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Solutions of the reference—hypernetted-chain equation with minimized free energy

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We use the Rosenfeld-Ashcroft procedure of modeling the bridge function in the reference—hypernetted-chain integral equation with its hard-sphere values, and choose the sphere diameter so that the free energy of the system is minimized. The resulting integral equation is solved for both the long-range Coulomb potential and the short-range Lennard-Jones potential. The results are in excellent agreement with Monte Carlo data for the thermodynamics and structure of both systems. The method provides an entirely first-principles approach to the theory of the structure and thermodynamics of simple classical liquids.

I. INTRODUCTION

Knowledge of the pair-distribution function $g(r)$ is the essential prerequisite for a complete static description of homogeneous classical liquids whose molecules are taken to interact through effective two-body forces. The context in which much of the work toward this goal has been carried out was established some time ago by a number of authors independently.[1] Their analysis of the density expansion of $g(r)$ has led to two equations which, however, involve *three* unknowns:

$$h(r)=c(r)+\rho\int d\vec{r}\,'h(|\vec{r}-\vec{r}\,'|)c(r') , \tag{1a}$$

$$c(r)=h(r)-\ln[g(r)e^{\beta\phi(r)}]+B(r) . \tag{1b}$$

The first of these is the Ornstein-Zernike equation defining the direct-correlation function $c(r)$ in terms of $g(r)=1+h(r)$. In the second, a closure equation, $\phi(r)$ is the pair potential and $B(r)$ is the sum of "bridge" or "elementary" graphs in the diagrammatic analysis of the two-point functions. Though the same analysis leads to a formal relationship between $B(r)$ and $g(r)$, it involves an infinite sum of highly connected diagrams and so cannot be utilized in practice. This apparent absence of a *simple* functional connecting $B(r)$ to $g(r)$ prevents this scheme from being fully closed and has led to a number of approximate closures, the best known being the Percus-Yevick[2] (PY) and hypernetted-chain[1] (HNC) approximations. These have widely varying theoretical motivations and domains of useful application.[3] In this paper, we present an alternative and entirely first-principles procedure based on a generalization of the HNC approximation,[4–6] a procedure which adheres closely to basic thermodynamic principles and is seen to be equally successful in practice when applied to systems described by both short- and long-range potentials.

In Sec. II, we give a brief derivation, based on a free-energy functional, of the modified— or reference—HNC (RHNC) equation,[4] which approximates $B(r)$ with the bridge function of a short-range (reference) potential $\phi_0(r)$. Following Rosenfeld and Ashcroft,[5] who proposed and extensively documented the view that $B(r)$ should be essentially the same function for all potentials $\phi(r)$, we view $\phi_0(r)$ as an adjustable function. The optimum $\phi_0(r)$ is then determined by requiring that it minimize the free energy,[6] a condition that greatly increases the internal consistency of the RHNC equation and eliminates the undetermined parameters found in earlier work with the RHNC approach. Finally, making the specific choice of a hard sphere $B_0(r)$ with adjustable core size (obtained from the Verlet-Weis[7] and Henderson-Grundke[8] parametrizations), we examine in Sec. III some numerical results for the Coulomb and Lennard-Jones (LJ) potentials. The results of the method, both for structure and for thermodynamics, are in excellent agreement with corresponding Monte Carlo data.

II. THEORY

A closed-form expression for the free energy is most readily obtained by the familiar device of "turning on" the potential $\phi(r)$, but doing so here in two stages; first, from the noninteracting state to the reference potential $\phi_0(r)$, and then from there to the full potential $\phi(r)$. To this end, we write

$$\phi(r;\lambda_0,\lambda_1)=\lambda_0\phi_0(r)+\lambda_1\Delta\phi(r) \tag{2}$$

with $\Delta\phi(r)=\phi(r)-\phi_0(r)$, and then introduce the configurational partition function for the partially interacting system: Thus,

$$Q(\lambda_0,\lambda_1)=V^{-N}\int d\vec{r}^{\,N}\exp\left[-\beta\sum_{\substack{i,j\\ i<j}}\phi(r_{ij};\lambda_0,\lambda_1)\right] . \tag{3}$$

