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Structure and thermodynamics of a simple fluid

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Monte Carlo results are found for a simple fluid with a pair potential consisting of a hard-sphere core and a Lennard-Jones attractive tail. They are compared with several of the most promising recent theoretical treatments of simple fluids, all of which involve the decomposition of the pair potential into a hard-sphere-core term and an attractive-tail term. This direct comparison avoids the use of a second perturbation scheme associated with softening the core, which would introduce an ambiguity in the significance of the differences found between the theoretical and Monte Carlo results. The study includes the optimized random-phase approximation (ORPA) and exponential (EXP) approximations of Andersen and Chandler, an extension of the latter approximation to nodal order three (the N3 approximation), the linear-plus-square (LIN + SQ) approximation of Høye and Stell, the renormalized hypernetted chain (RHNC) approximation of Lado, and the quadratic (QUAD) approximation suggested by second-order self-consistent Γ ordering, the lowest order of which is identical to the ORPA. As anticipated on the basis of earlier studies, it is found that the EXP approximation yields radial distribution functions and structure factors of excellent overall accuracy in the liquid state, where the RHNC results are also excellent and the EXP, QUAD, and LIN + SQ results prove to be virtually indistinguishable from one another. For all the approximations, however, the thermodynamics from the compressibility relation are poor and the virial-theorem results are not uniformly reliable. Somewhat more surprisingly, it is found that the EXP results yield a negative structure factor $S(k)$ for very small k in the liquid state and poor radial distribution functions at low densities. The RHNC results are nowhere worse than the EXP results and in some states (e.g., at low densities) much better. In contrast, the N3 results are better in some respects than the EXP results but worse in others. The authors briefly comment on the RHNC and EXP approximations applied to the full Lennard-Jones potential, for which the EXP approximation appears somewhat improved in the liquid state as a result of the softening of the potential core.

I. INTRODUCTION

Over the past decade there have been substantial new developments in the characterization of the structure and thermodynamics of a classical monatomic liquid at equilibrium.[1] The purpose of this paper is to examine in quantitative detail how far several of the most promising of these developments take us, and what they are still unable to do. This has entailed both generating new Monte Carlo results and extending existing theoretical work.

Almost all of the significant recent theoretical progress has involved adding an interparticle attraction as a perturbation to a reference-system potential that can most profitably be taken to be a hard-sphere potential. Application to pair potentials that do not already have a strictly hard core, such as the Lennard-Jones potential, entails a second perturbative scheme associated with softening the core, which inevitably brings with it additional errors and uncertainties. In order to avoid these difficulties, we have for the most part compared the various theories to new Monte Carlo results for a potential with a hard-sphere core and a Lennard-Jones tail.

Among the several different approaches we scrutinize is a nodally ordered approximation scheme applied to a cluster expansion developed by Andersen and Chandler[2] and, independently, by one of us.[3] Its lowest-order result, of nodal order 2, is the well-known exponential (EXP) approximation of Andersen and Chandler.[2] We consider here the result of nodal order 3, which we call the N3 approximation. We further show that if one sums the expansion to *all* orders but excludes the terms represented by diagrams of basic (i.e., "bridge" or "elementary") topological type, one recovers an approximation previously proposed by Lado, which we call here the renormalized hypernetted chain (RHNC) approximation.[4] We also consider an approximation proposed very recently by Høye and Stell,[5] the linear-plus-square (LIN + SQ) approximation, which was suggested to them by the structure of the mean spherical approximation (MSA). Finally we examine the results of the self-consistent Γ-ordered approach of Stell and co-workers.[6-11] It yields a readily computable lowest-order result, which in fact is identical to the optimized random-phase approximation (ORPA) result of Andersen and Chandler in their optimized mode-expansion theory.[12] For the pair potential under consideration the higher-order results are difficult to handle without quite drastic approximations that simplify their functional form (in contrast to the case of simple lattice models, the primitive model of an electrolyte, or a simple dipolar fluid, where they are tractable[11]). We give an argument leading to a simplification that results in two slightly different approximate second-order results. One proves to be the LIN + SQ approximation. The other we call the quadratic (QUAD) approximation.

Quantitative evaluation of the radial distribution function $g(r)$ and structure factor $S(k)$ in all of the approximations mentioned above has been made for a variety of densities. Although all of the comparisons with our hard-core Monte Carlo results are, strictly speaking, new, some of them only confirm conclusions that have already been clear from earlier work. For example, we find that the hard-sphere, MSA, and ORPA $g(r)$'s are already good approximations to the full $g(r)$ in the liquid state, while the EXP $g(r)$ is even better and is remarkably accurate. Similarly we find that the LIN + SQ $g(r)$'s are indistinguishable from the EXP $g(r)$'s in the liquid state, which is an immediate consequence of the very small differences there between the hard-sphere and ORPA $g(r)$'s. These expected results by and large only serve to further document the success of thermodynamic perturbation theories and their recent extensions when applied to simple fluids. However, other results are less satisfactory in somewhat unexpected ways. For example, we find that the EXP $g(r)$ is seriously inaccurate at typical compressed-vapor densities despite its exactitude in the zero-density limit. One must go to the RHNC to obtain a uniformly reliable approximation to $g(r)$ over the full range of fluid densities that includes the vapor and liquid state. Finally, some of our results are quite disappointing and surprising. For instance, the EXP, QUAD, and LIN + SQ structure factors become negative over a certain range of small k, and although $S(0)$ is positive in these approximations, it yields inaccurate thermodynamic results, as does even the $S(0)$ of the RHNC equation, the best of the approximations that we consider here. (The virial-theorem result for the RHNC approximation is also inaccurate.) A second disappointment is that the nodal-ordering scheme in which EXP and N3 are embedded does not converge rapidly enough to yield a three-node approximant that is uniformly better than the EXP result whenever the EXP result is already good.

Our work here suggests that the absence of negative $S(k)$ values in previous EXP studies of a Lennard-Jones fluid may be the result of compensating errors that tend to shrink the interval over which $S(k)$ is negative as the hard core of the reference-system potential is softened. (By directly comparing Monte Carlo and EXP $g(r)$'s for the full Lennard-Jones potential as well as for the repulsive Lennard-Jones core, we find further evidence that the core-softening scheme used by Andersen, Chandler, and Weeks to apply the EXP approximation to a Lennard-Jones potential increases the relative accuracy of that approximation through fortuitous cancellation of errors.) Our work further points up the fact that even the most successful of the theories we consider are incapable of yielding the equation of state of a simple fluid with high accuracy via the compressibility relation or virial theorem, and it confirms that we still do not have sufficiently reliable insight into the equilibrium state of simple fluids to be able to systematically and uniformly improve successful approximations such as the EXP by means of the formalisms that have been used to derive or justify them. In short, real progress still appears to involve much trial and error, and its significance is understood only with the aid of hindsight.

