ARPA Order No. 1479

Program Code 1E20

Contract No. N00014-69-A-0200-6018

Principal Investigator:
Kurt E. Shuler
Department of Chemistry
University of California, San Diego
La Jolla, California 92037

Name of Contractor:
The Regents of the University of California
Contract and Grant Officer
19B, Building 301, Matthews Campus
University of California, San Diego
La Jolla, California 92037

Short Title of Work:
Roles of Repulsive and Attractive
Forces in Liquids

Effective Date of Contract:
From: 1 August 1968 To: 31 July 1972

Amount of Contract: $180,000

D D C
JAN 24 1972
B

Sponsored by
Advanced Research Projects Agency
ARPA Order No. 1479

R

41

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY *(Corporate author)* Department of Chemistry University of California, San Diego La Jolla, California 92037	2a. REPORT SECURITY CLASSIFICATION UNCLASSIFIED 2b. GROUP

3. REPORT TITLE

Roles of Repulsive and Attractive Forces in Liquids: The Optimized Random Phase Approximation

4. DESCRIPTIVE NOTES *(Type of report and inclusive dates)*

5. AUTHOR(S) *(First name, middle initial, last name)*

Hans C. Andersen, David Chandler and John D. Weeks

6. REPORT DATE December 1971	7a. TOTAL NO. OF PAGES 44	7b. NO. OF REFS 26

8a. CONTRACT OR GRANT NO. N00014-69-A-0200-6018	9a. ORIGINATOR'S REPORT NUMBER(S) Technical Report No. ~~11~~ 10
b. PROJECT NO.	
c.	9b. OTHER REPORT NO(S) *(Any other numbers that may be assigned this report)*
d.	ARPA Order No. 1479

10. DISTRIBUTION STATEMENT

Distribution of this document is unlimited.

11. SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY Office of Naval Research Physics Branch Washington, D. C. 20360

13. ABSTRACT

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14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
pair correlation functions						
structure of liquids						
thermodynamics of liquids						
forces in liquids						

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Roles of Repulsive and Attractive Forces in Liquids: The Optimized Random Phase Approximation[*]

Hans C. Andersen
Department of Chemistry
Stanford University
Stanford, California 94305

David Chandler
School of Chemical Sciences
University of Illinois
Urbana, Illinois 61801

and

John D. Weeks[†]
Department of Chemistry
University of California, San Diego
La Jolla, California 92037

Abstract

The optimized random phase approximation (ORPA) is applied to the calculation of the thermodynamic properties and pair correlation function of simple liquids. General formulas are presented, together with results for the Lennard-Jones fluid, which are compared with Monte Carlo and molecular dynamic results. Excellent agreement is obtained for the entire single phase fluid region of the phase diagram, except for the critical region and the very low temperature vapor. The theory converges especially rapidly at high densities or at high temperatures. The importance of separating the intermolecular potential in the proper way to obtain most rapid convergence of perturbation theories is discussed. It is concluded that the structure of simple liquids is determined mostly by the rapidly varying parts of the potential. Further, the ORPA provides an accurate theory for calculating the contributions from different forces to the structure and thermodynamics of liquids.

I. Introduction

In a recent discussion of the equilibrium structure of simple liquids[1], we introduced a method for separating the intermolecular potential into two parts, an attractive part and a repulsive part, and discussed the conceptual advantages of this separation. In particular we concluded that the structure of the Lennard-Jones liquid is determined largely by the repulsive part of the potential at high density.

To test this conclusion, subsequent Monte Carlo calculations[2,3] were performed for hypothetical fluid whose potential is just the repulsive part of the Lennard-Jones potential. The differences between the structure of this fluid and the structure of the Lennard-Jones liquid (at the same temperature and density) clearly are due to the attractive forces. At high densities, these differences were indeed found to be small, but not negligible.

Any theory which neglects the effect of attractive forces on the structure of a liquid may be called a "high-temperature approximation (HTA)", since it is reasonable to expect such an approximation to be valid at high temperatures. This type of approximation may also be applied in thermodynamic perturbation theory. For the Lennard-Jones fluid, the HTA gives remarkably accurate thermodynamic properties not only at high temperatures but also at high densities for all temperatures, down to and including the triple point temperature[4,2].

Thus for the Lennard-Jones liquid, the HTA is useful for all high temperature states and for all high density states. Over this range it provides a qualitatively correct theory of structure and a quantitatively accurate theory of thermodynamic properties.

To obtain a more general theory of liquid structure and thermodynamics, one which is applicable to lower densities or temperature and to other types of fluids, it is necessary to have an accurate method for going beyond the HTA, i.e. for calculating the effect of attractive forces on the liquid structure. In this paper we apply the recently developed[5] "optimized random phase approximation (ORPA)" to this problem. For the Lennard-Jones liquid, the method is very accurate for the _entire_ single-phase fluid region of the phase diagram (except for the critical region and the vapor far below the critical temperature). The thermodynamic results agree with those of Monte Carlo and molecular dynamics calculations to within the estimated uncertainty of the latter, and the pair correlation functions and structure factors also agree well with those obtained from the computer calculations. The theory is very rapidly convergent for the Lennard-Jones liquid (much more so than the Barker-Henderson perturbation theory[6]), and so we expect that it will be applicable to a wide variety of liquids, including those in which the effect of attractions is great. For example, ORPA (in suitably generalized form[7]) can be applied to reasonable potential models[8] for liquid water. In addition, the ORPA provides a way of understanding why the effect of attractions is so small for simple liquids.

In the next section, we present some preliminary definitions and review the basic ideas of the HTA and the ORPA. Section III discusses the calculational procedures involved in applying the theory. The results for the Lennard-Jones fluid are presented in Section IV, and conclusions are discussed in Section V.

II. Definitions and General Theory

A. Definitions

The general system under consideration here is a classical fluid of N molecules in a volume V (the average number density is $\rho = N/V$). We shall assume that the total potential energy, W, can be written as a sum of spherically symmetric pair potentials, w:

$$W = \sum_{i<j=1}^{N} w(r_{ij}) , \tag{1}$$

where r_{ij} is the distance between molecules i and j.

The Helmholtz free energy for the system is given by

$$-\frac{\beta \Delta A}{V} = \mathcal{A} = V^{-1} \ln V^{-N} \int d\underset{\sim}{r}^{N} e^{-\beta W} , \tag{2}$$

where ΔA denotes the excess free energy with respect to the ideal gas at the same temperature, density and volume, and β^{-1} is Boltzmann's constant times the temperature. The thermodynamic properties are obtained by differentiating $\mathcal{A}$ with respect to β and ρ. The correlation functions can be obtained by functional differentiation. In particular,

$$g(r) = -(2/\rho^2) \; [\delta \mathcal{A} / \delta \beta w(r)] = h(r)+1 , \tag{3}$$

where g(r) is the radial distribution function, and h(r) is called the two-particle correlation function. The dimensionless Fourier transform of h(r) is

$$\hat{h}(k) = \rho \int d\underset{\sim}{r} \; h(r) \exp(-i\underset{\sim}{k}\cdot\underset{\sim}{r}) = \chi(k) - 1 , \tag{4}$$

where $\chi(k)$ is called the structure factor.

The methods we describe in this paper are applicable to classical fluids for which the pair interaction contains a harshly repulsive part that is short ranged (in addition to some attractive parts and/or long ranged repulsions):

$$w(r) = u_0(r) + u(r) \quad , \tag{5}$$

where $u_0(r)$ is the harsh repulsion. We call $u_0(r)$ the <u>reference potential</u>; it is the pair potential for the <u>reference fluid</u> in which the forces between the molecules are short ranged and harshly repulsive. The remainder, $u(r)$, is called the <u>perturbation potential</u>.

In saying that the potential u_0 is "short ranged and harshly repulsive" we mean that the Boltzmann factor for u_0, $\exp[-\beta u_0(r)]$, closely resembles the Boltzmann factor for a hard sphere interaction (which is a step function rising from 0 to 1 at a distance corresponding to the hard sphere diameter d). In particular, $\exp[-\beta u_0(r)]$ must be zero for small r, unity for large r, and it must rise from essentially zero to essentially unity over a range of r values which is small compared with the r at which it has the value of $\frac{1}{2}$.

