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On the Equilibrium Structure and Thermodynamics of Simple Liquids*

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ON THE EQUILIBRIUM STRUCTURE AND THERMODYNAMICS OF SIMPLE LIQUIDS*

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ABSTRACT

The equilibrium structure and thermodynamics of a simple liquid is discussed. The particular system considered in our calculations is the Lennard-Jones liquid in which the intermolecular interaction is the pairwise additive 6-12 potential, $w(r)=4\epsilon[(\sigma/r)^{12}-(\sigma/r)^6]$. The potential is separated into two parts, a reference part containing all the repulsive forces and a perturbation containing all the attractive forces. (This separation is distinctly different from the often-used separation of the potential into positive and negative parts.) It is found that the effects of the two parts of the potential on the structure of the liquid are most easily discussed in terms of the structure factor (or equivalently, the Fourier transform of the pair-correlation function) rather than the pair-correlation function itself. For values of the Fourier transform variable, k , greater than about π/σ , where σ is the distance at which the intermolecular potential is zero, the attractive part of the potential has very little effect on the structure factor for reduced densities greater than about .5; i.e., for these values of k , the structure factor is equal to that of a hypothetical reference fluid which has only the repulsive forces. The attractive part of the potential manifests itself primarily in the small k part of the structure factor, but this effect decreases as the density increases and is almost negligible at reduced densities of about .7. These conclusions are established by comparing Verlet's molecular dynamics structure factor for the Lennard-Jones fluid with the reference system structure factors calculated with the aid of a simple but accurate approximation described herein. On the basis of

these results a very simple prescription is given for calculating the radial distribution function of a simple liquid at high densities which is more accurate than those obtained by any previously reported theory. Calculations of the free energy, internal energy, and even the pressure with the aid of the pressure (virial) equation are remarkably accurate and provide additional support for the conclusions. In short, we find that the structure factor and pair distribution function of a simple fluid is dominated by the repulsive forces at high densities even at low temperatures. The implications of our conclusions to perturbation theories for liquids, and to the interpretation of x-ray scattering experiments is discussed.

1. 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 liquids⁽¹⁾ and by Barker and Henderson's ingenious application of the high-temperature expansion to obtain the thermodynamic properties of Lennard-Jones liquids starting from those of a hard-sphere system^(2,3).

The Verlet and Barker-Henderson work, as well as other considerations^(4,5), suggest to us that a theory of liquids should consider explicitly the role that the repulsions play in determining the structure and thermodynamics of simple liquids. In particular, we hypothesize that in some representation, the repulsive forces should dominate the equilibrium structure. As might be expected from Verlet's molecular dynamics investigation, a suitable representation is obtained by considering the structure factor or (equivalently) the Fourier transform of the two-particle correlation function. We find that at moderate and high densities, a significant portion of the structure factor is quantitatively dominated by the repulsive forces. This indicates that the separation of the Lennard-Jones potential into reference and perturbation parts used by Barker and Henderson is not the most physically appropriate. In this separation, the reference potential contains the positive part of the potential, and the perturbation contains the negative part of the potential (with the convention that the intermolecular potential is zero for infinite separation). Rather we find that it is physically significant and useful to separate the interaction into a part containing all the repulsive forces and a part containing all the attractive forces.

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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 is 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, we are able to discover a simple expression for the radial distribution function of a dense Lennard-Jones liquid that is more accurate than those obtained by any previously reported theory. Furthermore, our separation into repulsive and attractive parts leads to a quantitative description of the thermodynamics of dense simple liquids through the use of the high-temperature expansion to first order, which we call the high-temperature approximation. In addition to explaining the surprising success of our application of the high-temperature approximation at liquid temperatures, our results indicate that the straight-forward use of subsequent terms in the high-temperature expansion is not the most appropriate theory to correct the high-temperature approximation.

As stated above, we consider a Lennard-Jones fluid, that is, 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 units of length, and ϵ the units of energy. In terms of these parameters, the frequently used dimensionless representations of the number density, $\rho = N/V$, and the temperature are

$$\left. \begin{aligned} \rho^* &= \rho\sigma^3 \\ T^* &= (\beta\epsilon)^{-1} \end{aligned} \right\} \quad (2)$$

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

$$h(r) = g(r) - 1 \quad (3)$$

where $g(r)$ is the usual radial distribution function⁽⁶⁾. [Given that a particle is at the origin, $4\pi r^2 \rho g(r)$ is the probability distribution for finding a particle located a distance r away from the origin.] The dimensionless Fourier transform of the correlation function is

$$\hat{h}(k) = \rho \int d\mathbf{r} h(r) e^{-i\mathbf{k} \cdot \mathbf{r}} \quad (4)$$

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 ($\rho\sigma^3 \geq .4$) we hypothesize and then verify the following statements: 1. At intermediate and large wave-vectors ($k\sigma \geq \pi$), 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); 2. For high densities ($\rho\sigma^3 \geq .65$) the behavior of $\hat{h}(k)$ even at small wave-vectors ($k\sigma \leq \pi$) 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 appreciated.

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

$$w(r) = u_0(r) + u(r) \quad (5)$$

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 has a well-defined thermodynamic limit, this separation is unique:

$$\left. \begin{aligned} u_0(r) &= w(r) + \epsilon, & r < 2^{1/6}\sigma \\ &= 0, & r \geq 2^{1/6}\sigma \end{aligned} \right\} \quad (6)$$

$$\left. \begin{aligned} u(r) &= -\epsilon, & r < 2^{1/6}\sigma \\ &= w(r), & r \geq 2^{1/6}\sigma \end{aligned} \right\} \quad (7)$$

These functions are depicted in Figure 1.

The hypothesis we try to verify in this paper is that for some range of wave-vectors

$$\hat{h}(k) = \hat{h}_0(k) \quad (8)$$

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, Equation 8 is nearly exact for $k\sigma \geq \pi$, and at high densities Equation 8 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

$$w(r;\lambda) = u_0(r) + \lambda u(r), \quad 0 \leq \lambda \leq 1 \quad (9)$$

Then we can relate the Helmholtz free energy of the Lennard-Jones system to the reference system and the perturbation:⁽⁸⁾

$$(\beta \Delta A/N) = (\beta \Delta A_0/N) + (\beta \rho/2) \int_0^1 d\lambda \int g(r;\lambda) u(r) d\mathbf{r} \quad (10)$$

Here $g(r;\lambda)$ is the radial distribution function in the "test" system, ΔA is the excess free energy

$$(\beta \Delta A/N) = \int_0^\rho (\beta p/\rho' - 1) d\rho' \quad (11)$$

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 Equation 10 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 10 can also be written in terms of the Fourier transforms of the correlation functions:

$$\begin{aligned} (\beta \Delta A/N) = & (\beta \Delta A_0/N) + (\beta \rho/2) \hat{u}(0) + [\beta/2(2\pi)^3] \int \hat{h}_0(k) \hat{u}(k) d\mathbf{k} \\ & + [\beta/2(2\pi)^3] \int_0^1 d\lambda \int [\hat{h}(k;\lambda) - \hat{h}_0(k)] \hat{u}(k) d\mathbf{k} \end{aligned} \quad (12)$$

where

$$\hat{u}(k) = \int d\mathbf{r} u(r) e^{-i\mathbf{k} \cdot \mathbf{r}} \quad (13)$$

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 Equation 12. 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

$$(\beta\Delta A/N) \approx (\beta\Delta A_0/N) + (\beta\rho/2)\hat{u}(0) + (\beta/2)\int \hat{h}_0(k)\hat{u}(k)dk \quad (14)$$

will be at best qualitatively accurate (errors $\sim 10\%$) when the density is low, but will become quantitatively accurate as the density increases. The calculations presented in the next section show that this behavior does occur.