II. NOTATION AND SOME FORMALISM

This section has the dual purpose of introducing our notation and serving as a basis for our discussion of the several cluster-integral formalisms from which we derived the approximations we consider. For a pair potential with a hard-sphere (HS) core plus a softer part $[v(r)=v_{\mathrm{HS}}(r)+w(r)]$ all of these approximations can be regarded as having two functions as their basic building blocks. The first is just the hard-sphere radial distribution function $g_{\mathrm{HS}}(r)$. The second is a "chain function" we denote as $\mathcal{C}^*(12)$, which is defined below [Eq. (14)]. The lowest-order Γ-ordered approximation (LOGA) in the self-consistent Γ-ordered scheme of Stell and co-workers[6-11] as well as the optimized random-phase approximation of Andersen and Chandler,[12] which is identical to the LOGA, are both given by the pair distribution function

$$g(12)=g_{\mathrm{HS}}(r)+\mathcal{C}^*(12)\,. \qquad (1)$$

For the same potential $(v=v_{\mathrm{HS}}+w)$ the mean spherical approximation[13] is given by the same expression, but with $g_{\mathrm{HS}}(r)$ approximated by its MSA form [i.e., the MSA approximation to $g(12)$ when $v=v_{\mathrm{HS}}$, which is in turn identical to the Percus-Yevick[14] $g_{\mathrm{HS}}(r)$], and $\mathcal{C}^*(12)$, a functional of $g_{\mathrm{HS}}(r)$, likewise approximated through the use of the MSA $g_{\mathrm{HS}}(r)$ in its evaluation. Thus the MSA can itself be regarded as a convenient approximation to the ORPA or LOGA result, and for all but the most dense fluid states it is a good approximation. [Globally, however, the ORPA and MSA results appear to be crucially different, since it is to be anticipated that use of the exact $g_{\rm HS}(r)$ will in general lead to a phase diagram that includes a solid-fluid transition, which is almost universally expected to occur even in the absence of attractive forces, i.e., in the absence of the $\mathfrak{C}^*(12)$ of (1). Use of the Percus-Yevick (PY) $g_{\rm HS}(r)$, on the other hand, will suppress any such transition, since the PY $g_{\rm HS}(r)$ itself shows no evidence of the hard-sphere transition.[15]] In our work here we always use the best available[16] assessments of the exact $g_{\rm HS}$. These are indistinguishable from the PY values only for low densities.

We note that even the well-studied ORPA and MSA results have heretofore been subjected to little *direct* comparison with Monte Carlo (MC) or molecular-dynamics results, since almost all comparisons[17, 18] involving the ORPA or MSA and computer simulation for simple liquids have been made for the Lennard-Jones potential, which does not lend itself to immediate treatment by such approximation but instead requires the introduction of a hard-core potential, adjusted to be as nearly equivalent as possible to the Lennard-Jones potential.

The main purpose of this paper is to give a *direct* comparison between a number of theoretical results and MC results for a simple hard-core fluid, defined by an interparticle potential that is especially suitable in this connection:

$$v(r)=v_{\rm HS}(r)+w(r)\,,$$
$$v_{\rm HS}(r)=\begin{cases}\infty \text{ for } r<d\,,\\ 0 \text{ for } r>d\,,\end{cases}\qquad(2)$$
$$w(r)=\begin{cases}-\epsilon \text{ for } d<r<2^{1/6}d\,,\\ 4\epsilon[(d/r)^{12}-(d/r)^{6}] \text{ for } r>2^{1/6}d\,.\end{cases}$$

The $w(r)$ need not be prescribed for $r<d$ except by the condition $w(r)<\infty$.

For this potential the attractive $w(r)$ can be strictly regarded as a perturbation upon a hard-sphere reference potential rather than upon a reference potential that can only be related to hard-sphere results by further perturbative or variational treatment. We thus avoid having to untangle the results of two separate approximations that one faces in treating a Lennard-Jones system in terms of a hard-sphere reference potential, with the attendant ambiguities caused by compensating errors and related complications.

For any v that is the sum of a repulsive reference term v_0 and an attractive perturbing term w, the Andersen-Weeks-Chandler "high-temperature approximation"[16, 19] is based upon replacing the radial distribution function $g(r)$ by $e^{-\beta v_0}y_{\rm HS}(r/d)$, where $e^{-\beta v\ \ (r)}y_{\rm HS}(r/d)$ is $g_{\rm HS}(r)$, the hard-sphere $g(r)$, and d is chosen so that

$$\int[g(r)-e^{-\beta v_0(r)}y_{\rm HS}(r/d)]\,d\vec{r}=0\,.\qquad(3)$$

For the potential we treat here, this approximation becomes simply

$$g(r)=g_{\rm HS}(r)\,,\qquad(4)$$

which is also the lowest-order result for a straightforward expansion of $g(r)$ in β.[20] We find that the EXP, ORPA, and LIN + SQ approximations are all better than (4) over the full range of ρ and T that we have considered, as can be seen from our tables and figures. The first-order result in β, in the notation developed below, is given by our Eqs. (7) and (36), with $F^{\rm L}(12)$ given by

$$F^{\rm L}(12)=\int d(3)\,d(4)\,\hat{F}_0(13)\,\Phi(34)\,\hat{F}_0(42)\,.$$

We have not attempted the numerical evaluation of this result here, because of its complexity. We note in passing, however, that our representation has certain advantages over the usual one[21, 22] for β expansions; in particular, it is valid as it stands for both finite and infinite systems.

We turn now to some formal details relevant not only to a potential given by (2) but more generally to any pair potential v composed of a highly repulsive core term v_0 (for simplicity we retain a hard-core interaction) and a softer part w:

$$v=v_0+w\,.\qquad(5)$$

Then the cluster-integral formalism of Lebowitz, Stell, and Baer (LSB)[6] provides a decomposition of the correlation functions into a long-range (L) and a short-range (S) part, the contributions of which are dominating at respectively large and short separations of the particles. In particular, for the two-particle Ursell function, related to $g(12)$ by

$$F(12)=\rho^2 g(12)-\rho^2\equiv\rho^2 h(12)\qquad(6)$$

(ρ is the average density of the system, assumed homogeneous), we can write

$$F(12)=F^{\rm S}(12)+F^{\rm L}(12)\,;\qquad(7)$$

$F^{\rm S}(12)$ is defined graphically[23] as the subsum of all cluster integrals in a Φ-bond, f_0-bond representation of $F(12)$ such that the points 1 and 2 are connected by a path of f_0 bonds. Here

$$\Phi=-\beta w\qquad(8)$$

and

$$f_0=e^{-\beta v_0}-1\,.\qquad(9)$$

Defining

$$\hat{F}(12)=F(12)+\rho\delta(12)\qquad(10)$$

and $\hat{F}^{\rm S}(12)$ similarly, one can show[6] that $\hat{F}(12)$ is the sum of all irreducible graphs with Φ bonds and $\hat{F}^{\mathrm{S}}$ hypervertices[23] having two white vertices labeled by 1 and 2.

The graphs appearing in $F(12)$ can be ordered according to a parameter γ such that γ^{-1} measures the range of w:

$$w(r,\gamma)=\gamma^3\phi(\gamma r)\,. \tag{11}$$

As pointed out by LSB,[6] the orderings of the short- and long-range functions must be considered separately. For $F^{\mathrm{L}}(12)$ one obtains the following expansion:

$$\begin{aligned}F^{\mathrm{L}}(12)={}&\rho^2\mathcal{C}^*(12)+\tfrac{1}{2}\int d(3)\cdots d(6)\,\hat{F}^{\mathrm{S}}(134)\,\mathcal{C}(35)\,\mathcal{C}(46)\,\hat{F}^{\mathrm{S}}(562)\\&+\int d(3)\cdots d(8)\,\hat{F}^{\mathrm{S}}(134)\,\mathcal{C}(35)\,\mathcal{C}(46)\,\hat{F}^{\mathrm{S}}(567)\,\mathcal{C}(78)\,\hat{F}^{\mathrm{S}}(82)\\&+\tfrac{1}{2}\int d(3)\cdots d(10)\,\hat{F}^{\mathrm{S}}(13)\,\mathcal{C}(34)\,\hat{F}^{\mathrm{S}}(456)\,\mathcal{C}(57)\,\mathcal{C}(68)\,\hat{F}^{\mathrm{S}}(789)\,\mathcal{C}(9,10)\,\hat{F}^{\mathrm{S}}(10,2)\\&+\text{higher-order terms}\,,\end{aligned} \tag{12}$$

where $\mathcal{C}(12)$ is the "chain sum"

$$\begin{aligned}\mathcal{C}(12)={}&\Phi(12)+\int d(3)\,d(4)\,\Phi(13)\,\hat{F}^{\mathrm{S}}(34)\,\Phi(42)\\&+\int d(3)\cdots d(6)\,\Phi(13)\,\hat{F}^{\mathrm{S}}(34)\,\Phi(45)\\&\times\hat{F}^{\mathrm{S}}(56)\,\Phi(62)+\cdots\,,\end{aligned} \tag{13}$$

and $\mathcal{C}^*(12)$ is defined by

$$\rho^2\mathcal{C}^*(12)=\int d(3)\,d(4)\,\hat{F}^{\mathrm{S}}(13)\,\mathcal{C}(34)\,\hat{F}^{\mathrm{S}}(42)\,. \tag{14}$$

