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The Relationship Between the Hard Sphere Fluid and Fluids with Realistic Repulsive Forces*

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Abstract

We consider the equilibrium statistical mechanics of classical fluids in which the potential energy is decomposable into repulsive pair interactions. A generalized cluster expansion is derived relating the thermodynamic and structural properties of such systems to those of the hard sphere fluid. The expansion is ordered by a softness parameter ξ which is essentially the range of intermolecular distances in which the difference between the Mayer f functions for the repulsive potential and an appropriate reference hard sphere potential is non-zero. The first (lowest order) approximation generated by the expansion equates the free energy and $y(r)$ for the fluid to the respective functions appropriate to a system of hard spheres with diameter d. Here $y(r) = g(r) \exp[+\beta u(r)]$, where $g(r)$ and $u(r)$ denote the radial distribution function and repulsive pair potential respectively. A prescription is given for choosing a temperature and density dependent diameter d of the reference hard sphere fluid so that the first approximation for the free energy contains errors of order ξ^4 only, and the corrections to the first approximation for $g(r)$ are of order ξ^2. The method is used to calculate the properties of a fluid whose intermolecular potential varies as r^{-12}. The repulsive potential that produces the repulsive forces in the Lennard-Jones potential is also studied. Since the properties of the hard sphere fluid are known from the results of computer calculations and conveniently summarized by analytic equations, the application of the first approximation is numerically very simple. With this approximation, the results obtained for both model systems agree closely with those obtained by Monte Carlo calculations.

I. Introduction

At least since the time of van der Waals and Maxwell, the hard sphere or "billiard ball" model has been thought to represent many of the essential features of realistic intermolecular repulsive forces in equilibrium and non-equilibrium phenomena. As a result, much effort has been devoted to understanding the properties of hard sphere fluids. The Percus-Yevick equation[1] for hard spheres has been solved exactly,[2] giving convenient and accurate information about the equation of state and pair distribution function at low densities. The scaled particle theory[3] is of comparable accuracy for the thermodynamic properties. To extend our knowledge to higher densities, Monte Carlo and molecular dynamics computer calculations have been performed.[4-6] Recently, analytic expressions for the equilibrium properties have been presented which accurately summarize the results of the computer calculations at moderate and high densities and which have the proper functional form at low density.[6] In addition, molecular dynamics calculations have shown that hard spheres exhibit a first order phase transition,[7] which is similar in many respects to the liquid-solid transition of real fluids.[8,9]

The hard sphere model is obviously an idealization, and the purpose of this paper is to discuss, within the context of equilibrium statistical mechanics, the relationship between this idealized model and the smoothly varying repulsive forces found in real fluids. The usual method for doing this is a perturbation theory of some type, and several authors have developed theories to relate hard sphere data to the properties of fluids with other repulsive potentials. Rowlinson considered fluids whose repulsive intermolecular potential varied as the inverse n-th power of

the intermolecular separation.[10] He expanded the thermodynamic properties in powers of 1/n, the lowest order result corresponding to $n=\infty$ which is equivalent to the hard sphere potential. Barker and Henderson[11a] have shown how to generalize the Rowlinson method to apply to a wide class of repulsive potentials $u_R(r)$. In this generalized Rowlinson method a temperature-dependent hard sphere diameter is calculated according to

$$d_R = \int_0^\infty [1 - e^{-u_R(r)/kT}]\, dr$$

and the pressure and free energy are set equal to those of the associated hard sphere fluid with the same temperature and density and with a diameter d_R. Recently, Barker and Henderson have modified this basic approach by dividing the repulsive potential into two parts at some radius $r=\mu$.[11b] The contribution to the thermodynamic properties from the portion $r<\mu$ is calculated by the generalized Rowlinson method while that from the portion $r>\mu$ is given by the first term of the high temperature expansion. Finally, the parameter μ is chosen to minimize the excess free energy per particle as given by this combination of methods.

In our recent discussion of the equilibrium structure of dense simple liquids[12], we introduced a new method to relate both the thermodynamic properties and the equilibrium structure of a general repulsive system to those of a hard sphere system. We presented physical and heuristic arguments to justify the procedure. In this paper we show that the approximation method is in fact the first step in a rigorous and systematic procedure. In Sec. II we introduce and analyze the

theory, which is based on a generalization of the familiar Mayer cluster theory. In Sec. III we demonstrate the accuracy of our method for the thermodynamic properties of two systems composed of "soft sphere" particles. The first system is a fluid in which the intermolecular potential is inversely proportional to the twelfth power of the intermolecular separation (the r^{-12} potential). In the second system, the potential is chosen to have the same repulsive forces as those of the Lennard-Jones potential. In both cases, the results obtained compare favorably with those found by Monte Carlo calculations. The paper is concluded in Sec. IV with a discussion of our method for relating hard sphere and soft sphere fluids.

II. Theory

A conventional model for a liquid is a classical system of N interacting particles in a volume V, for which the total potential energy, U, is assumed to be a sum of pair energies which depend only on the scalar distances between particles

$$U = \sum_{\substack{i<j \\ 1}}^{N} u(r_{ij}) \quad .$$

When using the canonical ensemble, the central problem for this model is to determine how the excess Helmholtz free energy depends on the potential u. We let

$$\mathcal{A}(\rho,\beta;\varphi) = -\beta\Delta A/V = V^{-1} \ln Q$$

$$Q = V^{-N}\int d\underset{\sim}{r}^{N} \prod_{\substack{i<j \\ 1}}^{N} \varphi(r_{ij}) \ ,$$

$\rho = N/V$ is the thermodynamic particle density, β^{-1} is Boltzmann's constant, k, times the temperature, T, and $\varphi(r) = \exp[-\beta u(r)]$ is the usual Boltzmann factor for the pair potential u. The notation $\underset{\sim}{r}^N$ denotes the positions of the N particles, and ΔA is the excess Helmholtz free energy (compared with an ideal gas at the same temperature, density and volume). From $\mathcal{A}(\rho,\beta;\varphi)$ we can calculate the pressure, entropy, and other thermodynamic properties by straightforward differentiations with respect to ρ and β. Also, the radial distribution function, g(r), can be determined by functional differentiation with respect to $\varphi(r)$:

$$(\rho^2/2)\ g(\underset{\sim}{r}) = \varphi(\underset{\sim}{r})\ (\delta\mathcal{A}(\rho,\beta;\varphi)/\delta\varphi(\underset{\sim}{r})) \ .$$

For the present purposes, it is more convenient to deal not with g(r) directly but rather with y(r), which is defined as

$$y(\underset{\sim}{r};\rho,\beta;\varphi) = e^{\beta u(r)} g(\underset{\sim}{r};\rho,\beta;\varphi) .$$