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

$$\beta p/\rho = 1 + (\beta\rho/6)\int r(\partial w(r)/\partial r)g(r)dr \quad (15)$$

and the energy equation for the excess internal energy⁽⁶⁾,

$$\Delta E/N = (\rho/2)\int w(r)g(r)dr \quad (16)$$

These equations probe the quantitative behavior of the radial distribution function. According to our hypothesis, when the density is sufficiently high, $g(r)$ is accurately approximated by $g_0(r)$. Thus, by using this approximation to evaluate Equations 15 and 16, we have a sensitive test of the hypothesis. Such a calculation is carried out in the next section; the results obtained at high densities ($\rho^* \geq .65$) 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 $y_0(r)$ which is defined by the equation

$$g_0(r) = y_0(r) \exp[-\beta u_0(r)] . \quad (17)$$

Physically, $y_0(r)$ 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 $y_0(r)$ can be approximated by the similar function appropriate to a hard-sphere system of diameter d , $y_d(r)$. For this reason, we consider the following approximation:

$$g_0(r) \simeq y_d(r) \exp[-\beta u_0(r)] , \quad (18)$$

or

$$\hat{h}_0(k) \simeq \rho \int d\mathbf{r} [y_d e^{-\beta u_0} - 1] e^{-i\mathbf{k} \cdot \mathbf{r}} . \quad (18')$$

By recalling the role of $\hat{h}_0(k)$ as a linear response function, it is seen that Equation 18 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 :

$$\int d\mathbf{r} [y_d e^{-\beta u_0} - 1] = \int d\mathbf{r} [y_d e^{-\beta u_d} - 1] \quad (19)$$

where u_d denotes a hard-core repulsion of diameter d . Within the framework

of the compressibility theorem,

$$(\partial\rho/\partial\beta p)_\beta = 1 + \rho \int h(r) d\mathbf{r} \quad (20)$$

the criterion given in Equation 19 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 .

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 $\rho^* = .8$ we obtain

$(\beta p_0/\rho) = 6.11$, and $(\beta \Delta \Lambda_0/N) = 2.81$; the Monte Carlo results are $(\beta p_0/\rho) = 6.07 (\pm .05)$ and $(\beta \Delta \Lambda_0/N) = 2.81$. Incidentally, the Rowlinson "steepness" criterion⁽¹²⁾ used by Barker and Henderson⁽²⁾ 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 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, Equation 8, and the approximate treatment of the reference system, Equations 18 and 19. 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.

The Equilibrium Structure

In our treatment of the reference system, the function $y_o(r)$, defined in Equation 17, is approximated by the hard-sphere function $y_d(r)$. As a result, $\hat{h}_o(k)$ can be expressed as

$$\hat{h}_o(k) = \hat{h}_d(k) + \rho \int d\mathbf{r} y_d(r) (e^{-\beta u_o} - e^{-\beta u_d}) e^{-i\mathbf{k} \cdot \mathbf{r}} \quad (21)$$

where $\hat{h}_d(k)$ is the Fourier transform of the two-particle correlation function for the hard-sphere system of diameter d . 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 Equation 19 for the temperature and density dependent d , and calculate $\hat{h}_o(k)$ from Equation 21.

Plots of $d(\beta, \rho)$ for a few isochores are given in Figure 2. These graphs bear a striking resemblance to Verlet's empirical plots (Figure 17, Reference 1) of the temperature and density dependent diameter he found

could be used to fit a hard-sphere spectrum, $\hat{h}_d(k)$, to the Lennard-Jones spectrum, $\hat{h}(k)$. 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 that in the range $\pi \leq k\sigma \leq 5\pi$, 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 $k\sigma \geq \pi$, $\hat{h}(k)$ is dominated by the repulsive forces. These forces are what define the reference system in this paper. Furthermore, from Equation 21, 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, $k\sigma \geq 5\pi$.

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 Figure 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 Figure 3, the value of d obtained from Equation 19 and then used in Equation 21 is $(1.005)\sigma$; the reported value for Verlet's hard-sphere model d is $(1.0)\sigma$. In Figure 4, we see that at high densities the 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 Figure 4 is $(1.025)\sigma$, Verlet's hard-sphere model d is $(1.026)\sigma$.

While these results strongly indicate that our hypothesis is true, 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 Figure 5, a plot of $g_0(r)$ as described by Equation 18 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 Figure 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 k -space 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, $k\sigma \leq \pi$, the attractions and repulsions contribute (at low and moderate densities) to $g(r)$ for all $r \geq \sigma$. 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 Figure 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 Figure 6 a plot of $g_0(r)$ as described in Equation 16 is compared with the "exact" Lennard-Jones $g(r)$ for a thermodynamic state similar to that considered in Figure 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.

Thermodynamics

As discussed in Section 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 Equation 14),

$$(\beta \Delta A/N) \approx (\beta \Delta A_0/N) + (\beta \rho/2) \int d\mathbf{r} g_0(r) u(r) \quad (22)$$

should be only qualitatively accurate (errors ~10%) at low densities but become quantitatively accurate as the density increases.

We have evaluated the right-hand side of Equation 22 at various temperatures and densities. Some of our results are tabulated in Tables I and II, and graphed in Figure 7. The numerical integrations were performed by using our approximate treatment of the reference system, Equations 18 and 19, and the solution of the Percus-Yevick equation for a hard-sphere fluid⁽¹¹⁾. This solution gives the analytic form of $y_d(r)$ 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 Equation 22 (see Equation 20 and comments following it) was obtained from Levesque and Verlet's accurate polynomial fit of the machine calculations on hard-spheres⁽¹⁰⁾. The plots in Figure 7 show how the excess free energy as approximated in Equation 22 (or Equation 14) does converge at high densities ($\rho^* \geq .65$) to the values predicted by machine calculations^(10, 16). The temperatures considered are sufficiently low ($T^* \leq 1.35$) 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 number of approximate theories accurately predict the thermodynamic behavior of the Lennard-Jones gas^(2,3,17).

In Tables I and II we compare the numerical values arrived at through Equation 22 (or Equation 14) with those predicted by other theories and machine calculations. One important aspect of our work becomes apparent when the Barker-Henderson⁽²⁾ 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 lack of improvement 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 does 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 $\rho^* \geq .65$.