The $F^{\mathrm{S}}(123)$ is obtained from the three-particle Ursell function by

$$\begin{aligned}\hat{F}^{\mathrm{S}}(123)={}&F^{\mathrm{S}}(123)+\delta(12)F^{\mathrm{S}}(13)+\delta(13)F^{\mathrm{S}}(12)\\&+\delta(23)F^{\mathrm{S}}(12)+\rho\delta(12)\,\delta(13)\,.\end{aligned} \tag{15}$$

The first term on the right-hand side (RHS) of (12) is of order γ^3, the next three terms are of order γ^6, and the neglected terms of order γ^9. Thus, keeping only lowest-order terms in F^{L}, we have

$$F(12)=F^{\mathrm{S}}(12)+\rho^2\mathcal{C}^*(12)\,. \tag{16}$$

In the same way $F^{\mathrm{S}}(12)$ can be γ ordered, but truncation of such an expansion would yield an $F^{\mathrm{S}}+F^{\mathrm{L}}$ that would depend on the value of Φ inside the core (because for $v=v_0+w$ such that $v_0=\infty$ for $r<d$, w is not well defined for $r<d$) and for arbitrary Φ would yield an $h(12)$ different from -1 inside the core. Instead one can determine F^{S} in a way that satisfies this core condition. To see this, we define

$$\hat{c}(12)=c(12)-\delta(12)/\rho\,, \tag{17}$$

where $c(12)$ is the familiar direct correlation function, so that the Ornstein-Zernike (OZ) equation reads

$$-\delta(12)=\int\hat{c}(13)\hat{F}(23)d(3)\,. \tag{18}$$

The Fourier transform[24] of (16) gives, using (14) and (13),

$$\overline{F}(k)=\overline{F}^{\mathrm{S}}(k)/[1+\overline{F}^{\mathrm{S}}(k)\,\tilde{\Phi}(k)]\,, \tag{19}$$

while (18) gives

$$\overline{F}(k)=-1/\overline{c}(k)\,. \tag{20}$$

Equating the RHS of (19) and (20), we get

$$\overline{c}(k)=\overline{c}^{\,\mathrm{S}}(k)+\tilde{\Phi}(k) \tag{21}$$

or, in real space,

$$c(12)=c^{\mathrm{S}}(12)+\Phi(12)\,. \tag{22}$$

If for $r\geqslant d$ we further approximate $c^{\mathrm{S}}(12)$ by its lowest-order γ result $c_0(12)$, which is the direct correlation function of a system of particles interacting via v_0 only (i.e., of a hard-sphere system), and impose the core condition $h(12)=-1$ for $r<d$, then $c(12)$ is known for all r (via the OZ equation). We then *define*, for all r, a $c^s(12)$ given by

$$c^{\mathrm{S}}(12)=c(12)-\Phi(12)\,. \tag{23}$$

With this choice, $c(12)$ and $h(12)$ are independent of the value of $\Phi(12)$ for $r<d$. A particularly convenient choice of Φ is the one that yields $c^{\mathrm{S}}=c_0$ for $r<d$ as well as $r>d$, and hence

$$\hat{F}^{\mathrm{S}}=\hat{F}_0\,. \tag{24}$$

This choice,

$$\Phi(12)=c(12)-c_0(12)\,, \tag{25}$$

is identical with the "optimized" Φ of Andersen and Chandler[2] (i.e., chosen so that $\mathcal{C}^*=0$ for $r<d$) and will be used throughout this paper.

The $\mathcal{C}^*(12)$ defined by the lowest-order approximation

$$\rho^2\mathcal{C}^*(12)=F(12)-F_0(12) \tag{26}$$

is quite close to the MSA result for $F(12)-F_0(12)$

[MSA assumes $c_0(12)=0$ for $r>d$, already quite a good approximation]. Note that Eqs. (26) and (1) are the same, in slightly different notation. As noted previously, this equation defines both the LOGA[10] and ORPA[12] results.

Several systematic means have been devised to go beyond the MSA and LOGA/ORPA results. One of them is based upon the h_0-bond, $\mathcal{C}^*$-bond representation of $h(12)$ given by Andersen and Chandler[2] and, independently, by Stell.[3] If all graphs of nodal order greater than 2 are neglected in this expansion (where the nodal order of a graph is simply the number of its vertices), one recovers the EXP approximation of Andersen and Chandler[2]:

$$g_{\text{EXP}}=g_0 e^{\mathcal{C}^*}. \qquad (27)$$

Retaining instead all graphs of nodal order up through 3, we obtain an approximation that can be written[3,16]

$$g=g_{\text{EXP}}(1+2\rho\mathcal{S}*\mathcal{H}+\rho\mathcal{S}*\mathcal{S}), \qquad (28)$$

where

$$\mathcal{S}=g_0 e^{\mathcal{C}^*}-1-\mathcal{C}^*, \qquad (29a)$$

$$\mathcal{H}=h_0+\mathcal{C}^*=h_{\text{ORPA}}, \qquad (29b)$$

and we have used the convolution notation in (28):

$$A*B=\int d(3)A(13)B(23).$$

[In terms of $\mathcal{H}$ and $\mathcal{S}$ bonds the EXP approximation is just $h(12)=\mathcal{H}+\mathcal{S}$.] We refer to this as the N3 approximation for $g(12)$. On the basis of the arguments given in Refs. 2 and 3, one would expect the N3 approximation to be an improvement over the EXP approximation wherever one is considering a state in which the EXP approximation is a good one initially. And, on the basis of the same arguments, one is led to expect that an even better approximation might result if one instead retained *all* graphs in the h_0-bond, $\mathcal{C}^*$-bond representation of $h(12)$ except those that are of basic (elementary or bridge) form, i.e., those that include at least one subgraph with the topology

$$\Gamma(12)=\int d(3)\,d(4)A(13)A(14)A(23)A(24)A(34). \qquad (30)$$

We call the resulting approximation the renormalized hypernetted chain approximation (RHNC), in view of its inclusion of the same topological type of cluster integral retained in the hypernetted chain approximation,[25] but with a different set of bond functions. Each graph omitted in either the N3 or RHNC approximation for $h(12)$ represents a cluster integral that involves two or more volume integrations over at least one $\mathcal{C}^*$ bond and further $\mathcal{C}^*$ bonds or h_0 bonds, with each integration accompanied by a factor of ρ. At liquid densities the maximum amplitude of $\mathcal{C}^*$ is small, while both $\mathcal{C}^*$ and h_0 are oscillatory about the value zero (see our appendix for details); at such densities the cluster integrals neglected in either approximation represent a relatively small contribution, because each volume integration over a product of such oscillating functions is a smoothing operation tending to yield a function of maximum amplitude smaller than that of any of the bond functions. At lower densities (at which $\mathcal{C}^*$ is no longer small and oscillatory) the neglected integrals are still relatively small, because they are all of second or higher order in ρ. On the basis of this general argument—and in the absence of any further detailed information concerning the relation between the signs and magnitudes of the cluster integrals, etc.—one concludes that the RHNC approximation is likely to be somewhat better than the N3 approximation, because it retains those graphs that make the largest contribution to each nodal order rather than simply neglecting all graphs beyond third order. As we see in Sec. III A 1, the N3 approximation only marginally fulfills the expectations engendered by the above arguments, while the RHNC approximation is indeed a clear improvement over the EXP approximation.