Thus, we have

$$y(\underset{\sim}{r}) = (\partial/\partial\rho^2)\,(\partial Q/\partial\varphi(\underset{\sim}{r})) . \qquad (2.3)$$

Note that y(r) is a more slowly varying function of r than is g. (In fact, even for hard sphere potentials, y(r) is finite and continuous for all r, as can be seen from an inspection of its virial series or from the fact that it is equivalent to the pair distribution function of cavities in a hard sphere fluid.[13])

For soft sphere particles which have continuous, positive and purely repulsive potentials, the function $\varphi_s(r)$ is indicated schematically in Figure 1a. (In the following discussion, the subscript s always denotes a quantity for a soft sphere fluid.) The function rises smoothly from zero at small distances (where we assume u_s is extremely large) to unity at large distances. For comparison, the φ_d function for hard spheres with diameter d is shown in Figure 1b. (We denote all quantities for a hard sphere fluid with a subscript d.) If the continuous potential of interest is harshly repulsive, the φ_s function is very similar to the φ_d function, and since Q depends only on φ, we might expect that the thermodynamic properties and y(r) for a harshly repulsive potential might be quite similar to the corresponding quantities for hard spheres, provided that the diameter d is chosen properly. For a reasonable choice of d, $\varphi_s(r) - \varphi_d(r)$ is effectively non-zero only for a small range of values of r (See Figure 1c.). If that range is ξd, then ξ is a dimensionless parameter which is a measure of the softness of the potential.

The larger ξ is, the softer is the potential, and only for hard spheres is ξ equal to zero. We will now develop an expression for A in powers of this softness parameter. To do this we need to know how A changes when φ is changed.

In general, if $\varphi(r)$ is changed from one function to another (i.e. if $\varphi(r)$ is changed from $\varphi_0(r)$ to $\varphi_0(r) + \Delta\varphi(r)$), the resulting change in A can be expressed in terms of a functional Taylor series:

$$A(\rho,\beta;\varphi_0 + \Delta\varphi) = A(\rho,\beta;\varphi_0) + \int d\underset{\sim}{r}\, \frac{\delta A(\rho,\beta;\varphi_0)}{\delta\varphi(\underset{\sim}{r})}\, \Delta\varphi(\underset{\sim}{r})$$

$$+ \frac{1}{2}\int d\underset{\sim}{r}\, d\underset{\sim}{r}'\, \frac{\delta^2 A(\rho,\beta;\varphi_0)}{\delta\varphi(\underset{\sim}{r})\delta\varphi(\underset{\sim}{r}')}\, \Delta\varphi(\underset{\sim}{r})\, \Delta\varphi(\underset{\sim}{r}')$$

$$+ \cdots \qquad (2.4)$$

These functional derivatives can be evaluated in several ways (see Appendix A). The first derivative is given in Eq. (2.3). The second derivative is

$$\frac{\delta^2 A(\rho,\beta;\varphi)}{\delta\varphi(\underset{\sim}{r})\delta\varphi(\underset{\sim}{r}')}\bigg|_{\varphi=\varphi_0} = \rho^3 V^{-1}\int d\underset{\sim}{r}^3\, \delta(\underset{\sim}{r}_{12}-\underset{\sim}{r})\,\delta(\underset{\sim}{r}_{13}-\underset{\sim}{r}')\, y_0(r_{12})\, y_0(r_{13})\, J_0^{(3)}(\underset{\sim}{r}^3)$$

$$+ (\rho^4/4)\, V^{-1}\int d\underset{\sim}{r}^4\, \delta(\underset{\sim}{r}_{12}-\underset{\sim}{r})\,\delta(\underset{\sim}{r}_{34}-\underset{\sim}{r}')\, y_0(r_{12})\, y_0(r_{34})\, J_0^{(4)}(\underset{\sim}{r}^4) \qquad (2.5)$$

where $\delta(\underset{\sim}{r})$ is the three dimensional Dirac delta function, and $J_0^{(3)}$ and $J_0^{(4)}$ are certain correlation functions (see Appendix A). The subscript zero indicates that the correlation functions are those for the fluid in which $\varphi = \varphi_0$. (The ρ and β dependence of the correlation functions in Eq. (2.5) should be understood even though it is not indicated explicitly.)

When (2.3) and (2.5) and higher functional derivatives are substituted into (2.4), we obtain a formally exact infinite series for A. If φ_0 is chosen to be 1, i.e. $u_0 = 0$ which corresponds to an ideal gas, this series becomes the usual virial expansion. In this case $\Delta\varphi(r)$ is the Mayer f function, $e^{-\beta u(r)} - 1$, and the first functional derivative term becomes the familiar second virial coefficient contribution, since $y_0 = 1$ for an ideal

gas. The second functional derivative term vanishes because $J_o^{(3)}$ and $J_o^{(4)}$ are zero for an ideal gas. Higher functional derivatives give the remaining terms of the virial series.

To discuss soft spheres, however, we will use this expansion with the choice $\varphi_0 = \varphi_d$ and $\Delta\varphi = \varphi_s - \varphi_d$. The resulting equation is simplified if we define

$$B_d(r) = y_d(r)\left[\varphi_s(r) - \varphi_d(r)\right].$$

This function is shown in Figure 1d. As can be seen, it is natural to call this the "blip" function. Then Eq. (2.4) can be expressed as

$$\begin{aligned} Q(o,\beta;\varphi_s) = {} & Q(o,\beta;\varphi_d) + (\rho^2/2)\int d\underset{\sim}{r} B_d(r) \\ & + (\rho^3/2V)\int d\underset{\sim}{r}^3 B_d(r_{12})B_d(r_{13})J_d^{(3)}(\underset{\sim}{r}^3) \\ & + (\rho^4/8V)\int d\underset{\sim}{r}^4 B_d(r_{12})B_d(r_{34})J_d^{(4)}(\underset{\sim}{r}^4) \qquad (2.6) \\ & + \cdots \end{aligned}$$

The subsequent terms contain three or more factors of $B_d(r)$ (or $\varphi_s(r) - \varphi_d(r)$) which is non-zero only for a small range of values of r (namely, for $|r-d| \lesssim \xi d$). Hence we might expect that the contribution of the nth functional derivative term is of order ξ^n. We have not yet chosen d however. It is reasonable to choose d such that

$$\int d\underset{\sim}{r}\; y_d(r)\left[\varphi_s(r) - \varphi_d(r)\right] = \int d\underset{\sim}{r}\; B_d(r) = 0. \qquad (2.7)$$

This choice causes the first functional derivative term (which is apparently of order ξ and hence is potentially the largest term) to vanish identically. This is indeed a felicitous choice for d, since it makes the second derivative terms, which nominally appear to be of order ξ^2, actually become of order ξ^4 (see Appendix B). Indeed it can be shown that all the subsequent terms are of order ξ^4 or higher order. Thus we have the result that

$$A(\rho,\beta;\varphi_s) = A(\rho,\beta;\varphi_d)\ [1 + O(\xi^4)] \qquad (2.8)$$

when d is chosen to satisfy Eq. (2.7). Equation (2.8) provides a direct connection between the thermodynamic properties of hard spheres and soft spheres. The associated hard sphere diameter is density and temperature dependent, and (as will be seen below) has the physically reasonable property that d decreases as the temperature or the density is increased.