With the corresponding excess free energy defined as

$$\beta A(\lambda_0,\lambda_1)=-\ln Q(\lambda_0,\lambda_1) , \tag{4}$$

we then have

$$\frac{\partial[\beta A(\lambda_0,\lambda_1)]}{\partial\lambda_0}=\tfrac{1}{2}N\rho\int d\vec{r}\,g(r;\lambda_0,\lambda_1)\phi_0(r)$$

$$\equiv F_0(\lambda_0,\lambda_1)\ , \tag{5a}$$

and

$$\frac{\partial[\beta A(\lambda_0,\lambda_1)]}{\partial\lambda_1}=\tfrac{1}{2}N\rho\int d\vec{r}\,g(r;\lambda_0,\lambda_1)\Delta\phi(r)$$

$$\equiv F_1(\lambda_0,\lambda_1)\ . \tag{5b}$$

These may be solved for $A(\lambda_0,\lambda_1)$ by first integrating (5b) to give

$$\beta A(\lambda_0,\lambda_1)-\beta A(\lambda_0,0)=\int_0^{\lambda_1}d\lambda_1'F_1(\lambda_0,\lambda_1')+G(\lambda_0)\ , \tag{6}$$

with $G(\lambda_0)$ an arbitrary function of λ_0. Differentiating (6) with respect to λ_0 and comparing with Eq. (5a) to determine G, we get

$$F_0(\lambda_0,\lambda_1)=\frac{\partial[\beta A(\lambda_0,0)]}{\partial\lambda_0}+\int_0^{\lambda_1}d\lambda_1'\frac{\partial F_1(\lambda_0,\lambda_1')}{\partial\lambda_0}$$

$$+G'(\lambda_0)\ ,$$

i.e.,

$$F_0(\lambda_0,\lambda_1)=\frac{\partial[\beta A(\lambda_0,0)]}{\partial\lambda_0}+F_0(\lambda_0,\lambda_1)-F_0(\lambda_0,0)$$

$$+G'(\lambda_0)$$

$$=F_0(\lambda_0,\lambda_1)+G'(\lambda_0)\ , \tag{7}$$

where we have used $\partial F_1/\partial\lambda_0=\partial F_0/\partial\lambda_1$ to evaluate the integral. Thus, $G'=0$, or G must be a constant, which is easily seen (upon setting $\lambda_0=\lambda_1=0$) to be zero. Equation (6) now expresses the anticipated two-stage "charging" process

$$\beta A(\lambda_0,\lambda_1)=\int_0^{\lambda_0}d\lambda_0'F_0(\lambda_0',0)+\int_0^{\lambda_1}d\lambda_1'F_1(\lambda_0,\lambda_1') \tag{8}$$

or, for the fully interacting system,

$$\beta\frac{A}{N}=\tfrac{1}{2}\rho\int d\vec{r}\int_0^1 d\lambda_0 g(r;\lambda_0,0)\phi_0(r)$$

$$+\tfrac{1}{2}\rho\int d\vec{r}\int_0^1 d\lambda_1 g(r;1,\lambda_1)\Delta\phi(r)\ . \tag{9}$$

The first term in (9) can be evaluated[9] to give the reference-system free energy

$$\beta\frac{A^{(0)}}{N}=\beta\frac{A_1^{(0)}}{N}+\beta\frac{A_2^{(0)}}{N}+\beta\frac{A_3^{(0)}}{N}\ , \tag{10}$$

where

$$\beta\frac{A_1^{(0)}}{N}=-\tfrac{1}{2}\rho\int d\vec{r}\{\tfrac{1}{2}h_0^2(r)+h_0(r)$$

$$-g_0(r)\ln[g_0(r)e^{\beta\phi_0(r)}]\}\ , \tag{11a}$$

$$\beta\frac{A_2^{(0)}}{N}=-\frac{1}{2\rho}\int\frac{d\vec{k}}{(2\pi)^3}\{\ln[1+\rho\tilde{h}_0(k)]-\rho\tilde{h}_0(k)\}\ , \tag{11b}$$

and

$$\beta\frac{A_3^{(0)}}{N}=-\tfrac{1}{2}\rho\int d\vec{r}\int_0^1 d\lambda_0 B(r;\lambda_0,0)\frac{\partial g(r;\lambda_0,0)}{\partial\lambda_0}\ , \tag{11c}$$

with the tilde denoting a Fourier transform. Similarly, the increment in the free energy in turning on the rest of the potential is[4]

$$\beta\frac{\Delta A}{N}=\tfrac{1}{2}\rho\int d\vec{r}\int_0^1 d\lambda_1 g(r;1,\lambda_1)\Delta\phi(r)$$

$$=\beta\frac{\Delta A_1}{N}+\beta\frac{\Delta A_2}{N}+\beta\frac{\Delta A_3}{N}\ . \tag{12}$$