When one sums only the series-parallel diagrams in the h-bond expansion of $\ln g(12)+\beta v(12)$, the result is the original hypernetted chain (HNC) approximation[25]:

$$\ln g(12)+\beta v(12)=h(12)-c(12). \qquad (31)$$

The motivation for the series-parallel summation that yields (31) can be summarized by the same argument that we applied to the h_0-bond, $\mathcal{C}^*$-bond expansion of $h(12)$, except it is weaker: In the h-bond expansion of $\ln g+\beta v$ there is no $\mathcal{C}^*$ bond in each neglected basic graph that is guaranteed to be small at liquid densities.

The RHNC approximation that results from series-parallel summation of the h_0-bond, $\mathcal{C}^*$-bond expansion of $h(12)$ can also be expressed as a simple expression analogous to (31):

$$\ln[g(12)/g_0(12)]=h(12)-h_0(12)-[c(12)-c_0(12)]+\Phi(12). \qquad (32)$$

This proves to be identical to an approximation suggested by Lado[4] if his $v(12)-v_0(12)$ (indeterminate inside our hard core) is identified with our $\Phi(12)$. He arrived at his result by arguing that instead of neglecting completely the sum of basic graphs $b(12)$ in the h-bond expansion of $\ln g(12)+\beta v(12)$, whose inclusion yields the exact expression

$$\ln g(12)+\beta v(12)=h(12)-c(12)+b(12)\,, \tag{33}$$

one might sensibly approximate the sum by $b_0(12)$, which is the function that $b(12)$ becomes when $v(12)$ is $v_0(12)$. For $v=v_0$ one has from (33)

$$\ln g_0(12)+\beta v_0(12)=h_0(12)-c_0(12)+b_0(12)\,. \tag{34}$$

Letting $b(12)=b_0(12)$ in (33) and subtracting (34) from the result yields (32), if $v(12)-v_0(12)$ is chosen to be $\Phi(12)$ inside as well as outside the hard-core region of the potential. To complete the definition of the RHNC, the $c(12)$ appearing in (32) must be related to the $h(12)$ and $g(12)$ appearing there via the OZ equation [our Eq. (18)].

Another approximation that we evaluate in this paper was recently suggested by Høye and Stell[5] as a means of using the solution of the MSA to generate an approximation with improved thermodynamic self-consistency. They propose

$$g(12)=g_0(r)[1+\mathcal{C}^*(12)]+\tfrac{1}{2}[\mathcal{C}^*(12)]^2\,, \tag{35}$$

with g_0 and $\mathcal{C}^*$ evaluated in the MSA for analytic simplicity (but here we evaluate g_0 and $\mathcal{C}^*$ using the best available hard-sphere results). We call (35) the LIN + SQ approximation. It is clear that in the liquid state of a simple fluid, where $\mathcal{C}^*(12)$ has a small amplitude, the LIN + SQ approximation will be quite similar to the EXP approximation (except possibly for r immediately outside the hard-core diameter d, where g_0 can be quite large). What is not clear *a priori* is just *how* similar it is quantitatively, and how it differs from the EXP compared to the N3 and RHNC results. We consider these equations in Sec. III.

In considering dipolar liquids, Verlet and Weis[26] were led to an even simpler LIN approximation,

$$g(12)=g_0(r)[1+\mathcal{C}^*(12)]\,,$$

dictated by the special symmetries of a dipolar potential, for which it proved far superior to the EXP approximation. Preliminary results also suggested to them that the LIN approximation would likewise prove superior in a simple Lennard-Jones liquid; our results here do not bear out that conclusion, however.

The final set of approximations we consider before turning to our numerical results are those generated by the self-consistent second-order Γ-ordered result, in which [cf. Eq. (2.15) of Ref. 6]

$$F^{\mathrm{S}}(12)=F_0(12)+\tfrac{1}{2}\int\frac{\delta^2F_0(12)}{\delta\rho(3)\,\delta\rho(4)}F^{\mathrm{L}}(34)\,d(3)\,d(4) \tag{36}$$

and $F^{\mathrm{L}}(12)$ is given by the four terms exhibited in (12). [In $F^{\mathrm{L}}(12)$ it is appropriate to use the lowest-order results for $\hat{F}^{\mathrm{S}}(12)$, $\mathcal{C}(12,\hat{F}^{\mathrm{S}})$, and $\hat{F}^{\mathrm{S}}(123)$, namely, $\hat{F}_0(12)$, $\mathcal{C}(12,\hat{F}_0)$, and $\hat{F}_0(123)$.] This result, involving as it does three-body and four-body correlation functions, is intractably difficult to evaluate as it stands. One direction in which simplification lies was already discussed by Hemmer[27] in his pioneering γ-expansion study; if one further γ-expands the RHS of Eq. (36), one obtains

$$F^{\mathrm{S}}(12)=F_0(12)+\frac{1}{2}\,\frac{\partial^2F_0(12)}{\partial\rho^2}F^{\mathrm{L}}(12)$$
$$+\text{higher-order terms in }\gamma\,. \tag{37}$$

One can similarly γ-expand the terms shown in Eq. (12) to eliminate all the three- and four-body correlation functions there in favor of thermodynamic factors plus higher-order terms in γ. As one of us has discussed at length in Ref. 11, the resulting "nodally contracted" expressions are probably accurate enough to be useful in making order-of-magnitude comparisons among the original cluster integrals in (12) under liquid-state conditions. We have concluded, however, that they are not likely to be accurate enough to yield quantitatively satisfactory approximations as they stand, for the following reason: Only if functions such as $F^{\mathrm{L}}(12)$, $\mathcal{C}(12)$, and $\mathcal{C}^*(12)$ were weak, long-ranged, nonoscillatory functions [as they would be, for example, if $w(12)$ were weak, long ranged, and nonoscillatory], would the lowest-order terms in the resulting γ-expanded results be quantitatively accurate. But the F^{L}, $\mathcal{C}$, and $\mathcal{C}^*$, although weak, are oscillatory under liquid-state conditions. Therefore the arguments most relevant to further simplification of expressions such as (36) and (12) are instead those that we have already discussed in considering the motivation for the N3 and RHNC approximations. Rewriting the integral of (36) to get

$$F^{\mathrm{S}}(12)-F_0(12)$$
$$=h_0(12)F^{\mathrm{L}}(12)+2\rho\int\frac{\delta h_0(12)}{\delta\rho(3)}F^{\mathrm{L}}(32)\,d(3)$$
$$+\tfrac{1}{2}\rho^2\int\frac{\delta^2h_0(12)}{\delta\rho(3)\,\delta\rho(4)}F^{\mathrm{L}}(34)\,d(3)\,d(4)\,, \tag{38}$$

we see that under liquid-state conditions, where $F^{\mathrm{L}}(ij)$ is expected to be small in amplitude and spatially oscillatory, and $\delta h_0(12)/\delta\rho(3)$ and $\delta^2h_0(12)/[\delta\rho(3)\,\delta\rho(4)]$ are also expected to be oscillatory, the last two terms on the RHS of (38) can be expected to be small compared to the first term. At low densities this must also be true, since the last two terms are of higher order in ρ than the first. This leaves us, for both low and liquid-state densities,