When $w(r)$ contains short ranged, strongly repulsive forces for $0 \leq r \leq r_0$ only, we want to choose $u_0(r)$ to have the same forces, and so u_0 and u can be defined by Eq. (5) and the following:

$$\begin{aligned} du_0(r)/dr &= dw(r)/dr, & r &< r_0 \\ u_0(r) &= 0 & r &\geq r_0 \; . \end{aligned} \tag{6}$$

For this separation it follows that

$$u(r) = \text{constant} = u(r_0), \quad r < r_0 \; .$$

Also $u(r)$ is continuous and more slowly varying than if we had not included all the short ranged repulsive forces in $u_0(r)$. An example of this kind of potential separation is depicted in Fig. 1 for the case in which $w(r)$ is the Lennard-Jones potential and r_0 is chosen to be the minimum of the potential. For this separation of the Lennard-Jones potential, the perturbation contains all the attractive forces and no repulsive forces and is more slowly varying than u_0. In the most general situation $u(r)$ may also contain some slowly varying and/or long ranged repulsive interactions.

There are two major reasons for separating $w(r)$ into a harshly repulsive reference potential plus a slowly varying perturbation. First, a fluid in which the interactions are short ranged and harshly repulsive is obviously similar to a hard sphere fluid.[9] It is thus possible to exploit this similarity and define a new fluid, called the trial system, in which the pair interaction is given by

$$w_T(r) = u_d(r) + u_T(r) \tag{7a}$$

where

$$u_T(r) = u(r), \quad r \geq d , \tag{7b}$$

$$u_d(r) = \infty, \quad r < d \\ = 0, \quad r \geq d \tag{8}$$

and $d \leq r_0$. We call this the trial system because it is necessary to "try" (see below) various different values of d to find the one which is most closely related to the fluid with the pair potential $w(r)$. For distances smaller than d, the perturbation in the trial system, $u_T(r)$, can take on any finite value. The trial system differs from the fluid of interest only in that u_0 has been replaced by the hard sphere potential u_d. This difference makes the trial system more amenable to statistical mechanical analysis than the actual fluid of interest. In particular, the short ranged repulsions of the trial system are hard sphere repulsions, and a great deal of information about the hard sphere fluid is available from the results of computer experiments. Further, our technique for describing the effects of the perturbation on the structure relies on the physical constraint that $g(r) = 0$ for $r < d$ when the pair interactions contain a hard core repulsion. Once the thermodynamic and structural properties of the trial system are obtained (in some degree of approximation), it is then quite easy to relate these results to the corresponding properties of the fluid in which the pair potential is $w(r)$ rather than $w_T(r)$. This is the program we adopt in the present work.

A second reason for separating $w(r)$ into a harshly repulsive reference potential plus a slowly varying perturbation has to do with the convergence of perturbation theories. While the effects of a quickly varying perturbation on the structure of a fluid can be very large,[6] the effects of a slowly varying perturbation are small by comparison.[1] As a result, when it is possible to separate $w(r)$ in such a way that $u(r)$ is slowly varying, a perturbation theory for describing the effects produced by $u(r)$ can be rapidly convergent. It is for this reason that the potential separation exhibited in Fig. 1 leads to a first order perturbation theory[4] that is significantly more accurate than that of Barker and Henderson[6] who used the negative part of the Lennard-Jones potential (rather than the attractive part) for their perturbation.

The notation we use to distinguish the properties of various systems is the following: Properties of the hard sphere fluid are denoted by a subscript "d" which stands for the diameter of the spheres. The properties of the trial system are identified with a subscript "T". Those of the reference system are denoted with a "0". Properties of the fluid of interest have no subscripts. Thus, for example, $\chi(k)$ denotes the structure factor for the system with pair potential $w(r)$, while $\chi_d(k)$, $\chi_T(k)$ and $\chi_0(k)$ denote the structure factors for the hard sphere, trial and reference systems, respectively.

In the next part of this section, we establish the fundamental relationship between the trial system and the actual system under consideration. In Part C, the high temperature approximation (HTA) will be applied to the trial system, and the relationship will be used to obtain the corresponding approximation for the fluid of interest. In Part D, the optimized random phase approximation (ORPA) will be used in the same way to obtain more accurate results. Some limitations of HTA and ORPA are discussed in Part E.

B. Relationship Between Trial System and Actual System

The properties of a system with realistic repulsive forces can be related to a system with hard core repulsions by a cluster expansion. The expansion developed below is a generalization of one recently presented by the authors[9].

Note that $\mathcal{A}$ is a functional of the Mayer function $f(r) = \exp(-\beta w)-1$. The corresponding quantity for the trial system, $\mathcal{A}_T$, depends in the same way on $f_T(r;d) = \exp(-\beta w_T)-1$. These cluster functions are drawn in Fig. 2a. The difference between them, $\Delta f = f - f_T$, is depicted in Fig. 2b. If the trial system diameter d is chosen well, the distance over which $\Delta f(r)$ is non-zero, ξd, is small. This immediately suggests that $\mathcal{A}$ and $\mathcal{A}_T$ can be related by the following functional Taylor series:

$$\mathcal{A} = \mathcal{A}_T + \int \left[\frac{\delta \mathcal{A}}{\delta f(r)}\right]_T \Delta f(r)\, d\underset{\sim}{r} + \dots \ .$$

The subsequent terms are higher order functionals of $\Delta f(r)$. The effective expansion parameter in this series is ξ, which can be regarded to be approximately equal to

$$d^{-1} \int_0^\infty |\Delta f(r)|\, dr \ .$$

By performing the indicated functional differentiation, we obtain

$$\mathcal{A} = \mathcal{A}_T + \frac{1}{2}\rho^2 \int y_T(r)\ \Delta f(r)\ d\underset{\sim}{r} + \dots , \qquad (9)$$

where $y_T(r)$ is related to the radial distribution function in the trial system by

$$y_T(r) = \exp[+\beta w_T(r)]\ g_T(r) \ . \qquad (10)$$

From Eq. (9) it is apparent that a good choice of d is that value for which the first correction to $\mathcal{A} \simeq \mathcal{A}_T$ vanishes. Thus, d is chosen to satisfy

$$\int y_T(r;d)\ \Delta f(r;d)\ d\underset{\sim}{r} = 0\ . \tag{11}$$

It can be shown[9] that when d is determined by Eq. (11),

$$\mathcal{A} = \mathcal{A}_T(d) + O(\xi^4)\ . \tag{12}$$

That is, Eq. (11) not only makes the term of order ξ in Eq. (9) equal to zero, it also forces further corrections to be of order ξ^4 (and not ξ^2). From the usual virial expansion for $\mathcal{A}$, it is also evident that $\mathcal{A} \simeq \mathcal{A}_T(d)$ is exact in the limit of small ρ when d is chosen by Eq. (11).

A similar functional Taylor series can be generated to relate h(r) to the trial system correlation function. In particular, when d is chosen by Eq. (11), it is found[9] that

$$y(r) \equiv \exp[+\beta w(r)]\ g(r) = y_T(r;d)\ [1 + O(\xi^2)]\ . \tag{13}$$

As a result, the structure factor is given by

$$\chi(k) = \chi_T(k;d) + \rho \int d\underset{\sim}{r}\ y_T(r;d)\ \Delta f(r)\ \exp(-i\underset{\sim}{k}\cdot\underset{\sim}{r}) + O(\xi^2) \tag{14}$$

The second term makes appreciable contributions (in the form of a damping) at intermediate and large wave-vectors.[10]

Equations (11)-(14) provide the desired relationship between the trial system and the system in which the pair potential is w(r). We now consider two approximate solutions to the problem of calculating properties of the trial system.

