

Role of Repulsive Forces in Determining the Equilibrium Structure of Simple Liquids*†

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The different roles the attractive and repulsive forces play in forming the equilibrium structure of a Lennard-Jones liquid are discussed. It is found that the effects of these forces are most easily separated by considering the structure factor (or equivalently, the Fourier transform of the pair-correlation function) rather than the pair-correlation function itself. At intermediate and large wave vectors, the repulsive forces dominate the quantitative behavior of the liquid structure factor. The attractions are manifested primarily in the small wave vector part of the structure factor; but this effect decreases as the density increases and is almost negligible at reduced densities higher than 0.65. These conclusions are established by considering the structure factor of a hypothetical reference system in which the intermolecular forces are entirely repulsive and identical to the repulsive forces in a Lennard-Jones fluid. This reference system structure factor is calculated with the aid of a simple but accurate approximation described herein. The conclusions lead to a very simple prescription for calculating the radial distribution function of dense liquids which is more accurate than that obtained by any previously reported theory. The thermodynamic ramifications of the conclusions are presented in the form of calculations of the free energy, the internal energy (from the energy equation), and the pressure (from the virial equation). The implications of our conclusions to perturbation theories for liquids and to the interpretation of x-ray scattering experiments are discussed.

I. INTRODUCTION

The investigation described in this paper was motivated by Verlet's interesting work on a hard-sphere model for the equilibrium structure of simple liquids¹ and by Barker and Henderson's² application of the high-temperature expansion^{3a} to obtain the thermodynamic properties of Lennard-Jones fluids starting from those of a hard-sphere system. The Verlet and Barker-Henderson work, as well as several other considerations,^{4,5} suggests to us that a theory of liquids should explicitly consider the role the repulsive forces play in determining the structure and thermodynamics of simple liquids. Indeed according to Longuet-Higgins and Widom,⁶ the basic assumption in their successful theory of freezing was that "at high densities the structure of the liquid is mainly determined by the repulsive forces..." Thus we believe it is physically significant and useful to separate the interaction potential into a part containing all the repulsive forces and a part containing all the attractive forces. This separation is distinctly different from the separation into positive and negative parts of the potential frequently used in perturbation theories of liquids.

At liquid temperatures and densities, energy considerations make a nearest neighbor pair of molecules tend to be separated by a distance corresponding to the minimum in the potential, while the effect of the surrounding molecules is to push them closer together. In the balance between these effects, that part of the potential which lies between the minimum of the potential and the zero of the potential is certainly important. As far as the dynamics of nearest-neighbor pairs are concerned, the molecules do not "know" the sign of their mutual potential energy (relative to a zero of

energy in which they are infinitely far apart). They are, however, very much aware of the derivative of that potential (i.e., the force).

By considering the different roles the attractive and repulsive forces play in determining the liquid structure factor, we are able to discover a simple expression for the radial distribution function of a dense Lennard-Jones liquid which is more accurate than that obtained from any previously reported theory. Furthermore, our separation into repulsive and attractive parts leads to an accurate description of the thermodynamics of dense simple liquids using only the first-order term of the high-temperature expansion, which we call the high-temperature approximation. Our method helps explain the surprising accuracy of the high-temperature approximation at the low temperatures we consider.

As stated above, we consider a Lennard-Jones fluid, i.e., a classical system of N molecules in a volume V whose total potential energy can be written as a sum of spherically symmetric pair potentials of the 6-12 type

$$w(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6]. \quad (1)$$

Here, σ has the dimensions of length, and ϵ the dimensions of energy. In terms of these parameters, the frequently used dimensionless representations of the number density, $\rho = N/V$, and the temperature are $\rho^* = \rho\sigma^3$ and $T^* = (\beta\epsilon)^{-1}$, where β is the reciprocal of Boltzmann's constant times the temperature. The structure of the Lennard-Jones system is conveniently described in terms of the two-particle correlation function and its Fourier transform. The correlation function is $h(r) = g(r) - 1$, where $g(r)$ is the usual radial distribution function.⁶ The dimensionless Fourier transform of the

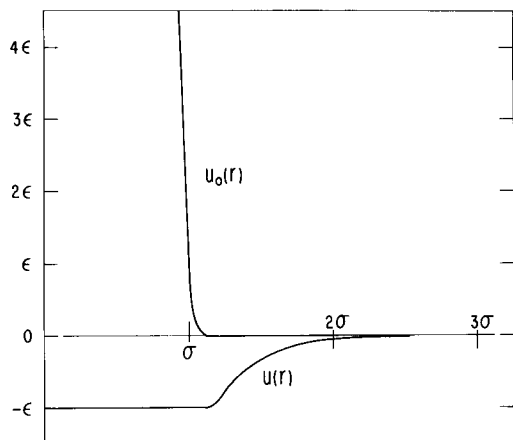


FIG. 1. Separation of the Lennard-Jones potential, $w(r)$, into a part containing all the repulsive forces, $u_0(r)$, and a part containing all the attractive forces, $u(r)$.

correlation function is

$$\hat{h}(k) = \rho \int d\mathbf{r} h(r) \exp(-i\mathbf{k} \cdot \mathbf{r}). \quad (2)$$

The structure factor, $\chi(k)$, is simply $\hat{h}(k)+1$, and it is measured directly by scattering experiments performed on a fluid.

In this paper, attention is focused on $\hat{h}(k)$ for the Lennard-Jones liquid. In particular, for liquid densities ($\rho\sigma^3 \gtrsim 0.4$) we hypothesize and then verify the following statements: (i) *At intermediate and large wave vectors ($k\sigma \gtrsim \pi$), the quantitative behavior of $\hat{h}(k)$ is dominated by the repulsive forces* (the attractive forces are primarily manifested in the small wave vector portion of the spectrum); (ii) *For high densities ($\rho\sigma^3 \gtrsim 0.65$) the behavior of $\hat{h}(k)$ even at small wave vectors ($k\sigma \lesssim \pi$) is at least qualitatively determined by the repulsive forces.* Physically, the first statement is understood once it is recalled that $\hat{h}(k)+1$ represents the linear response of the fluid structure to a disturbance of wavelength $2\pi/k$.⁷ While a short wavelength disturbance will probe both the repulsive and attractive forces in a fluid, it is reasonable that the harsh repulsions, rather than the slowly varying longer ranged attractions, will dominate the response of the fluid to such a disturbance. The second statement is equivalent to asserting that the correlations in a simple liquid are almost entirely due to excluded volume effects when the density is high. While this latter part of our hypothesis has been stated qualitatively by many authors,^{1,2,4,5} its quantitative validity has not been fully exploited.

