Reformulation of Weeks−Chandler−Andersen Perturbation Theory Directly in Terms of a Hard-Sphere Reference System[†]

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A new variant of fluid thermodynamic perturbation theory is constructed by building on approximations developed by Andersen, Chandler, and Weeks (WCA), directly using a hard-sphere (HS) reference system rather than indirectly via a soft-repulsive reference system. The resulting HS-WCA theory is more forgiving with respect to the choice of a reference HS diameter than the original WCA theory. For example, a simple analytical Boltzmann factor criteria, which relates the reference HS diameter to the distance at which the repulsive pair-potential is equal to kT, is shown to produce global Lennard-Jones fluid thermodynamic predictions that are essentially identical to those of the original WCA theory (or its self-consistent refinement by Lado).

I. Introduction

The thermodynamic perturbation theory of liquids traces its roots back to ideas developed by van der Waals[1] and Boltzmann,[2] who suggested that the structure of a liquid is dictated primarily by repulsive intermolecular interactions, whereas cohesive interactions determine its energy.[3,4] This implies that repulsive and attractive portions of an intermolecular pair-potential contribute more-or-less independently to fluid thermodynamics and may each best be described using different types of approximation strategies. In particular, the structure and entropy of a fluid may be equated with that of an appropriately chosen repulsive reference fluid, while cohesive interactions may be treated as a perturbation, evaluated by averaging over the reference fluid structure. This fundamental understanding has held up remarkably well over the intervening years and has in fact played a central role in the later evolution of fluid statistical mechanics,[5−12] culminating in the elegant liquid perturbation theory of Weeks−Chandler−Andersen (WCA).[5,6] In this work we revisit WCA theory and show that it may be viewed as a special case of a family of perturbation theories which differ in subtle but significant ways from either WCA or other previous formulations of liquid perturbation theory.[5−14] This work is focused on demonstrating the fundamental soundness and exceptional accuracy of this new formulation, as well as its significant practical advantages.

The original WCA theory extended prior perturbation theories by introducing two key refinements: the first involves the way in which the intermolecular potential is separated into repulsive and attractive contributions, and the second pertains to the method used to relate the thermodynamic properties of a soft-repulsive reference fluid to that of hard-sphere (HS) fluid.[5,6] The combination of these features produced a firmly grounded theory of unrivaled accuracy. The new perturbation theory described in this work retains the essential features of WCA theory but introduces a subtle change in the way these are combined.

The original WCA theory may be viewed as a perturbation theory with a soft-repulsive reference fluid, whose properties are in turn approximated using a HS fluid. The new formulation differs from WCA only in that it is better described as a HS perturbation theory, with a WCA correction introduced to represent the influence of soft-repulsive interactions. Thus, the difference between the two theories is almost a matter of semantics—but not quite. Predictions of the new formulation reduce exactly to those of WCA theory when the reference HS diameter is defined as prescribed by WCA theory. However, the two theories differ in the way that the perturbation free energy is evaluated. As a result, the new formulation proves to be more forgiving with regard to the selection of a reference HS diameter. This feature is of significant practical importance, as it implies that one may use any one of several trivially simple prescriptions for defining an appropriate reference HS diameter, rather than having to numerically minimize an integral equation, as required by earlier formulations of WCA theory.[6,7]

Although the WCA HS diameter is necessarily a function of both temperature and density, $\sigma_{HS}(T,\rho)$, the new theory can accommodate diameters which are functions of temperature only, $\sigma_{HS}(T)$, without loss in predictive accuracy. For example, we find that one may use a simple Boltzmann factor criteria[15,16] to equate $\sigma_{HS}(T)$ with that value of the intermolecular separation at which the interaction potential is equal to kT (or RT if one prefers using molar units). For many types of pair-potentials, including those of Lennard-Jones or generalized Lennard-Jones (GLJ) form,[13] this prescription reduces $\sigma_{HS}(T)$ to an algebraic function. Thus, determining $\sigma_{HS}(T)$ becomes even easier than it is when implementing the perturbation theory of Barker−Henderson,[5,8] which requires numerically integrating over the repulsive potential to determine $\sigma_{HS}(T)$, and whose first-order predictions are not as accurate as those of WCA or our new variant thereof.[5,13]

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Because the new formulation builds on approximations developed by WCA but immediately regards the reference fluid to be a HS fluid, we refer to the new theory as HS-WCA. The fundamental basis of this theory, and other variants of WCA theory, are described in section II. Section III compares predictions of these theories with each other and with computer simulation measurements. Our conclusions are summarized and discussed in section IV.