In this last equation

$$\beta\frac{\Delta A_j}{N}=\beta\frac{A_j}{N}-\beta\frac{A_j^{(0)}}{N}\ ,\ j=1,2 \tag{13a}$$

and

$$\beta\frac{\Delta A_3}{N}=-\tfrac{1}{2}\rho\int d\vec{r}\int_0^1 d\lambda_1 B(r;1,\lambda_1)\frac{\partial g(r;1,\lambda_1)}{\partial\lambda_1}\ , \tag{13b}$$

where A_1,A_2 are defined as in Eqs. (11) for the *full* potential $\phi(r)$ and its corresponding correlation functions. The excess free energy with potential $\phi(r)$ is then seen to be given by

$$\beta\frac{A}{N}=\beta\frac{A^{(0)}}{N}+\beta\frac{\Delta A}{N}$$

$$=\beta\frac{A_1}{N}+\beta\frac{A_2}{N}+\beta\frac{A_3^{(0)}}{N}+\beta\frac{\Delta A_3}{N}\ . \tag{14}$$

This is an exact expression. The first two terms are computable, and the third is assumed known through Eq. (10). Only the final term resists evaluation. Clearly, the behavior of $B(r;1,\lambda_1)$ in the core region does not affect the last integral [Eq. (13b)]. Further, what is known about the bridge function suggests that it is relatively short ranged. Hence, it is only the form of $B(r;1,\lambda_1)$ in the region of the first peak of $g(r;1,\lambda_1)$ that matters physically.[5] If we assume that $B(r;1,\lambda_1)$ in this region is indeed relatively insensitive to the change in potential from $\phi_0(r)$ to $\phi(r)$, we may evaluate (13b) approximately as

$$\beta\frac{\Delta A_3}{N}\approx-\tfrac{1}{2}\rho\int d\vec{r}B(r;1,0)[g(r;1,1)-g(r;1,0)]$$

$$\approx-\tfrac{1}{2}\rho\int d\vec{r}B_0(r)[g(r)-g_0(r)]\ . \tag{15}$$

This produces a readily computable expression for the free energy and constitutes the RHNC approximation.

Aside from the need for a repulsive core (as required on general physical grounds) the reference potential $\phi_0(r)$ to this point has been essentially arbitrary. We can now impose a constraint on the selection of ϕ_0 by insisting that it comply with the fundamental condition of the canonical ensemble, namely, the requirement of a minimum free energy. As expressed in Eq. (14), A is a functional of $g(r)$, $g_0(r)$, and $B_0(r)$. Accordingly, a straightforward variation of these functions [using the approximation (15)] then leads to

$$\beta\frac{\delta A}{N}=\tfrac{1}{2}\rho\int d\vec{r}\{c(r)-h(r)+\ln[g(r)e^{\beta\phi(r)}]-B_0(r)\}\delta g(r)-\tfrac{1}{2}\rho\int d\vec{r}[g(r)-g_0(r)]\delta B_0(r)\;. \tag{16}$$

It follows that (i)

$$c(r)=h(r)-\ln[g(r)e^{\beta\phi(r)}]+B_0(r)\;, \tag{17}$$

which is the RHNC closure, and (ii)

$$\rho\int d\vec{r}[g(r)-g_0(r)]\delta B_0(r)=0\;, \tag{18}$$

which is the constraint. If we specialize now to some selected reference potential $\phi_0(r)=\phi_0(r;\sigma,\epsilon)$ which incorporates adjustable length and energy parameters σ and ϵ, Eq. (18) becomes

$$\rho\int d\vec{r}[g(r)-g_0(r)]\sigma\frac{\partial B_0(r)}{\partial\sigma}=0 \tag{19a}$$

and

$$\rho\int d\vec{r}[g(r)-g_0(r)]\epsilon\frac{\partial B_0(r)}{\partial\epsilon}=0\;. \tag{19b}$$

These are the conditions that will determine the optimum values of σ and ϵ that minimize the free energy.

