeats the pattern found in Fig. 3, except that the valid range of the SB approximation shrinks to $T^* < 4.0$. At the new valid range, the SB approximation appears to be slightly better than the CSP, while outside the range the SB approximation deteriorates severely. This observation indicates that the temperature derivative is more sensitive to an approximation and deserves to pay an extra attention.

The findings above can be utilized to interpret a number of abnormalities found in our MSA theory, using the SB diameter. First, the deterioration at high temperatures is resulted from the poor performance of the SB expression, noting that it remains good at low and moderate temperatures. Second, since the derivative of diameter with respect to temperature is more sensitive to an approximation, the resulting internal energy could be worse than pressure. To illustrate this, the system in Figs. 1 and 2 is recalculated using the exact BH diameter and the results are depicted in Figs. 5 and 6. The two figures show that the two diameters yield very close results in pressure calculations and using the exact diameter improves dramatically internal energy calculations. It is also noted that the improvement is only appreciable at $T^* > 4.0$, which coincides with the finding in Fig. 4. To further justify the above arguments, pressure and internal energy of 100-mer LJ chains are calculated and plotted in Figs. 7 and 8, respectively, using our MSA+SAFT theory.[8] Again, these figures suggest that the SB and BH expressions yield almost identical results for pressure and substantial differences are found at $T^* = 5.0$ for internal energy. Figures 6 and 8 also indicate that the differences between the two expressions are more conspicuous at high densities, and they are diminished at low densities.

The observations above seem to suggest that the problems of thermodynamic calculations rise only at high temperatures and only for internal energy calculations. However, this assertion is rather premature for LJ mixtures. Using the recently developed mixture MSA+SAFT theory,[10] we calculate pressure and internal energy at $T^* = 3.5$ through both SB and BH expressions. The results are demonstrated in Figs. 9 and 10, respectively. It is evident that the predicted pressures from the SB approximation are substantially below the exact and MC ones, while these results of internal energy are much higher. It is somewhat astonished to see that the performance of the SB approximation is very poor even at a moderate temperature and the poor performance spreads to pressure

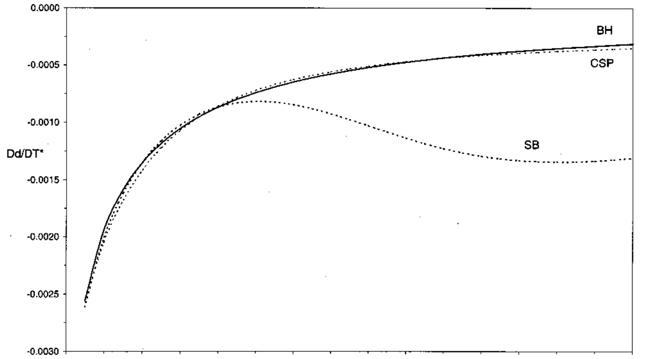

FIG. 4. Derivatives of the BH, CSP, and SB diameters with respect to temperature.

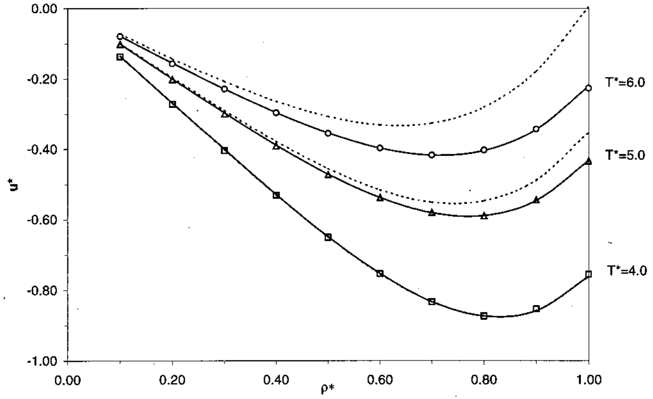

FIG. 6. Same as in Fig. 5 except for internal energy.