$$F^{\mathrm{S}}(12)\approx F_0(12)+h_0(12)F^{\mathrm{L}}(12)\,. \tag{39}$$

Similar arguments applied to the terms in (12) indicate that the first integral on the RHS there dominates the last two for both low and high ρ. Having gotten this far, we are still left with a term coming from (12),

$$\frac{1}{2}\int d(3)\cdots d(6)\hat{F}_0(134)\,\mathcal{C}(35)\,\mathcal{C}(46)\hat{F}_0(562)\,, \qquad (40)$$

that is essentially unmanageable, largely because of the two three-body F_0's that remain in the integrand, but also because it is $\mathcal{C}^*$ [rather than the $\mathcal{C}$ appearing in (40)] that is a readily available function from the first-order results. However, since $\hat{F}_0(123)$ has an h_0-bond expansion and $\mathcal{C}^*(ij)$ itself can be reexpressed in terms of $\mathcal{C}$ bonds and h_0 bonds, we can write the difference between expression (40) and $\frac{1}{2}[\mathcal{C}^*(12)]^2$ as an h_0-bond, $\mathcal{C}$-bond expansion to get

$$\begin{aligned}\frac{1}{2}\int d(3)\cdots d(6)\hat{F}_0(134)\,\mathcal{C}(35)\,\mathcal{C}(46)\hat{F}_0(562)\\ =\frac{1}{2}[\mathcal{C}^*(12)]^2+\frac{1}{2}\rho\int d(3)\,\mathcal{C}^2(13)\,h_0(23)\\ +\frac{1}{2}\rho^2\int d(3)\,d(4)\,h_0(13)\,\mathcal{C}^2(34)\,h_0(42)+\cdots\,. \qquad (41)\end{aligned}$$

Applying the by now familiar arguments that we have invoked several times before in this section leads us to expect that the integrals on the RHS of (41) will be small compared to $\frac{1}{2}[\mathcal{C}^*(12)]^2$, so we expect a reasonable approximation will be given by

$$F^{\mathrm{L}}(12)=\rho^2\mathcal{C}^*(12)+\frac{1}{2}\rho^2[\mathcal{C}^*(12)]^2\,. \qquad (42)$$

Combining (39) and (42), we get the approximation

$$g_{\mathrm{QUAD}}=g_0(1+\mathcal{C}^*+\tfrac{1}{2}\mathcal{C}^{*2})\,. \qquad (43)$$

[This approximation will be called QUAD (quadratic).]

If only the lowest-order term $\rho^2\mathcal{C}^*$ in F^{L} is retained in calculating F^{S} from (39), i.e., if we let

$$F^{\mathrm{S}}=F_0+h_0\rho^2\mathcal{C}^*\,, \qquad (44)$$

then we recover the structurally simpler LIN+SQ approximation discussed earlier,

$$g_{\mathrm{LIN+SQ}}=g_0(1+\mathcal{C}^*)+\tfrac{1}{2}\mathcal{C}^{*2}\,. \qquad (45)$$

Thus the second-order γ-ordered result does not suggest approximations that are different in any fundamental way from those already discussed. The QUAD and LIN+SQ bear the hallmark of "second orderness" in γ ordering by being intrinsically quadratic rather than exponential (in γ^3, and therefore in $\mathcal{C}^*$); this proves not to be a handicap in the liquid region (where they are indistinguishable from EXP). In the low-density region, where they are inferior to EXP for small r, EXP proves poor enough for larger r to be of only limited use in the first place.

The main advantage that LIN+SQ has over EXP is analytic simplicity. A Lennard-Jones potential can be very well approximated by either its positive part, or its repulsive part, plus a linear combination of two Yukawa potentials; the positive (or repulsive) part can in turn be treated by means of either the Andersen-Chandler-Weeks[17] or the Barker-Henderson[20] perturbation procedures, respectively, which perturb off the hard-sphere result. But $\mathcal{C}^*(12)$ for a potential given by a linear combination of two Yukawas plus a hard-sphere core can be treated wholly analytically[28,29]; as a result, for this potential the LIN+SQ approximation can be solved in essentially closed analytic form for the structure factor and for its thermodynamics as well as for $g(12)$ itself. This is true neither for the EXP nor the QUAD approximations.

III. NUMERICAL RESULTS

A. Hard-sphere potential with attractive Lennard-Jones tail

To test the accuracy of the approximations we have discussed, we performed MC calculations [864 particles, $(1-2)\times10^6$ configurations] and at low density solved the PY equation for a hypothetical fluid where the particles interact through the potential v given by (2). Numerical computations for this interaction (rather than for a Lennard-Jones interaction) avoid the further approximations necessary to take into account the finite steepness of the repulsive part of the Lennard-Jones interaction, and thus allow for a more stringent test in the region immediately outside the hard core. For the Lennard-Jones interaction, differences in $g(r)$ near the core tend to be suppressed to some extent by the $e^{-\beta v_0}$ factor in $g(r)$.

$\mathcal{C}^*$ was calculated by minimizing the ring-diagram contribution to the free energy with respect to a variation of Φ inside the core, as explained in the work of Andersen and Chandler.[2] For the pure hard-sphere $g_{\mathrm{HS}}(r)$, we used the phenomenological expressions of Ref. 16 for $\rho d^3>0.5$ and the PY solution for $\rho d^3<0.5$.

Typical gaseous and liquid densities for the potential given by Eq. (2) are much the same as those for a Lennard-Jones potential. [To be more precise, the liquid-state density range is shifted to slightly higher density values compared to the Lennard-Jones (LJ) case. A typical liquid point for an LJ system is the point $\rho\sigma^3=0.84$, $kT/\epsilon=0.75$. The correspondong hard-sphere diameter, according to the Weeks-Chandler-Andersen recipe,[16,17] is $d=1.022$. This gives an "equivalent" density for our potential of $\rho d^3=0.897$.] In all our tables, figures, and discussion of the potential given by Eq. (2) we take $d=1$ and $k/\epsilon=1$.

In describing our results, we are faced with a problem familiar to all who wish to present and analyze many data points representing functions that have considerable structure. On the one hand, a figure can convey at a glance key features and significant trends that a table cannot; on the other hand, as source material a figure is frustrating and often virtually useless compared to a table because of the relatively low accuracy of the information that can be read from it. Because of the role as reference material that most of our numerical output is likely to assume, we have chosen to give most of it as tables rather than figures, supplemented by the brief verbal descriptions below. These descriptions are, however, highly subjective—what we characterize as a "barely adequate" approximation may be the next man's "nearly exact" result. The problem here is not simply a matter of differing opinion either, but involves the fact that the adequacy of an approximation is a function of how one intends to use it. So we warn readers *not* to take too seriously the verbal descriptions below and urge them instead to consult our tabulated data whenever a precise comparison of relative accuracies is needed. In the interest of brevity we reproduce in the main body of the text only tables and figures that we single out for special comment in our discussion below. An appendix consisting of a full set of supplementary tables for the eight thermodynamic states we have investigated is available upon request from either author.