The physical appeal of these integral constraints on $\phi_0(r)$ is underscored when we note that without them the RHNC approximation leads to thermodynamic inconsistency.[4] Specifically, from the free energy we have for the pressure p and internal energy U

$$\beta\frac{p}{\rho}-1=\rho\frac{\partial(\beta A/N)}{\partial\rho}\;, \tag{20}$$

$$\beta\frac{U}{N}=\beta\frac{\partial(\beta A/N)}{\partial\beta}\;. \tag{21}$$

On the other hand, we have the quadratures

$$\beta\frac{p}{\rho}-1=-\tfrac{1}{6}\rho\int d\vec{r}g(r)r\beta\phi'(r)\;, \tag{22}$$

$$\beta\frac{U}{N}=\tfrac{1}{2}\rho\int d\vec{r}g(r)\beta\phi(r)\;. \tag{23}$$

In RHNC these separate determinations disagree. With Eqs. (19), this inconsistency is removed.[6] Further, the thermodynamic relation

$$\left[\frac{\partial U}{\partial V}\right]_T=T\left[\frac{\partial p}{\partial T}\right]_V-p \tag{24}$$

proposed by Hiroike[10] as a test of approximate integral equations [when p and U are obtained, for instance, from Eqs. (22) and (23)] is satisfied.

III. RESULTS

At present the only model of a simple liquid sufficiently well explored to serve as a reference system in the proposed scheme is the hard-sphere fluid. For this system, Verlet and Weis[7] (VW) have constructed a very accurate parametrization of $g_0(r)$, based on the PY equation and augmented with a correction, which incorporates thermodynamic consistency through the Carnahan-Starling[11] equation of state. Henderson and Grundke[8] have provided an extension into the hard-core region for the function

$$y_0(r)=g_0(r)e^{\beta\phi_0(r)}\;, \tag{25}$$

which is then known over the entire range of r. The "series" or "nodal" function for the hard-sphere fluid $S_0(r)=h_0(r)-c_0(r)$ can also be obtained by numerical inversion of $\tilde{S}_0(k)$, where

$$\tilde{S}_0(k)=\frac{\rho\tilde{h}_0^2(k)}{1+\rho\tilde{h}_0(k)}\;. \tag{26}$$

Here $\tilde{h}_0(k)$ is given by the analytic transform of $h_0(r)$. The bridge function then follows from these by using Eq. (1b), i.e.,

$$B_0(r)=\ln y_0(r)-S_0(r)\;. \tag{27}$$

For the hard-sphere potential, Eq. (19b) is of course trivially satisfied since the hard-sphere system has no energy scale. The function $\partial B_0(r)/\partial\sigma$ needed in Eq. (19a) to fix the hard-sphere diameter is determined in the same way as $B_0(r)$. From the explicit differentiation of the parametrized $y_0(r)$, we obtain first

$$\frac{\partial\tilde{S}_0(k)}{\partial\sigma}=\{1-[1+\rho\tilde{h}_0(k)]^{-2}\}\frac{\partial\tilde{h}_0(k)}{\partial\sigma} \tag{28}$$

and, after numerical inversion,

$$\frac{\partial\tilde{B}_0(r)}{\partial\sigma}=\frac{\partial\ln y_0(r)}{\partial\sigma}-\frac{\partial S_0(r)}{\partial\sigma}\;. \tag{29}$$

Because the VW parametrization incorporates into the PY hard-sphere solution a core diameter that is slightly smaller than the actual value of σ, there is a mismatch of the analytic properties of the fitted functions at multiples of σ. Thus, the $\partial B_0(r)/\partial\sigma$ obtained through Eqs. (28) and (29) shows a small but clearly unphysical discontinuity at $r=2\sigma$. It appears to be the case that this anomaly has no significant consequences. Nevertheless, despite the success of the VW model, an equally good parametrization of the hard sphere $g_0(r)$ that more faithfully preserves its analytic character seems desirable for uses such as the present one.