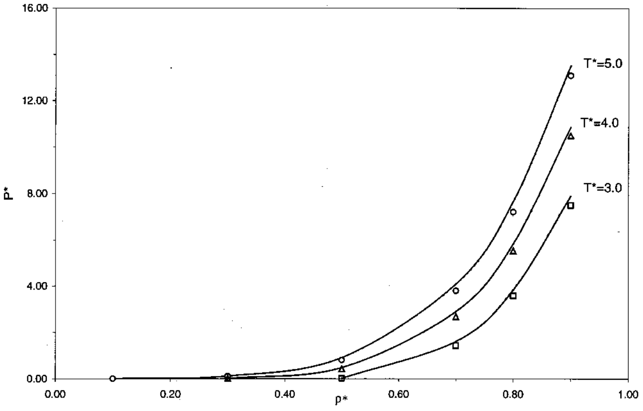

FIG. 7. Pressure of LJ chains with 100 mers obtained from computer simulation (symbols) (Ref. 20) and from the MSA+SAFT (Ref. 8), using the SB (dashed lines) and BH (solid lines) diameter, respectively.

calculations. However, a subtle analysis of the LJ chain mixtures reveals that although the reduced temperature with respect to $\varepsilon_{11}$ is moderate $(=3.5)$, its value is extremely high $(=10.5)$ if it is reduced with respect to $\varepsilon_{22}$. The latter reduced temperature is actually used to calculate the diameter of component 2, which is far beyond the valid range of the SB approximation found in Figs. 3 and 4. Such a poor diameter gives rise to distorted profiles for pressure and internal energy. When the exact diameter is employed, the SAFT theory is in much closer agreement with the MC data. Therefore, the diameters of LJ mixtures should be selected more cautiously.

From the calculations above for the LJ fluid, chains and chain mixtures, we can conclude that the SB approximation to the BH diameter is improper in a number of cases. The exact BH diameter has to be adopted to prevent misleading results. In these testing cases, we find that the CSP expression reproduces the BH results very closely, although they are not depicted in those figures for brevity. The expression has been proven earlier to represent very well the BH diameter and its derivative over a wider range of temperatures than the other does. Therefore, at this point, the CSP expression is recommended for practical calculations.

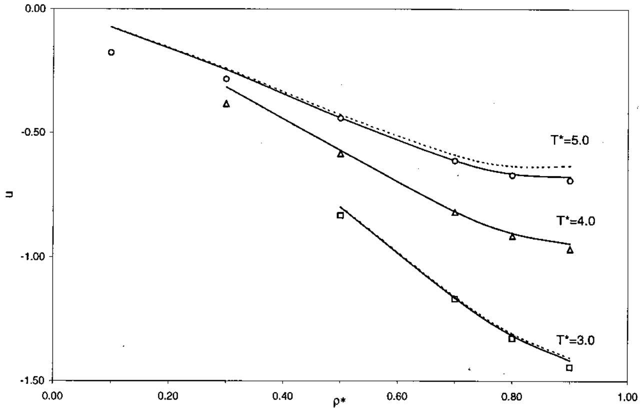

FIG. 8. Same as in Fig. 7 except for internal energy.

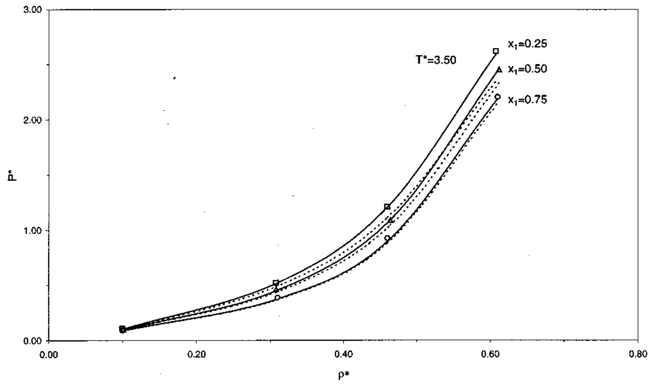

FIG. 9. Pressure of binary LJ chain mixtures obtained from computer simulation (symbols) (Ref. 21) and from the MSA+SAFT (Ref. 10), using the SB (dashed lines) and BH (solid lines) diameter, respectively. These mixtures consist of an identical chain length of 4, identical segment size, and a ratio of $\varepsilon_{11}/\varepsilon_{22}=1/3$ for energy parameters.