II. Theoretical Formulation

The starting point of many thermodynamic perturbation theories is the decomposition of a spherically symmetric intermolecular pair-potential, $u(r)$, into the sum of a repulsive, $u_0(r)$, and a perturbation, $u_1(r)$, potential.

$$u(r) = u_0(r) + u_1(r) \qquad (1)$$

Although various such separations are possible, a particularly appealing general method was suggested by WCA[5,6] who defined $u_0(r)$ as the repulsive potential obtained from that portion of $u(r)$ with a negative derivative, $du/dr < 0$, while $u_1(r)$ is the remaining attractive potential. More specifically, $u_0(r)$ is shifted up in energy by the well-depth, ϵ, and $u_1(r)$ is extended into the core region so as to render both $u_0(r)$ and $u_1(r)$ (and their derivatives) continuous over all r

$$u_0(r) = \begin{cases} u(r) + \epsilon & r \le r_0 \\ 0 & r > r_0 \end{cases} \qquad (2)$$

$$u_1(r) = \begin{cases} -\epsilon & r \le r_0 \\ u(r) & r > r_0 \end{cases} \qquad (3)$$

where r_0 is the position of the potential minimum.

In developing their perturbation theory, WCA assumed that the reference fluid is one composed of soft-repulsive particles with a pair-potential identical to $u_0(r)$. Thus, the excess Helmholtz free energy of the full fluid, $\tilde{A} \equiv A^\times/NkT = \beta A^\times/N$, may be expressed as the following sum of the reference fluid free energy, $\tilde{A}^{(0)} \equiv A^{(0)}/NkT$, plus a remainder, $\Delta\tilde{A}^{(1)} \equiv [A^\times - A^{(0)}]/NkT$.

$$\tilde{A} = \tilde{A}^{(0)} + \Delta\tilde{A}^{(1)} \qquad (4)$$

If it is assumed that the structural and thermodynamic properties of the reference fluid are known in advance, then the following first-order (mean-field) approximation may be invoked to calculate $\Delta\tilde{A}^{(1)}$, where $g_0(r)$ is the radial distribution of the soft-repulsive reference fluid.

$$\Delta\tilde{A}^{(1)} = 2\pi\rho\beta \int_0^\infty g_0(r) u_1(r) r^2 \, dr \qquad (5)$$

However, because the required reference fluid properties are not in general known, WCA proposed the following additional approximations in order to complete their perturbation theory.

In particular, WCA approximated $g_0(r)$ by assuming that the cavity distribution function of the soft-repulsive fluid is identical to that of an appropriately chosen HS fluid, $y_0(r) = y_{HS}(r)$.[5,6] Because the radial and cavity distribution functions associated with a given pair-potential are fundamentally related by $g_0(r) = y_0(r) \exp[-\beta u_0(r)]$, the above approximation implies that

$$g_0(r) \approx y_{HS}(r) \exp[-\beta u_0(r)] \qquad (6)$$

Furthermore, by functionally differentiating $A^{(0)}$ with respect to $\exp[-\beta u_0(r)]$, WCA obtained the following first-order

expression for $A^{(0)}$ in terms of the excess Helmholtz free energy of the HS fluid, A^{HS}.[5,6]

$$\tilde{A}^{(0)} = \tilde{A}^{HS} + 2\pi\rho \int_0^\infty [g_{HS}(r) - g_0(r)] r^2 \, dr \qquad (7)$$

Andersen, Weeks, and Chandler showed that the above expression for $\tilde{A}^{(0)}$ (which may also be derived by other means[6d,17]) is accurate through third-order in a parameter ξ, representing the length scale over which the "blip function", $g_{HS}(r) - g_0(r)$, has a magnitude that is appreciably larger than zero. On the other hand, the WCA predictions for $\Delta\tilde{A}^{(1)}$ are only accurate to first-order in ξ.[18] Thus, *one should expect eq 7 to remain valid over a wider range of σ_{HS} values than eq 5.*