TABLE I. Various approximations and Monte Carlo values for $g(r)$ of a system of particles interacting through a hard-core term plus the attractive part of a Lennard-Jones potential [cf. Eq. (2)]. Notations are explained in text. This table is for $\rho = 0.1$ and $T = 1.20$.

r/d	HS	$\mathcal{C}^*$	EXP	N3	RHNC	LIN + SQ	QUAD	PY
1.000	1.143	0.730	2.372	2.144	2.500	2.244	2.282	2.490
1.040	1.131	0.729	2.344	2.120	2.462	2.221	2.256	2.453
1.080	1.120	0.728	2.319	2.099	2.430	2.200	2.232	2.420
1.120	1.110	0.728	2.297	2.081	2.401	2.182	2.211	2.390
1.160	1.099	0.702	2.217	2.016	2.313	2.117	2.141	2.302
1.200	1.089	0.639	2.064	1.892	2.150	1.989	2.008	2.138
1.240	1.080	0.563	1.896	1.756	1.975	1.846	1.859	1.963
1.280	1.071	0.486	1.742	1.628	1.813	1.710	1.719	1.802
1.320	1.063	0.415	1.609	1.518	1.675	1.589	1.595	1.663
1.360	1.055	0.351	1.498	1.425	1.559	1.486	1.490	1.549
1.400	1.047	0.295	1.407	1.349	1.465	1.400	1.402	1.455
1.440	1.040	0.248	1.332	1.286	1.389	1.328	1.330	1.379
1.480	1.034	0.207	1.272	1.235	1.327	1.270	1.270	1.318
1.520	1.028	0.174	1.223	1.193	1.278	1.221	1.222	1.268
1.560	1.022	0.146	1.183	1.160	1.238	1.182	1.182	1.229
1.600	1.017	0.123	1.151	1.133	1.207	1.150	1.150	1.198
1.640	1.013	0.105	1.125	1.111	1.182	1.125	1.125	1.173
1.680	1.009	0.090	1.104	1.095	1.162	1.104	1.104	1.154
1.720	1.005	0.079	1.088	1.081	1.148	1.087	1.087	1.140
1.760	1.002	0.070	1.075	1.072	1.137	1.075	1.075	1.129
1.800	1.000	0.063	1.065	1.065	1.130	1.065	1.065	1.122
1.840	0.998	0.059	1.058	1.060	1.125	1.058	1.058	1.117
1.880	0.997	0.056	1.054	1.058	1.124	1.054	1.054	1.115
1.920	0.996	0.054	1.051	1.058	1.125	1.051	1.051	1.116
1.960	0.996	0.054	1.051	1.060	1.127	1.051	1.051	1.118
2.000	0.996	0.055	1.052	1.063	1.132	1.052	1.052	1.122
2.040	0.997	0.056	1.054	1.067	1.137	1.054	1.054	1.126
2.080	0.998	0.056	1.055	1.069	1.140	1.055	1.055	1.129
2.120	0.998	0.057	1.056	1.070	1.141	1.056	1.056	1.129
2.160	0.998	0.057	1.057	1.070	1.140	1.056	1.056	1.128
2.200	0.999	0.056	1.056	1.069	1.137	1.056	1.056	1.125
2.240	0.999	0.054	1.055	1.067	1.133	1.055	1.055	1.121
2.280	0.999	0.053	1.053	1.064	1.128	1.053	1.053	1.116
2.320	1.000	0.050	1.051	1.060	1.122	1.051	1.051	1.110
2.360	1.000	0.048	1.049	1.056	1.115	1.049	1.049	1.104
2.400	1.000	0.045	1.046	1.052	1.109	1.046	1.046	1.098
2.440	1.000	0.043	1.044	1.049	1.102	1.044	1.044	1.092

1. Results for g(r)

Results for eight thermodynamic states covering the whole density region were obtained by us. Besides the LIN + SQ, QUAD, EXP, and RHNC results for all states, the results give the pure hard-sphere pair correlation function g_{HS}, $\mathfrak{C}^*$ and essentially exact results, either MC or PY, depending upon the density. (At $\rho = 0.1$ the PY results can be regarded as exact; at $\rho = 0.2$ the MC and PY results are roughly of the same degree of reliability and we give them both.) The LOGA/ORPA result is simply obtained from our results as $g_{\text{HS}} + \mathfrak{C}^*$. We also give N3 results.[30]

Briefly, we find that the EXP, QUAD, and LIN + SQ approximations are all of essentially equal accuracy in the liquid state. They are all of somewhat greater overall accuracy than the LOGA/ORPA results, which are already of satisfactory accuracy for many purposes in the liquid region. On the face of it, one of the attractive features of the EXP approximation lacking in the ORPA, QUAD, and LIN + SQ results is that the EXP $g(12)$ goes to the exact limiting result, $e^{-\beta v(12)}$, when $\rho \to 0$. This would suggest that the EXP approximation might be usefully accurate all the way from typical liquid densities to zero density, in contrast to the ORPA, QUAD, and LIN + SQ approximations, which one has no reason to expect to remain accurate as $\rho \to 0$. Our results show, however, that the EXP breaks down badly at low density ($\rho = 0.1$) and relatively low temperature (e.g., at $T = 1.2$) for $r \geq 1.5$, as do the ORPA, QUAD, and LIN + SQ g's. The fact that the EXP approximation becomes exact as $\rho \to 0$ is reflected at $\rho = 0.1$ in the behavior of g_{EXP}, mainly in the interval $1 \leq r \leq 1.5$, where g_{EXP} is

TABLE II. As Table I, with $\rho = 0.1$ and $T = 1.35$.

r/d	HS	$\mathfrak{C}^*$	EXP	N3	RHNC	LIN + SQ	QUAD	PY
1.000	1.143	0.633	2.151	2.401	2.163	2.066	2.094	2.181
1.040	1.131	0.632	2.128	2.371	2.138	2.046	2.072	2.153
1.080	1.120	0.632	2.107	2.345	2.115	2.028	2.052	2.128
1.120	1.110	0.632	2.088	2.322	2.095	2.011	2.033	2.106
1.160	1.099	0.610	2.023	2.242	2.029	1.956	1.974	2.038
1.200	1.089	0.555	1.897	2.087	1.903	1.847	1.861	1.909
1.240	1.080	0.488	1.759	1.919	1.765	1.726	1.735	1.769
1.280	1.071	0.420	1.630	1.764	1.636	1.609	1.616	1.639
1.320	1.063	0.357	1.518	1.631	1.525	1.506	1.510	1.527
1.360	1.055	0.300	1.424	1.520	1.432	1.417	1.419	1.433
1.400	1.047	0.251	1.346	1.429	1.354	1.342	1.343	1.355
1.440	1.040	0.209	1.282	1.355	1.291	1.280	1.281	1.291
1.480	1.034	0.174	1.230	1.296	1.240	1.228	1.229	1.240
1.520	1.028	0.144	1.187	1.248	1.199	1.186	1.186	1.198
1.560	1.022	0.120	1.152	1.209	1.165	1.151	1.152	1.164
1.600	1.017	0.100	1.124	1.178	1.138	1.123	1.123	1.138
1.640	1.013	0.083	1.101	1.153	1.116	1.100	1.100	1.116
1.680	1.009	0.070	1.082	1.134	1.100	1.082	1.082	1.099
1.720	1.005	0.060	1.067	1.119	1.087	1.067	1.067	1.087
1.760	1.002	0.052	1.056	1.108	1.077	1.056	1.056	1.077
1.800	1.000	0.047	1.048	1.101	1.070	1.048	1.048	1.071
1.840	0.998	0.043	1.042	1.096	1.066	1.042	1.042	1.066
1.880	0.997	0.040	1.038	1.094	1.064	1.038	1.038	1.064
1.920	0.996	0.039	1.036	1.094	1.064	1.036	1.036	1.064
1.960	0.996	0.039	1.035	1.096	1.065	1.035	1.035	1.066
2.000	0.996	0.040	1.036	1.099	1.069	1.036	1.036	1.069
2.040	0.997	0.041	1.038	1.103	1.072	1.038	1.038	1.072
2.080	0.998	0.041	1.040	1.106	1.074	1.040	1.040	1.074
2.120	0.998	0.042	1.041	1.106	1.076	1.041	1.041	1.075
2.160	0.998	0.042	1.041	1.106	1.076	1.041	1.041	1.075
2.200	0.999	0.041	1.041	1.103	1.074	1.041	1.041	1.074
2.240	0.999	0.040	1.040	1.099	1.072	1.040	1.040	1.071
2.280	0.999	0.039	1.039	1.095	1.069	1.039	1.039	1.068
2.320	1.000	0.037	1.038	1.089	1.065	1.038	1.038	1.065
2.360	1.000	0.036	1.036	1.084	1.061	1.036	1.036	1.061
2.400	1.000	0.034	1.034	1.078	1.058	1.034	1.034	1.057
2.440	1.000	0.032	1.032	1.072	1.054	1.032	1.032	1.053