The same "blip function" expansion can be used to obtain an expression for $y_s(r)$ using Eqs. (2.6) and (2.3).

$$y(r;\varphi_s) = y(r;\varphi_d)\ [1 + (2\rho/V)\int d\underset{\sim}{r}^3\, \delta(\underset{\sim}{r}_{12}-\underset{\sim}{r})B_d(r_{13})J_d^{(3)}(\underset{\sim}{r}^3) + (\rho^2/2V)\int d\underset{\sim}{r}^4\, \delta(\underset{\sim}{r}_{12}-\underset{\sim}{r})B_d(r_{34})J_d^{(4)}(\underset{\sim}{r}^4) + \ldots]\ .$$

In general it is not possible to choose d such that the first functional derivative correction term for y vanishes identically for all r. This first correction appears to be of order ξ. However, if we use the same value of d as we chose above for the free energy series, it can be shown (see Appendix B) that this term is actually of order ξ^2 for all r. Indeed all subsequent terms are of order ξ^2 or smaller. Thus we have

$$y_s(r) = y_d(r)\ [1 + O(\xi^2)] \qquad (2.9)$$

or

$$g_s(r) = e^{-\beta u_s(r)}\ y_d(r)\ [1 + O(\xi^2)] \qquad (2.9')$$

This equation gives a relationship between the structure of a soft sphere fluid and that of a hard sphere fluid.

Equations (2.8) and (2.9'), together with (2.7), provide convenient approximate expressions for the excess Helmholtz free energy and pair correlation function of a fluid with a repulsive intermolecular potential. To apply these formulas it is necessary to have information about the excess Helmholtz free energy and y(r) for the hard sphere fluid. Fortunately,

Verlet and Weis[6] have presented analytic expressions for these functions which accurately summarize the results of computer calculations on hard-sphere systems.

In previous work by the present authors concerning the effect of repulsive forces on the structure of the Lennard-Jones fluid, Eqs. (2.8) and (2.9), without the correction terms, and (2.7) were postulated (on the basis of some intuitive arguments) to be the relationships between hard sphere and soft sphere fluids. It is now seen that these postulates are really the leading terms in systematic expansions in powers of the softness of the potential. It can also be seen that the thermodynamic relationship (2.8) is inherently more accurate than the structural one (2.9). One might expect the former to be accurate even for quite soft potentials since the first correction is of fourth order in the softness.

When the excess energy and excess pressure are obtained by differentiating the lowest order result for the free energy, Eq. (2.8), the errors are of order ξ^4. If these excess quantities are calculated from the radial distribution function using the energy and virial equations,

$$\beta\Delta E/N = (\beta\rho/2)\int d\underset{\sim}{r}\; g(r)\; u(r)\;, \tag{2.10}$$

$$\beta\Delta p/\rho = -(\beta\rho/6)\int d\underset{\sim}{r}\; g(r)\; r\; (du(r)/dr)\;, \tag{2.11}$$

the errors in each will be of the same order as the errors in g, namely ξ^2 if the lowest order g is used and ξ^3 if the next approximation is used. It can be shown however that the ratio of the excess energy to the excess pressure is the same for both approximations for g and is the same as the ratio obtained when the energy and pressure are calculated from the lowest approximation to the free energy. Since this latter ratio has error only of order ξ^4, it follows that the ratio of excess energy to excess pressure calculated from either of the two lowest order approximations for g is more accurate than the individual values.

The blip function expansion was developed specifically to apply to dense fluids. However, it is easily shown that the theory is exact in the limit of low density. The correct second virial coefficient is obtained from Eq. (2.8), and the correct g(r) is obtained from Eq. (2.9'). As a necessary corollary of this it follows that the numerical value of a correction of given order in ξ depends on the density and may be significant at high density although negligible at low density.

In the next section we examine the numerical predictions of the theory.

III. Numerical Results

A. Inverse Twelfth Power Potential

Recent Monte Carlo calculations for a "soft sphere" fluid with an inverse twelfth power pair interaction potential

$$u(r) = \epsilon(\sigma/r)^{12} \tag{3.1}$$

provide accurate thermodynamic data with which to compare our theory. This potential is sufficiently "soft" that it provides a severe test of the accuracy of our method.

There is no temperature-independent characteristic length in an inverse power potential. As a result, the excess thermodynamic functions have simple scaling properties. For example, for the potential in Eq. (3.1) it can be shown that $\beta\Delta A/N$ $(= -a/\rho)$ is a function only of the single variable $(\beta\epsilon)^{1/4}\rho\sigma^3$. This scaling law has two immediate consequences. From the thermodynamic equations

$$\beta\Delta p/\rho = -\rho\left(\frac{\partial}{\partial\rho}(a/\rho)\right)_\beta \tag{3.2}$$

and

$$\beta\Delta E/N = -\beta\left(\frac{\partial}{\partial\beta}(a/\rho)\right)_\beta \tag{3.3}$$

it follows that $\beta\Delta p/\rho$ and $\beta\Delta E/N$ are also functions of $(\beta\epsilon)^{1/4}\rho\sigma^3$ only and are related by

$$\beta\Delta p/\rho = 4\,\beta\Delta E/N\ . \tag{3.4}$$

An analogous scaling law holds for the radial distribution function $g(r;\beta,\rho)$ and $y(r;\beta,\rho)$. These functions actually depend on only two

independent variables, a scaled length which is $r/\sigma(\beta\epsilon)^{1/12}$ and the single thermodynamic variable $(\beta\epsilon)^{1/4}\,\rho\sigma^3$; i.e.

$$g(r;\beta,\rho) = G\left(r/\sigma(\beta\epsilon)^{1/12};\ (\beta\epsilon)^{1/4}\,\rho\sigma^3\right) \tag{3.5}$$

where G is a universal function for the r^{-12} potential.