We consider and attempt to verify the consequence of our hypothesis within the framework of a simple computational scheme. The relevant statistical mechanics are discussed in Sec. II. The numerical ramifications, and thus justification, of the hypothesis are presented in Sec. III. The paper is concluded in Sec. IV with a discussion of the significance of our work.

II. THEORY

For the physical reasons stated above, we separate the intermolecular potential into two parts:

$$w(r) = u_0(r) + u(r). \quad (3)$$

We call $u_0(r)$ the reference system pair potential and $u(r)$ the perturbation potential. For the particular separation in which we are interested, $u_0(r)$ includes all the repulsive forces in the Lennard-Jones potential and $u(r)$ all the attractions. With the additional condition that the reference system pair potential obey the thermodynamic requirement $u_0(r) \rightarrow 0$ as $r \rightarrow \infty$, this separation is unique:

$$u_0(r) = w(r) + \epsilon, \quad r < 2^{1/6}\sigma \\ = 0, \quad r \geq 2^{1/6}\sigma \quad (4)$$

$$u(r) = -\epsilon, \quad r < 2^{1/6}\sigma \\ = w(r), \quad r \geq 2^{1/6}\sigma. \quad (5)$$

These functions are depicted in Fig. 1.

The hypothesis we try to verify in this paper is that for some range of wavevectors $\hat{h}(k) \cong \hat{h}_0(k)$, where $\hat{h}_0(k)$ is the Fourier transform of the reference system two-particle correlation function. In particular, we assert that at moderate and high densities, this approximation is very accurate for $k\sigma \gtrsim \pi$ and at high densities it is accurate for smaller wave vectors as well. In the next section we show that the assertion appears to be true, and as a result we are able to construct a simple approximation for $g(r)$ that is very accurate at high densities.

The thermodynamic ramifications of our postulate can also be discussed. First, we consider the free energy. This is done by introducing a "test" potential

$$w(r; \lambda) = u_0(r) + \lambda u(r), \quad 0 \leq \lambda \leq 1. \quad (6)$$

Then we can relate the Helmholtz free energy of the Lennard-Jones system to the reference system and the perturbation⁸:

$$\frac{\beta \Delta A}{N} = \frac{\beta \Delta A_0}{N} + \frac{\beta \rho}{2} \int_0^1 d\lambda \int g(r; \lambda) u(r) d\mathbf{r}. \quad (7)$$

Here $g(r; \lambda)$ is the radial distribution function in the "test" system, ΔA is the excess free energy (with respect to the ideal gas at the same volume temperature and density):

$$\frac{\beta \Delta A}{N} = \int_0^{\rho} \frac{1}{\rho'} \left(\frac{\beta p}{\rho'} - 1 \right) d\rho', \quad (8)$$

where p is the pressure, and ΔA_0 is the excess free energy in the reference system. With our choice of reference and perturbation interactions, the integral over λ in Eq. (7) represents the effect of turning on the attractive forces in the Lennard-Jones fluid: when $\lambda=0$, $g(r; \lambda)$ is the radial distribution function for the reference system, $g_0(r)$; and when $\lambda=1$, $g(r; \lambda)$ is the

Lennard-Jones $g(r)$. Equation (7) can also be written in terms of the Fourier transforms of the correlation functions:

$$\frac{\beta\Delta A}{N} = \frac{\beta\Delta A_0}{N} + \frac{1}{2}(\beta\rho)\hat{u}(0) + \frac{\beta}{2(2\pi)^3} \int \hat{h}_0(k)\hat{u}(k)d\mathbf{k} + \frac{\beta}{2(2\pi)^3} \int_0^1 d\lambda \int [\hat{h}(k;\lambda) - \hat{h}_0(k)]\hat{u}(k)d\mathbf{k}, \quad (9)$$

where

$$\hat{u}(k) = \int d\mathbf{r} u(\mathbf{r}) \exp(-i\mathbf{k}\cdot\mathbf{r}) \quad (10)$$

and $\hat{h}(k;\lambda)$ is the Fourier transform of the correlation function in the "test" system. According to our hypothesis, only the small wave vector contributions will be significant in the last integral of Eq. (9). Furthermore, the last integral should effectively vanish when the density becomes sufficiently high. Thus, if the hypothesis is true, then for *low* temperatures as well as high the high-temperature approximation

$$\frac{\beta\Delta A}{N} \simeq \frac{\beta\Delta A_0}{N} + [\frac{1}{2}(\beta\rho)\hat{u}(0)] + \frac{\beta}{2(2\pi)^3} \int \hat{h}_0(k)\hat{u}(k)d\mathbf{k} \quad (11)$$

will be only approximately valid, i.e., errors 10% when the density is low, but will become much more accurate as the density increases. The calculations presented in the next section show that this behavior does occur.

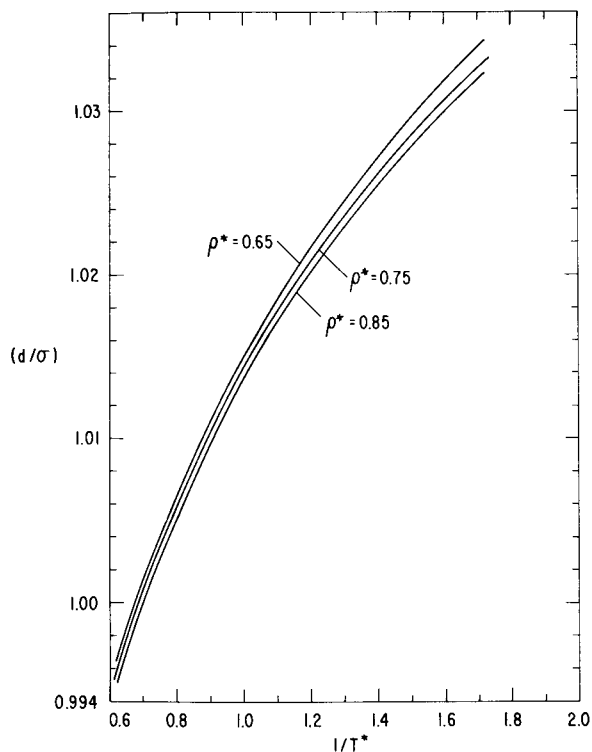


FIG. 2. Plots of $d(\beta, \rho)$ for a few isochores.