With $B_0(r)$ determined, a solution of Eqs. (1) for the potential of interest proceeds in the conventional fashion. We first rewrite Eqs. (1) in terms of the series function

$$S(r)=h(r)-c(r)\;. \tag{30}$$

This yields

$$c(r)=\exp[-\beta\phi(r)+S(r)+B_0(r)]-1-S(r) \tag{31a}$$

and

$$\tilde{S}(k)=\rho\frac{\tilde{c}^2(k)}{1-\rho\tilde{c}(k)} \tag{31b}$$

which are to be solved iteratively for $S(r)$. Then $g(r)$ is obtained from

$$g(r)=\exp[-\beta\phi(r)+S(r)+B_0(r)]\ . \tag{32}$$

The algorithm may thus be summarized as follows: Determine $B_0(r)$ and $\partial B_0(r)/\partial\sigma$ for hard spheres of diameter σ, solve Eqs. (31), and test the vanishing of Eq. (19a). Repeat this process altering σ until (19a) is satisfied to a numerically adequate degree. Standard root-finding techniques may be used to generate new estimates of σ from earlier guesses; the convergence is generally quite rapid.

To test this method, we have carried out solutions for two physically disparate models of interactions in simple liquids: the long-range Coulomb potential (one-component plasma) and the short-range LJ potential.

A. Coulomb potential

The simplest model of fluids of charged particles, the one-component plasma[12] (OCP) consists of N point particles of charge e immersed in a uniform neutralizing background. This is actually a two-component system in which the second component is taken to be completely structureless. Its state-dependent potential energy

$$U(\vec{r}^N)=\sum_{\substack{i,j\\ i<j}}\frac{e^2}{r_{ij}}-\tfrac{1}{2}N\rho\int d\vec{r}\,\frac{e^2}{r}\ , \tag{33}$$

leads to a thermal average U of the form

$$\beta\frac{U}{N}=\tfrac{1}{2}\rho\int d\vec{r}\,[g(r)-1]\beta\frac{e^2}{r}\ , \tag{34}$$

which differs from Eq. (23) because of the background terms. A similar replacement of $g(r)$ by $g(r)-1$ occurs in other formulas whenever $g(r)$ multiplies $\phi(r)=e^2/r$. Thus, for example, A_1 becomes

$$\beta\frac{A_1}{N}=-\tfrac{1}{2}\rho\int d\vec{r}\,\{\tfrac{1}{2}h^2(r)+h(r)-g(r)\ln[g(r)e^{\beta\phi(r)}]+\beta\phi(r)\} \tag{35}$$

while the pressure is given by

$$\beta\frac{p}{\rho}-1=\tfrac{1}{6}\rho\int d\vec{r}\,[g(r)-1]\beta\phi(r)=\tfrac{1}{3}\beta\frac{U}{N}\ . \tag{36}$$

Finally, the inverse compressibility is obtained from

$$\beta\frac{\partial p}{\partial\rho}=1-\rho\int d\vec{r}\,[c(r)+\beta\phi(r)] \tag{37}$$

rather than the usual expression in which $\beta\phi(r)$ is absent.

Equations (31), with sphere diameter σ adjusted to satisfy (19a), have been solved for the OCP at ten values of

$$\Gamma=\beta\frac{e^2}{a}\ , \tag{38}$$

where a is the ion-sphere radius, i.e.,

$$\tfrac{4}{3}\pi\rho a^3=1\ . \tag{39}$$

Table I lists the computed free energy, internal energy, and inverse compressibility, along with the required σ for each value of Γ. Also shown are the corresponding thermodynamic quantities obtained from a recent parametrization of extensive Monte Carlo (MC) data constructed by Slattery *et al.*[13] The computed free and internal energies are seen to be essentially exact; differences with the MC values are generally less than 0.1%. The inverse compressibility data, while a great improvement over HNC values, do not share the same degree of success; at $\Gamma=100$, for example, the error is 6.3%. An example of the structural data obtained from the solutions is given in Fig. 1, which compares the computed pair-correlation function $g(r)$ with Monte Carlo results[14,15] for $\Gamma=100$. The agreement is seen to be very good. [The odd dip in the computed $g(r)$ curve at $r=2\sigma=3.10a$ is an artifact of the hard sphere $B_0(r)$. It appears to be a reflection of the analytic deficiencies of the VW $g_0(r)$ as mentioned above.] These calculations are based on a grid of 2048 points with an interval size $\Delta r/a\approx 0.01$. Additional details of the numeri-

TABLE I. Exact (Ref. 13) and computed thermodynamics of the OCP.