As a result of these scalings laws, Monte Carlo calculations for this potential need be performed for only one temperature. The thermodynamic properties and the radial distribution functions along one isotherm can be used to obtain the results for any other temperature and density.

The scaling laws hold for the exact thermodynamic properties and pair correlation function. The results of an approximate theory might not obey these relationships. The Rowlinson theory, for example, does not obey the scaling laws. For the blip function expansion, however, it can be shown that each of the terms in the series for $\beta\Delta A/N$ satisfies the scaling law exactly, i.e. is a function only of $(\beta\epsilon)^{1/4}\,\rho\sigma^3$, provided that the hard sphere diameter d is chosen according to Eq. (2.7). Furthermore, each term in the blip function expansion for y satisfies the scaling law implied by Eq. (3.5).

We now compare the results of the theory with Monte Carlo calculations and other theoretical methods. We will use only the leading term in the blip function expansion for both the free energy, Eq. (2.8), and $y(r)$, Eq. (2.9). The computational procedure is very simple. Along one isotherm, Eq. (2.7) is solved at a number of densities to give the associated hard sphere diameter $d(\beta,\rho)$. (See Appendix C for a discussion of the hard sphere information that is needed for this calculation.) At each density the excess free energy of the associated hard sphere system is calculated, and by Eq. (2.8) this is equal to the excess free energy of the soft spheres under

consideration. The compressibility factor, $\beta p/\rho$, is obtained from Eq. (3.2). Note that since d is a (decreasing) function of the density, the pressure of the soft spheres is not simply equal to that of the associated hard sphere system. Instead we have

$$\beta \Delta p/\rho = \left(\frac{\beta \Delta p_d}{\rho}\right) \left[1 + \frac{3\rho}{d}\left(\frac{\partial d}{\partial \rho}\right)_\beta\right] + O(\xi^4) \qquad (3.6)$$

The second term in square brackets lowers the pressure.

In Table I, we compare the results of our theory with the Monte Carlo calculations,[14,15] the theory of Rowlinson[10] (as generalized by Barker and Henderson[16]), and the variational theory of Barker and Henderson[11b] on the isotherm $\beta\epsilon = 1$. These theories are briefly described above in Section I.

It can be seen that the Rowlinson method gives reasonably accurate free energies and pressures at lower densities, but it breaks down at high density. This is to be expected from a theory which attempts to describe soft spheres with a density-independent effective hard sphere diameter. The Barker-Henderson variational method allows the hard sphere diameter to be density dependent and hence gives consistently better results over a range of density (except for low densities where apparently the variational method fails to give the correct second virial coefficient). The results of the blip function expansion are better still. They are exact in the limit of low density. The free energy values (over the entire density range indicated) and the pressures (except for the highest density) are all within a percent of the Monte Carlo values.

Thus we can conclude that Eqs. (2.8) and (2.7) provide a very accurate relationship between the thermodynamic properties of hard spheres and soft spheres with inverse twelfth power repulsions.

Since Monte Carlo pair correlation functions have not been published for this potential we cannot test the structural relationship, Eq. (2.9'), directly. We can provide an indirect test, however, by using (2.9') to calculate virial pressures according to (2.11). The virial pressure results are not expected to be as accurate as the free energy pressures in Table Ib, since the latter have errors of order ξ^4 and the former have errors of order ξ^2. It can be seen from Table II that the virial pressures are accurate at low densities but are in error by as much as 12% at the highest density.

In summary, Eq. (2.8) for the free energy of a soft sphere fluid is very accurate for the inverse twelfth power potential, but Eq. (2.9') for the radial distribution function is very accurate only at low densities for this soft a potential. For a harder potential both equations are more accurate, as we shall see in the following portion of this section.

B. The Potential Which has the Same Repulsive Forces as the Lennard-Jones Potential

In an earlier discussion of the role of repulsive forces in determining liquid structure,[12] we considered a fluid whose intermolecular potential was purely repulsive and had exactly the same repulsive intermolecular force as the Lennard-Jones potential $w_L(r)$. For this fluid, the pair interaction is

$$u_{RL}(r) = w_L(r) + \epsilon \qquad r \leq 2^{1/6}\sigma$$

$$= 0 \qquad r > 2^{1/6}\sigma$$

where $-\epsilon$ is the depth of $w_L(r)$ at its minimum value. The potentials w_L and u_{RL} have exactly the same repulsive forces but the latter has no attractive forces. For the purpose of this paper, u_{RL} is of interest because it is purely repulsive and because Monte Carlo calculations of its structure and thermodynamic properties have been performed.[6,17]

The Monte Carlo values of the pressure and excess internal energy are shown in Table III, where they are compared with results obtained from Eq. (2.8), together with (3.3) and (3.4). This provides a test of the thermodynamic relationship between soft and hard spheres. The pressures predicted by the generalized Rowlinson method are also shown. At high densities the latter differ from the Monte Carlo values by about 6%.

The blip function free energy pressures (Eqs. (2.8) and (3.6)) agree with the Monte Carlo results to within a percent for all temperatures and densities considered. The difference is of the same size as the

errors of the Monte Carlo calculations and of the hard sphere data that are needed for the present calculations.[18] The excess energies are also very accurate. Thus we conclude that Eq. (2.8) is a very accurate thermodynamic relationship between hard spheres and soft spheres with this potential.

To test the structural relationship, Eq. (2.9'), the pressure and energy can be calculated from Eqs. (2.11) and (2.10). The results are shown in Table IV. The maximum difference between the blip function expansion and Monte Carlo results is 2%.

We can provide a more direct test of the structural relationship in the Lennard-Jones repulsion system because Barker and Henderson have obtained Monte Carlo values for g(r).[17] The comparison is shown in Figure 2 for the first peak in the pair correlation function for one temperature and density. The major noticeable differences between the Monte Carlo and blip function expansion results are that the peak heights differ by 5% and the depths of the minimum near $r = 1.5\sigma$ differ by about .05. At other parts of the curve, the difference is at most .03. (A part of this difference can be explained by the inherent errors of the Monte Carlo method.[18]) This represents remarkably close agreement and provides a very strong confirmation of the structural relationship (2.9') between soft and hard spheres for this hard a repulsive potential.

In summary, for this potential, which is much harder than the inverse twelfth power repulsion, Eqs. (2.8) and (2.9'), together with (2.7), are very accurate equations for the thermodynamic and structural properties of the fluid.