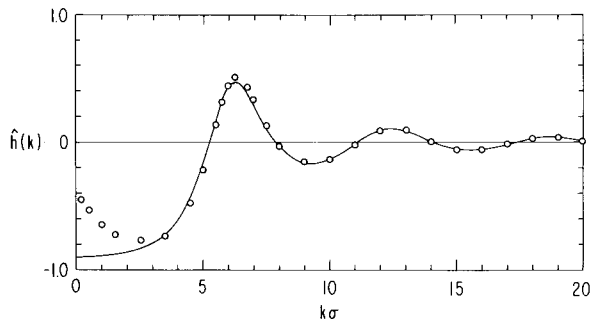


FIG. 3. Plot of $\hat{h}(k)$ for $\rho^*=0.5426$, $T^*=1.326$. The line represents Eq. (15'); the circles are the molecular dynamics results (Ref. 1).

Further tests of our ideas concerning the equilibrium structure of simple liquids are found in the application of the pressure (virial) equation,⁶

$$\beta p/\rho = 1 - \frac{1}{6}(\beta\rho) \int \mathbf{r}(\partial w(\mathbf{r})/\partial \mathbf{r})g(\mathbf{r})d\mathbf{r} \quad (12)$$

and the energy equation for the excess internal energy,⁶

$$\Delta E/N = (\rho/2) \int w(\mathbf{r})g(\mathbf{r})d\mathbf{r}. \quad (13)$$

These equations probe the quantitative behavior of the radial distribution function. According to our hypothesis, when the density is sufficiently high, $g(\mathbf{r})$ is accurately approximated by $g_0(\mathbf{r})$. Thus, by using this approximation to evaluate Eqs. (12) and (13), we have a sensitive test of the hypothesis. Such a calculation is carried out in the next section; the results obtained at high densities ($\rho^* \gtrsim 0.65$) are in good agreement with molecular dynamics results.

To perform the numerical evaluations necessary to verify our hypothesis, we need the thermodynamic properties and two-particle correlation function in the reference system. Rather than perform expensive machine calculations to obtain this information, we have invented an approximation method to describe the reference system. The method appears to be sufficiently accurate for the purposes of this paper. To discuss it, we introduce the function $y_0(\mathbf{r})$ which is defined by the equation

$$g_0(\mathbf{r}) = y_0(\mathbf{r}) \exp[-\beta u_0(\mathbf{r})]. \quad (14)$$

Physically, $y_0(\mathbf{r})$ gives the correlations that exist in the reference system beyond the range of the reference interaction. Since this interaction is harshly repulsive, it seems probable that $y_0(\mathbf{r})$ can be approximated by the similar function appropriate to a hard-sphere system of diameter d , $y_d(\mathbf{r})$. For this reason, we consider the following approximation:

$$g_0(\mathbf{r}) \simeq y_d(\mathbf{r}) \exp[-\beta u_0(\mathbf{r})], \quad (15)$$

or

$$\hat{h}_0(k) = \hat{h}_d(k) + \rho \int d\mathbf{r} y_d(\mathbf{r}) [\exp(-\beta u_0) - \exp(-\beta u_d)] \times \exp(-i\mathbf{k}\cdot\mathbf{r}), \quad (15')$$

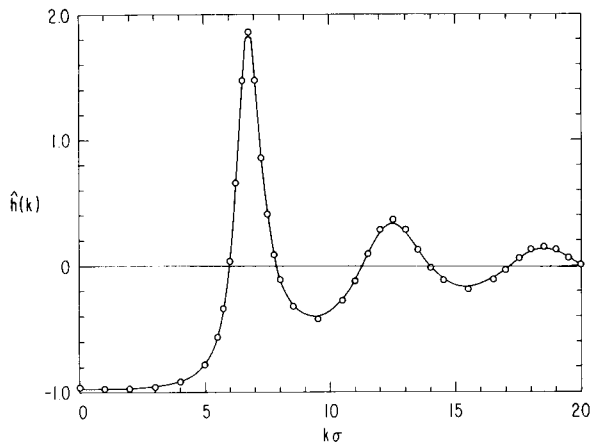


FIG. 4. Plot of $\hat{h}(k)$ for $\rho^*=0.844$, $T^*=0.723$. The line represents Eq. (15'); the circles are the molecular dynamics results (Ref. 1).

where u_d denotes a hard-core repulsion of diameter d . By recalling the role of $\hat{h}_0(k)$ as a linear response function, it is seen that the idea that gives rise to Eq. (15) is equivalent to assuming that for intermediate and long wavelength disturbances, the response of the reference system is accurately given by the response of a hard-sphere system. Thus, by equating the long-wavelength (small k) responses of the reference and hard-sphere systems, we have a physically reasonable density and temperature-dependent criterion for determining d :

$$\int d\mathbf{r}[y_d \exp(-\beta u_0) - 1] = \int d\mathbf{r}[y_d \exp(-\beta u_d) - 1]. \quad (16)$$

Within the framework of the compressibility theorem,

$$(\partial\rho/\partial\beta p)_\beta = 1 + \rho \int h(r) d\mathbf{r}, \quad (17)$$

the criterion given in Eq. (16) approximates the thermodynamics of the reference system with the thermodynamics of the hard-sphere system. For the computations presented in the next section, we use the compressibility theorem to obtain the thermodynamic properties of the reference system. That is, once a value for d is obtained for a particular ρ and β , the free energy of the reference system is taken to be the free energy of the hard-sphere system with diameter d and density ρ .

Note added in proof: Recently, we have shown that the approximate treatment of the reference system described herein is the first step in a rigorous and systematic procedure arising from a cluster-type expansion for the reference system free energy. Both theoretical analysis and direct comparison to Monte-Carlo computer "experiments" indicate that the corrections are very small. [See H. C. Andersen, J. D. Weeks, and D. Chandler, Phys. Rev. (to be published).]

In the treatment described above, the reference system thermodynamics is obtained from the thermodynamics of a hard-sphere fluid; and reliable analytic

expressions for the pressure and free energy of such a fluid do exist in the literature.^{9,10} Unfortunately, this is not all we need. Also required is an analytic form (or tabulated values) for the correlation function (or its Fourier transform) in a hard-sphere system. For lack of anything better, we use the analytic solution of the Percus-Yevick equation.¹¹ Though it is fairly accurate, it represents our major source of error in the computations presented in the next section.