		$-\beta(A/N)$		$-\beta(U/N)$		$-\beta(\partial p/\partial\rho)$	
Γ	σ/a	Exact	Comp.	Exact	Comp.	Exact	Comp.
10	1.2072	7.102	7.092	7.996	7.990	2.619	2.793
20	1.3318	15.297	15.284	16.670	16.666	6.498	6.606
30	1.3956	23.713	23.698	25.442	25.440	10.414	10.326
40	1.4369	32.238	32.224	34.259	34.259	14.345	13.996
50	1.4669	40.833	40.818	43.103	43.106	18.287	17.642
60	1.4901	49.475	49.461	51.966	51.970	22.235	21.265
70	1.5089	58.152	58.138	60.842	60.848	26.189	24.881
80	1.5246	66.856	66.843	69.729	69.737	30.146	28.485
90	1.5379	75.582	75.571	78.623	78.636	34.105	32.105
100	1.5497	84.327	84.316	87.524	87.539	38.068	35.680

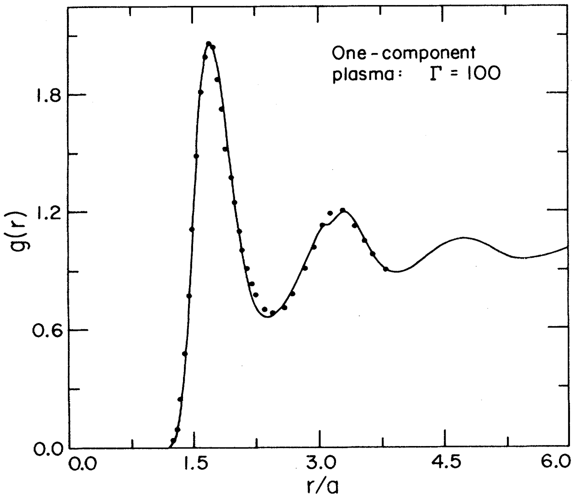

FIG. 1. Computed (line) and MC (circles) pair-distribution function for the OCP at $\Gamma=100$. The anomaly in the full line at $r\approx 3a$ is attributable to the VW fitting procedure for the hard-sphere system (see text).

cal procedure are given by Ng.[16]

Finally, it is worth noting that the OCP results reported above are notably better than those of an otherwise identical calculation using the PY equation for the hard-sphere functions.[6,17] This demonstrates the necessity of actually implementing the requirement of thermodynamic consistency of the reference system that was implicit in the derivation presented in Sec. II.

B. Lennard-Jones potential

As an example of a short-ranged potential typical of insulating liquids, we have applied this procedure to the well-known LJ fluid characterized by the potential

$$\phi(r)=4\epsilon\left[\left[\frac{\sigma}{r}\right]^{12}-\left[\frac{\sigma}{r}\right]^{6}\right], \tag{40}$$

where ϵ and σ set the energy and length scales, respectively. The results below are reported in the reduced units $\rho^*=\rho\sigma^3$ and $T^*=kT/\epsilon$. The free energy, pressure, and internal energy have been computed from Eqs. (14), (22), and (23), respectively. For the compressibility we have used the standard relation

$$\beta\frac{\partial p}{\partial\rho}=S^{-1}(k\to 0)=1-\rho\tilde{c}(k\to 0)\ . \tag{41}$$

Our results are summarized in Table II. The pressure and internal energy are compared with the simulation values obtained by Verlet.[18] For all cases considered, the difference between the present calculations and simulation studies are comparable to the uncertainties in the simulation data. As seen in Table II, we compare the free energy and compressibility values with the semiempirical equation of state for the LJ fluid originating with Levesque and Verlet.[19] The agreement for these quantities is somewhat less impressive, but nevertheless is far better than the results obtained with the standard integral equations. Note that the free energies are always (by calculation) above the desired results. If the exact free-energy functional (14) was used to compute A from the g's obtained by this method, the free energy is required to be above the exact value. The fact that this inequality still appears to hold *in practice* suggests that approximation (15) is indeed an accurate treatment of the free energy. Better results for the compressibility (correct to about 1%, for $T^*\gtrsim 1$) can be obtained by differentiating the pressure given by Eq. (22) along a given isotherm. This makes clear the fact that thermodynamic inconsistencies, though markedly reduced, have not been entirely eliminated.