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, it is important to understand how different forces effect the

structure. In so doing, we learn what kind of perturbation theory will yield a quantitative description of the equilibrium structure and thermodynamics of the liquid state. Although the high-temperature approximation can be very accurate, we do not expect that the next few terms in the high-temperature expansion will provide an appropriate theory of liquids even when our separation is used. To understand why we recall the hypothesis we have tried to verify in this paper: the repulsions dominate $\hat{h}(k)$ for $k\sigma \gtrsim \pi$, and the presence of attractions is manifested mainly in $\hat{h}(k)$ for $k\sigma \lesssim \pi$. A comprehensive theory for Lennard-Jones fluids would be one which explains and uses this hypothesis. The straightforward application of the high-temperature expansion will not explain this behavior in any simple way. This is true because of the complications involved in calculating higher order terms in this expansion. As far as the structure is concerned, the first correction to $g(r) \approx g_0(r)$ requires the knowledge of the three- and four-particle correlation functions in the reference system, and even for hard-sphere systems, reliable representations of these functions are not known. Furthermore, the higher order terms for the thermodynamic properties are difficult to evaluate or approximate accurately⁽³⁾. A reasonable estimation of the second order term in the high-temperature expansion must be obtained by expensive machine calculations (the local- or macroscopic-compressibility approximations⁽²⁾ for this term are inadequate^(3,10)). Barker and Henderson have published⁽³⁾ the results of a Monte Carlo calculation of the second order term for their interaction separation which indicate that the high-temperature expansion is slowly convergent at liquid temperatures ($T^* < 1.35$). However, we have been informed that the reported results are in error⁽³⁾; and the corrected results are better. This may be an indication that while it is

computationally difficult, the high-temperature expansion is rapidly convergent at low temperatures.

We believe that a theory which recognizes the validity of our hypothesis may provide a simpler method to obtain the thermodynamic corrections to the high-temperature approximation and in addition give an accurate description of the liquid structure.

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

$$g(r) \approx g_0(r) \quad (23)$$

is very accurate at high densities. As further verification, we use this approximation to evaluate $\beta p/\rho$ and $\Delta E/N$ through Equations 15 and 16 respectively. Once again the integrals are performed within the context of our approximate treatment of the reference system: Equations 18, 19 and the analytic solution of the Percus-Yevick equation for hard-spheres. The results are tabulated and compared with molecular dynamics data⁽¹⁹⁾ 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 compare our results with those obtained from numerical solutions of the Percus-Yevick equation for the Lennard-Jones fluid⁽¹⁴⁾; Here, our superior accuracy is pertinent to some recent calculations performed by Barker, et.al.⁽²⁰⁾ using the Percus-Yevick equation. This work is discussed briefly in the Appendix.

Of course, values for the pressure (or any other thermodynamic function)

can also be obtained by numerically differentiating the free energy (see Equation 11). 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 $\rho^* \sim .7$), 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 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 approximation^(2,3) 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⁽³⁾. 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.

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 $.5^{(21)}$, 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 $g(r) \approx g_0(r)$. 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⁽²²⁾.

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 Pings⁽²³⁾ which is depicted by Verlet⁽¹⁾ in his Figure 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 Equation 19 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. Until densities are so high that $\rho d^3 > .9$, we think that our calculated values of the excess free energy and excess internal energy should agree to better than a percent with those that might be obtained from an exact treatment of the reference system. This is born out by a comparison between the Monte-Carlo and approximate (Percus-Yevick) evaluation of the high-temperature approximation for the Barker-Henderson separation of the

Lennard-Jones potential (see Reference 10 and column 5 of our Table I). When the density does become very large, however, the Percus-Yevick approximation for hard-spheres is not reliable, and significant errors must be expected. For example, in Table III, our results for the internal energy are in excellent agreement with molecular dynamics except for the states $\rho^* = .85$, $T^* = .658$; $\rho^* = .85$, $T^* = .591$; and $\rho^* = .88$, $T^* = .591$. The values for ρd^3 at these states are .93, .95, and .97 respectively. All the other states considered in that table correspond to smaller effective hard-sphere densities. It would be worthwhile if extensive tables of reliable computations (e.g., machine calculations) 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 Section III, are sensitive to small errors in the reference system even at densities smaller than $\rho d^3 = .9$.

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We wish to thank J. Rasaiah for sending us some of the results of his computations. Two of us (J.D.W. and D.C.) thank Kurt E. Shuler for his hospitality and support during our stay at the University of California, San Diego. We are also grateful to Katja Lakatos and Dick Bedeaux for many informative discussions.

APPENDIX

We consider the correspondence between the calculation of the free energy discussed herein and the recent adaptation of the Percus-Yevick theory by Barker, et.al.⁽²⁰⁾. These workers use the Percus-Yevick equation for the Lennard-Jones potential to obtain the internal energy via the energy equation (Equation 16), numerically integrate these results with respect to β to get the free energy, and numerically differentiate with respect to ρ to obtain the pressure. They are motivated to proceed in this fashion since the energy equation is a less sensitive test of inaccuracies in $g(r)$ than is the pressure equation (Equation 15). An indication of the errors to be expected in the energy when the Percus-Yevick $g(r)$ is used at high densities and low temperatures is given in Table IV.

To understand the correspondence of their procedure to the free energy calculation discussed in this paper, we introduce the notation

$$\phi(r) = \beta w(r) \tag{A-1}$$

and the "test" function, $\phi(r;\lambda)$, which defines the test system

$$\phi(r;\lambda) = \phi_0(r) + \lambda \phi_1(r) \quad , \quad 0 \leq \lambda \leq 1 \tag{A-2}$$

such that $\phi(r;1) = \phi(r)$. The function $\phi_0(r)$ defines a reference system. After differentiating the canonical partition function with respect to λ , it is easy to show that

$$\beta \Delta A/N = (\beta \Delta A/N) \Big|_{\lambda=0} + (\rho/2) \int_0^1 d\lambda \int \phi_1(r) g(r;\lambda) d\mathbf{r} \tag{A-3}$$

Equation A-3 is Equation 10 when our choice of test system and perturbation

parts, $\phi_0 = \beta u_0$ and $\phi_1 = \beta u$, is made. However, the choice of $\phi_0 = \beta_0 w$ and $\phi_1 = (\beta - \beta_0)w$ for some β_0 can also be made in which case Equation A-3 is equivalent to integrating the energy equation between two inverse temperatures, β_0 and β , to obtain the free energy. The correspondence is explicitly seen by changing variables in Equation A-3 from λ to β' , the effective inverse temperature in the test system where $\beta' = \beta_0 + \lambda(\beta - \beta_0)$. This procedure is the one carried out by Barker, et.al.⁽²⁰⁾. It is seen that determining the "constant of integration", $(\beta \Delta A/N)|_{\lambda=0}$, is equivalent to determining a reference system excess free energy. Previously⁽²³⁾, Barker and Henderson chose as their reference system the system with the positive part of the interaction potential at temperature $(\beta\epsilon)^{-1}$. In their recent work⁽²⁰⁾, they have chosen the Lennard-Jones fluid at a different temperature, $(\beta_0\epsilon)^{-1}$, as the reference system and used machine calculation data to determine $\Delta A(\beta_0)$ for the Lennard-Jones fluid at several densities. They then solve the Percus-Yevick equation for the Lennard-Jones fluid to give $g(r, \lambda) \equiv g(r, \beta')$ and numerically perform the λ integration as well as the r integration in Equation A-3 to go from the reference system (state) to the total system (final state).

Although Equation A-3 is valid for an arbitrary choice of reference system and perturbation parts, the separation we have suggested is particularly convenient at high densities since here $g(r, \lambda) \simeq g_0(r)$ to a very good approximation. The λ integration in Equation A-3 is then trivial and the calculation of the free energy is greatly simplified.