To check the accuracy of our treatment of the reference system, we have applied the method to a fluid in which the pair interactions are the Lennard-Jones potential for $r < \sigma$, and zero for $r > \sigma$. Levesque and Verlet have analyzed this system with Monte Carlo calculations.¹⁰ We find that the agreement between our treatment and the "exact" machine calculations is excellent. For example, at $T^*=1.35$ and $\rho^*=0.8$ we obtain $(\beta p_0/\rho) = 6.11$, and $(\beta \Delta A_0/N) = 2.81$; the Monte Carlo results are $(\beta p_0/\rho) = 6.07 (\pm 0.05)$ and $(\beta \Delta A_0/N) = 2.81$. Incidentally, the Rowlinson "steepness" criterion¹² used by Barker and Henderson² for this reference system is of comparable accuracy. This is not surprising since the Rowlinson criterion and ours should converge to one another in the limit of a very steep reference system repulsion. However, the reference interaction considered in this paper is slightly less harsh than the one considered by Levesque and Verlet, and by Barker and Henderson. The relevance of this fact is apparent when one considers one important difference between our method and the Rowlinson criterion. Ours fits a temperature and density dependent hard-core repulsion to the reference interaction, while Rowlinson's fits a hard core that is only temperature dependent. As a result, our criterion gives the physically reasonable behavior that the effective hard-sphere diameter decreases as density increases (with the temperature fixed) while the Rowlinson method predicts a diameter that is constant. In general we find that for a particular

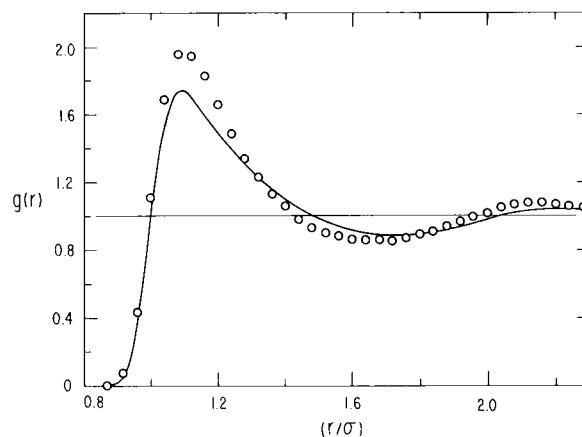


FIG. 5. Plot of $g(r)$ at a moderate density: $\rho^*=0.50$, $T^*=1.36$. The line represents Eq. (15); the circles are the molecular dynamics results (Ref. 1).

repulsive interaction the value of our d is slightly larger than Rowlinson's at low densities and slightly smaller than his at high densities.

III. VERIFICATION

The numerical consequences of our ideas concerning the equilibrium structure of the Lennard-Jones fluid are presented in this section.¹³ First, the structure is considered directly; we present calculations of $\hat{h}(k)$ and $g(r)$ that are performed within the framework of our hypothesis, $\hat{h}(k) \cong \hat{h}_0(k)$ and the approximate treatment of the reference system, Eqs. (15) and (16). Second, we consider the thermodynamic ramifications of our postulate. Comparisons of our results with machine calculations and other theories for Lennard-Jones fluids are given throughout the section.

A. The Equilibrium Structure

The solution of the Percus-Yevick equation for hard spheres gives convenient analytic expressions for $\hat{h}_d(k)$ and $y_d(r)$ ($0 \leq r \leq 2d$). By using these expressions, we solve Eq. (16) for the temperature- and density-dependent d , and calculate $\hat{h}_0(k)$ from Eqs. (15').

Plots of $d(\beta, \rho)$ for a few isochores are given in Fig. 2. These graphs bear a striking qualitative resemblance to Verlet's empirical plots (Fig. 17, Ref. 1) of the temperature- and density-dependent diameter he found could be used to fit a hard-sphere $\hat{h}_d(k)$ to the Lennard-Jones $\hat{h}(k)$. In that work, Verlet first calculated $\hat{h}(k)$ from molecular dynamics experiments. He then found the effective hard-sphere system in which $\hat{h}_d(k)$ resembled $\hat{h}(k)$ with regard to the height of the main peak and the position of the second zero of $\hat{h}(k)$. (The number density of his effective hard-sphere system is only approximately equal to that of the Lennard-Jones system.) The interesting observation that followed was

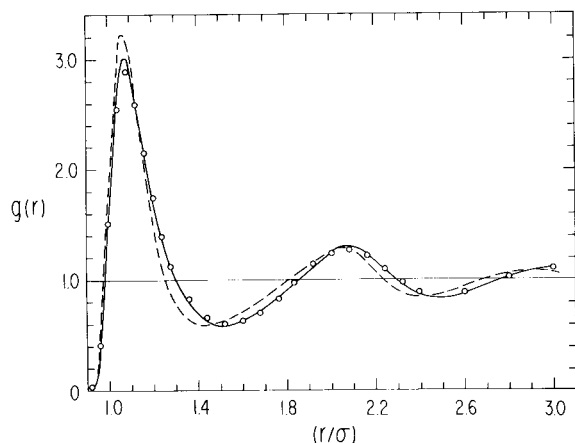
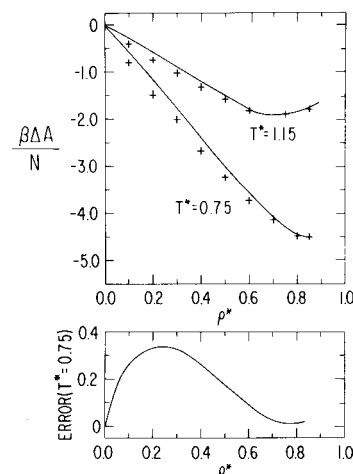


FIG. 6. Plot of $g(r)$ at a high density: $\rho^*=0.85$, $T^*=0.88$. The line represents Eq. (15); the circles are the molecular dynamics results (Ref. 1); and the dashed line represents the numerical solution of the Percus-Yevick equation for the Lennard-Jones potential (Ref. 14).

FIG. 7. Plots of $\beta\Delta A/N$ for two isotherms. In the upper graph, the line represents Eq. (18); the crosses are the Monte Carlo results (Ref. 16). In the lower graph, the "Error" denotes the difference at $T^*=0.75$ between the $\beta\Delta A/N$ as obtained from Eq. (18) and $\beta\Delta A/N$ as obtained from Monte Carlo calculations.



that in the range $\pi \lesssim k\sigma \lesssim 5\pi$, the hard-sphere function, $\hat{h}_d(k)$, and the Lennard-Jones function, $\hat{h}(k)$, were very similar even though the hard-sphere parameters (d and ρ) were chosen to match only a small number of properties of $\hat{h}(k)$. We believe that Verlet was actually observing the behavior which we have postulated to be true: for $k\sigma \gtrsim \pi$, $\hat{h}(k)$ is dominated by the repulsive forces. These forces are what define the reference system in this paper. Furthermore, from Eq. (15'), it can be verified that differences between the reference system and the appropriate hard-sphere system are not appreciable in $\hat{h}(k)$ until we reach large wave vectors, $k\sigma \gtrsim 5\pi$.