Furthermore, WCA suggested a criteria for determining $\sigma_{HS}(T,\rho)$ by requiring that the integral on the right-hand side of eq 7 vanishes. This amounts to assuming that the soft-repulsive reference fluid and HS fluids have the same compressibility.[19] Note that the entire WCA construct hinges on this approximation, as it ensures the accuracy of both $g_0(r)$ and $A^{(0)}$, as long as σ_{HS} is determined by iteratively minimizing the integral in eq 7 at each temperature and density.

On the other hand, Verlet and Weis showed that the thermodynamic self-consistency of WCA theory may be improved by using $\sigma_{HS}(T,\rho)$ values that differ very slightly from those obtained using the equal-compressibility criteria.[18] Lado proposed an elegant analytical implementation of this refinement of WCA theory, which retains eqs 1−7 but replaces the equal-compressibility assumption by a self-consistency criteria that requires iterative minimization of a slightly different integral equation in order to determine $\sigma_{HS}(T,\rho)$.[7] The resulting diameters are invariably slightly smaller than those obtained from the original WCA theory.[7,13,14,18] The predictions of Lado's theory are somewhat more accurate than those of the original WCA theory when applied to fluids with repulsive-core potentials that are softer than the Lennard-Jones $u_0(r)$.[7,14] However, when applied to a Lennard-Jones fluid the predictions of both variants of WCA theory are virtually indistinguishable and in essentially perfect agreement with simulation results (except in the near-critical and low-density regions, where the predictions of both theories deviate slightly from simulation results).

Our new HS-WCA theory differs from the above formulations primarily in that we take from the beginning a HS fluid rather than a soft-repulsive fluid to be the reference system with respect to which all perturbations are determined. This implies that the full fluid free energy may be expressed as follows

$$\tilde{A} = \tilde{A}^{HS} + \Delta\tilde{A}^{(0)} + \Delta\tilde{A}^{(1)} \qquad (8)$$

where $\Delta\tilde{A}^{(0)}$ and $\Delta\tilde{A}^{(1)}$ are the first-order perturbation free energies associated with $u_0(r)$ and $u_1(r)$, respectively. We approximate $\Delta\tilde{A}^{(0)}$, as in WCA theory, using eq 7.

$$\Delta\tilde{A}^{(0)} = 2\pi\rho \int_0^\infty [g_{HS}(r) - g_0(r)] r^2 \, dr \qquad (9)$$

So, up to this point all of the above theories are functionally equivalent, except for the criteria used to define the optimal HS diameter. However, because HS-WCA theory assumes a HS reference fluid, the attractive perturbation free energy in this case becomes

$$\Delta\tilde{A}^{(1)} = 2\pi\rho\beta \int_0^\infty g_{HS}(r) u_1(r) r^2 \, dr \qquad (10)$$

This is again very similar to eq 5 except that $g_0(r)$ is replaced by the HS radial distribution function $g_{HS}(r)$. Note that if the

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WCA criteria is used to determine $\sigma_{HS}(T,\rho)$ then the integrals in eqs 5 and 10 become identical. This is because the only region over which $g_{HS}(r)$ and $g_0(r)$ differ is when $r < r_0$; because $u_1(r)$ is constant over this region (see eq 3), the WCA equal-compressibility approximation implies that the integrals over $g_0(r)$ and $g_{HS}(r)$ are identical. Thus, there is strictly speaking no difference at all between HS-WCA and WCA predictions, when the equal-compressibility criterion is used to define $\sigma_{HS}(T,\rho)$.