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TABLE I. Approximate and Monte-Carlo results for the excess free energy on the $T^* = .75, 1.15$ 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 References 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.

TABLE I

		- $\beta\Delta A/N$			
T^*	ρ^*	Eq. 22	Monte-Carlo	Barker-Henderson	Rasaiah-Stell
.75	.1	.55	.81	.57	.57
	.2	1.15	1.48	1.16	1.15
	.3	1.78	2.11	1.77	1.76
	.4	2.42	2.68	2.38	2.37
	.5	3.06	3.23	2.96	2.96
	.6	3.65	3.74	3.48	3.48
	.7	4.14	4.17	3.90	3.88
	.8	4.46	4.47	4.16	4.08
	.84	4.51	4.54	4.20	
1.15	.1	.29	.39	.30	.30
	.2	.60	.73	.61	.60
	.3	.92	1.05	.92	.89
	.4	1.23	1.33	1.20	1.17
	.5	1.51	1.59	1.46	1.41
	.55	1.63	1.69	1.56	
	.6	1.74	1.79	1.65	1.58
	.65	1.82	1.84	1.72	
	.75	1.88	1.88	1.76	
	.85	1.77	1.78	1.63	
1.35	.1	.22	.30	.23	.22
	.2	.45	.56	.46	.44
	.3	.68	.90	.69	.65
	.4	.90	1.00	.89	.84
	.5	1.09	1.16	1.05	.99
	.6	1.22	1.26	1.16	1.07
	.7	1.26	1.29	1.18	1.05
	.8	1.16	1.19	1.07	.88

TABLE II. Approximate results for the excess free energy on the $\rho^* = .88, .85, .75$ and $.65$ 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, Reference 10) are listed. These values for $-\beta\Delta A/N$ are generally too high at temperatures below $T^* \leq 1.35$, 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.

TABLE II

		$-\beta \Delta A/N$		
ρ^*	T^*	Eq. 22	Empirical	Barker-Henderson
.88	1.095	1.94	1.99	1.80
	.94	2.64	2.88	2.65
	.591	6.80	6.86	6.30
.85	2.889	- .93	- .86	- .94
	2.202	- .44	- .37	- .47
	1.214	1.51	1.55	1.39
	1.128	1.86	1.91	1.73
	.880	3.32	3.35	3.10
	.782	4.18	4.21	3.90
	.786	4.14	4.17	3.86
	.760	4.41	4.44	4.10
	.719	4.87	4.90	4.53
	.658	5.66	5.71	5.26
	.591	6.74	6.81	6.25
.75	2.849	- .56	- .50	- .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
	.881	3.27	3.30	3.06
	.827	3.66	3.69	3.43
.65	2.557	- .18	- .20	- .11
	1.585	.79	.85	.73
	1.036	2.24	2.30	2.12
	.900	2.90	2.96	2.74

TABLE III. Approximate and molecular dynamics results for the pressure and internal energy. Columns 3 and 5 contain our results obtained by applying Equation 23 to Equations 15 and 16 respectively. Molecular dynamics results (References 19 and 10) are listed in Columns 4 and 6; the error bounds for these machine calculations are $\pm .05$.

TABLE III

		$\beta p/\rho$		$-\Delta E/N\epsilon$	
ρ^*	T^*	Pressure Equation	Molecular Dynamics	Energy Equation	Molecular Dynamics
.88	1.095	3.42	3.48	5.92	5.85 ^a
	.94	2.87	2.77	6.08	6.04 ^a
	.591	.18	- .18	6.47	6.53
.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
	.88	1.82	1.64	5.96	5.94
	.782	1.20	.98	6.06	6.04
	.786	1.23	.99	6.05	6.05
	.76	1.03	.82 ^a	6.08	6.07
	.719	.69	.36 ^c	6.12	6.12
	.658	.09	-.20	6.19	6.39 ^b
	.591	-.75	- 1.20	6.26	6.46 ^b
.75	2.849	3.05	3.10	4.09	4.07
	1.304	1.63	1.61	4.99	5.02
	1.069	.90	.90	5.15	5.19
	1.071	.91	.89	5.15	5.17
	.881	-.02	-.12	5.28	5.31
	.827	-.38	-.54	5.32	5.38
.65	2.557	2.08	2.14	3.78	3.78
	1.585	1.21	1.25	4.20	4.23
	1.036	-.23	-.11	4.46	4.52
	.90	-.91	-.74	4.52	4.61

^a Revised results (see Reference 10).

^b Revised results (see Reference 10). The unrevised values were 6.19 at $T^* = .658$, and 6.26 at $T^* = .591$.

^c Molecular dynamics results for $\rho^* = .85$ and $T^* = .72$ (Reference 10) predict $\beta p/\rho = .43$.

TABLE IV. Approximate and molecular dynamics results for the pressure and internal energy as obtained from Equations 15 and 16 respectively. Columns 3 and 6 give the values obtained by applying the approximation $g(r) \simeq g_0(r)$. Columns 4 and 7 give the molecular dynamics results (Reference 19); the error bounds here are $\pm .05$. The results obtained by using the solution of the Percus-Yevick equation for $g(r)$ (Reference 14) are given in Columns 5 and 8.

TABLE IV

ρ^*	T^*	$\beta p/\rho$			$-\beta \Delta E/N$		
		This Work	MD	PY	This Work	MD	PY
.85	1.128	2.82	2.78	3.57	5.08	5.05	4.98
	.88	1.82	1.64	3.17	6.77	6.75	6.61
	.786	1.23	.99	2.97	7.70	7.70	7.51
	.719	.69	.36	2.82	8.52	8.51	8.28

FIGURE CAPTIONS

- Figure 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, $u(r)$.
- Figure 2. Plots of $d(\beta, \rho)$ for a few isochores.
- Figure 3. Plot of $\hat{h}(k)$ for $\rho^* = .5426$, $T^* = 1.326$. The line represents Equation 21; the circles are the molecular dynamics results (Reference 1).
- Figure 4. Plot of $\hat{h}(k)$ for $\rho^* = .844$, $T^* = .723$. The line represents Equation 21; the circles are the molecular dynamics results (Reference 1).
- Figure 5. Plot of $g(r)$ at a moderate density: $\rho^* = .50$, $T^* = 1.36$. The line represents Equation 18; the circles are the molecular dynamics results (Reference 1).
- Figure 6. Plot of $g(r)$ at a high density: $\rho^* = .85$, $T^* = .88$. The line represents Equation 18; the circles are the molecular dynamics results (Reference 1); and the dashed line represents the numerical solution of the Percus-Yevick equation for the Lennard-Jones potential (Reference 14).
- Figure 7. Plots of $\beta\Delta A/N$ for two isotherms. In the upper graph, the line represents Equation 22; the crosses are the Monte-Carlo results (Reference 16). In the lower graph, the "Error" denotes the difference at $T^* = .75$ between the $\beta\Delta A/N$ as obtained from Equation 22 and $\beta\Delta A/N$ as obtained from Monte-Carlo calculations.