To strengthen our argument, we plot our $\hat{h}_0(k)$ for two thermodynamic states and compare with Verlet's molecular dynamics at the same states. In Fig. 3, the density is sufficiently low to illustrate the dramatic discrepancy and then similarity between $\hat{h}_0(k)$ and the true Lennard-Jones $\hat{h}(k)$ as we pass from small to large wave vectors. Incidentally, for the state considered in Fig. 3, the value of d obtained from Eq. (16) and then used in Eq. (15') is $(1.005)\sigma$; the reported value for Verlet's hard-sphere model d is $(1.0)\sigma$. In Fig. 4, we see that at high densities that excluded volume effects dominate the correlations to such an extent that $\hat{h}_0(k)$ is also in good agreement with the Lennard-Jones $\hat{h}(k)$ for small wave vectors. The value of d for the thermodynamic state considered in Fig. 4 is $(1.025)\sigma$, Verlet's hard-sphere model d is $(1.026)\sigma$.

While these results above provide support for our hypothesis, we also want to discuss the structure as described by the Fourier inversion of $\hat{h}(k)$, namely the radial distribution function, $g(r)$. In Fig. 5, a plot of $g_0(r)$ as described by Eq. (15) is compared with the "exact" molecular dynamics Lennard-Jones $g(r)$.¹ Here, the thermodynamic state is similar in density and temperature to the one considered in Fig. 3. The rather poor agreement between $g_0(r)$ and $g(r)$ for all r is simply a manifestation of the discrepancy between $\hat{h}_0(k)$ and $\hat{h}(k)$ for small k . This juxtaposition of the

TABLE I. Approximate and Monte Carlo results for the excess free energy on the $T^*=0.75, 1.15$ and 1.35 isotherms. Column 3 lists results obtained from the high-temperature approximation with our potential separation and our treatment of the reference system. Machine calculation results from Refs. 10 and 16 are given in Column 4. The results obtained from the Barker-Henderson and Rasaiah-Stell treatments of the high-temperature approximation are given in Columns 5 and 6, respectively. The Barker-Henderson results were calculated by us. Though several thermodynamic states on the 0.75 and 1.15 isotherms are metastable, comparison between the approximate and Monte Carlo results are meaningful since both calculations constrain the system in the same way to a one-phase fluid.

T^*	ρ^*	$-\beta\Delta A/N$			
		Eq. (21)	Monte Carlo	Barker-Henderson	Rasaiah-Stell
0.75	0.1	0.55	0.81	0.57	0.56
	0.2 ^a	1.15	1.48	1.16	1.15
	0.3 ^a	1.78	2.11	1.77	1.76
	0.4 ^a	2.42	2.68	2.38	2.37
	0.5 ^a	3.06	3.23	2.96	2.96
	0.6 ^a	3.65	3.74	3.48	3.48
	0.7 ^a	4.14	4.17	3.90	3.88
	0.8 ^a	4.46	4.47	4.16	4.15
1.15	0.84	4.51	4.54	4.20	
	0.1	0.29	0.39	0.30	0.30
	0.2	0.60	0.73	0.61	0.60
	0.3	0.92	1.05	0.92	0.89
	0.4 ^a	1.23	1.33	1.20	1.17
	0.5 ^a	1.51	1.59	1.46	1.41
	0.55 ^a	1.63	1.69	1.56	
	0.6 ^a	1.74	1.79	1.65	1.58
	0.65	1.82	1.84	1.72	
	0.75	1.88	1.88	1.76	
0.85	1.77	1.78	1.63		
1.35	0.1	0.22	0.30	0.23	0.22
	0.2	0.45	0.56	0.46	0.44
	0.3	0.68	0.80	0.69	0.65
	0.4	0.90	1.00	0.89	0.84
	0.5	1.09	1.16	1.05	0.99
	0.6	1.22	1.26	1.16	1.07
	0.7	1.26	1.29	1.18	1.05
	0.8	1.16	1.19	1.07	0.90

^a Corresponds to one-phase metastable states in the liquid-gas two-phase region.

k and r -space representations of the structure emphasizes the convenience of considering the Fourier transform of the correlation function rather than the actual correlation function. While the attractive forces appreciably contribute to only a small part of the spectrum, $k\sigma \lesssim \pi$, the attractions and repulsions contribute (at low and moderate densities) to $g(r)$ for all $r \gtrsim \sigma$. Thus, it is difficult to say what type of interaction produces a certain effect in $g(r)$. Our results indicate that this difficulty is not encountered when $\hat{h}(k)$ is considered.

When we reach high enough densities, the repulsions are the dominant force in both the r and k -space representations of the structure. In viewing Fig. 4, this is no surprise, since we see that at high densities the Fourier transform of the correlation function for the reference system is similar to that of the Lennard-Jones system at small k as well as large. In Fig. 6 a plot of $g_0(r)$ as described in Eq. (15) is compared with the "exact" Lennard-Jones $g(r)$ for a thermodynamic state similar to that considered in Fig. 4. The agreement between $g_0(r)$ and $g(r)$ is excellent. To emphasize how good the agreement is, we have also plotted the $g(r)$ obtained by solving the Percus-Yevick equation for the Lennard-Jones fluid.¹⁴ Although the Percus-Yevick theory is fairly accurate when applied to harshly repulsive systems, it is seen that at high densities it is considerably less accurate when applied to systems with longer-ranged attractive forces.

B. Thermodynamics

As discussed in Sec. II, the truth of our hypothesis on the equilibrium structure has direct ramifications on the thermodynamic properties of a fluid. In particular, the high-temperature approximation [see Eq. (11)],

$$(\beta\Delta A/N) \simeq (\beta\Delta A_0/N) + \frac{1}{2}(\beta\rho) \int d\mathbf{r} g_0(r) u(r) \quad (18)$$

should be only approximately valid (errors $\sim 10\%$) at low densities but become increasingly more accurate as the density increases.