C. High Temperature Approximation for the Trial System

The simplest theory for the trial system is obtained by neglecting entirely the effects of the perturbation on the structure. This approximation, which becomes exact in the limit of small β, is called the high temperature approximation (HTA). For the trial system, it is

$$[g_T(r)]_{HTA} = g_d(r) \tag{15}$$

and

$$[\mathcal{A}_T]_{HTA} = \mathcal{A}_d - \frac{1}{2}\beta\rho^2 \int g_d(r)\, u_T(r)\, d\underset{\sim}{r} \, . \tag{16}$$

With the aid of Eqs. (11)-(13) we obtain from (15) and (16) the HTA for the actual system with the pair potential $w(r)$:

$$g_{HTA}(r) = \exp[-\beta u_0(r)]\ y_{d_0}(r) = g_0(r)\ [1 + O(\xi^2)] \tag{17}$$

and

$$\mathcal{A}_{HTA} = \mathcal{A}_{d_0} - \frac{1}{2}\beta\rho^2 \int g_{HTA}(r)\, u(r)\, d\underset{\sim}{r} \, . \tag{18}$$

The quantity d_0 is the solution to Eq. (11) when the HTA is used for $y_T(r;d)$; that is

$$\int y_{d_0}(r)\, \Delta f_0\, d\underset{\sim}{r} = 0 \tag{19}$$

where

$$\Delta f_0 = \exp(-\beta u_0) - \exp(-\beta u_{d_0}) \, .$$

Equations (17)-(19) are the principal equations employed by the authors in their recent discussions on the perturbation theory and structure of simple liquids.[1,4] At high densities they afford an exceptionally accurate (as well as simple) theory of Lennard-Jones liquids.

At low densities, however, the structure is no longer dominated entirely by the repulsive forces, and the attractions must be accounted for. Further, it is probable that important classes of systems exist (e.g., those in which the attractive forces vary rapidly in space) for which the attractions play an important role in forming the liquid structure even at high densities. Thus, we now turn to the problem of describing the effects of the perturbation on the structure.

D. Optimized Random Phase Approximation for the Trial System

Discussions of the random phase approximation (RPA) and the optimized random phase approximation (ORPA) for classical fluids have already been published.[5,11-13] Thus, we present below only a brief outline of the basic ideas, together with the formulas necessary for the present work.

The RPA for the trial system describes the effects of the perturbation on the structure of that system by the equation

$$[\chi_T(k)]_{RPA} = \frac{\chi_d(k)}{1+p(k)\chi_d(k)} \, , \tag{20}$$

where

$$p(k) = \beta\rho\,\hat{u}_T(k) = \rho \int d\underset{\sim}{r}\;\beta u_T(r)\,\exp(-i\underset{\sim}{k}\cdot\underset{\sim}{r}) \tag{21}$$

This approximation can be expressed in terms of the direct correlation function, c(r):

$$[c_T(r)]_{RPA} = c_d(r) - \beta u_T(r) \, . \tag{22}$$

Thus, it is the first order approximation in the perturbation expansion for $c_T(r)$ about $c_d(r)$ (where the ordering parameter is the strength of the perturbation potential). In terms of the radial distribution function, the approximation is

$$[g_T(r)]_{RPA} = g_d(r) + \left[\begin{array}{l}\text{sum of all singly connected chains in}\\ \text{the cluster expansion for } g_T(r) \text{ involv-}\\ \text{ing one or more } -\beta u_T(r) \text{ bonds, and zero}\\ \text{or more } h_d(r) \text{ bonds.}\end{array}\right]$$

$$= g_d(r) - (2\pi)^{-3} \int d\underset{\sim}{k}\;\chi_d^{\,2}(k)\;\beta\hat{v}(k)\,\exp(i\underset{\sim}{k}\cdot\underset{\sim}{r}) \, , \tag{23}$$

where

$$\hat{v}(k) = \hat{u}_T(k)/[1 + p(k)\ \chi_d(k)] \ . \tag{24}$$

The cluster diagrams described in Eq. (23) are depicted in Fig. 3a. The RPA for the Helmholtz free energy is

$$[\mathcal{A}_T]_{RPA} = \mathcal{A}_d - \frac{1}{2}\beta\rho^2 \int d\underset{\sim}{r}\ g_d(r)\ u_T(r)$$
$$+ \frac{1}{2}(2\pi)^{-3}\int d\underset{\sim}{k} \left\{p(k)\chi_d(k) - \ln[1 + p(k)\chi_d(k)]\right\} \ . \tag{25}$$

Equations (20), (22) or (23) are obtained by taking the appropriate functional derivatives of (25) [see Eq. (3)]. The first two terms on the right hand side of Eq. (25) form the HTA for $\mathcal{A}_T$. The last term is the sum over all ring graphs in the cluster expansion for $\mathcal{A}_T$ involving $h_d(r)$ bonds and two or more $-\beta u_T(r)$ bonds. These diagrams are depicted in Fig. 3b. It is seen that the RPA can also be appropriately called the "ring picture approximation".

Since the RPA represents the sum of a class of graphs in the cluster series, systematic corrections to the approximation can be obtained by accounting for subsequent terms in the cluster expansion. At least two such theories have been presented: the γ-ordered expansion[13] and the mode expansion.[5,11,12] The former utilizes diagrammatic methods explicitly, while the latter uses a collective coordinate formalism. Both theories give corrections to the RPA in the form of an infinite series expressed entirely in terms of reference (i.e. hard sphere) fluid correlation functions and a screened potential $v(r)$, which is the inverse Fourier transform of $\hat{v}(k)$ defined in Eq. (24).

The ORPA is a method for enhancing the convergence of such infinite series. To introduce the ORPA we note that the short ranged repulsive interaction in the trial system is the hard core potential $u_d(r)$. Thus intermolecular separations smaller than d are physically inaccessible. As a result, the exact evaluation of $g_T(r)$ would yield $g_T(r) = 0$ for $r<d$. However, the RPA does not necessarily obey this condition since the second term on the right side of Eq. (23) may be non-zero for $r<d$. This improper description of excluded volume effects is related to the fact that the predictions of the RPA depend on the perturbation in this physically inaccessible region[12]. By changing $u_T(r)$ for $r<d$ we can change $u_T(k)$ (and $\hat{v}(k)$) for any value of k. Such changes obviously alter the value and hence the accuracy of $[\mathcal{A}_T]_{RPA}$ and the form of $[g_T(r)]_{RPA}$. In recent work on model electrolytes[5,12] it was found that by choosing $u_T(r)$ for $r<d$ such that $[g_T(r)]_{RPA} = 0$ for $r<d$, the RPA can be made very accurate. Thus we are motivated to extend the ideas used in the electrolyte calculations to the problem under consideration here. In particular, we shall pick u(r) for $r<d$ so that

$$[g_T(r)]_{RPA} = -(2/\rho^2)\,\frac{[\delta\,\mathcal{A}_T]_{RPA}}{\delta\beta u(r)} = 0\;, \quad r<d\;, \tag{26}$$

From Eq. (25) it is seen that the addition of this physical constraint to the RPA is equivalent to demanding that

$$[\delta\, a_{RPA}/\delta\, u(r)] = 0\;, \quad r<d\;, \tag{27}$$

where a_{RPA} is the random phase integral

$$a_{RPA} = \frac{1}{2}\,(2\pi)^{-3}\int d\underset{\sim}{k}\,\left\{p(k)\chi_d(k) - \ln[1+p(k)\chi_d(k)]\right\} \tag{28}$$

which corrects the HTA to $\mathcal{A}_T$ in the RPA.

In summary, the ORPA is any one of Eqs. (20), (22), (23) or (25) supplemented with Eq. (27). Further discussion of this approximation is contained in Reference 5.

E. Limitations of HTA and ORPA

Published calculations show that at high densities the HTA gives a very accurate theory of thermodynamic properties if the appropriate potential separation is used.[1,2,4] Further, the calculations presented in Section IV of this paper show that the ORPA is very accurate at high and moderate densities for both thermodynamic and structural properties. This state of affairs does not, however, persist in the region of low densities. In particular, the HTA and ORPA do not give the exact second virial coefficient. The correct second virial coefficient for $\mathcal{A}$ is

$$B_2 = \frac{1}{2} \int d\underset{\sim}{r} \, [\exp(-\beta u_0 - \beta u) - 1] \ .$$

The HTA gives

$$[B_2]_{HTA} = \frac{1}{2} \int d\underset{\sim}{r} \, [(1-\beta u) \ \exp(-\beta u_0) - 1] \ ,$$

and the ORPA gives

$$[B_2]_{ORPA} = \frac{1}{2} \int d\underset{\sim}{r} \, [(1 - \beta u + \frac{1}{2} \beta^2 \ u^2) \ \exp(-\beta u_0) - 1] \ .$$

The error in the ORPA result is small at high temperatures but can be large at low temperatures. (The corresponding errors in the low density g(r) are similar.) Away from the critical region, the errors in ORPA at low density make relatively little difference in the measurable thermodynamic properties, since for temperatures sufficiently below the critical temperature the maximum density of the gas is very small.