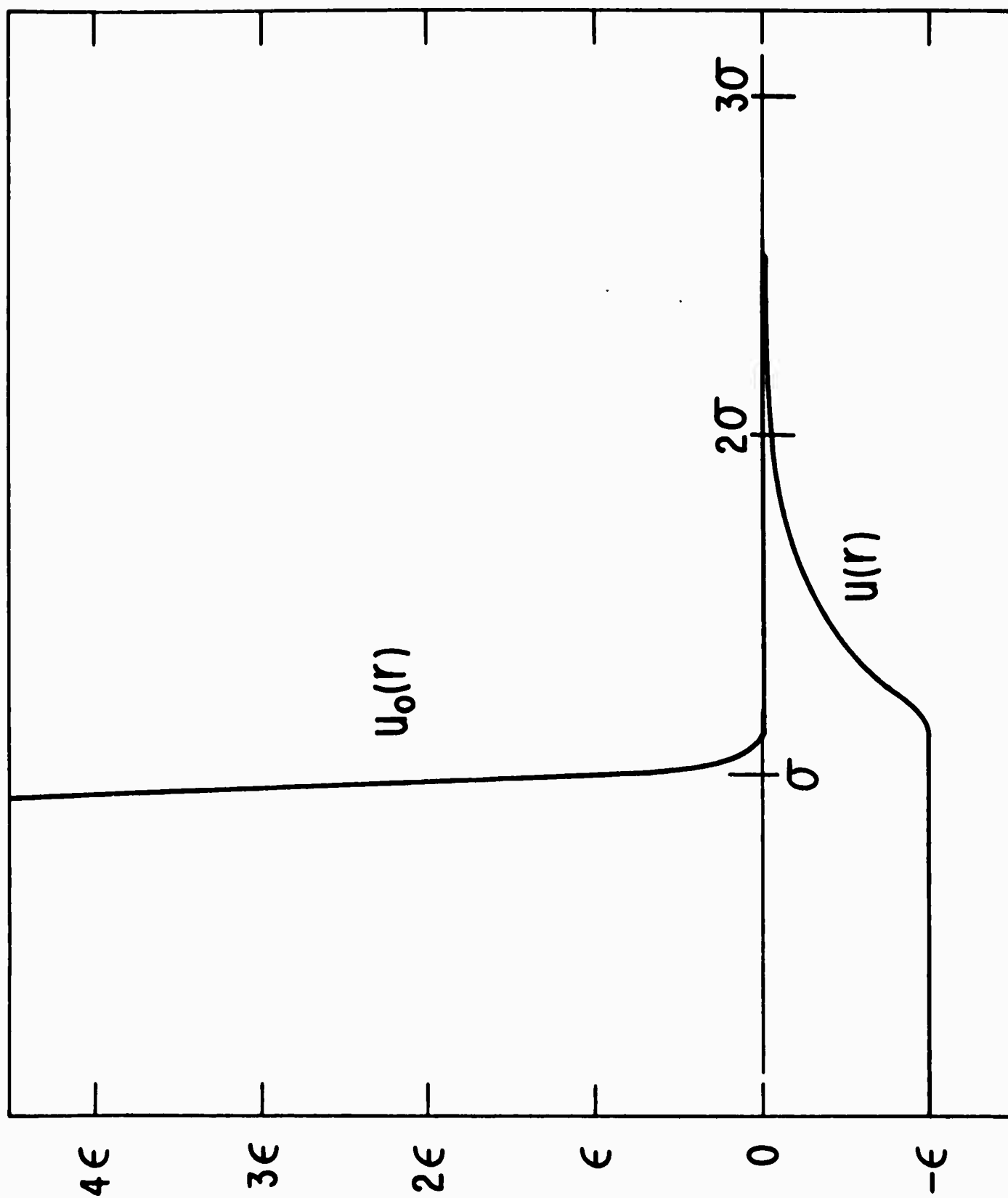


FIGURE 1

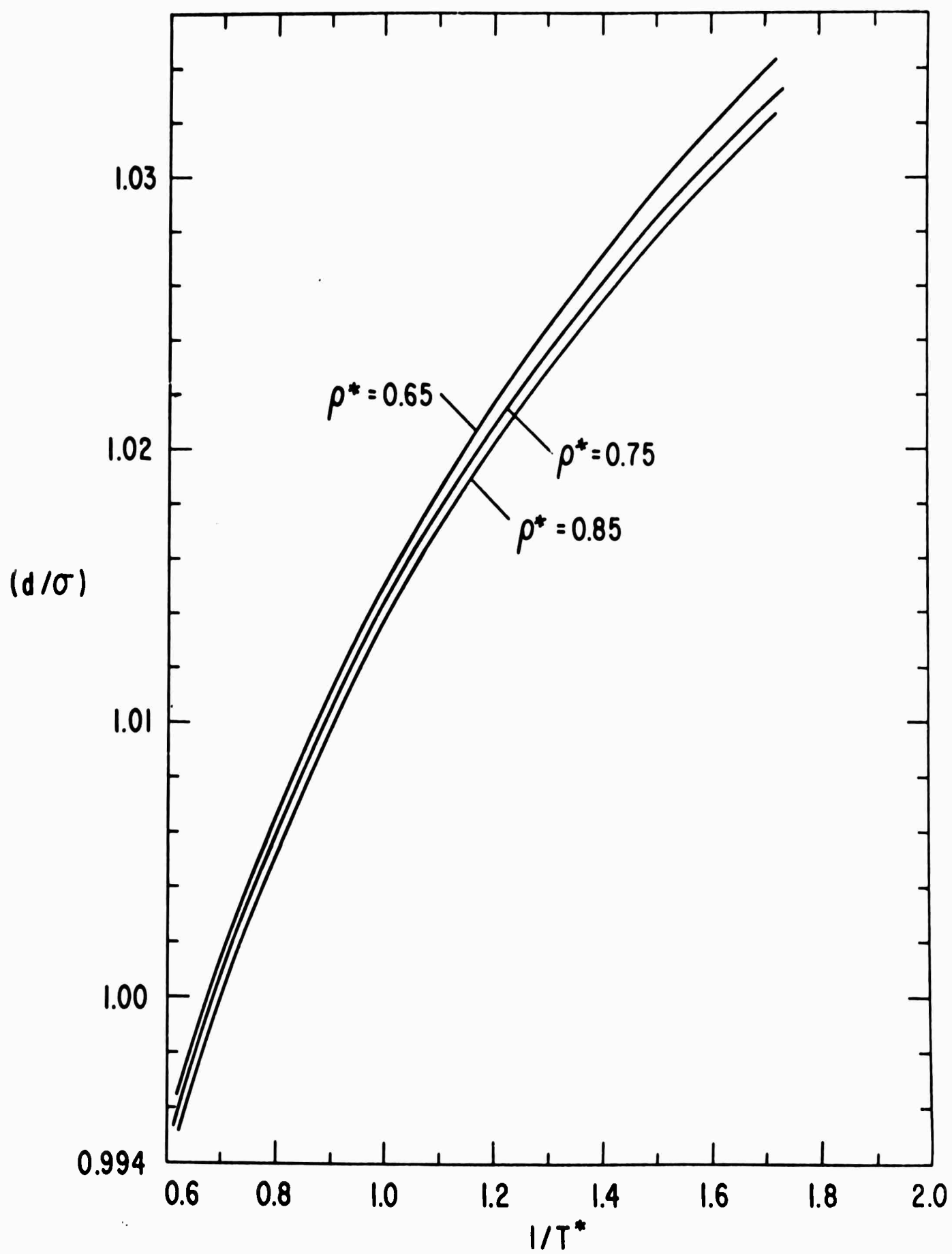


FIGURE 2

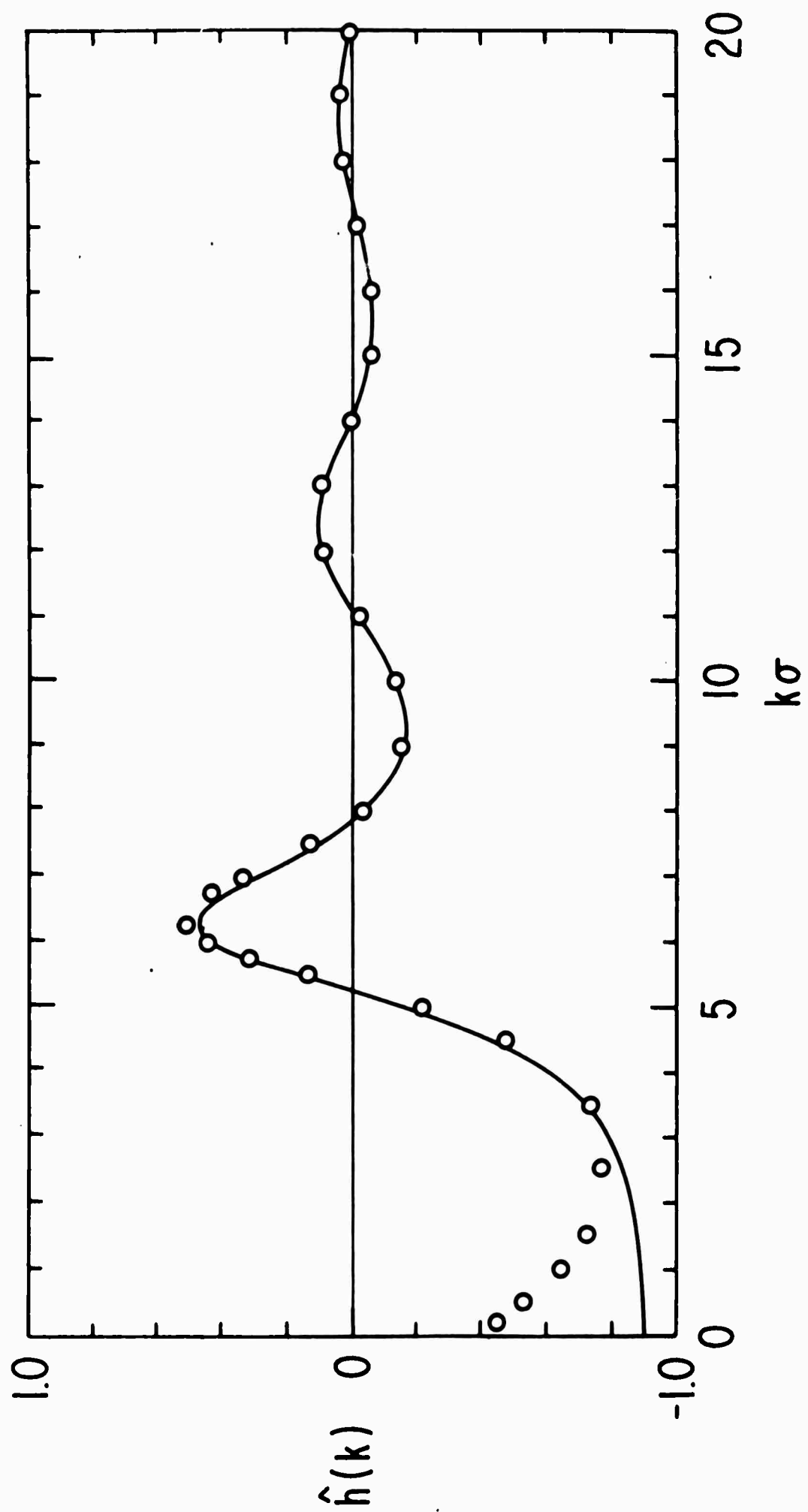


FIGURE 3

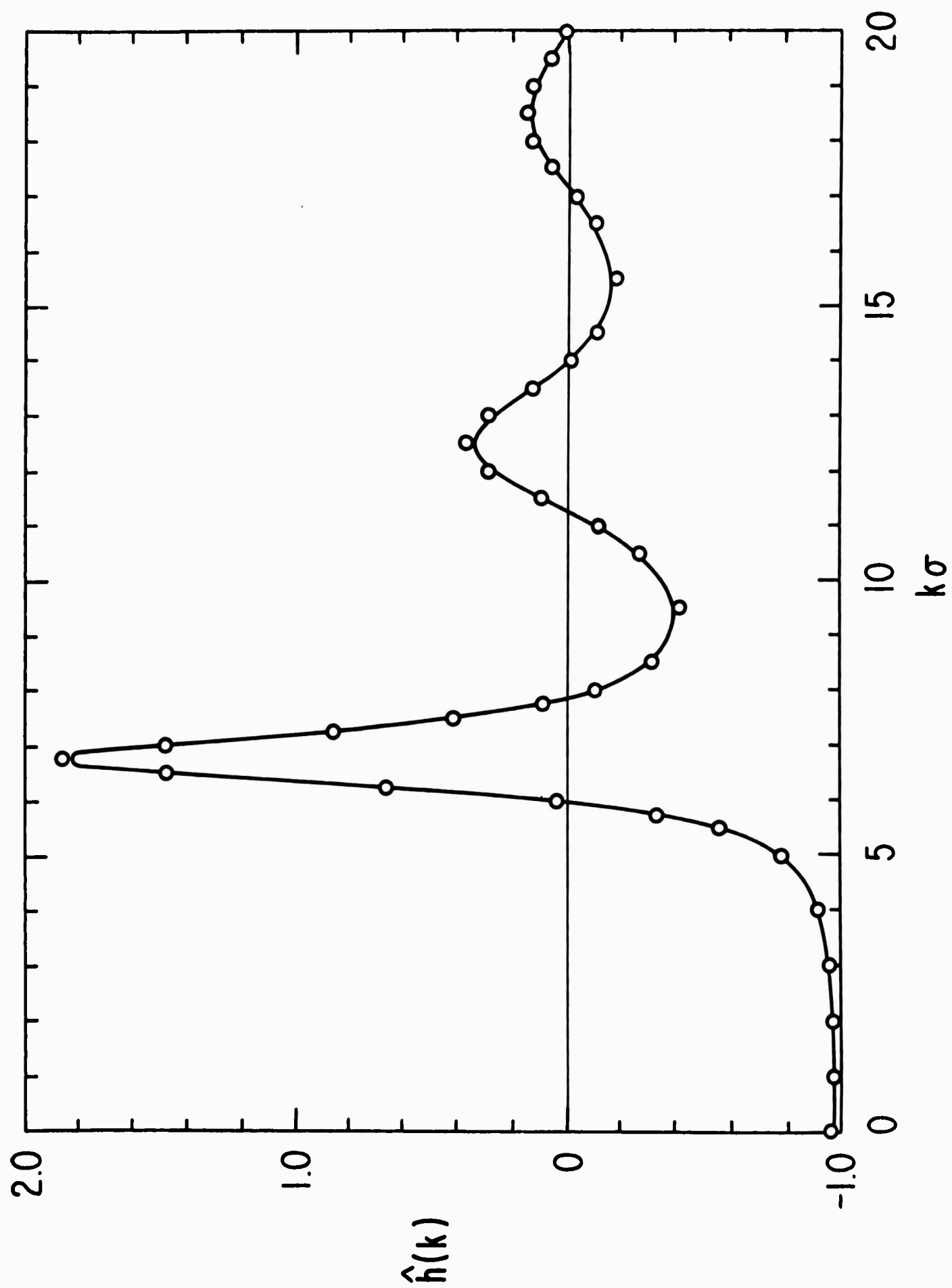


FIGURE 4

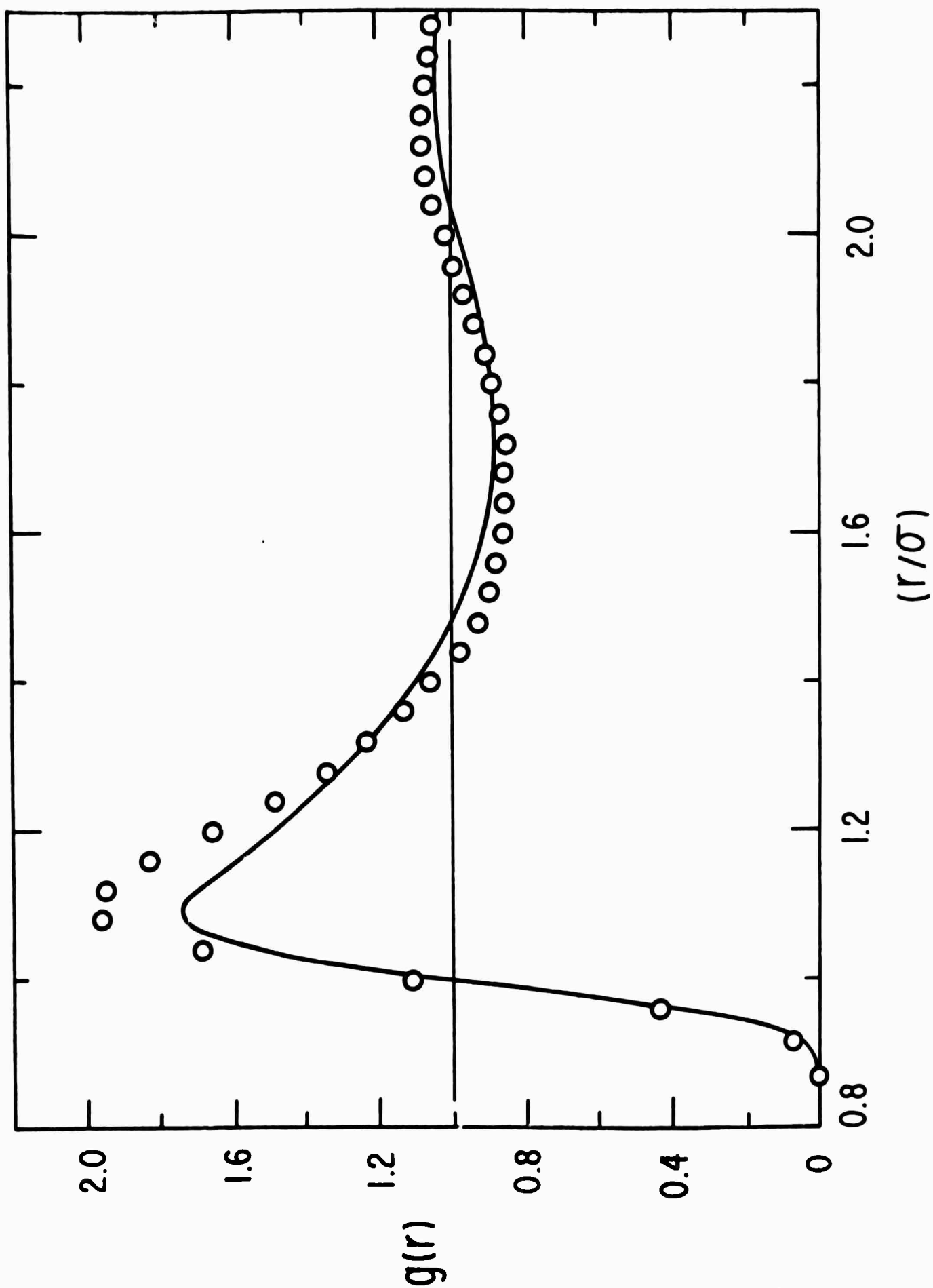


FIGURE 5

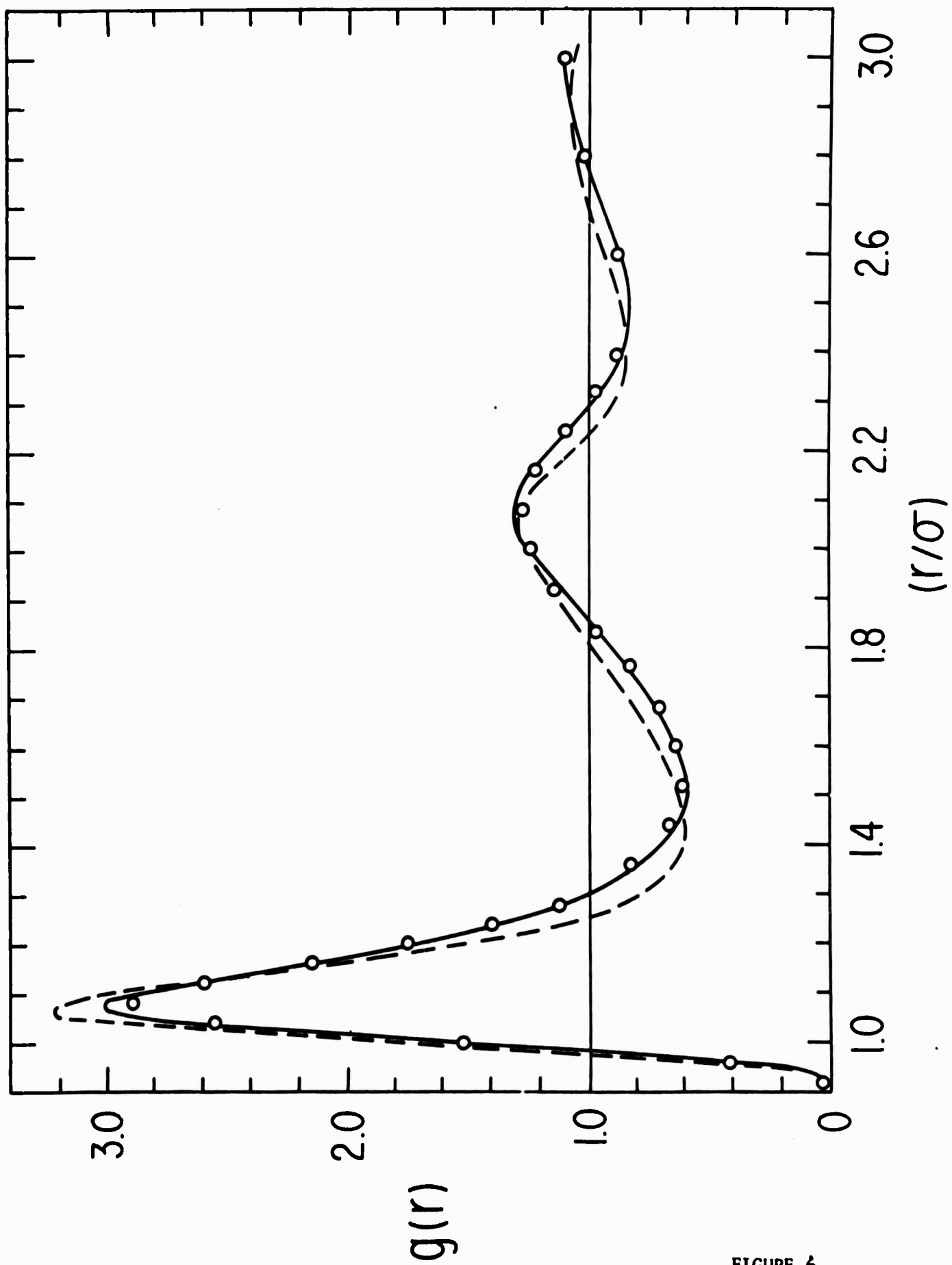


FIGURE 6

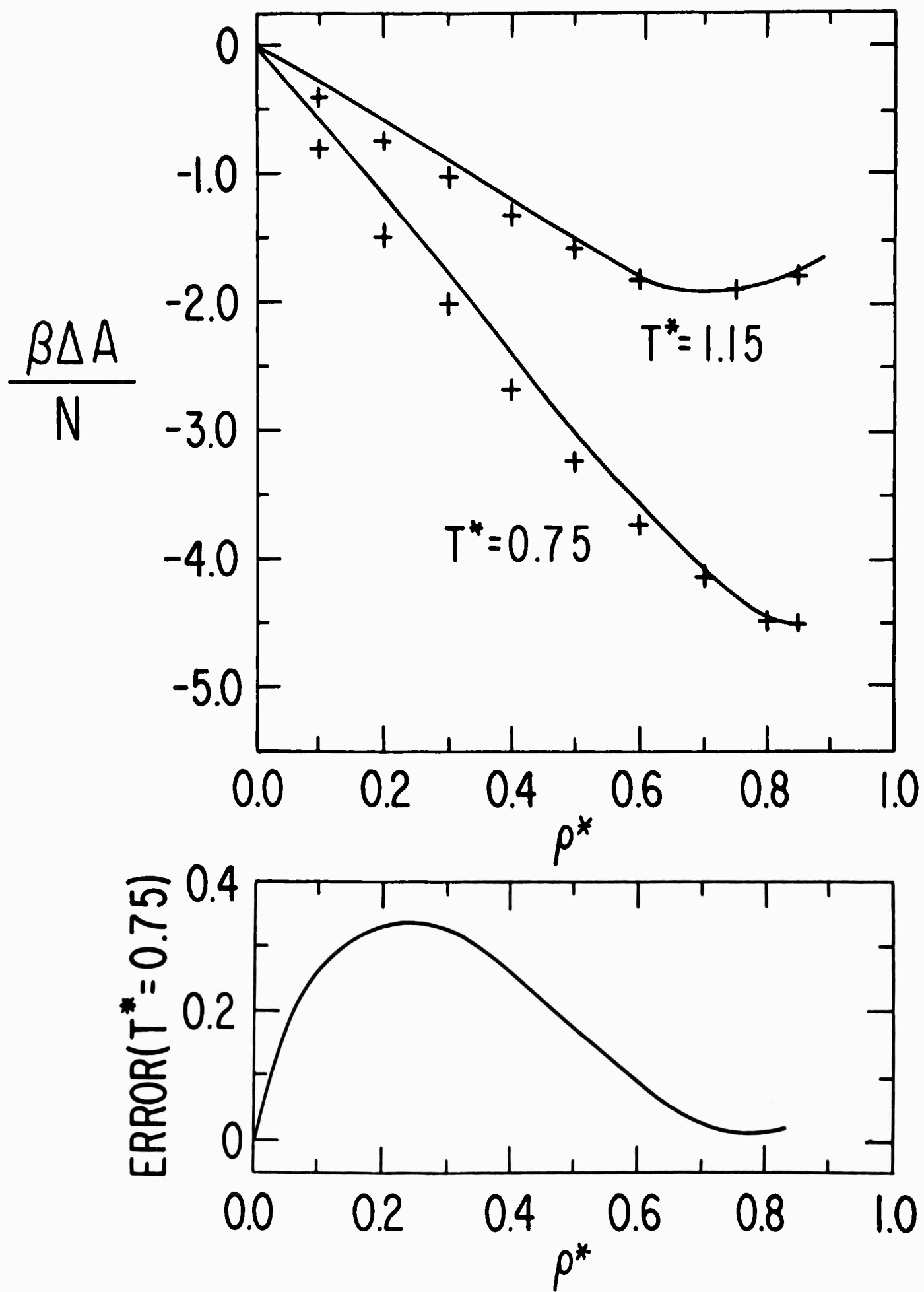


FIGURE 7

ABSTRACT CONTD.

even the pressure with the aid of the pressure (virial) equation are remarkably accurate and provide additional support for the conclusions. In short, we find that the structure factor and pair distribution function of a simple fluid is dominated by the repulsive forces at high densities even at low temperatures. The implications of our conclusions to perturbation theories for liquids, and to the interpretation of x-ray scattering experiments is discussed.