We have evaluated the right-hand side of Eq. (18) at various temperatures and densities. Some of our results are tabulated in Tables I and II, and graphed in Fig. 7. The numerical integrations were performed by using our approximate treatment of the reference system, Eqs. (15) and (16), and the solution of the Percus-Yevick equation for a hard-sphere fluid.¹¹ This solution gives the analytic form of $y_a(r)$ for $0 \leq r \leq 2d$, and the analytic form of the Laplace transform of r times the hard-sphere radial distribution function. With this information, a simple extension of a method proposed by Frisch *et al.*¹⁵ allows us to perform the integrations quickly and accurately [the only errors being the Percus-Yevick equation itself and our approximate treatment of $g_0(r)$]. Furthermore, the hard-sphere thermodynamic data needed to complete the evaluation of Eq. (18) [see Eq. (17) and comments following it] were obtained from Levesque and Verlet's accurate polynomial fit of the machine calculations on hard spheres.¹⁰ Tables I and II, and the plots in Fig. 7 show how the excess free energy as approximated in Eq. (18) [or Eq. (11)] does converge at high densities ($\rho^* \gtrsim 0.65$) to the values predicted by machine calculations.^{10,16} The temperatures considered are sufficiently low ($T^* \lesssim 1.35$) that the accuracy is not a trivial consequence of the possible rapid convergence of the high-temperature expansion. The critical temperature is approximately 1.35 (or slightly lower); at higher temperatures a num-

ber of approximate theories accurately predict the thermodynamic behavior of the Lennard-Jones gas.^{2,17}

In Tables I and II we also compare the numerical values arrived at through Eq. (18) [or Eq. (11)] with those predicted by other theories and machine calculations. One important aspect of our work becomes apparent when the Barker-Henderson² results are considered. These are the values for the excess free energy obtained from the high-temperature approximation in the following way: The reference interaction is the Lennard-Jones potential for $r < \sigma$, the perturbation is the Lennard-Jones potential for $r > \sigma$; the reference system is then approximated by a hard-sphere system via the Rowlinson criterion, and the Percus-Yevick approximation for $g_d(r)$ is used. From the tables it is seen that with this treatment, the high-temperature approximation gives free energies with an error of the order of 10% for liquid temperatures ($T^* < 1.35$), and the accuracy does not improve as the density increases. This 10% error in the high-temperature approximation is simply a consequence of the interaction separation. For the high-temperature approximation to be accurate, the structure of the reference system must closely resemble the structure of the total Lennard-Jones system. The Barker-Henderson reference system does not satisfy this condition at liquid temperatures. However, our separation into repulsive and attractive forces satisfies this condition when the density is high enough, and as a result, our values of the free energy are virtually indistinguishable from the Monte Carlo predictions for $\rho^* \gtrsim 0.65$.

We have also tabulated the values for the excess free energy recently obtained by Rasaiah and Stell.¹⁷ In these calculations, the pair potential is written as a hard-core repulsion plus a perturbation part which is defined as the Lennard-Jones potential minus the hard core. Rasaiah and Stell recall the fact that the high-temperature approximation gives an upper bound to the Helmholtz free energy,¹⁸ and use it as a variational principle to determine the hard-core diameter. Their results, while indeed upper bounds to the "exact" machine calculations, are not quite as accurate as the Barker-Henderson results. Our results would also be rigorous upper bounds to the excess free energy if we had an exact treatment of the reference system. We use an approximation scheme and thus cannot guarantee that we do obtain such a bound, though in all cases tested, we do obtain free energies higher than those predicted by machine calculations.

The thermodynamic results presented here emphasize the importance of considering the precise nature of the equilibrium structure in fluids. In particular, we believe it is important to understand how different forces affect the liquid structure. In so doing, we may learn what kind of theory will yield a useful description of the equilibrium structure and thermodynamics of the entire liquid state. We believe a theory which explains and uses our hypothesis may provide a simple

TABLE II. Approximate results for the excess free energy on the $\rho^* = 0.88, 0.85, 0.75,$ and 0.65 isochores. Column 3 lists results obtained from the high-temperature approximation with our potential separation and our treatment of the reference system. In Column 4 the results from an empirical equation of state (obtained by fitting a polynomial to molecular dynamics results for the pressure, Ref. 10) are listed. These values for $-\beta\Delta A/N$ are generally too high at temperatures below $T^* \lesssim 1.35$, and not very reliable for higher temperatures. In Column 5 the results for the Barker-Henderson treatment (calculated by us) of the high-temperature approximation are given.

ρ^*	T^*	$-\beta\Delta A/N$		
		Eq. (21)	Empirical	Barker-Henderson
0.88	1.095	1.94	1.99	1.80
	0.94	2.84	2.88	2.65
	0.591	6.80	6.86	6.30
0.85	2.889	-0.93	-0.86	-0.94
	2.202	-0.44	-0.37	-0.47
	1.214	1.51	1.55	1.39
	1.128	1.86	1.91	1.73
	0.880	3.32	3.35	3.10
	0.782	4.18	4.21	3.90
	0.786	4.14	4.17	3.86
	0.760	4.41	4.44	4.10
	0.719	4.87	4.90	4.53
	0.658	5.66	5.71	5.26
0.591	6.74	6.81	6.25	
0.75	2.849	-0.56	-0.50	-0.58
	1.304	1.36	1.41	1.27
	1.069	2.22	2.26	2.08
	1.071	2.21	2.25	2.07
	0.881	3.27	3.30	3.06
	0.827	3.66	3.69	3.43
0.65	2.557	-0.18	-0.20	-0.11
	1.585	0.79	0.85	0.73
	1.036	2.24	2.30	2.12
	0.900	2.90	2.96	2.74

means to this end. A simple method is desirable since the straightforward use of subsequent terms in the high-temperature expansion is computationally difficult: Expensive machine calculations are required to determine the second-order term in the thermodynamic high-temperature expansion^{3a} (the local- and macroscopic-compressibility approximations^{2a} are inadequate^{2b,10}); and the second-order term for structure^{3b} may be impossible to evaluate (with current generation computers).

Finally, we consider the calculations of the pressure from the virial equation, and the excess internal energy from the energy equation. In the first part of this section we tried to verify that the approximation $g(r) \cong g_0(r)$ is very accurate at high densities. As further verification, we use this approximation to evaluate $\beta p/\rho$ and $\Delta E/N$ through Eqs. (12) and (13), respectively.

TABLE III. Approximate and molecular dynamics results for the pressure and internal energy. Columns 3 and 5 contain our results obtained by using the approximation $g(r) \cong g_0(r)$ in Eqs. (12) and (13), respectively. Molecular dynamics results (Refs. 19 and 10) are listed in Columns 4 and 6; the error bounds for these machine calculations are ± 0.05 .