TABLE III. Various approximations and Monte Carlo values for $S(k)$ of a system with potential given by Eq. (2). See text for notations; this table is for $\rho = 0.90$ and $T = 0.75$.

kd	HS	MC	RHNC	ORPA	EXP
0.400	0.024	0.089	0.043	0.045	0.158
0.800	0.025	0.075	0.041	0.043	0.067
1.200	0.027	0.064	0.039	0.040	−0.007
1.600	0.029	0.056	0.037	0.039	−0.045
2.000	0.032	0.052	0.037	0.039	−0.049
2.400	0.035	0.050	0.039	0.041	−0.032
2.800	0.041	0.051	0.042	0.044	−0.004
3.200	0.049	0.055	0.049	0.050	0.029
3.600	0.062	0.063	0.059	0.061	0.065
4.000	0.082	0.077	0.076	0.078	0.102
4.400	0.115	0.102	0.104	0.108	0.145
4.800	0.170	0.147	0.153	0.158	0.202
5.200	0.270	0.232	0.242	0.249	0.292
5.600	0.462	0.405	0.420	0.429	0.465
6.000	0.861	0.793	0.813	0.819	0.842
6.400	1.662	1.669	1.687	1.667	1.672
6.800	2.549	2.796	2.755	2.698	2.686
7.200	2.292	2.433	2.364	2.360	2.334
7.600	1.566	1.545	1.522	1.540	1.506
8.000	1.094	1.032	1.037	1.054	1.018
8.400	0.837	0.773	0.790	0.802	0.772
8.800	0.698	0.644	0.662	0.672	0.652
9.200	0.628	0.587	0.602	0.610	0.601
9.600	0.604	0.577	0.585	0.592	0.595

TABLE IV. Same as Table III, with $\rho = 0.91$ and $T = 1.35$.

kd	HS	MC	RHNC	ORPA	EXP
0.400	0.023	0.124	0.030	0.031	0.072
0.800	0.024	0.106	0.030	0.031	0.025
1.200	0.025	0.088	0.030	0.031	−0.011
1.600	0.027	0.073	0.031	0.032	−0.026
2.000	0.030	0.062	0.033	0.033	−0.023
2.400	0.034	0.055	0.035	0.036	−0.008
2.800	0.039	0.052	0.039	0.040	0.014
3.200	0.047	0.052	0.046	0.047	0.038
3.600	0.058	0.057	0.057	0.058	0.064
4.000	0.077	0.068	0.074	0.076	0.094
4.400	0.109	0.089	0.103	0.105	0.130
4.800	0.161	0.129	0.152	0.155	0.182
5.200	0.255	0.210	0.241	0.245	0.270
5.600	0.438	0.383	0.416	0.421	0.441
6.000	0.821	0.788	0.795	0.799	0.810
6.400	1.615	1.698	1.626	1.617	1.617
6.800	2.581	2.758	2.694	2.663	2.653
7.200	2.367	2.396	2.410	2.406	2.388
7.600	1.599	1.577	1.573	1.584	1.562
8.000	1.102	1.073	1.069	1.079	1.058
8.400	0.835	0.803	0.809	0.816	0.799
8.800	0.693	0.662	0.673	0.678	0.668
9.200	0.621	0.595	0.606	0.611	0.608
9.600	0.595	0.579	0.585	0.589	0.593

reasonably accurate at such densities and temperatures, whereas g_{ORPA}, g_{QUAD}, and $g_{\mathrm{LIN+SQ}}$ are not. However, at $\rho = 0.1$ and $T = 1.2$, g_{EXP}, g_{ORPA}, g_{QUAD}, and $g_{\mathrm{LIN+SQ}}$ all give identical (and unsatisfactory) results for somewhat larger r. The RHNC approximation, on the other hand, is essentially exact for all r at this state. At $\rho = 0.1$ and $T = 1.35$, g_{EXP} remains unsatisfactory for larger r, whereas RHNC remains satisfactory for all r. At $\rho = 0.2$ and $T = 1.6$, the RHNC and EXP results are of comparable overall accuracy (and the EXP and QUAD results have become virtually indistinguishable). See Tables I and II.

At intermediate density ($\rho = 0.6$) and $T = 1.6$ [convergence difficulties in the MC process seemed to indicate that for the potential (2) the state with $T = 1.35$ was already in the metastable region], $\mathcal{C}^*$ is small, especially in the core region, so that g_{QUAD}, $g_{\mathrm{LIN+SQ}}$, and g_{EXP} give virtually identical answers which are, moreover, in excellent agreement with g_{RHNC} and the "exact" MC result.

As the density is increased, $\mathcal{C}^*$ becomes negative for r close to the core and the different $g(r)$'s are smaller than g_{HS} in this region, in agreement with MC calculations. However, g_{EXP}, g_{QUAD}, and $g_{\mathrm{LIN+SQ}}$, which are practically identical, differ from the "exact" result by as much as 0.15 in the region immediately outside the core. We note also that for this low temperature ($T = 0.75$) the pair correlation function still differs noticeably from the pure hard-sphere value (high-temperature limit).

At high densities the RHNC and EXP results for $g(r)$ are of comparable accuracy, so the superiority of the RHNC results for low densities, as well as its high-density superiority in terms of $S(k)$ that we discuss below, give it an overall advantage. The N3 approximation, on the other hand, does not seem globally superior to the EXP approximation. At lower and intermediate densities (through $\rho = 0.6$), N3 is superior to the EXP for larger r, but a bit worse in the region close to the core. For $\rho = 0.9$, $T = 0.75$, close to the core the N3 approximation becomes superior to the EXP, but its long-range oscillations are somewhat less accurate.

2. *Results for S(k)*

The structure factor $S(k)$ is the three-dimensional Fourier transform of $\rho h(r) + \delta(r)$:

$$S(k) = \int e^{i\vec{k}\cdot\vec{r}}[\rho h(r) + \delta(r)]d\vec{r}\,. \tag{46}$$

For the $S(k)$ associated with the potential given by Eq. (2) we compare various results in our tables.

TABLE V. Internal energy per particle, compressibility factor, and contact values of $g(r)$ for the system with potential given by Eq. (2). RHNC and EXP approximations are compared with Percus-Yevick values for $\rho = 0.1$ (essentially exact at this density) and Monte Carlo values for higher densities.