The HS-WCA and WCA theory predictions only differ when the reference HS fluid diameter is varied from the value prescribed by the equal-compressibility approximation, and this brings us to the main advantage of our present treatment. The results presented in the following section demonstrate that HS-WCA theory is less sensitive to the precise value of σ_{HS} than WCA theory. Because of this relative insensitivity, there is no need to precisely optimize the value of σ_{HS} used at each temperature and density. One may, for example, use either the WCA or Lado prescriptions. However, one may equally effectively use other criteria, including some which express σ_{HS} as a function of temperature only. A particularly appealing such method is based on a Boltzmann factor criteria (BFC) which sets σ_{HS} to that value of r at which $\beta u_0(r) = 1$ or $\exp[-\beta u_0(r)] = 1/e$. For a Lennard-Jones fluid (with the WCA potential separation, eq 2) the BFC implies that

$$\sigma_{HS}(T) = \sigma\left[\frac{2}{1 + \sqrt{\frac{1}{\beta\epsilon}}}\right]^{1/6} \qquad (11)$$

More generally, one may set $\exp[-\beta u_0(r)] = 1/a$ to obtain the following expression for σ_{HS}, whose predictions are within about $\pm2\%$ of those obtained using eq 11 when $2 \leq a \leq 5$.

$$\sigma_{HS}(T) = \sigma\left[\frac{2}{1 + \sqrt{\frac{\ln(a)}{\beta\epsilon}}}\right]^{1/6} \qquad (12)$$

Furthermore, similar expressions may be used to obtain σ_{HS} values associated with GLJ or inverse-power potentials.[13,14] For a GLJ potential one need only replace the exponent of $1/6$ in the above two equations by $2/n_0$, where n_0 is the exponent which characterizes the steepness of the GLJ repulsive core.[13] For an inverse-power potential, $u(r) = \epsilon(\sigma/r)^n$, the BFC equations reduce to $\sigma_{HS}(T) = \sigma[\beta\epsilon]^{1/n}$ and $\sigma_{HS}(T) = \sigma[\beta\epsilon/\ln(a)]^{1/n}$, respectively. The accuracy of predictions obtained using the simple and explicit BFC compared to the WCA equal-compressibility criterion represents one of the main observations of this work and one of its main advantages.

The physical significance for the BFC is implicit in an expression which arises in the elementary kinetic theory of chemical reaction rates. This states that the fraction of collisions in a thermally equilibrated HS gas which have a relative kinetic energy greater than E^* is exactly equal to $\exp[-\beta E^*]$.[20] Thus the BFC is equivalent to setting σ_{HS} to a value which ensures that only $1/e$ of all collisions will have a relative kinetic energy sufficient to allow two particles with a given soft-core potential to penetrate to a separation that is smaller than σ_{HS}. The results described in the next section demonstrate that virtually identical HS-WCA predictions are obtained when using variants of the BFC with values of $2 < a < 5$, which corresponds to requiring that no more than 50% or fewer than 20% of collisions have a relative kinetic energy sufficient to penetrate to values of $r < \sigma_{HS}$.

Previous fluid thermodynamic and transport property studies have used the BFC, with different values of a, to obtain effective σ_{HS} values for various experimental and theoretical systems.[15,16] In particular, it has variously been suggested that σ_{HS} should be set to the value of r at which $\beta u_0(r)$ is equal to 1, $3/2$ or 2 (which correspond to $a \approx 2.7$, 4.5, or 7.4, respectively). The first of these was proposed Hsu, Chandler, and Loweden, the second by Andrews, and the third by Speedy and co-workers.[15] Although all of the above criteria may be formally justified, the criterion of Speedy et al. predicts diameters that are somewhat too small to be useful as HS-WCA reference systems, whereas the other two criteria produce acceptable σ_{HS} values. On the other hand, other possible criteria for relating σ_{HS} to a given continuous potential predict σ_{HS} values that are somewhat too large for the present purposes. These include a criterion derived by requiring that the HS and soft-repulsive reference system have the same second virial coefficient. This predicts $\sigma_{HS}(T)$ values that are similar to those obtained using eq 12 when setting $a \approx 1.5$. Alternatively, the $\sigma_{HS}(T)$ values obtained using Barker−Henderson perturbation theory (with the WCA potential separation, eq 2) are approximately equivalent to setting $a \approx 1.7$. Both of the latter criteria (with $a < 2$) predict σ_{HS} values that are a few percent too large for use as HS-WCA reference fluid diameters, particularly at high densities.