ρ^*	T^*	$\beta p/\rho$		$-\Delta E/N\epsilon$	
		Pressure equation	Molecular dynamics	Energy equation	Molecular dynamics
0.88	1.095	3.42	3.48	5.92	5.85 ^a
	0.94	2.87	2.77	6.08	6.04 ^a
	0.591	0.18	-0.18	6.47	6.53
0.85	2.889	4.27	4.36	4.35	4.25
	2.202	4.11	4.20	4.85	4.76
	1.214	3.05	3.06	5.65	5.60
	1.128	2.82	2.78	5.73	5.69
	0.88	1.82	1.64	5.96	5.94
	0.782	1.20	0.98	6.06	6.04
	0.786	1.23	0.99	6.05	6.05
	0.76	1.03	0.82 ^a	6.08	6.07
	0.719	0.69	0.36 ^c	6.12	6.12
	0.658	0.09	-0.20	6.19	6.39 ^b
	0.591	-0.75	-1.20	6.26	6.46 ^b
	0.75	2.849	3.05	3.10	4.09
1.304		1.63	1.61	4.99	5.02
1.069		0.90	0.90	5.15	5.19
1.071		0.91	0.89	5.15	5.17
0.881		-0.02	-0.12	5.28	5.31
0.827		-0.38	-0.54	5.32	5.38
0.65	2.557	2.08	2.14	3.78	3.78
	1.585	1.21	1.25	4.20	4.23
	1.036	-0.23	-0.11	4.46	4.52
	0.90	-0.91	-0.74	4.52	4.61

^a Revised results (see Ref. 10).

^b Revised results (see Ref. 10). The unrevised values were 6.19 at $T^* = 0.658$, and 6.26 at $T^* = 0.591$.

^c Molecular dynamics results for $\rho^* = 0.85$ and $T^* = 0.72$ (Ref. 10) predict $\beta p/\rho = 0.43$.

Once again the integrals are performed within the context of our approximate treatment of the reference system: Eqs. (15), (16), and the analytic solution of the Percus-Yevick equation for hard spheres. The results are tabulated and compared with molecular dynamics data¹⁹ in Table III. Since the virial and energy equations are sensitive probes of the structure, the agreement between our simple calculations and the machine calculations is seen to afford further verification of our hypothesis. In Table IV we also compare our results with those obtained from numerical solutions of the Percus-Yevick equation for the Lennard-Jones fluid.¹⁴ Again we emphasize that our present method yields results of this accuracy only at high densities ($\rho^* \gtrsim 0.65$). At lower densities, and for a number of other purposes, the numerical solution of the Percus-Yevick equation for the Lennard-Jones fluid is to be preferred.

Of course, values of the pressure (or any other thermodynamic function) can also be obtained by numerically differentiating the free energy [see Eq. (8)].

We have found the use of the high-temperature approximation to obtain the pressure in this way is even more accurate than the application of the virial equation. However, such results are not relevant to the theme of this paper which is to verify a specific hypothesis regarding the structure of simple liquids. One finds that the reference system pressure is a large positive number ($\beta p_0/\rho$ is around 8 at $\rho^* \sim 0.7$), and the perturbation contribution is about the same size but negative. The two add together to give a small number, the quantitative accuracy of which is not entirely meaningful. We say this because errors of less than 1% in the reference pressure can produce a 10% error (or worse) in the total pressure, and such errors must be expected due to the approximate treatment of the reference system. These inaccuracies arise from the attempt to relate properties of an effective hard-sphere system with those of the reference system, and the errors inherent in the expressions used to represent the hard-sphere properties. The differences between our results and the machine calculation results for the

TABLE IV. Approximate and molecular dynamics results for the pressure and internal energy as obtained from Eqs. (12) and (13), respectively. Columns 3 and 6 give the values obtained by applying the approximation $g(r) \cong g_0(r)$. Columns 4 and 7 give the molecular dynamics results (Ref. 19); the error bounds here are ± 0.05 . The results obtained by using the solution of the Percus–Yevick equation for $g(r)$ (Ref. 14) are given in Columns 5 and 8.

ρ^*	T^*	$\beta p/\rho$			$-\beta \Delta E/N$		
		This work	MD	PY	This work	MD	PY
0.85	1.128	2.82	2.78	3.57	5.08	5.05	4.98
	0.88	1.82	1.64	3.17	6.77	6.75	6.61
	0.786	1.23	0.99	2.97	7.70	7.70	7.51
	0.719	0.69	0.36	2.82	8.52	8.51	8.28

pressure are comparable to the possible errors in the description of the reference system. We note that at liquid temperatures the numerical differentiation of the free energy obtained from the Barker–Henderson treatment of the high-temperature approximation² yields pressures that are slightly better than the ones we obtain. However, their results are worse when they use a Monte Carlo (rather than Percus–Yevick) hard-sphere radial distribution function.^{2b} This merely indicates that the accuracy of calculations of the pressure by differentiating the free energy obtained from the high-temperature approximation is sensitive to slight errors in the reference system pressure and pair-correlation function. Hence, the quantitative accuracy (or lack of it) for pressures obtained in this way is not an entirely meaningful test of the high-temperature approximation and certainly does not provide a meaningful test of the present ideas concerning the pair-correlation function.

IV. DISCUSSION

The four basic conclusions of this paper are the following: (a) For simple liquids with pairwise additive intermolecular potentials at moderate to high densities, it is conceptually worthwhile to regard the pair potential as a sum of repulsive and attractive parts, rather than a sum of positive and negative parts. (b) To unravel the effects of the various parts of the potential on the structure of the liquid, it is useful to consider the structure factor of the liquid (the Fourier transform of the pair correlation function) rather than the pair correlation function itself. (c) For $k\sigma \gtrsim \pi$, the attractive part of the potential has very little effect on the structure factor for reduced densities greater than about 0.5,²⁰ i.e., for these values of k , the structure factor is nearly equal to that of a hypothetical fluid which has only the repulsive forces. (d) The attractive part of the potential manifests itself primarily in the small k ($k\sigma \lesssim \pi$) part of the structure factor, but this effect decreases as the density increases.

The purpose of this paper is to establish the validity of our basic hypothesis [(c) and (d) above]. Many of the results tabulated and graphed above are sufficiently

accurate as to constitute an empirical justification for the hypothesis. We have given physical arguments to make these ideas plausible and used them to develop a numerically accurate way of obtaining thermodynamic properties for dense liquids. We have also discovered a very simple and accurate approximation for the radial distribution function for dense liquids, namely $g(r) \cong g_0(r)$. But we are still lacking a fundamental statistical mechanical theory to explain our ideas. If we had such a theory and could understand why the attractive part of the potential has such a small effect on the structure of the liquid, we could probably calculate this effect and the net result would be a highly accurate theory of the liquid state extending over a wide range of temperature and density.