The HTA and ORPA are not acceptable theories of critical phenomena. Neither gives a free energy which satisfies thermodynamic stability criteria. Even if one supplements the theoretical free energy with a Maxwell construction, a purely classical coexistence curve is obtained from both theories.[14] Also the ORPA (like the HTA) is inconsistent in the sense that at the critical point (as determined by the free energy) the compressibility as determined by the correlation function is finite.

One pleasant feature of ORPA as opposed to the RPA is that the ORPA does not contain the catastrophic singularities which are found in the RPA and frequently (and incorrectly) associated with phase transitions.[15]

III. Calculational Procedure and Summarizing Equations

The first step when applying the ORPA is the determination of the optimized form of $u_T(r)$ for $r<d$. This optimized potential is the solution to the variational problem stated by Eq. (27). We find this solution numerically. The perturbation in the unphysical region, $r<d$, is expanded in a series of basis functions. In particular, $u_T(r)$ is expressed as

$$-\beta u_T(r) = -\beta u(r) + q\, H(d-r) - (s/d)\, G(r-d)$$

$$+ H(d-r)\, (1-r/d)^2 \sum_{n=0}^{m} c_n P_n^*(r/d) \qquad (29)$$

where q, s, and c_n are constants, H(x) is the step function

$$H(x) = 1,\ x \geq 0$$
$$= 0,\ x<0\ ,$$

G(x) is the function whose derivative is the step function

$$G(x) = x,\ x \geq 0$$
$$= 0,\ x<0\ ,$$

and $P_n^*(x) = P_n(2x-1)$, where $P_n(y)$ is a Legendre polynomial. The Fourier transform of $u_T(r)$ thus depends on the values of q, s, c_0, ... As a result, a_{RPA} also depends on these coefficients. The optimized $u_T(r)$ is obtained by finding the set of coefficients for which a_{RPA} is stationary with respect to small changes in the coefficients. [We note that a_{RPA} is a positive definite functional of $\hat{u}_T(k)$. One solution of Eq. (27) corresponds to an absolute minimum, and it is apparently this solution that we find. We do not know if other solutions of (27) exist.]

With the coefficients q, s, c_0, c_1, ... determined by the variational procedure, the RPA, Eqs. (20)-(25), is applied directly to yield the equilibrium properties of the trial system. In particular, Eq. (23) is applied to obtain $g_T(r)$. In order to relate the trial system properties to the actual systems properties, we also need $y_T = \exp(+\beta w_T) g_T$. For $r > d$, there is no problem. However, the ORPA does not directly yield information about $y_T(r)$ for $r < d$. Fortunately, we need $y_T(r)$ for values of r close to d only. Thus, we simply extrapolate into the hard core using the fact that $y_T(r)$ and its first derivative are continuous functions of r. The y_T function and its derivative can be evaluated at $r = d$ accurately since $g_T(r) - c_T(r)$ and its first three derivatives are continuous at that point. Thus, for example,

$$g_T(d+) = c_d(d+) - c_d(d-) + \beta u_T(d-) \ .$$

The direct correlation function for hard spheres, $c_d(r)$, is known analytically,[2] and $\beta u_T(d-)$ can be evaluated from Eq. (29).

With the $y_T(r;d)$ calculated for a range of d values, we then calculate the d which satisfies Eq. (11). It is found that when the perturbation $u(r)$ is very much more slowly varying than $u_0(r)$, the value of d obtained from Eq. (11) is essentially the same as d_0 which is the solution to Eq. (19). With the value of d determined, Eqs. (12), (13) and (14) are used to produce the final ORPA results for the system in which the pair potential is $w(r)$. In particular, the free energy is

$$\mathcal{a}_{ORPA} = \mathcal{a}_{HTA} + \Delta a_{HTA} + a_{RPA} \qquad (30)$$

where $\mathcal{a}_{HTA}$ is defined by Eqs. (17) and (18) (it is a function of the diameter d_0), a_{RPA} is the random phase integral, Eq. (28), evaluated with hard sphere diameter d and the optimized $u_T(r)$, and

$$\Delta a_{HTA} = \mathcal{a}_d - \mathcal{a}_{d_0} - \frac{1}{2}\beta\rho^2 \int d\underset{\sim}{r}\,(g_d - g_{d_0})\,u(r)\ . \tag{31}$$

In deriving Eq. (31), we make use of Eq. (19). Since for many systems, d is very close in value to d_0, the Δa_{HTA} is frequently negligible, and $a_{RPA}(d)$ can be replaced by $a_{RPA}(d_0)$.

IV. Application to Lennard-Jones Fluid

We have applied the procedure described in the previous section to the Lennard-Jones fluid, which is a hypothetical fluid of spherical particles which interact with each other through a distance dependent potential of the following form:

$$w(r) = 4\epsilon\,[(\sigma/r)^{12} - (\sigma/r)^{6}] \;. \qquad (32)$$

The total potential energy of the fluid is assumed to be equal to the sum of all the pair interactions.

This simple model is known to be inadequate as an exact description of even the noble gases, because of the restricted form of the potential and the neglect of three-body forces.[16] For our purposes its major virtue is that Monte Carlo and molecular dynamics calculations have been performed for this model, giving information about the thermodynamic and structural properties. Thus for checking the accuracy of the ORPA, the Lennard-Jones fluid is more ideal than a real fluid such as argon, for which we do not know the intermolecular interactions so accurately.

The potential separation employed in our calculations is the one depicted in Fig. 1. That is,

$$\begin{aligned} u_0(r) &= w(r) + \epsilon \;, & r &< r_0 \\ &= 0 \;, & r &\geq r_0 \end{aligned} \qquad (33a)$$

$$\begin{aligned} u(r) &= -\epsilon \;, & r &< r_0 \\ &= w(r) \;, & r &\geq r_0 \;, \end{aligned} \qquad (33b)$$

where $r_0 = 2^{1/6}\sigma$ is the position of the minimum in w(r). This separation of w(r) satisfies all the conditions desirable for reference and perturbation interactions (see Section II A). In particular, $u_0(r)$ is a harsh repulsion, and u(r) is slowly varying.

The Lennard-Jones parameters ϵ and σ can be used as the units of energy and length, respectively; all the thermodynamic properties can be expressed in terms of the dimensionless density, $\rho^* \equiv \rho\sigma^3$, and the dimensionless temperature, $T^* \equiv (\beta\epsilon)^{-1}$. In these units the critical point occurs for $T_c^* = 1.26$ and $\rho_c^* = .30$, and the triple point is at $T_t^* = .70$ and $\rho_t^* = .84$. The accuracy of the critical point parameters is uncertain.[17]

The calculations were performed for a wide variety of states for reduced densities from about .1 to 1 and reduced temperatures from about .6 to 2.74. For each state the hard sphere diameter, d_0, associated with the repulsive part of the potential was evaluated [Eq. (19)], followed by the HTA free energy, structure factor, and pair correlation function. For the optimization procedure on the trial system we used the series in Eq. (29) truncated after the P_1^* term. [This trial function with only four basis functions was found to be accurate enough. Extending the series up to the P_5^* term had no appreciable effect.] The trial system hard sphere diameter, d, associated with the repulsive part of the potential in the <u>presence</u> of attractions was evaluated according to Eq. (11). For each state the difference between d_0 and d was found to be negligible (approximately $1\text{-}2 \times 10^{-4}\ \sigma$). The optimized RPA integral provides the ORPA contribution to the free energy, and the optimized coefficients were used to calculate the ORPA corrections to the structure factor and pair correlation functions.[18]

These calculations require a knowledge of the excess free energy $\mathcal{A}_d$ and the pair correlation function $g_d(r)$ for the hard sphere fluid for range of densities. We used the results of Verlet and Weis[2], who performed Monte Carlo calculations for hard spheres and presented very convenient analytic forms for the functions.