C. Remarks

I. A limitation of the method. This method relies on knowledge of the equation of state and pair correlation function of the hard sphere fluid. Since hard spheres undergo a phase transition to a solid-like phase when $\rho d^3 \approx .93$, this provides an upper limit on the densities at which the method as we have described it can be applied. However, at higher densities we can at least obtain the thermodynamic properties by a variational procedure similar to that of Barker and Henderson,[11b] except using the blip function method rather than the generalized Rowlinson method to treat the hard sphere aspects of the calculation. Real liquids of course have attractive as well as repulsive forces, and the present considerations are only the starting point for more complete descriptions of liquids. At high densities, real liquids as well as hard sphere liquids solidify, and so the density limitations of the present method are not important.

II. Density and temperature dependence of the hard sphere diameter. The crucial link between hard and soft sphere fluids is provided by Eq. (2.7) which tells how to choose the associated hard sphere diameter for a soft potential. Numerical solution of this equation shows that the diameter depends on density and temperature in a physically reasonable way (see Tables II and IV and Fig. 2 of Ref. 12). As the temperature is increased (at constant density), the diameter decreases. This reflects the physical fact that at higher temperatures the intermolecular configurations of high potential energy become more probable, and these configurations correspond to smaller intermolecular separations. Also, as the density is increased at constant temperature, the diameter decreases. This reflects the physical fact that

at higher densities the pressure is greater and the molecules are squeezed closer and closer together.

IV. Conclusion

The purpose of this paper is to present and justify a certain way of relating the hard sphere fluid model to more realistic soft sphere repulsive potentials in the equilibrium statistical mechanics of fluids. We have shown that the Helmholtz free energy and the function $y(r) = e^{\beta u(r)} g(r)$ for a soft sphere fluid are approximately the same as the corresponding quantities for a hard sphere fluid at the same density, provided that the hard core diameter is chosen properly. A prescription is given for calculating this diameter which has the physically reasonable property of being a decreasing function of temperature and density. These results are derived from well defined expansions of the Helmholtz free energy and $y(r)$ in powers of a parameter which is a measure of the softness of the repulsive potential or, in other words, the extent to which the potential differs from the hard sphere model potential. Calculations based on this theory are not computationally difficult. They require detailed but available knowledge of the equilibrium properties of hard sphere fluids. The theory becomes exact in the limit of low density, but the results remain useful and accurate up to quite high densities, depending on the softness of the potential. The upper limit to the density at which the calculations can be performed is determined by the highest density at which we have accurate hard sphere radial distribution functions. This density is approximately that at which the hard sphere system undergoes its phase transition.

In this paper we have restricted our attention to intermolecular potentials which are positive and repulsive. In real fluids, however, the intermolecular forces are attractive for some ranges of intermolecular separations. Nevertheless, at high densities (and at high temperatures for all densities) the structure of a fluid is dominated by the repulsive forces,[12] and so an accurate theory of repulsive forces can provide a foundation for an equilibrium theory of liquids.[12,6]

Acknowledgements

We are grateful to L. Verlet, and to J. A. Barker and D. Henderson for sending us preprints of their work prior to publication. One of us (J.D.W.) wishes to thank K. E. Shuler for his hospitality and support at the University of California, San Diego.

Appendix A: Evaluation of Functional Derivatives of a

The functional derivatives of a with respect to $\varphi(\underset{\sim}{r})$ can be evaluated in at least two ways. One way is to express a in terms of the configuration integral Q (Eq. (2.1)) and take the functional derivative for finite V. The result can be expressed in terms of reduced correlation functions in the canonical ensemble for a finite volume. Then the thermodynamic limit can be taken. For second and higher derivatives, this method is tedious because in the canonical ensemble the Ursell cluster functions do not approach zero as the position coordinates are separated, but rather there are extra 1/V components to these functions.

A somewhat easier method is to begin with the thermodynamic limit virial (cluster) series for a. The functional derivatives of this infinite series are relatively easy to calculate, and the resulting infinite series can be expressed in terms of correlation functions with the aid of diagrammatic manipulations and the product theorem for generating functions of classes of diagrams.[19]

By using this latter procedure, Eq. (2.5) is straightforwardly obtained. The function $J^{(3)}(\underset{\sim}{r}^3)$ is defined as

$$\sum_{m=0}^{\infty} \frac{\rho^m}{m!} \int d\underset{\sim}{r}_4 \cdots d\underset{\sim}{r}_{m+3} \, J^{(3)}(\underset{\sim}{r}^{m+3};m)$$

where $J^{(3)}(\underset{\sim}{r}^{m+3};m)$ is the sum of contributions from all distinct labeled graphs with 3 root points at $\underset{\sim}{r}_1, \underset{\sim}{r}_2, \underset{\sim}{r}_3$, and m field points at $\underset{\sim}{r}_4, \ldots, \underset{\sim}{r}_{m+3}$ such that: (a) at most one Mayer f bond ($=e^{-\beta u}-1$) connects each pair of points, (b) no f bond connects points 1 and 2, (c) no f bond connects 1 and 3, (d) the diagram becomes a star (multiply connected) if f_{12} and f_{13} are added, (e) the diagram does not become disconnected if points 1 and 2 are removed; and (f) the diagram does not become disconnected if points 1 and 3 are removed. It can be shown that this is precisely the series for the function on the right hand side of the following equation

$$J^{(3)}(\underset{\sim}{r}^3) = h(r_{23}) + g(r_{23}) \left[\frac{g^{(3)}(\underset{\sim}{r}^3)}{g(r_{12})g(r_{13})g(r_{23})} - 1\right] \qquad (A.1)$$

where $h(r) = g(r) - 1$, and $g^{(3)}$ is the three particle correlation function. This final expression now contains no reference to diagrams. (The same result can also be obtained by the first method described in this Appendix.) If one makes the Kirkwood superposition approximation,[20] we would have simply

$$J^{(3)}(\underset{\sim}{r}^3) = h(r_{23}). \qquad (A.2)$$

Similarly the function $J^{(4)}(\underset{\sim}{r}^4)$ is

$$\sum_{m=0}^{\infty} \frac{\rho^m}{m!} \int d\underset{\sim}{r}_5 \ldots d\underset{\sim}{r}_{m+4}\, J^{(4)}(r^{m+4}, m)$$

where the integrand is the sum of contributions from all distinct labeled graphs with 4 root points (1,2,3,4) and m field points (5, ..., m+4) such that: (a) at most one f bond connects each pair of points, (b) no f bond connects 1 and 2 (c) no f bond connects 3 and 4, (d) the diagram becomes a star if f_{12} and f_{34} are added. (e) the diagram does not become disconnected if points 1 and 2 are removed, and (f) the diagram does not become disconnected if points 3 and 4 are removed. An expression for $J^{(4)}$ in terms of four, three, and two particle distribution functions can also be obtained. If, in addition, we make the superposition approximation, we have

$$\begin{aligned} J^{(4)}(\underset{\sim}{r}^4) = {} & h(r_{13})h(r_{24}) + h(r_{14})h(r_{23}) + h(r_{13})h(r_{23})h(r_{24}) \\ & + h(r_{13})h(r_{14})h(r_{24}) + h(r_{13})h(r_{14})h(r_{23}) \\ & + h(r_{14})h(r_{23})h(r_{24}) + h(r_{13})h(r_{14})h(r_{23})h(r_{24}). \end{aligned} \qquad (A.3)$$

This result can also be obtained by using the diagrammatic expansion for $J^{(4)}$ and summing only those graphs which are consistent with the superposition approximation.[20]

Appendix B: Estimating the ξ Dependence of Various Integrals

The effective hard core diameter d is chosen according to Eq. (2.7). As a result of this choice, many integrals are automatically of higher order in ξ than one might ordinarily expect. In this Appendix we discuss the reason for this.