Although the range of acceptable σ_{HS} values is limited, virtually identical HS-WCA predictions are obtained over a range of values centered around the BFC $\sigma_{HS}(T)$ (with $a = e$) which includes diameters obtained using the original WCA and Lado criteria. The latter diameters retain a special physical significance in HS-WCA theory. The WCA σ_{HS} is that for which the soft- and hard-sphere fluids have the same Helmholtz free energy. Thus the WCA criteria identifies the HS fluid whose thermodynamic properties most closely resemble those of the soft-repulsive fluid (with a pair-potential defined by eq 3). The Lado σ_{HS}, on the other hand, is optimal in the sense that it ensures thermodynamic self-consistency of the soft-repulsive fluid pressures and energies.[7]

All of the calculations required to implement the above perturbation theories are performed using analytical approximation strategies which we have recently described.[13] In particular, an extended virial expansion[13,21] is used to algebraically evaluate integrals over $g_{HS}(r)$ and the hard-fluid approximation[13,22] is used to evaluate integrals over $g_0(r)$ (using eq 6).[13]

III. Results

Figure 1 shows the effects of varying σ_{HS} on the repulsive and attractive Helmholtz free energies obtained when applying different theoretical expressions, at two temperature−density values. Note that the critical point and triple point of a Lennard-Jones fluid occur at $kT_c/\epsilon = 1.29$, $\rho_c\sigma^3 = 0.32$ and $kT_t/\epsilon = 0.72$, $\rho_t\sigma^3 = 0.83$, respectively (as estimated from the experimental values for argon fit to a Lennard-Jones fluid equation of state).[5,23] So, the left-hand panel pertains to a high-density supercritical fluid, whereas the right-hand panel pertains to a liquid near the triple point.

The upper portions of Figure 1 compare the Helmholtz free energies of a HS fluid (calculated using the Carnahan−Starling equation of state)[24] with that of a soft-repulsive reference fluid (calculated using the WCA approximation obtained by combining eqs 6 and 7). Thus, although the HS free energy is a strong function of σ_{HS}, WCA $A^{(0)}$ predictions are more weakly dependent on σ_{HS}. The degree to which the WCA $A^{(0)}$ predictions depend on σ_{HS} is a measure of the limits of validity of eq 7, because the true $A^{(0)}$ is necessarily independent of σ_{HS}. The

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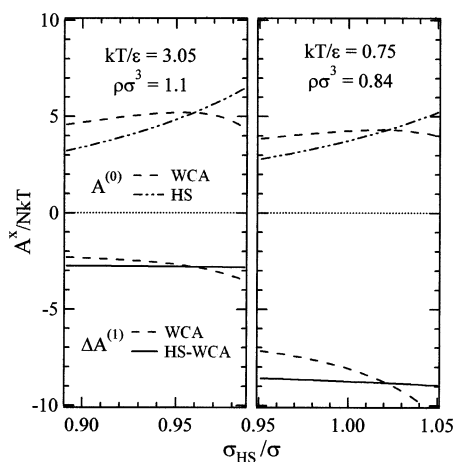
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Figure 1. Dependence of HS, WCA, and HS-WCA Helmholtz free energy predictions on σ_{HS}, at two different Lennard-Jones temperatures and densities. The crossing points of each pair of curves occur at the WCA equal-compressibility σ_{HS} value. The flatness of the HS-WCA $\Delta A^{(1)}$ predictions is the primary reason for the relative insensitivity of the HS-WCA theory to σ_{HS}.
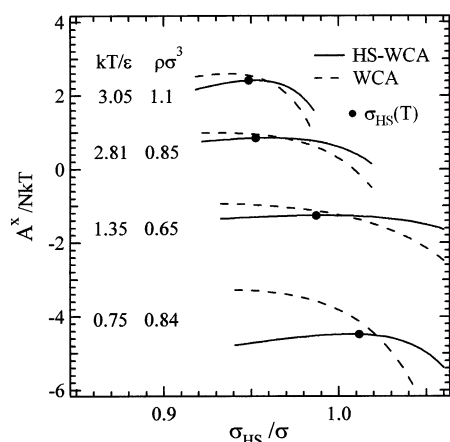

Figure 2. Comparison of WCA and HS-WCA total $A^{\times}$ predictions at four temperatures and densities, plotted as a function of σ_{HS}. The points mark the BFC σ_{HS} values (obtained using eq 11) and the corresponding HS-WCA $A^{\times}$ predictions. The curve-crossing points mark the WCA equal-compressibility σ_{HS} values and $A^{\times}$ predictions.

lower portions of Figure 1 show $\Delta A^{(1)}$ predictions obtained using eq 5 (WCA) and eq 10 (HS-WCA). In this case the WCA predictions are evidently more strongly dependent on σ_{HS} than the HS-WCA predictions.