The thermodynamic results are presented in Tables I-III. The free energy was obtained from Eqs. (18) and (30), and the pressure and energy were obtained by numerical differentiations of the free energy with respect to density and temperature, respectively:

$$\beta p/\rho = -\rho \left(\frac{\partial \mathcal{A}/\rho}{\partial \rho}\right)_\beta ,$$

and

$$\Delta E/N = -\left(\frac{\partial \mathcal{A}/\rho}{\partial \beta}\right)_\rho ,$$

where ΔE stands for the excess (with respect to the ideal gas) internal energy. These results are compared with the molecular dynamics results of Verlet[19] and the Monte Carlo calculations of Levesque and Verlet, and Hansen.[20] A convenient summary of much of the available computer data is found in Ref. 2.

Excellent agreement between ORPA and computer results are obtained for most of the states investigated. For example, Verlet estimated that for the high density, low temperature states, the error in the molecular dynamics results for $\beta p/\rho$ may reach .05. Table II shows that for most of the high density states the differences between the ORPA and molecular dynamics results are equal to or less than this amount. The only serious discrepancies between ORPA and Monte Carlo occur for the low temperature low density gas, i.e. the vapor well below the critical temperature.

The HTA and ORPA structure factors and pair correlation functions are compared with molecular dynamics results[21] in Figs. 4-7. Figure 4 shows the structure factor for $\rho^* = .844$, $T^* = .723$, a state near the triple point. The major discrepancy between the HTA and molecular dynamics results occur only in the height of the first peak. The ORPA raises the peak, eliminating much of the discrepancy, and makes other changes which are not visible on the scale of this graph. Fig. 5 shows the pair correlation function for a nearby state. The HTA is remarkably accurate but peaks slightly too high and for too small an intermolecular distance. The ORPA improves the agreement with computer experiments.

These two figures illustrate the accuracy of the hypothesis that at high density repulsive forces dominate the structure of a simple liquid.[1] The HTA result is not accurate enough to give good pressures via the virial equation.[2] This, however, is an extremely sensitive test of a correlation function. When directly compared with the results of the computer experiment, the HTA can be seen to account quite well for the important features of g(r).

Figures 6 and 7 show the corresponding results for states at about critical temperature but at a density somewhat higher than critical. For g(r) the HTA is only qualitatively correct. For the structure factor, the HTA is again remarkably good except for small k. The ORPA to a large extent corrects these discrepancies. For the structure factor, the ORPA results essentially coincide with the molecular dynamics results, except at small k. (The small k errors in the ORPA are a reflection of the fact that the ORPA does not properly account for the long range correlations in the critical region.) These results confirm the conclusions of our previous work[1] about the density and k dependence of the effect of repulsive forces on the structure of liquids[22]

The ORPA results also agree quite closely with the second order perturbation theory of Barker and Henderson.[6] For example, along the isotherm $T^* = 1.15$, the free energies $(-\mathcal{A}/\rho)$ of the two theories differ by at most .02 and the compressibility factors $\beta p/\rho$ by at most .06.

A major difference between the two theories is that at high densities the free energy series whose first two terms are the HTA and ORPA, converge much more rapidly than the BH perturbation theory. The HTA is already essentially correct at high densities, and the ORPA makes a very small correction (see for example Table III). By comparison the BH first order theory is not nearly so accurate[4] and the BH second order correction is about 20 times larger than the RPA correction. A similar difference in the convergence of $g(r)$ and $\chi(k)$ exists for the two theories. The origin of these differences is the methods used to separate the potential into reference and perturbation parts. Barker and Henderson choose the positive part of the Lennard-Jones potential as their reference interaction. The negative part is taken to be the perturbation. However, the negative part of the Lennard-Jones potential is <u>not</u> slowly varying, and thus it makes large contributions to the structure at all densities. The separation into purely repulsive and purely attractive parts which we use is more useful, since at high densities the purely attractive part (which is slowly varying) has only a very small effect on the structure.

A second major difference is that in the BH theory, it is necessary to have information about the three- and four-particle correlation functions in the hard sphere fluid in order to calculate the effect of the perturbation potential on the structure. On the other hand, the ORPA requires only the more easily obtained two-particle $g(r)$ for hard spheres.[23]

V. Discussion

In this section, we summarize the principal conclusions of this work and discuss the advantages associated with using the ORPA to study classical fluids.

Principal conclusions. The structure of dense simple classical fluids is determined mostly by the rapidly varying parts of the intermolecular potential. If all the rapidly varying parts are short ranged and purely repulsive, a quickly convergent theory of the equilibrium properties of the dense fluid can be constructed. In this theory the effect of the harshly varying repulsions is related to the properties of the hard sphere fluid, and the effect of the remaining perturbation on the structure is calculated from the optimized random phase approximation. The resulting theory, in addition to being rapidly convergent at high densities is accurate and useful for the entire single-phase fluid region of the phase diagram, excepting the critical region and the very low temperature vapor. At high density the effect of the perturbation on the structure can be neglected completely, giving a very accurate thermodynamic theory and a fairly accurate and extremely simple approximation for the pair correlation function, $g(r) \simeq g_0(r)$.

If the attractive part of the potential has spatial variations much greater than those of the attractive part of the Lennard-Jones potential (or if there are some long ranged rapidly varying repulsive forces or oscillations in the potential such as are postulated for liquid metals), then these parts of the potential can influence the structure significantly. In particular, according to the ORPA Eq. (20) for $\chi(k)$, if the perturbation has appreciable negative Fourier components near $k = 2\pi/\sigma$, where $\chi_0(k)$ is large, then the perturbation will affect the structure at high density.[24]

Advantages of the optimized random phase approximation. Computations involving the optimized random phase approximation requires detailed but available[2] information about the free energy and pair correlation function of the hard sphere fluid. The accuracy obtained with just this information is comparable to that obtained when one carries the Barker-Henderson perturbation series for $\mathcal{A}$ to second order in the perturbation.[6] However, the second order term in the perturbation series requires knowledge about of three- and four-particle correlations as well as the two-particle correlation in the hard sphere fluid. With the same information needed to carry the straightforward perturbation series to second order, one can use either the mode expansion[5,11,12] or γ-ordered expansion[13] to calculate corrections to the ORPA. For some fluids the corrections may be necessary to obtain quantitative results when the perturbation is significantly different from the Lennard-Jones perturbation.

Another advantage of the ORPA is that it, unlike the weak interaction perturbation expansion,[25] is particularly well suited for describing long ranged interactions, such as the Coulomb potential.[5,11,12] Finally, the ring and chain summations which give the random phase approximation can also be performed for a certain class of highly anisotropic molecular potentials.[7,26] The generalized RPA formula for these angular dependent forces are only slightly more complicated than those for spherically symmetric forces. Thus, techniques similar to those discussed in this paper can be applied to many types of fluids which are more interesting and complex than single liquids.

Acknowledgments

We thank D. Henderson and J. A. Barker for supplying us with extensive tables of the results of their thermodynamic perturbation theory. One of us (J.D.W.) wishes to thank K. E. Shuler for his hospitality and support at the University of California, San Diego.

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*This research was supported by the National Science Foundation, the donors of the Petroleum Research Fund administered by the American Chemical Society, and the U. S. Department of Defense administered by the Office of Naval Research (Grant N00014-69A-0200-6018).

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22. In our earlier discussions of simple liquids (Ref. 1), the HTA curves in Figs. 4-7 also were given, except that at that time for lack of anything better we used the Percus-Yevick (PY) hard sphere correlation functions in our calculations. The present calculations use the more accurate hard sphere information of Verlet and Weis (Ref. 2), and hence are a more accurate test of the HTA. Because of the errors introduced by the PY functions, small differences between the two sets of results for the structure factor are noticeable.

23. The three-and four-particle hard sphere functions which are required for the second order Barker-Henderson perturbation theory (Ref. 6) could be used to calculate corrections to the ORPA, using for example the mode expansion theory (Ref. 5). There is no point in doing so in the present case. For other fluids this might be worthwhile.

24. It should be noted that the $p(k)$ used in Eq. (20) should be calculated using (21) and the optimized perturbation. The optimized potential for $r < d$ adjust itself so that $\hat{u}_T(k) > -(\rho\beta)^{-1}\hat{X}_d(k)$ for all k in order to make a_{RPA} finite. [See Eqs. (28) and (21).] If $\hat{u}_T(k)$ has appreciable negative Fourier components for $k \simeq 2\pi/\sigma$, the optimization procedure will partially cancel these components. The cancellation will not be complete, however, and hence the structure of the fluid will be affected.