By converting the integral in Eq. (2.7) into a one dimensional integral we find

$$\int_0^\infty r^2 dr\, B_d(r) = 0. \tag{B.1}$$

Consider an integral of the following type

$$\int_0^\infty r^2 dr\, B_d(r)\, F(r;s) \tag{B.2}$$

where F is any smooth function of r and may depend on some other variables, denoted by s, which are held constant in the r integration. Since $B_d(r)$ is effectively non-zero for $|r-d| \lesssim \xi d$ only, we might expect this integral to be of first order in ξ. However, because of Eq. (B.1), we have

$$\int_0^\infty r^2 dr\, B_d(r)\, F(r;s) = \int_0^\infty r^2 dr\, B_d(r)[F(r;s) - F(d;s)]$$

If F(r;s) is a slowly varying function of r (i.e., if F is differentiable) then the quantity in square brackets is of order ξ and the integral is of order ξ^2, not ξ.

To apply this result let us now consider the integral containing $J_d^{(3)}$ in the right hand side of Eq. (2.6). Fix $\underset{\sim}{r}_1$ and $\underset{\sim}{r}_3$ and consider doing the $\underset{\sim}{r}_2$ integration. The above result cannot be applied directly because $J_d^{(3)}(\underset{\sim}{r}^3)$ is not a continuous function of $|r_{12}|$ at fixed $\underset{\sim}{r}_1$, $\underset{\sim}{r}_3$, and fixed direction for $\underset{\sim}{r}_{12}$ (see Eqs. (A.1) and (A.2)). However, we first integrate over all

the angles associated with $\underset{\sim}{r}_{12}$, holding $|\underset{\sim}{r}_{12}|$ fixed. The discontinuities are smoothed out and now the integration over $|\underset{\sim}{r}_{12}|$ gives a result of order ξ^2. The remaining integral over $|\underset{\sim}{r}_{13}|$ gives <u>another</u> factor of ξ^2. Thus the complete integral is of order ξ^4.

This method can be employed to verify all the statements given in the text concerning the ξ dependence of various integrals.

Appendix C: Information about the Hard Sphere Fluid

To perform calculations using the present method, it is necessary to know the equation of state for hard sphere fluids as well as the function $y_d(r)$.

The equation of state which we use is the one suggested by Carnahan and Starling,[21]

$$\beta p_d/\rho = (1+\eta+\eta^2-\eta^3)/(1-\eta)^3 ,$$

where $\eta = \pi\rho d^3/6$ and d is the hard sphere diameter. This formula summarizes the available molecular dynamics and Monte Carlo results within the statistical accuracy of these computer calculations. By integrating with respect to density, the excess Helmholtz free energy corresponding to this equation of state can be obtained:

$$A_d/\rho = -\eta(4-3\eta)/(1-\eta)^2 .$$

The $y_d(r)$ function is also needed for all values of $r \geq d$ as well as for r slightly less than d, i.e. just inside the hard core. For $r \geq d$, $y_d(r) = g_d(r)$, which can be obtained from Monte Carlo and molecular dynamics calculations. We use the empirical formula of Verlet and Weis[6], which expresses g_d as the sum of two parts:

$$y_d(r) = g_d(r) = g_1(r) + g_2(r), \quad r \geq d , \qquad (C.1)$$

where $g_1(r)$ is simply related to the Wertheim-Theile[2] analytic solution of the hard-sphere Percus-Yevick equation[1] and $g_2(r)$ is a small correction (also in convenient analytic form). Verlet and Weis state that $g_d(r)$ obtained in this simple way differs from their Monte Carlo results by at most 0.03 and estimate the statistical error to be approximately 0.01. To obtain y_d for r near d inside the core, we assume we can

use the same formula. Inside the core, the Percus-Yevick y_d is known analytically, and the value of g_2 is obtained by extrapolation. We adopted the procedure of extrapolating the logarithm of g_2 quedretically into the core. This procedure is clearly arbitrary; however, comperison of different extrapolation methods indicates that an error of et most a few parts in 10^4 are introduced into the calculated d by the arbitrariness of the extrapolation. For exemple, the values for d given in Table IV differ from those calculated by Verlet end Weis by a different extrapolation procedure by at most .0002. The error is so small because d depends on y_d inside the core only for values of r which are very close to d end any reasonably extrepoletion procedure gives much the same results. This error makes e negligible difference for the thermodynamic properties celculeted from the free energy. The extrapolation procedure can obviously have e small effect on the value of g(r) for r<d when it is calculated from Eq. (2.9'), especially for very soft potentials. This effect is minimized, however, by the exponentiel factor which approaches zero rapidly es r is decreased from d. Nevertheless, this small effect on g(r) could heve en effect on the virial pressure and energy calculeted from Eqs. (2.11) and (2.10) beceuse of the sensitivity of these equations to slight errors in g. We estimate that for the inverse twelfth power potantial, the viriel pressures might contain an error of the order of et most 5% et the highest density (and much less at lower densities), while for the much harder Lennard-Jones repulsive potential, u_{RL}, the error in the viriel pressure due to the uncertainty in the extrapoletion is negligible compared with errors erising from inaccuracies in our $g_d(r)$ for r outside the core. These latter errors are of the order of a percent.[18]

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Table Ia. Reduced Excess Free Energy per Particle for a Fluid of Molecules Interacting Through an Inverse Twelfth Power Repulsion[a] -- A Test of the Thermodynamic Relationship between Hard-Sphere and Soft-Spheres.