Note that the value of σ_{HS} at which the HS and WCA $A^{(0)}$ curves cross is the same as that at which the WCA and HS-WCA $\Delta A^{(1)}$ curves cross. These crossings all occur at the σ_{HS} value obtained from the WCA equal-compressibility approximation, as that is the value of σ_{HS} at which the volume integral of $g_0(r)$ is, by construction, equal to that of $g_{HS}(r)$.

Figure 2 shows how the total excess Helmholtz energy predictions, $A^{\times}$, depend on σ_{HS}, at four different temperatures and densities. The stronger σ_{HS} dependence of the WCA predictions (dashed curves) as opposed to the HS-WCA predictions (solid curves) derives primarily from the stronger dependence of the WCA $\Delta A^{(1)}$ on σ_{HS} (see Figure 1). The points on each of the HS-WCA curves mark the σ_{HS} values obtained from the BFC (eq 11) and the corresponding HS-WCA $A^{\times}$ predictions. Again the crossing point of each pair of curves occurs at the σ_{HS} value associated with the WCA equal-compressibility assumption. Note the nearly identical values of $A^{\times}$ predicted using HS-WCA theory with the BFC diameter
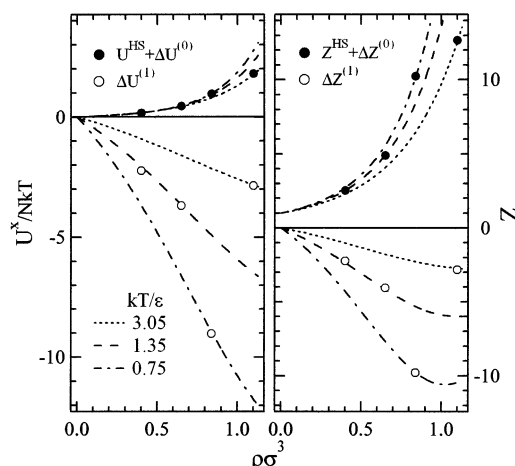

Figure 3. Comparison of repulsive and attractive thermodynamic predictions (curves) with simulation results (points). Virtually identical theoretical predictions are obtained using HS-WCA theory with the BFC $\sigma_{HS}(T)$ or WCA theory with the equal-compressibility $\sigma_{HS}(T,\rho)$.

(points) and WCA theory with the equal-compressibility diameter (the curve-crossing points).

Figure 3 shows a comparison of theoretical and simulation results for the repulsive and attractive contributions to $\tilde{U}$ and $Z = \widetilde{PV} + 1$, along three isotherms. The solid points represent the Lennard-Jones repulsive-core fluid simulation results of Verlet and Weis.[25] The open points represent attractive simulation results obtained by subtracting the Verlet−Weis simulation measurements from the Lennard-Jones $U^{\times}$ and Z simulation results compiled (and algebraically interpolated) by Johnson, Zollweg, and Gubbins,[26] $U^{(1)} = U^{\times} - U^{(0)}$ and $Z^{(1)} = Z - Z^{(1)}$. The excellent agreement between the simulation results and HS-WCA predictions is clearly evident. These theoretical curves are also essentially identical to WCA predictions (approximately within the thickness of the curves in Figure 3). However, notice that obtaining the WCA predictions requires iteratively minimizing the integral in eq 9 at every temperature and density, whereas the HS-WCA predictions require simply evaluating eq 11. Furthermore, the HS-WCA predictions are much less sensitive to the precise value of σ_{HS}, whereas WCA predictions deteriorate rapidly when σ_{HS} is varied, as described below.