25. When the perturbation contains Coulombic interactions, infinite classes of terms in the weak interaction series must be regrouped and summed in order to avoid divergences due to the long ranged potentials. See Reference 13, and H L. Friedman, Ionic Solution Theory (Interscience, New York, 1962).

26. The class consists of molecules which contain several interaction "sites" such that the total potential energy of interaction between two molecules is the sum of the interactions between each site on one molecule with each site on the other. The interaction between two sites depends only on the scalar distance between the sites, but, since the sites are not necessarily all located at the molecular centers, the resulting potential can be highly anisotropic.

Table I. Excess free energy for Lennard-Jones fluid. Column 3 gives the value for $\rho^{-1}\mathcal{A} = -\beta\Delta A/N$ obtained from the high temperature approximation (HTA). Column 4 gives the optimized random phase approximation (ORPA) contribution to $\rho^{-1}\mathcal{A}$. The total ORPA result (i.e., the sum of the previous two columns) is given in Column 5. The values obtained from Monte Carlo computer experiments are given in Column 6. Δ is the difference $\rho^{-1}\mathcal{A}_{MC} - \rho^{-1}\mathcal{A}_{ORPA}$.

T^*	ρ^*	$\rho^{-1}\mathcal{A}_{HTA}$	$\rho^{-1}a_{RPA}$	$\rho^{-1}\mathcal{A}_{ORPA}$	MC	Δ
.75	.1	.55	.20	.75	.80	.05
	.6	3.66	.07	3.73	3.73	.00
	.7	4.15	.04	4.19	4.17	-.02
	.8	4.46	.02	4.48	4.47	-.01
	.84	4.51	.02	4.53	4.53	.00
1.15	.1	.29	.08	.37	.38	.01
	.2	.60	.11	.71	.73	.02
	.3	.92	.11	1.03	1.05	.02
	.4	1.24	.08	1.32	1.34	.02
	.5	1.52	.05	1.57	1.59	.02
	.6	1.74	.03	1.77	1.78	.01
	.65	1.83	.02	1.85	1.84	-.01
	.75	1.89	.01	1.90	1.89	-.01
	.85	1.78	.01	1.79	1.78	.01
	.92	1.57	.01	1.58	1.56	-.02
1.35	.1	.22	.06	.28	.29	.01
	.2	.45	.08	.53	.56	.03
	.3	.69	.08	.77	.80	.03
	.4	.91	.06	.97	1.00	.03
	.5	1.10	.04	1.14	1.16	.02
	.55	1.17	.03	1.20	1.22	.02
	.7	1.27	.01	1.28	1.29	.01
	.8	1.18	.01	1.19	1.19	.00
	.9	.90	.01	.91	.91	.00
	.95[a]	.66	.01	.67	.67	.00
2.74	.1	.02	.01	.03	.03	.00
	.2	.03	.02	.05	.05	.00
	.3	.03	.02	.05	.05	.00
	.4	.00	.01	.01	.01	.00
	.55	-.12	.01	-.11	-.06	.05
	.70	-.37	.00	-.37	-.37	.00
	.80	-.64	.00	-.64	-.65	-.01
	.90	-1.04	.00	-1.04	-1.04	.00
	1.00	-1.59	.00	-1.59	-1.58	.01
	1.08[a]	-2.18	.00	-2.18	-2.16	.02

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a. For this thermodynamic state, $\rho d^3 > .93$. The analytic $g_d(r)$ and $\mathcal{A}_d$ used in the theoretical calculations presented here are reliable only for $\rho d^3 \leq .93$.

Table II. Pressure and internal energy for Lennard-Jones fluid along several isotherms.

		$\beta p/\rho$			$-\Delta E/N\epsilon$		
T*	ρ*	HTA[a]	ORPA[b]	MC[c]	HTA[a]	ORPA[b]	MC[c]
.75	.1	.42	.25	.23	.56	.85	1.15
	.7	-1.87	-1.69	-1.71	5.01	5.06	5.07
	.8	-.53	-.45	-.53	5.75	5.77	5.78
	.84	.38	.45	.37	6.01	6.03	6.04
1.15	.1	.70	.64	.61	.55	.74	.86
	.2	.36	.33	.35	1.17	1.47	1.55
	.3	.04	.09	.12	1.84	2.14	2.24
	.4	-.20	-.09	-.09	2.55	2.77	2.85
	.5	-.30	-.17	-.13	3.30	3.43	3.47
	.6	-.12	-.02	.07	4.04	4.11	4.14
	.65	.13	.22	.31	4.41	4.46	4.45
	.75	1.07	1.12	1.17	5.09	5.12	5.13
	.85	2.85	2.88	2.86	5.66	5.68	5.67
	.92	4.82	4.84	4.72	5.95	5.97	5.96
1.35	.1	.77	.73	.72	.55	.71	.78
	.2	.53	.51	.50	1.16	1.39	1.51
	.3	.31	.34	.35	1.82	2.04	2.09
	.4	.17	.24	.27	2.52	2.69	2.75
	.5	.18	.27	.30	3.24	3.35	3.37
	.55	.27	.35	.41	3.61	3.68	3.70
	.70	1.12	1.17	1.17	4.64	4.67	4.68
	.80	2.40	2.43	2.42	5.24	5.26	5.25
	.90	4.59	4.61	4.58	5.67	5.68	5.66
	.95[d]	6.14	6.15	6.32	5.79	5.81	5.71
2.74	.1	.98	.97	.97	.52	.60	.61
	.2	.99	.99	.99	1.08	1.19	1.21
	.3	1.04	1.05	1.04	1.67	1.77	1.78
	.4	1.18	1.19	1.20	2.28	2.36	2.37
	.55	1.63	1.65	1.65	3.17	3.21	3.21
	.7	2.58	2.59	2.64	3.92	3.94	3.90
	.8	3.65	3.66	3.60	4.26	4.28	4.28
	.9	5.22	5.23	5.14	4.39	4.40	4.41
	1.00	7.48	7.48	7.39	4.21	4.22	4.18
	1.08[d]	9.96	9.96	9.58	3.75	3.76	3.80

a. Obtained from numerical differentiation of $\mathcal{A}_{HTA}$.

b. Obtained from numerical differentiation of $\mathcal{A}_{ORPA}$.

c. Monte Carlo computer experiment results (see Ref. 2).

d. For this thermodynamic state, $\rho d^3 > .93$. The analytic $g_d(r)$ and $\mathcal{A}_d$ used in the theoretical calculations presented here are reliable only for $\rho d^3 \leq .93$.

Table II. Pressure and internal energy for Lennard-Jones fluid along several isotherms.

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T^*	ρ^*	HTA[a]	ORPA[b]	MC[c]	HTA[a]	ORPA[b]	MC[c]
.75	.1	.42	.25	.23	.56	.85	1.15
	.7	-1.87	-1.69	-1.71	5.01	5.06	5.07
	.8	-.53	-.45	-.53	5.75	5.77	5.78
	.84	.38	.45	.37	6.01	6.03	6.04
1.15	.1	.70	.64	.61	.55	.74	.86
	.2	.36	.33	.35	1.17	1.47	1.55
	.3	.04	.09	.12	1.84	2.14	2.24
	.4	-.20	-.09	-.09	2.55	2.77	2.85
	.5	-.30	-.17	-.13	3.30	3.43	3.47
	.6	-.12	-.02	.07	4.04	4.11	4.14
	.65	.13	.22	.31	4.41	4.46	4.45
	.75	1.07	1.12	1.17	5.09	5.12	5.13
	.85	2.85	2.88	2.86	5.66	5.68	5.67
	.92	4.82	4.84	4.72	5.95	5.97	5.96
1.35	.1	.77	.73	.72	.55	.71	.78
	.2	.53	.51	.50	1.16	1.39	1.51
	.3	.31	.34	.35	1.82	2.04	2.09
	.4	.17	.24	.27	2.52	2.69	2.75
	.5	.18	.27	.30	3.24	3.35	3.37
	.55	.27	.35	.41	3.61	3.68	3.70
	.70	1.12	1.17	1.17	4.64	4.67	4.68
	.80	2.40	2.43	2.42	5.24	5.26	5.25
	.90	4.59	4.61	4.58	5.67	5.68	5.66
	.95[d]	6.14	6.15	6.32	5.79	5.81	5.71
2.74	.1	.98	.97	.97	.52	.60	.61
	.2	.99	.99	.99	1.08	1.19	1.21
	.3	1.04	1.05	1.04	1.67	1.77	1.78
	.4	1.18	1.19	1.20	2.28	2.36	2.37
	.55	1.63	1.65	1.65	3.17	3.21	3.21
	.7	2.58	2.59	2.64	3.92	3.94	3.90
	.8	3.65	3.66	3.60	4.26	4.28	4.28
	.9	5.22	5.23	5.14	4.39	4.40	4.41
	1.00	7.48	7.48	7.39	4.21	4.22	4.18
	1.08[d]	9.96	9.96	9.58	3.75	3.76	3.80