## III. DENSITY-DEPENDENT BH DIAMETER

In the BH theory, the LJ potential (2) is split into the repulsive and attractive parts as follows:

$$u_{\mathrm{rep}}(r)=\begin{cases}4\varepsilon\left(\dfrac{\sigma^{12}}{r^{12}}-\dfrac{\sigma^{6}}{r^{6}}\right), & r<\sigma\\[2ex] 0, \quad r>\sigma, & \end{cases} \tag{5}$$

$$u_{\mathrm{att}}(r)=\begin{cases}0, \quad r<\sigma & \\[2ex] 4\varepsilon\left(\dfrac{\sigma^{12}}{r^{12}}-\dfrac{\sigma^{6}}{r^{6}}\right), & r>\sigma.\end{cases} \tag{6}$$

Note that the split occurs at $r=\sigma$, in contrast to at $r=\sqrt[6]{2}\sigma$ for the WCA theory. The reference system in the BH theory, a pseudo fluid, consists of molecules interacting through the potential (5), while the contribution from the attractive part is a perturbation about the reference. Since both the free energy and RDF of the reference system is not analytically attainable, the reference system is mapped into hard spheres, whose diameter remains to be determined. Note that such a reference system is more tractable than its soft counterpart in the WCA theory. In order to determine the diameter, Barker and Henderson[2] carried out an expansion of the Helmholtz

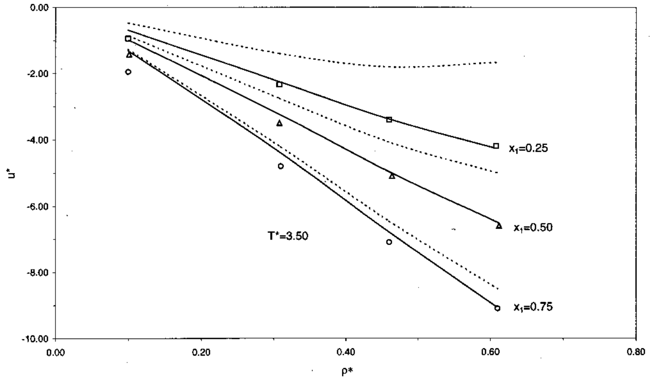

FIG. 10. Same as in Fig. 9 except for internal energy.

free energy with respect to $\alpha$ and $\gamma$, representing the steepness and depth of their modified potential function, respectively. The first-order term in the expansion turned out to be

$$a=a_0-2\pi\rho g_0(d)d^2\left(d-\int_0^\sigma(1-e^{-\beta u(r)})dr\right)+\cdots, \tag{7}$$

where the subscript 0 denotes the system of hard spheres, $d$ the hard-sphere diameter, $g(r)$ the RDF. Other terms in Eq. (7) are omitted due to their irrelevance to the present discussion. A simple choice for the diameter is to force that the first-order term vanishes, leading to the BH diameter (1). The diameter can be alternatively derived by a scheme through a functional expansion with respect to the Mayer function[22,23] The scheme appears to be more general than the original derivation and it reveals the detailed omissions implied in using the BH diameter. Making a perturbation expansion of the Helmholtz free energy of the pseudo fluid about a hard-sphere system with the diameter $d$, to first order, yields

$$\begin{aligned}a_{\text{rep}}&=a_0+\int\left(\frac{\partial a}{\partial f(r)}\right)_0(f_{\text{rep}}(r)-f_0(r))d\mathbf{r}\\&=a_0-\frac{1}{2}\rho\int y_0(r)(e^{-\beta u_{\text{rep}}(r)}-e^{-\beta u_0(r)})d\mathbf{r},\end{aligned} \tag{8}$$