It should be emphasized that all the conclusions drawn in this paper have been tested on the Lennard–Jones system only. This indicates another reason for pursuing a theoretical explanation of our hypothesis. In so doing one should be able to determine the class of systems for which our ideas are valid. A principal difference between the repulsive and attractive forces in the Lennard–Jones fluid is that the former varies far more rapidly in space than the latter. This difference may explain the different effects of the two on the structure of the liquid. Thus, when the spatial variations of the repulsions and attractions are comparable (as in a square-well system), our hypothesis may be invalid.²¹

Though we are stressing the need for further research, many of our ideas are simple enough computationally that they can now be applied to experimental studies. For example, when Verlet calculated $\hat{h}(k)$ from his molecular dynamics “experiments” he compared his results with those obtained from x-ray scattering experiments on liquid argon. The particular experiment of interest here is that of Mikolaj and Pings²² which is depicted by Verlet¹ in his Fig. 6. Verlet’s work shows that the main peak in $\hat{h}(k)$ for argon is slightly higher than, and slightly out of phase with, the peak in the Lennard–Jones $\hat{h}(k)$. In the context of our work, a discrepancy of this sort would indicate that the Lennard–Jones potential, with the parameters used by Verlet,

is not an accurate representation of the *repulsive* forces in liquid argon. Information about the repulsive forces could be obtained from the study of x-ray structure factors if the experiment were performed for a wide variety of densities and temperatures. For each density and temperature, an effective hard-sphere diameter could be obtained by fitting the Percus-Yevick hard-core structure factor to the experimental data for $k \geq \pi/\sigma$. (According to our hypothesis, this one parameter is all the information that can be obtained about the repulsive forces from an experiment done at one temperature and density.) From the density and temperature dependence of this parameter, information about the repulsive part of the potential can be obtained with the aid of Eq. (16) in much the same way as intermolecular potential information is obtained from the temperature dependence of the second virial coefficient of a gas with the aid of the statistical mechanical expression for this latter quantity. This program can be carried out even before we have an adequate theory of the effect of the attractive part of the potential on the small k part of the structure factor. (Our work also indicates that at high densities it may be impossible to get meaningful information about the attractive part of the potential from x-ray experiments.)

In the effort to avoid expensive calculations, we have used an approximate treatment of the reference system which does produce some error. Probably the most significant source of the inaccuracies was the use of the Percus-Yevick equation for y_d . However, we do not think the errors are significant enough to alter the conclusions of this paper. A comparison of the Percus-Yevick y_d with the molecular dynamics y_d given by Alder and Hecht²³ shows that the main error in the Percus-Yevick y_d occurs at values of r near the point of contact ($r/d \gtrsim 1.1$). However, the effect of this error is made less significant in our final expression for g_0 , Eq. (15), because of the exponential decrease of g_0 within the range of the reference system potential u_0 . We believe that, except perhaps at the highest densities, our calculated values for $\beta\Delta A/N$ and $\beta\Delta E/N$ should agree within about a percent or two with those that might be obtained from an exact treatment of the reference system. When the density does become very large, however, the Percus-Yevick approximation for hard spheres is not reliable, and significant errors must be expected. It would be worthwhile if extensive tables of reliable computations of hard-sphere functions were published. This would help us add to the credibility of our work, and help workers who wish to use perturbation theories to calculate pressures, which, as we have discussed in Sec. III, are sensitive to small errors in the reference system even at moderate densities.

Note added in proof: L. Verlet and J. J. Weis (to be published) have performed Monte-Carlo calculations for our reference potential and for the test potential, Eq. (6), and have shown that the high temperature

approximation is very accurate near the triple point. They also have shown that Eqs. (15) and (16) give an excellent representation of the reference system radial distribution function if accurate hard sphere data is used, rather than the Percus-Yevick approximation used herein. Barker and Henderson (to be published) have also calculated the reference system $g_0(r)$ by Monte-Carlo methods and have explicitly shown that the differences between $g_0(r)$ and the Lennard-Jones $g(r)$ are indeed small. However, an extremely accurate radial distribution function is required to obtain good results for the pressure from the virial equation, and Verlet has shown that the differences between $g(r)$ and $g_0(r)$ are sufficient to cause the latter to give inaccurate virial pressures for the Lennard-Jones system at low temperatures. The errors in the Percus-Yevick equation used herein apparently reduces the differences between $g(r)$ and the approximate $g_0(r)$ and cause the surprisingly accurate results for the virial pressure given in Tables III and IV.

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⁵ The idea of considering the different roles played by repulsive and attractive forces in fluids probably originates with Van der Waals. The usual derivations of the Van der Waals equation of state implicitly assumes (among other things) that the fluid structure is formed by the repulsive forces [see N. G. van Kampen, *Phys. Rev.* **135**, 362A (1964)].

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⁷ The formula cited here is $-\delta\hat{\rho}(k)/\delta\beta U(k) = \hat{h}(k) + 1$, where $\hat{\rho}(k)$ is the Fourier transform of the ensemble average of the particle density, and $U(k)$ is a Fourier coefficient of an external disturbance. See J. Yvon, *Nuovo Cimento Suppl.* **9**, 144 (1958).

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¹⁶ J. Hansen and L. Verlet, *Phys. Rev.* **184**, 151 (1969). In Table I of this paper, βF_i is $(\beta\Delta A/N) + \ln\rho^* - 1$.

¹⁷ J. Rasaiah and G. Stell, *Mol. Phys.* **18**, 249 (1970). In Table II of this paper, $\beta F/\rho$ is $(\beta\Delta A/N) + \ln\rho^* - 1$. Calculations of the pressure and other properties using the variational procedure employed by Rasaiah and Stell were reported by G. A. Mansoori and F. B. Canfield, *J. Chem. Phys.* **51**, 4958 (1969).

¹⁸ See, e.g., T. Lukes and R. Jones, *J. Phys. A* **1**, 29 (1968); G. H. Hardy, J. E. Littlewood, and G. Polya, *Inequalities* (Cambridge U. P., New York, 1952), Sec. 6.14.

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²⁰ This might be true even for lower densities. Verlet's molecular dynamics results (Ref. 1) do not extend much below this density, so at present we can not establish the lower limit of density at which this statement is accurate.

²¹ It is noted, however, that the $g(r)$ for square-well and hard-sphere fluids are similar at high densities; see Ref. 4.

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