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a. Obtained from numerical differentiation of $\mathcal{A}_{HTA}$.

b. Obtained from numerical differentiation of $\mathcal{A}_{ORPA}$.

c. Monte Carlo computer experiment results (see Ref. 2).

d. For this thermodynamic state, $\rho d^3 > .93$. The analytic $g_d(r)$ and $\mathcal{A}_d$ used in the theoretical calculations presented here are reliable only for $\rho d^3 \leq .93$.

Table III. Pressure and internal energy for Lennard-Jones fluid along several high density isochores.

		$\beta p/\rho$			$-\Delta E/N\epsilon$		
ρ^*	T^*	HTA[a]	ORPA[b]	MD[c]	HTA[a]	ORPA[b]	MD[c]
.88	1.095	3.44	3.47	3.48	5.86	5.87	5.85
.88	.940	2.82	2.85	2.77	6.03	6.04	6.04
.88	.591	-.32	-.26	-.18	6.44	6.46	6.53
.85	2.889	4.38	4.39	4.36	4.25	4.26	4.25
.85	2.202	4.22	4.23	4.20	4.77	4.78	4.76
.85	1.214	3.04	3.07	3.06	5.60	5.62	5.60
.85	1.128	2.78	2.81	2.78	5.69	5.70	5.69
.85	.88	1.64	1.69	1.64	5.93	5.95	5.94
.85	.782	.93	.98	.98	6.04	6.05	6.04
.85	.76	.74	.79	.82	6.06	6.08	6.07
.85	.658	-.35	-.29	-.20	6.17	6.19	6.39
.85	.591	-1.32	-1.24	-1.20	6.25	6.27	6.46
.75	2.849	3.10	3.11	3.10	4.05	4.07	4.07
.75	1.304	1.55	1.59	1.61	4.99	5.01	5.02
.75	1.069	.75	.81	.90	5.15	5.18	5.19
.75	1.071	.76	.82	.89	5.15	5.17	5.17
.75	.881	-.27	-.18	-.12	5.29	5.32	5.31
.75	.827	-.67	-.57	-.54	5.33	5.36	5.38
.65	2.557	2.11	2.12	2.14	3.77	3.80	3.78
.65	1.585	1.19	1.24	1.25	4.20	4.24	4.23
.65	1.036	-.32	-.21	-.11	4.47	4.52	4.52
.65	.90	-1.04	-.89	-.74	4.54	4.60	4.61

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[a] Obtained from numerical differentiation of a_{HTA}.

[b] Obtained from numerical differentiation of a_{ORPA}.

[c] Molecular Dynamics computer experiment results (see Ref. 2).

Figure Captions

Fig. 1. Intermolecular interactions. The Lennard-Jones potential is $w(r) = u_0(r) + u(r)$. The trial system interaction is the hard core potential, $u_d(r)$, plus $u(r)$.

Fig. 2. Mayer cluster functions. a. f and f_T are the cluster functions for the actual system and trial system, respectively. b. The difference $\Delta f = f-f_T$. The distance r_0 is the range of the repulsive potential $u_0(r)$, while d is the hard sphere diameter in the trial system.

Fig. 3. Cluster diagrams in the random phase approximation. a. The radial distribution function. b. The free energy. Solid lines denote $-\beta u_T(r)$ bonds, dashed lines are $h_d(r) = g_d(r)-1$ bonds, root points are open circles, and density field points are filled circles. $[\mathcal{A}_T]_{HTA}$ is the high temperature approximation for $\mathcal{A}_T$ (i.e., the first two terms on the right hand side of Eq. (25)).

Fig. 4. High density structure factor for the Lennard-Jones fluid. The circles denote the molecular dynamics results (Ref. 21); the dashed line represents the high temperature approximation (i.e., $\chi(k) \simeq \chi_0(k)$); the solid line is the <u>optimized</u> random phase approximation.

Fig. 5. High density pair correlation function for the Lennard-Jones fluid. The circles denote the molecular dynamics results (Ref. 21); the dashed line represents the high temperature approximation (i.e., $g(r) \simeq g_0(r)$); the solid line is the <u>optimized</u> random phase approximation.

Fig. 6. Moderate density structure factor for the Lennard-Jones fluid. The circles denote the molecular dynamics results (Ref. 21); the dashed line represents the high temperature approximation (i.e., $\chi(k) \simeq \chi_0(k)$); the solid line is the optimized random phase approximation.

Fig. 7. Moderate density pair correlation function for the Lennard-Jones fluid. The circles denote the molecular dynamics results (Ref. 21); the dashed line represents the high temperature approximation (i.e., $g(r) \simeq g_0(r)$); the solid line is the optimized random phase approximation.