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The equilibrium structure and thermodynamics of a simple liquid is discussed. The particular system considered in our calculations is the Lennard-Jones liquid in which the intermolecular interaction is the pairwise additive 6-12 potential, $w(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6]$. The potential is separated into two parts, a reference part containing all the repulsive forces and a perturbation containing all the attractive forces. (This separation is distinctly different from the often-used separation of the potential into positive and negative parts.) It is found that the effects of the two parts of the potential on the structure of the liquid are most easily discussed in terms of the structure factor (or equivalently, the Fourier transform of the pair-correlation function) rather than the pair-correlation function itself. For values of the Fourier transform variable, k , greater than about π/σ , where σ is the distance at which the intermolecular potential is zero, the attractive part of the potential has very little effect on the structure factor for reduced densities greater than about .5; i.e., for these values of k , the structure factor is equal to that of a hypothetical reference fluid which has only the repulsive forces. The attractive part of the potential manifests itself primarily in the small k part of the structure factor, but this effect decreases as the density increases and is almost negligible at reduced densities of about .7. These conclusions are established by comparing Verlet's molecular dynamics structure factor for the Lennard-Jones fluid with the reference system structure factors calculated with the aid of a simple but accurate approximation described herein. On the basis of these results a very simple prescription is given for calculating the radial distribution function of a simple liquid at high densities which is more accurate than those obtained by any previously reported theory. Calculations of the free energy, internal energy, and

(See attached sheet.)

KEY WORDS

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Statistical Mechanics