Figure 2 compares the pair-correlation function $g(r)$ with simulation data for conditions near the triple point.

TABLE II. Computed thermodynamics of the LJ (first lines) compared with simulation and equation-of-state results (second line). Equation-of-state derived values are in parentheses.

ρ^*	T^*	σ	$\beta(A/N)$	$\beta(p/\rho)$	$\beta(U^{\text{ex}}/N)$	$\beta(\partial p/\partial\rho)$
0.85	0.719	1.0196	−4.712	0.424	−6.116	22.9
			(−4.91)	0.36	−6.12	(27.4)
0.85	2.889	0.9537	0.964	4.364	−4.240	16.6
			(0.85)	4.36	−4.25	(17.4)
0.75	1.071	1.0019	−2.160	0.852	−5.166	10.5
			(−2.25)	0.89	−5.17	(9.7)
0.65	1.036	0.9963	−2.240	−0.155	−4.522	3.73
			(−2.30)	−0.11	−4.52	(3.16)
0.65	2.557	0.9619	0.185	2.136	−3.786	6.67
			(0.11)	2.14	−3.78	(6.58)
0.45	1.552	0.9576	−0.769	0.552	−2.982	1.143
				0.57	−2.98	
0.45	2.935	0.9471	0.088	1.377	−2.608	2.67
				1.38	−2.60	
0.40	1.424	0.9438	−0.872	0.382	−2.728	0.461
				0.38	−2.73	

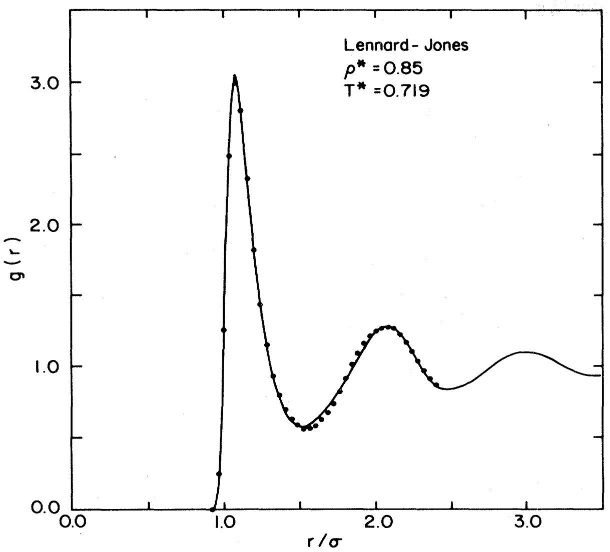

FIG. 2. Computed (line) and molecular dynamics (circles) pair-distribution function for the LJ at $\rho^* = 0.85$ and $T^* = 0.719$.

The agreement is very good, though there remains a small but discernible error in the region from the first minimum to the second maximum. The results at lower densities share the same qualitative deficiency but the magnitude of the error is substantially reduced. As is the case for OCP, there is a small irregularity at $r = 2\sigma$. It is less pronounced for the LJ potential though, and disappears rapidly with decreasing density.

IV. SUMMARY

The approach to simple liquids described in this paper is based on a "universal," widely tested[5] representation of the bridge function $B(r)$, coupled with the fundamental condition of free-energy minimization. It is thus an entirely first-principles approach that can be used with any potential. It is interesting to note that, when applied to the hard-core fluid, this procedure yields a minimum free energy for precisely the *true* hard-sphere diameter. The "computed" results are then just those of the reference—hard-sphere system. Numerical tests of the method for the long-range Coulomb and short-range LJ potentials produce excellent agreement with simulation data for both the thermodynamics and structure of these models. Thermodynamic consistency, however, is only partially achieved. Our results clearly suggest that future improvements in the parametrization of the hard-sphere pair-distribution function $g(r)$ are necessary.

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