$-a/\rho = \beta\Delta A/N$

$\rho\sigma^3$	Monte Carlo[b]	Monte Carlo[c]	This Work[d]	Barker-Henderson Variational	Generalized Rowlinson
.1414	.40	.40	.40	.39	.39
.2828	.91	.91	.91	.89	.89
.4243	1.53	1.53	1.54	1.54	1.54
.5657	2.32	2.33	2.33	2.37	2.42
.7071	3.33	3.34	3.34	3.43	3.68
.8485	4.60	4.61	4.65	4.77	5.58

a. These calculations are for the isotherm $\beta\epsilon = 1$.

b. Reference 14.

c. Reference 15.

d. Calculated from Eqs. (2.8) and (2.7).

Table Ib. Pressure of a Fluid of Molecules Interacting Through an Inverse Twelfth Power Repulsion[a] -- A Test of the Thermodynamic Relationship Between Hard-Spheres and Soft-Spheres.

	$\beta p/\rho$				
$\rho\sigma^3$	Monte Carlo[b]	Monte Carlo[c]	This Work[d]	Barker-Henderson Variational	Generalized Rowlinson
.1414	1.45	1.45	1.45	1.36	1.44
.2828	2.12	2.12	2.12	2.11	2.13
.4243	3.10	3.12	3.12	3.18	3.25
.5657	4.56	4.58	4.57	4.72	5.16
.7071	6.64	6.66	6.71	6.93	8.57
.8485	9.46	9.56	9.89	9.98	15.18

a. These calculations are for the isotherm $\beta\epsilon = 1$.

b. Reference 14.

c. Reference 15.

d. Calculated from Eqs. (2.8), (2.7) and (3.2).

Table II. Virial Pressure and Associated Hard Sphere Diameter of a Fluid of Molecules Interacting Through an Inverse Twelfth Power Repulsion[a] -- A Test of the Structural Relationship Between Hard-Spheres and Soft-Spheres.

	$\beta p/\rho$		
$\rho\sigma^3$	Monte Carlo[b]	This Work[c]	d/σ[d]
.1414	1.45	1.45	1.0663
.2828	2.12	2.16	1.0614
.4243	3.11	3.23	1.0552
.5657	4.57	4.85	1.0477
.7071	6.65	7.23	1.0390
.8485	9.51	10.60	1.0295

a. These calculations are for the isotherm $\beta\epsilon = 1$.

b. The average of the two Monte Carlo values (see Table Ib).

c. Calculated from Eqs. (2.9'), (2.7), and (2.11).

d. The associated hard sphere diameter, in units of σ, calculated from Eq. (2.7).

Table III. Pressure and Reduced Excess Internal Energy per Particle for a Fluid of Molecules Interacting Through the Repulsive Part of the Lennard-Jones Potential -- A Test of the Thermodynamic Relationship between Hard-Spheres and Soft-Spheres.

		$\beta p/\rho$			$\beta \Delta E/N$	
$\rho\sigma^3$	T^{*a}	Monte Carlo[b]	This Work[c]	Generalized Rowlinson	Monte Carlo[b]	This Work[d]
.85	2.81	6.92	6.92	7.38	.84	.84
.84	.75	10.23	10.33	10.99	.97	.98
.65	1.35	4.89	4.94	5.06	.46	.46
.40	1.35	2.53	2.54	2.55	.17	.18
.85	.72	10.87	10.83	11.55		1.03
.50	1.36	3.28	3.29	3.31		.27

a. The reduced temperature, kT/ε.

b. The first four states are from Ref. 6 and the last two are from Ref. 17.

c. Calculated from Eqs. (2.8), (2.7), and (3.2).

d. Calculated from Eqs. (2.8), (2.7), and (3.3).

Table IV. Virial Pressure, Reduced Excess Internal Energy Per Particle, and Associated Hard Sphere Diameter for a Fluid of Molecules Interacting Through the Repulsive Part of the Lennard-Jones Potential -- A Test of the Structural Relationship between Soft-Spheres and Hard-Spheres.

		$\beta p/\rho$		$\beta \Delta E/N$		
$\rho\sigma^3$	T^{*a}	Monte Carlo[b]	This Work[c]	Monte Carlo[b]	This Work[d]	d/σ[e]
.85	2.81	6.92	7.04	.84	.86	.9699
.84	.75	10.23	10.40	.97	.99	1.0224
.65	1.35	4.89	4.99	.46	.47	1.0029
.40	1.35	2.53	2.55	.17	.18	1.0048
.85	.72	10.87	10.89		1.04	1.0237
.50	1.36	3.28	3.31		.27	1.0039

a,b. See Footnotes of Table III.

c. Calculated from Eqs. (2.9'), (2.7), and (2.11).

d. Calculated from Eqs. (2.9'), (2.7), and (2.10).

e. The associated hard sphere diameter, in units of σ, calculated from Eq. (2.7).

Figure Captions

Figure 1. Schematic plots of some functions considered in the blip expansion:

a. The exponential of β times the negative of a soft sphere potential.

b. The exponential of β times the negative of a hard sphere potential.

c. The difference between (a) and (b) showing the significance of the softness parameter ξ.

d. The blip function, $B_d(r)$. According to Eq. (2.7), the diameter d is chosen to make the net areas under $r^2 B_d(r)$ equal to zero.

Figure 2. The radial distribution function for a dense fluid of molecules interacting through the repulsive part of the Lennard-Jones potential -- A test of the structural relationship between hard-spheres and soft-spheres. The density is $\rho\sigma^3 = .85$. The temperature is $kT/\epsilon = .72$. The dots are the Monte Carlo results of Barker and Henderson, Ref. 17. The smooth curve was calculated from Eqs. (2.9') and (2.7).