where $f(r)$ is the Mayer function, $y(r)$ the cavity function. There are a number of relations among these functions, namely

$$\frac{\partial a}{\partial f(r)}=-\frac{1}{2}\rho y(r), \tag{9}$$

$$y(r)=e^{\beta u(r)}g(r), \tag{10}$$

$$f(r)=e^{-\beta u(r)}-1. \tag{11}$$

Equation (8) can be reduced to

$$a_{\text{rep}}=a_0-2\pi\rho\int_0^\sigma y_0(r)(e^{-\beta u_{\text{rep}}(r)}-e^{-\beta u_0(r)})r^2dr. \tag{12}$$

The integral in Eq. (12) can be worked out more explicitly by the following argument: The integrand is peaked at $r=\sigma$ and, therefore, in the integration, $y_0(r)$ can be approximated by its value at contact, $g_0(d)$. Then Eq. (12) is reduced to

$$a_{\text{rep}}=a_0-2\pi\rho g_0(d)d^2\left(d-\int_0^\sigma(1-e^{-\beta u(r)})dr\right), \tag{13}$$

which is exactly the same as in Eq. (7) for deriving the BH diameter.

The argument above suggests an important fact: The BH diameter is so selected as to make the first-order correction to the free energy approximately vanished. In other words, the free energy of the hard spheres should match as closely as possible with the reference system. One better matching is obviously to force the first-order correction vanish exactly, i.e.,

$$2\pi\rho\int_0^\sigma y_0(r)(e^{-\beta u_{\text{rep}}(r)}-e^{-\beta u_0(r)})r^2dr=0 \tag{14}$$

or

$$\int_0^\sigma y_0(r)e^{-\beta u_{\text{rep}}(r)}r^2dr=\int_d^\sigma y_0(r)r^2dr, \tag{15}$$

which implicitly determines the hard-sphere diameter $d$. One important outcome from (15) is that the resulted diameter depends on both density and temperature, in contrast to the original BH diameter, a sole function of temperature. It appears that the density dependence is derivable from (7) by taking into account higher-order terms. However, at the time of Barker and Henderson's work, computation is very expensive and using the BH diameter is a good compromise for computation efficiency. For simplicity in the later discussion, $d$ calculated from (15) is referred to as the density-dependant BH diameter. Interestingly, the new diameter is derived in a similar manner to that in the WCA theory for calculating the cavity function of the reference system. Despite of differences in the range and depth of the repulsive force, both theories require the free energy of the pseudo fluid to be identical, to first order, to that of hard spheres. It may be rephrased that the two systems have the closest compressibility or the closest structure factor.[3,22] In fact, there have been attempts[22,24] to adopt the BH-type diameter in the WCA theory to facilitate calculation at normal conditions. This work is obviously proceeding in a reverse way.

There are a number of questions surrounding the derived density-dependent BH diameter: What is the relation between the new diameter and the original one? Are there any substantial differences possibly from the new diameter, and when should we use it? These questions motivate us to make detailed calculations, seeing its impact on thermodynamics at various conditions.

To perform the solution of Eq. (15) for $d$, we exploit the PY cavity function, namely

$$y_0(r)=\begin{cases}-c_0(r), & r<d\\ g_0(r), & r>d\end{cases} \tag{16}$$

and

$$\begin{aligned}c_0(r)=&-\frac{\eta(1+2\eta)^2}{2(1-\eta)^4}\left(\frac{r}{d}\right)^3+\frac{6\eta(1+\eta/2)^2}{(1-\eta)^4}\frac{r}{d}\\&-\frac{(1+2\eta)^2}{(1-\eta)^4},\end{aligned} \tag{17}$$

$$\begin{aligned}g_0(r)=&\frac{1+\eta/2}{(1-\eta)^2}\frac{d}{r}+\frac{1-5\eta-5\eta^2}{(1-\eta)^3}\frac{r-d}{r}\\&+\frac{-3\eta+6\eta^2+21/2\eta^3}{(1-\eta)^4}\frac{(r-d)^2}{rd},\end{aligned} \tag{18}$$

where $c_0(r)$ is the PY direct correlation function,[4] and $g_0(r)$ the PY RDF around $d$ developed recently.[8] A simple iterative calculation of (15) would yield the new diameter, and the original BH diameter may serve as an initial guess for the iteration.