The greater sensitivity of WCA predictions to the value of σ_{HS} is illustrated in Figure 4 which compares simulation results[26] and theoretical predictions obtained using a range of σ_{HS} values that vary by ±2% relative to the BFC diameter (eq 11). Note the much larger spread of the WCA predictions (dashed curves) as opposed to the HS-WCA predictions (dotted curves) over the same range of σ_{HS} values. The solid curves represent the HS-WCA predictions obtained using the BFC diameter, which are again virtually identical to those obtained using WCA with the equal-compressibility diameter (however, significantly poorer WCA predictions would be obtained, particularly at high densities and low temperatures, if the BFC rather than the equal-compressibility criteria were used to define σ_{HS}).

IV. Conclusions

The perturbation theory of WCA is widely acclaimed for being the only first-order theory to predict the thermodynamic properties of Lennard-Jones fluids with an accuracy that rivals computer simulation measurements.[5,6] The key to its exceptional accuracy may be traced to the way in which the pair-potential is decomposed into attractive and repulsive contributions and the way in which the properties of the resulting soft-repulsive reference fluid are related to those of a HS fluid.
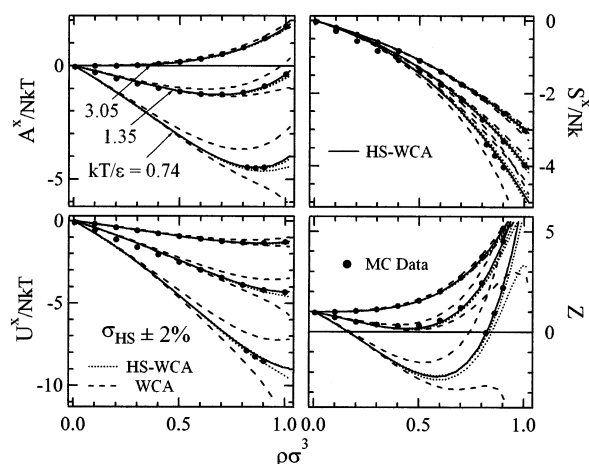
Figure 4. Comparison of global Lennard-Jones thermodynamic predictions and simulation results. The solid curves represent HS-WCA predictions obtained using the BFC σ_{HS} (and are virtually identical WCA predictions the equal-compressibility σ_{HS}). The dotted and dashed curves show the variation in HS-WCA and WCA predictions, respectively, when σ_{HS} is varied by $\pm 2\%$.

In this work we have presented a new variant of WCA theory which retains all of the essential features of WCA but differs only in that the new formulation is better described as a HS rather than a soft-sphere perturbation theory. The resulting HS-WCA theory reduces exactly to the original WCA theory when the equal-compressibility criteria is used to define σ_{HS}. The utility of the new formulation is that it is less sensitive to variations in σ_{HS} and thus affords greater flexibility and ease of implementation, without sacrificing predictive accuracy. In particular, use of the simple BFC to determine σ_{HS} leads to highly accurate results.

The reason for the greater sensitivity WCA predictions to σ_{HS} is linked to the fact that the WCA approximation for $g_0(r)$ (eq 6) closely resembles the true $g_0(r)$ only when σ_{HS} is defined as prescribed by WCA theory (or its refinement by Lado).[5,6,7] This also implies that the cavity distribution functions of soft-repulsive and HS fluids only resemble each other under the above conditions. On the other hand, the HS-WCA radial distribution function, $g_{HS}(r)$, continues to accurately represent the HS reference fluid structure at all values of σ_{HS}. Thus, the perturbation free energies, $\Delta A^{(1)}$, predicted by the HS-WCA theory remain accurate as σ_{HS} is varied, whereas those predicted by WCA are only accurate when σ_{HS} is very near the equal-compressibility value.

All of the variants of WCA theory, including that proposed by Lado and our new HS-WCA theory, use the same WCA approximation to represent the difference between the free energies of a HS fluid and a soft-repulsive fluid (eq 9). The accuracy of this approximation is evident in the upper curves in Figure 1, which show that WCA $A^{(0)}$ predictions remain relatively constant as σ_{HS} is varied. A perfectly accurate theory would predict $A^{(0)}$ values that are strictly independent of σ_{HS}, because the value of $A^{(0)}$ should not depend on the HS reference fluid with respect to which it is calculated.