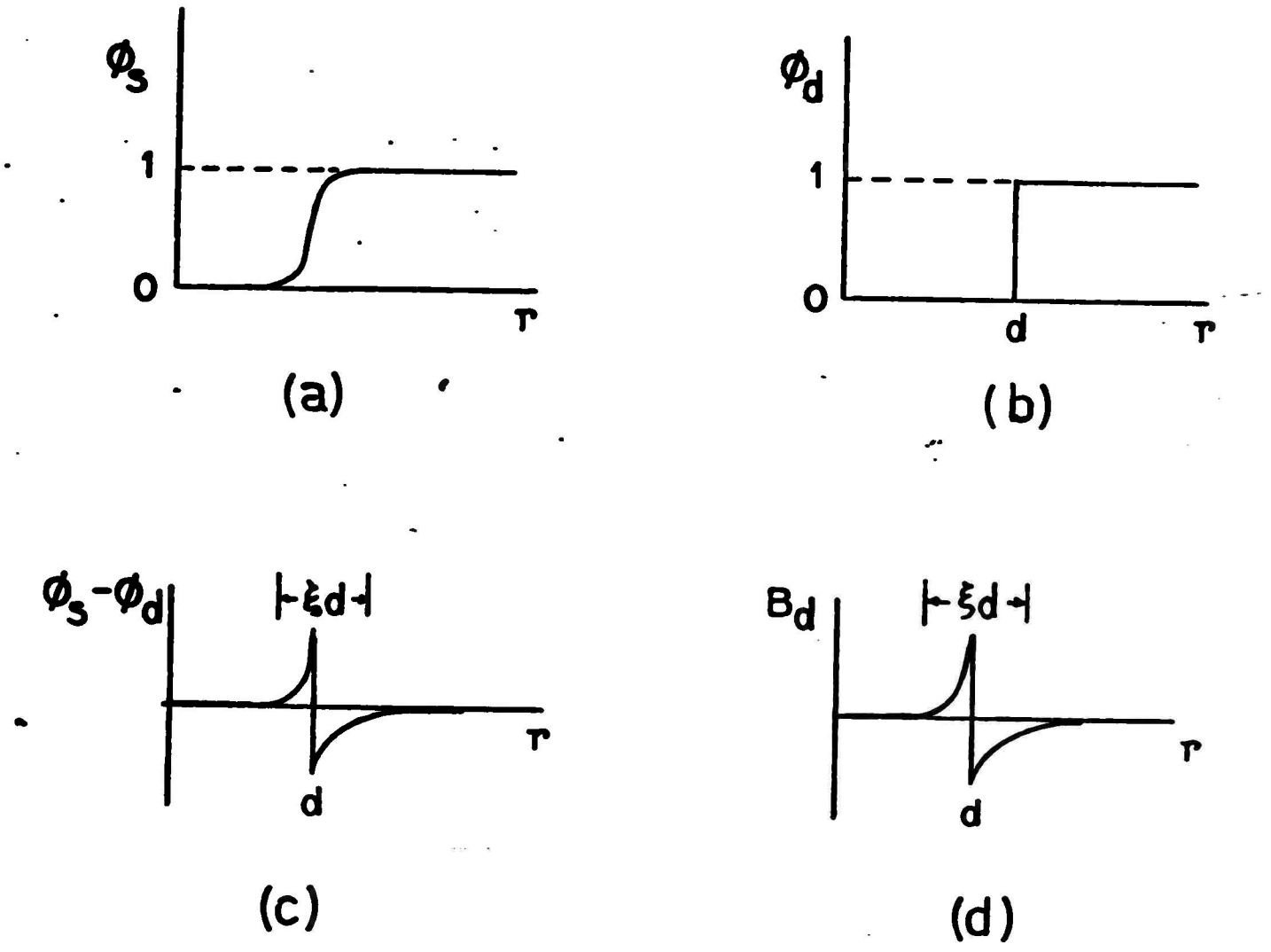

Figure 1

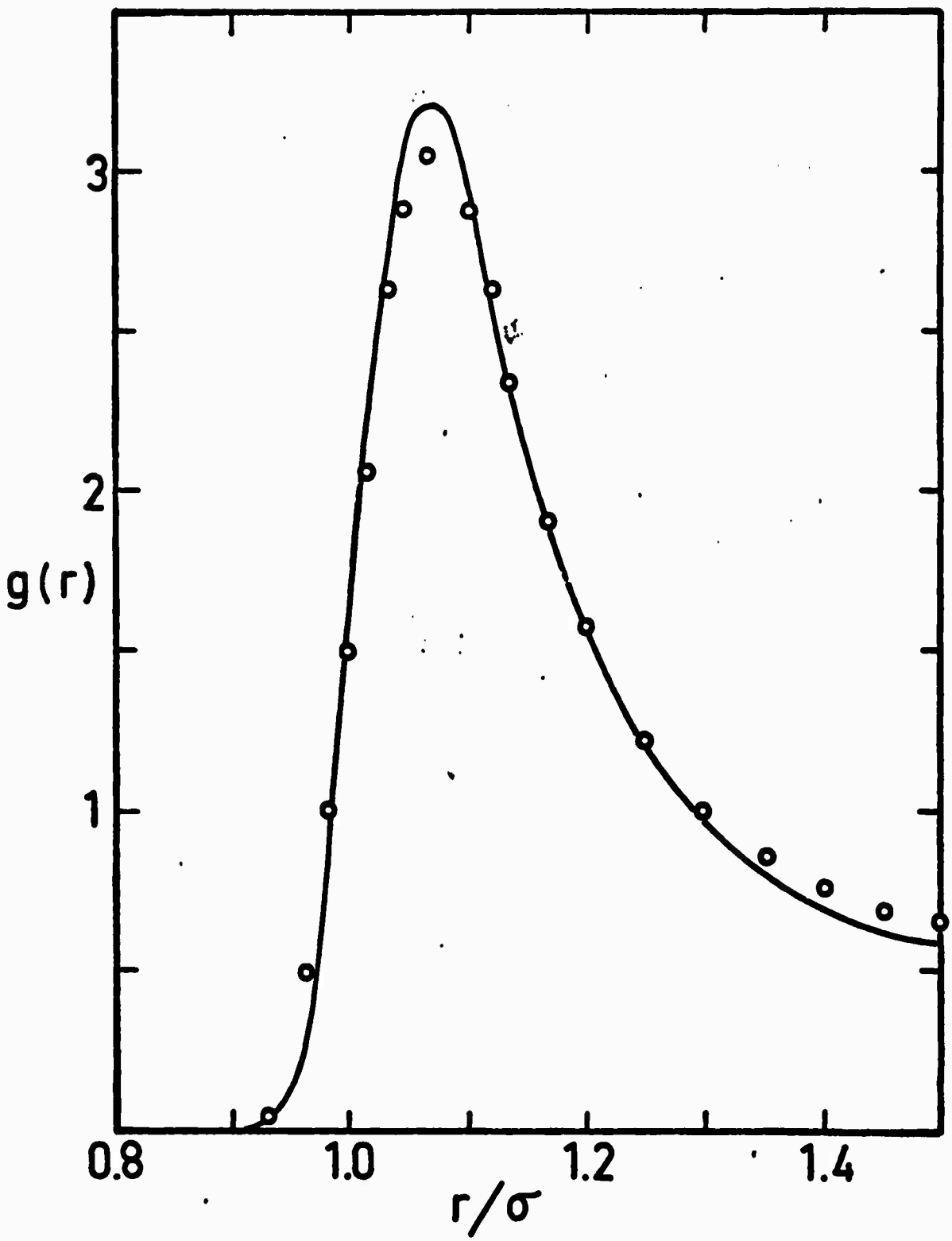

Figure 2