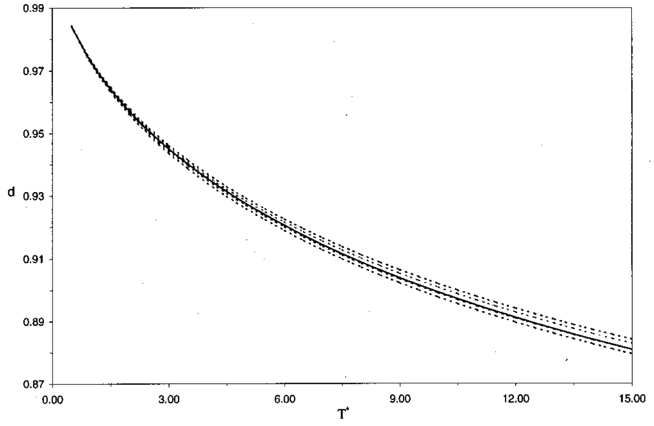

FIG. 11. Profiles of the original BH diameter (solid line) and density-dependent BH diameters (dashed lines) at $\rho^*=0.0$, 0.4, 0.8, and 1.0 from top to bottom, respectively.

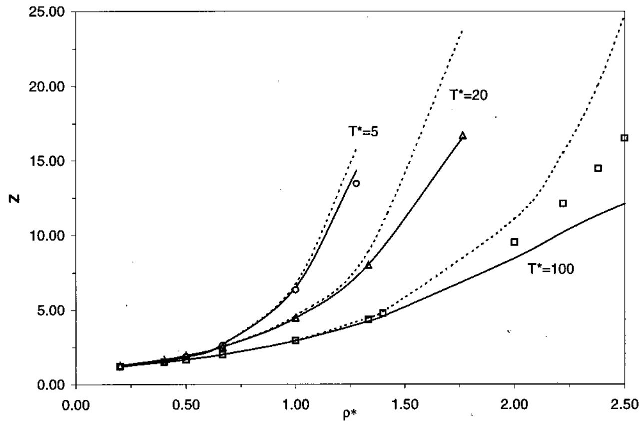

FIG. 12. Compressibility factor of the LJ fluid obtained from computer simulation (symbols) (Ref. 17) and from the MSA theory (Ref. 6) at extreme conditions. The solid lines are calculated through the original BH diameter, and the dashed lines through the density-dependent BH diameter.

In Fig. 11, the density-dependent diameters at four densities $-0.0$, 0.4, 0.8, and 1.0 are plotted against the original BH diameter. It is found that up to $T^*=15.0$, there are apparently close agreements among those diameters. For instance, at the temperature $T^*=15.0$ where the largest discrepancies are observed, the four density-dependent and original BH diameters are given by 0.8841, 0.8828, 0.8808, 0.8794, and 0.8808, respectively, with deviations within 0.4%. It is also seen that the BH diameter curve falls inside those density-dependent lines, matching most closely with that of $\rho=0.8$. Therefore, the BH diameter can be viewed as a median of those density-dependent ones. This can be used to explain why the original BH diameter is satisfactory in usual conditions. However, this assumption may be invalid at extreme conditions, since with increasing temperatures and densities the discrepancies from the BH diameter are becoming more and more evident. For example, in the neighborhood of the freezing line, the deviation between the two diameter is 1.2% at $T^*=20.0$ and $\rho=1.765$, and rises to 2.2% at $T^*=100.0$ and $\rho=2.50$. The resulting discrepancies for compressibility are more astonishingly 31% and 100%, respectively. It appears that thermodynamics is much more sensitive to the chosen diameter at those extreme conditions. To further illustrate this, compressibility and internal energy determined through the two diameters and the MSA theory are plotted against simulation data[17] in Figs. 12 and 13 for three sets of temperatures. It is seen that the original BH diameter works well at low to high densities, but deteriorates severely at very high densities even that the temperature is moderately high. The proposed density-dependent BH diameter is a good improvement: It yields very close results to those from the original diameter at low to high densities and amends the latter's deficiencies at very high densities for $T^*=5$ and $T^*=20$. It appears that an over-amending is somehow made at $T^*=100$. The over-amending is probably brought by the adopted PY cavity function, which is inaccurate at the extreme condition. Another possible reason is that the proposed diameter (15) is only the first-order correction to the free energy, and higher-order corrections may be necessary for obtaining a reliable diameter at those extreme states, where thermodynamics is extremely sensitive to the diameter.