Our new HS-WCA theory is a HS perturbation theory in which two different types of first-order approximations are used to calculate perturbations associated with the soft-repulsive and cohesive portions of the pair-potential. The roots of these two approximations may be traced back to the seminal perturbation theories of Zwanzig and Rowlinson.[10,11] Zwanzig's formulation of HS perturbation theory[10] predicts the same expression which we use to calculate $\Delta A^{(1)}$ (eq 10), when the attractive potential, $u_1(r)$ is defined as suggested by WCA (eq 3). Rowlinson's HS

perturbation theory, on the other hand, predicts the effects of the stiffness of a repulsive potential on the difference between the free energy of a HS and a soft-repulsive fluid.[11] Andersen, Weeks, and Chandler's derivation of eq 9 is a generalization of Rowlinson's inverse-stiffness parameter expansion.[5,6,11] Thus, the HS-WCA $\Delta A^{(0)}$ and $\Delta A^{(1)}$ predictions derive from first-order HS perturbative approximation strategies proposed by Rowlinson and Zwanzig, respectively.

We have presented results showing the high accuracy of both WCA and HS-WCA predictions when applied to a Lennard-Jones fluid. Fluids with softer repulsive-core potentials than a Lennard-Jones fluid are known to present additional challenges to HS perturbation theories.[7,13] In particular, predictions of the original WCA theory deteriorate rapidly when applied to inverse-power potentials with $n < 12$. Lado's self-consistent refinement of WCA theory is better able to represent soft fluids, but it too becomes unacceptably inaccurate when $n \leq 6$. Our new HS-WCA perturbation theory has the same limitations as other WCA theories when dealing with very soft-core fluids. The BFC (with $a = e$) may be applied to fluids with repulsive-core pair-potentials that are somewhat softer than that a Lennard-Jones fluid, but not too much softer. In particular, for densities up to $\rho\sigma^3 = 1$ and temperature $kT/\epsilon \geq 1$ HS-WCA $\tilde{A}^{(0)}$ predictions remain accurate to better than ± 0.1 for GLJ potentials[13] with $n_0 \geq 6$ or for inverse-power potentials with $n \geq 12$ (note that the core of a Lennard-Jones potential resembles an inverse-power potential with $n \approx 20$).[13] Lado's variant of WCA theory is applicable to somewhat softer-core potentials, as it remains accurate for inverse-power potentials as soft as $n \approx 9$.[14] For fluids with even softer-core potentials the perturbation theory of Mansoori−Canfield−Rasaiah−Stell (MCRS)[9] has been found to be more accurate than any variants of first-order WCA theory.[14,27] Furthermore, the MCRS theory has very recently been extended to yield predictions that are in virtually exact agreement with simulation results up to the freezing point of inverse-power fluids as soft as $n = 4$.[14,28]

The length scale of attractive intermolecular interactions can profoundly influence fluid−solid-phase transitions and the extent of the liquid phase.[29,30] In fact, for fluids composed of particles resembling C_{60} molecules,[31] which have a significantly shorter attractive length scale than a Lennard-Jones fluid, there is an ongoing debate as to whether a vapor−liquid critical point and equilibrium liquid phase could theoretically exist. The applicability of perturbation theories to fluids with such short attractive length scales has also been investigated.[32] For example, recent comparisons of simulation results and WCA predictions for a fluid composed of C_{60} molecules suggest that WCA predictions remain quite accurate, although the near-critical and low-density deviations typically found for Lennard-Jones fluids appear to be about twice as large for the C_{60} fluid.[13] For fluids with longer-range cohesive interactions than a Lennard-Jones fluid there is little doubt regarding the accuracy of WCA perturbation theories, since the structure of such fluids should even more closely resemble that of the corresponding WCA repulsive reference fluid. Thus, it is anticipated that the accuracy of both WCA and HS-WCA predictions should extend to non-Lennard-Jones fluids, except those with very soft cores and/or extremely short-range cohesive interactions.

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