		βu			$Z = p/\rho kT$			$g(1)$		
ρ	T	MC	RHNC	EXP	MC	RHNC	EXP	MC	RHNC	EXP
0.1	1.20	−0.785	−0.790	−0.755	0.628	0.624	0.637	2.490	2.500	2.372
0.1	1.35	−0.638	−0.638	−0.632	0.716	0.711	0.716	2.181	2.163	2.151
0.2	1.60	−0.96	−0.964	−0.974	0.67	0.651	0.665	1.94	1.903	1.949
0.3	1.35		−1.762	−1.774		0.278	0.313		2.106	2.151
0.5	1.35		−2.766	−2.827		0.06	0.126		2.112	2.209
0.6	1.60	−0.284 ± 0.01	−2.825	−2.858	1.12	1.045	1.089	2.57 ± 0.02	2.507	2.560
0.85	0.85	−7.89 ± 0.01	−7.876	−7.842	0.41 ± 0.1	0.71	0.24	3.94 ± 0.04	4.086	3.860
0.9	0.75	−9.51 ± 0.01	−9.502	−9.414	0.54 ± 0.1	0.96	0.16	4.44 ± 0.04	4.65	4.29
0.91	1.35	−5.32 ± 0.01	−5.33	−5.29	5.41 ± 0.1	5.64	5.15	4.90 ± 0.04	5.01	4.77
0.91	2.74	−2.62 ± 0.01	−2.62	−2.61	8.75 ± 0.1	8.42	8.16	5.15 ± 0.05	5.16	5.03
0.94	1.35		−5.52	−5.47		6.21	6.79		5.47	5.19

For all densities represented except $\rho = 0.1$, Monte Carlo results are shown. At $\rho = 0.1$ the PY results can be regarded as essentially exact, except perhaps for $k = 0.2$, 0.4, and 0.6, where the disparity between the PY and RHNC results [both of which coincide through $O(\rho^2)$ and are therefore expected to be of comparable accuracy in this regime] becomes non-negligible. All MC $S(k)$'s were obtained by Fourier-transforming the MC $g(r)$'s (extended beyond $r = 2.5d$ by the procedure described by Verlet[31]).

For all k, including the first peak and beyond (i.e., $k \geq 5.0$), the EXP and RHNC results are both highly accurate, with the ORPA already more than adequate for many purposes and even the HS result remarkably similar to the MC curve at liquid densities. However, striking differences emerge among the HS, ORPA, EXP, and RHNC results, and between each of them and the MC results, for smaller k. Since

$$\lim_{k \to 0} S(k) = 1 + \rho \int h(r) d\vec{r} = kT \left(\frac{\partial \rho}{\partial p} \right)_T , \tag{47}$$

this means in particular that in these approximations there will be large differences between, and errors in, the thermodynamics computed according to (47). (We have not tabulated QUAD and LIN + SQ results for $S(k)$, because they are so similar in all essential respects to the EXP results.) The most unexpected and disquieting feature of these small-k results is that EXP takes on negative values at liquid-state densities and temperatures. See Tables III and IV.

3. Thermodynamic results

The $S(k)$ tabulation, along with Eq. (47), already provides one route to thermodynamics, via the isothermal compressibility. As we have just seen in Sec. III A 3, it is not an accurate route when used with even the best of the approximations we are considering. The virial theorem

$$Z = \frac{\beta p}{\rho} = 1 - \frac{\beta \rho}{6} \int r g(r) \frac{\partial v(r)}{\partial r} d\vec{r} \tag{48}$$

provides another route, which is more satisfactory but still poor in the low-temperature liquid regime ($\rho = 0.85$, $T = 0.85$; and $\rho = 0.9$, $T = 0.75$), as shown in Table V. Still a third route is via the internal energy, computed from the equation for

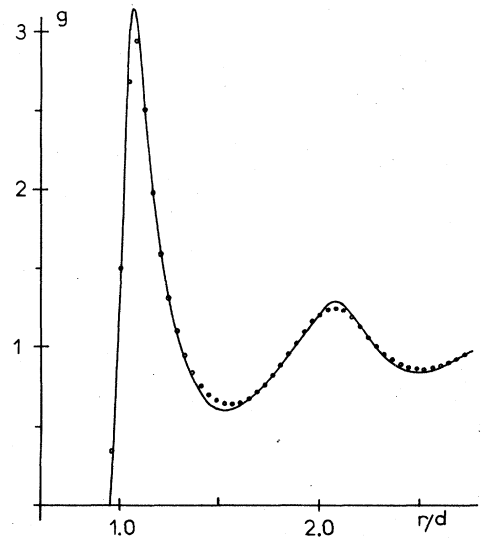

FIG. 1. Radial distribution function $g_0(r)$ for the repulsive part $v_0(r)$ of the Lennard-Jones potential $v_{\mathrm{LJ}} = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6]$, where $v_0(r) = v_{\mathrm{LJ}}(r) + \epsilon$ for $r < 2^{1/6}\sigma$, and $v_0(r) = 0$ for $r > 2^{1/6}\sigma$. Monte Carlo values (open circles) are compared with Andersen-Chandler-Weeks values (solid line) given by Eq. (50), as described in Ref. 17; $\rho\sigma^3 = 0.84$, $kT/\epsilon = 0.75$.

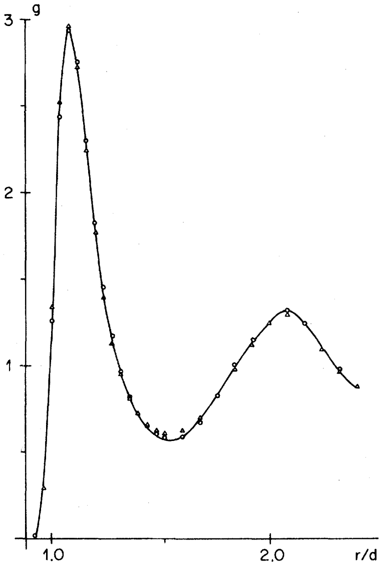

FIG. 2. Radial distribution function for the full Lennard-Jones potential v_{LJ} compared with Monte Carlo (MC) values (open circles) for $\rho\sigma^3 = 0.84$, $kT/\epsilon = 0.75$. For v_{LJ} the EXP values (solid line) are computed as discussed in Ref. 17; RHNC values (triangles) are computed using the MC values for $g_0(r)$, as discussed in text.

the configurational energy per particle, i.e.,

$$u = \tfrac{1}{2}\rho \int g(r)\, v(r)\, d\vec{r}\,. \tag{49}$$

As shown in Table V, the EXP and RHNC approximations both yield highly accurate results for the energy over a wide range of thermodynamic states.

B. Lennard-Jones potential

The use of the potential given by Eq. (2) has enabled us to avoid the problem of introducing a second set of approximations associated with softening a hard core to obtain the repulsive core of the LJ potential. Here we wish to address that question for one typical liquid-state LJ point ($\rho = 0.84$, $T = 0.75$). We plot in Fig. 1 a comparison of the Monte Carlo $g_0(r)$ and the Andersen-Chandler-Weeks (ACW)[17] $g_0(r)$ for the repulsive part $v_0(r)$ of the LJ potential v_{LJ} [i.e., $v_0(r) = v_{LJ}(r) + \epsilon$ for $r < 2^{1/6}\sigma$ and zero for $r > 2^{1/6}\sigma$]. The ACW $g(r)$ is

$$g_0(r) = e^{-\beta v_0(r)}\, y_{HS}(r/d)\,, \tag{50}$$

where y_{HS} is the hard-sphere y function and $d = 1.0222\sigma$. The approximation is adequate but not good. In Fig. 2 we compare on the same scale $g(r)$'s for the full Lennard-Jones potential at $\rho = 0.84$, $T = 0.75$, showing MC, EXP, and RHNC points, using the $g_0(r)$ of (50) in the EXP approximation, as prescribed in Ref. 17, and the MC $g_0(r)$ of Fig. 1 in the RHNC equation (32), with $\Phi = -\beta(v_{LJ} - v_0)$. We see that the EXP approximation is excellent and that the RHNC result is not appreciably better despite our use of exact g_0's in computing it. If we had used exact g_0's in the computation of the EXP $g(r)$, however, it would have been a somewhat inferior approximation, especially in the vicinity of the first minimum ($r \approx 1.5\sigma$). Our conclusion is that there is a serendipitous cancellation of errors involved in the application of the EXP approximation to v_{LJ} via Eq. (50). The result is a highly accurate approximation for a Lennard-Jones liquid that is not surpassed by any of the other approximations considered here. For lower-density states, however, the RHNC approximation is appreciably better; as a result, we would expect it to yield a slightly more accurate approximation globally for a Lennard-Jones fluid.

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