From both the functional expansion of the Helmholtz free energy in Eq. (12) and the calculations shown in Figs. 12 and 13, we firmly conclude that a density-dependent diameter is fundamentally more appropriate to map the reference system by hard spheres, and to extend the MSA theory to extreme conditions. The traditional BH diameter is only reliable at $\rho<1.0$ and beyond the region a new diameter may be obtained from (15). Within the framework of the MSA theory, the present method has a number of attractive features: It is computationally very simple, in which only extra work is to solve Eq. (15). RDF of this LJ fluid can be analytically obtained, although its accuracy in the high-density region remains to be investigated. In contrast to a WCA-type theory with poor performance at low densities, the MSA was previously known to perform consistently well from low densities to high densities.[25] The consistency is important for describing vapor–liquid phase transition. This work presents a continuous and consistent extension of the MSA theory to very high and freezing densities. Analogously, this extension is very beneficial for describing gas-solid/liquid-solid phase

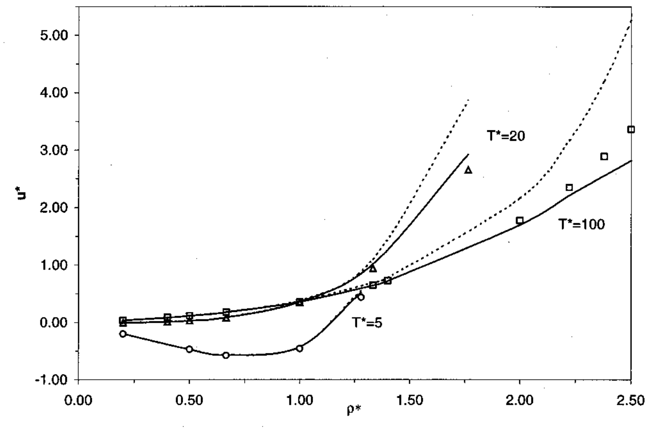

FIG. 13. Same as in Fig. 12 except for internal energy.

transition. To date, the density functional theory is the most efficient to study the phase transition. A reliable piece of information about the free energy and structure of the corresponding uniform fluid is the prerequisite to implement the theory.[26]

## IV. CONCLUSION

The effect of the BH diameter on thermodynamics of LJ systems is examined. It is found that the internal energy calculation is more sensitive to the diameter than is pressure and the sensitivity is more manifest for mixtures. Among the two approximations to the BH diameter examined, the CSP expression is found to match perfectly with the original BH diameter in the range up to $T^*=15.0$, while the SB expression is valid only at $T^*<5.0$ for pressure and $T^*<4.0$ for internal energy.

Through a functional expansion of Helmholtz free energy, a density-dependent BH diameter is proposed. The new diameter is found to be very close to the BH one at normal conditions and to yield much improved results at very high to extreme high densities, at a small cost of extra computation. The original BH diameter is applicable at $\rho<1.0$ and its density-dependent extension is fundamentally more appropriate for thermodynamic calculations.

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