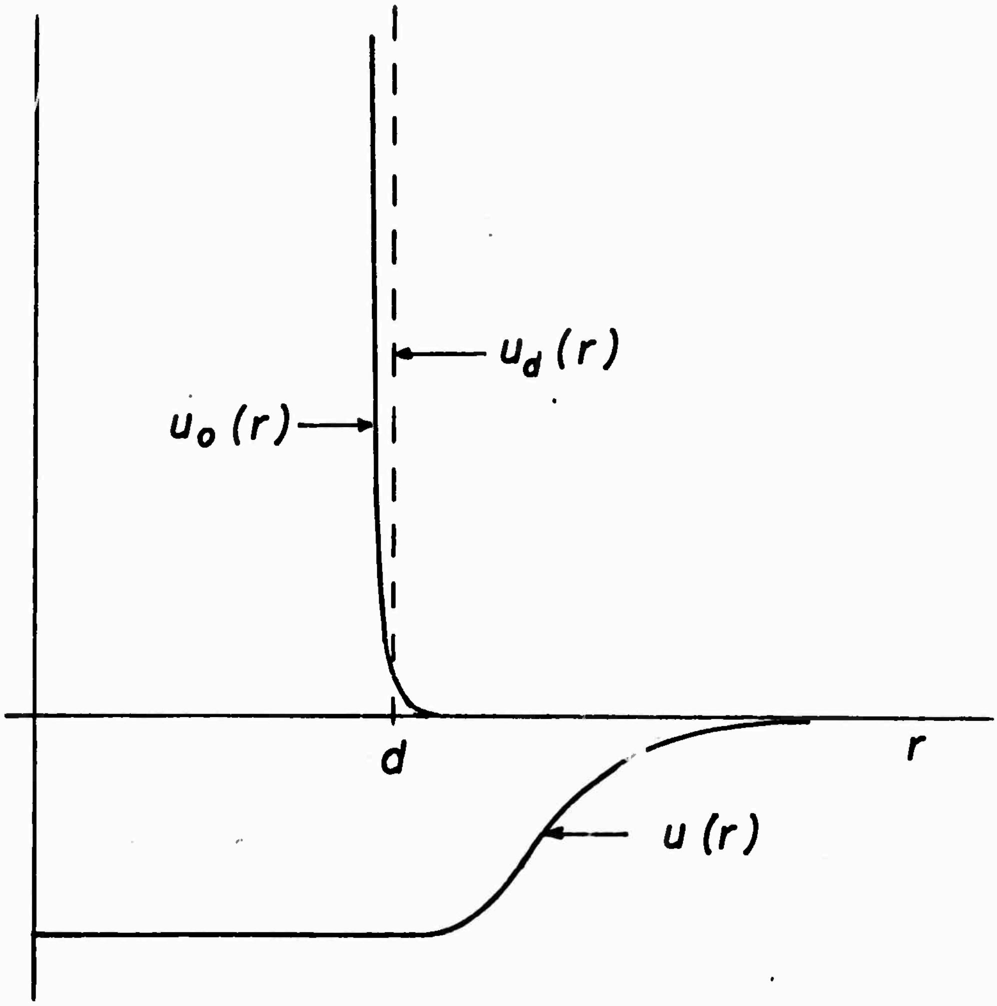
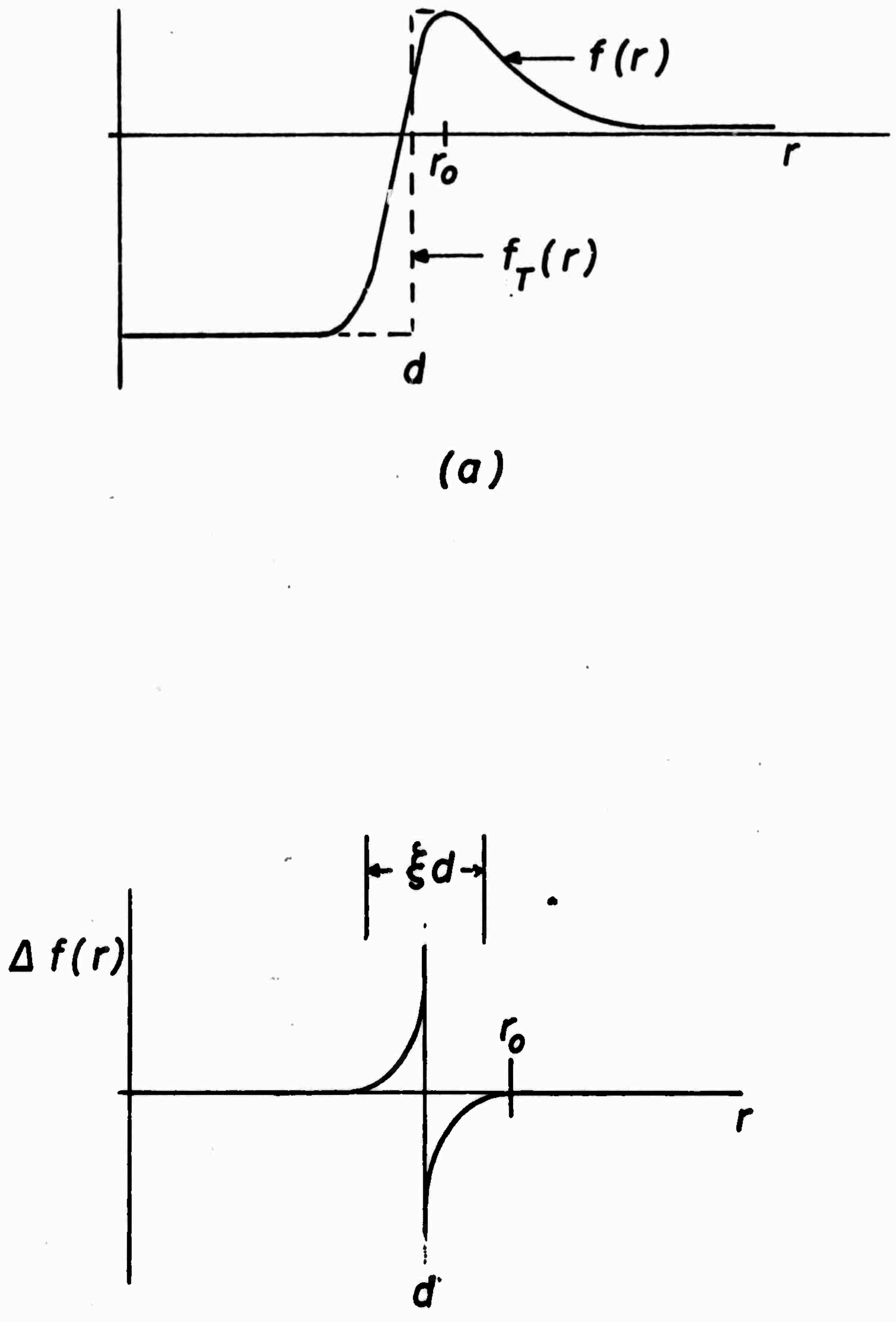


Figure 1



(a)

(b)

Figure 2

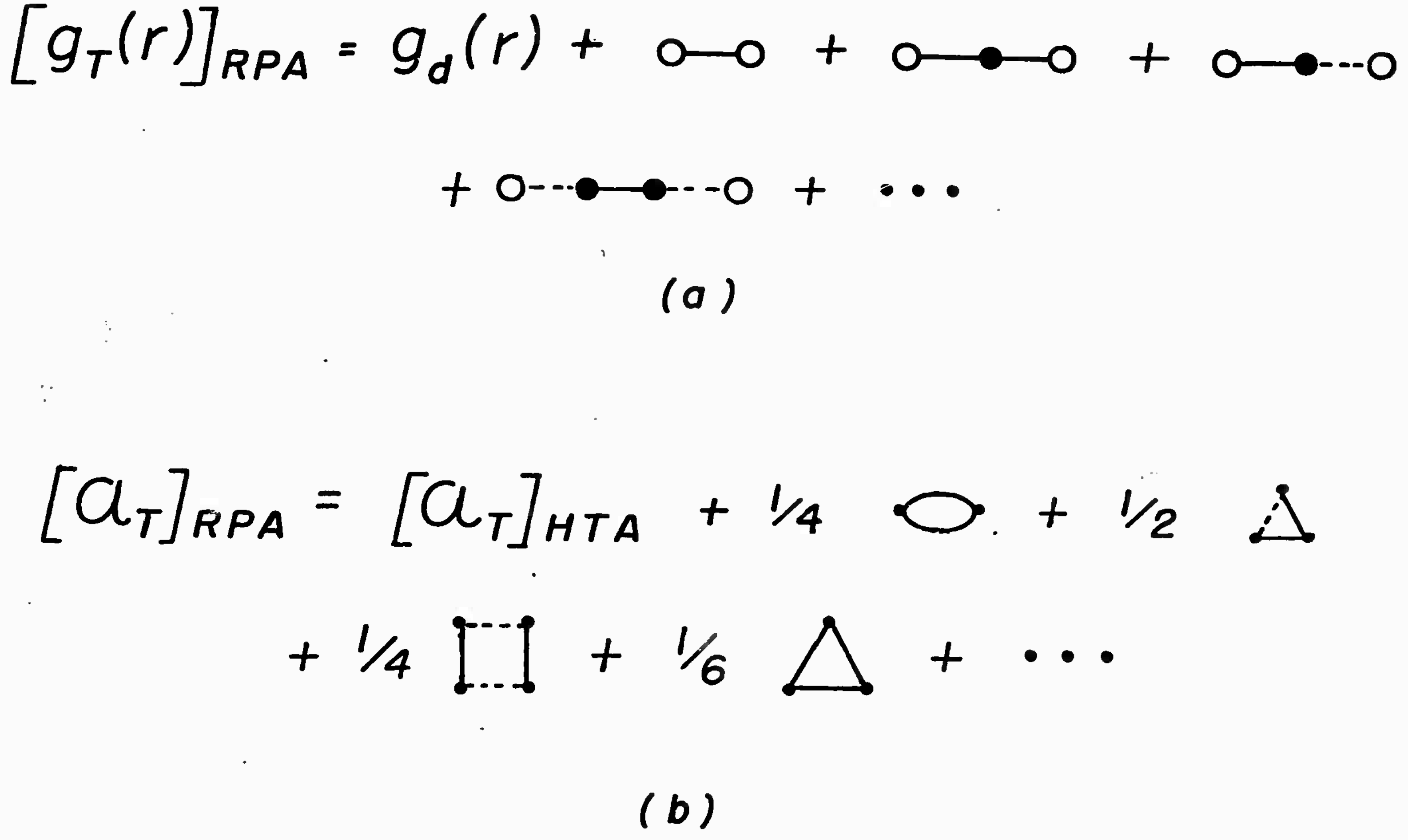


Figure 3

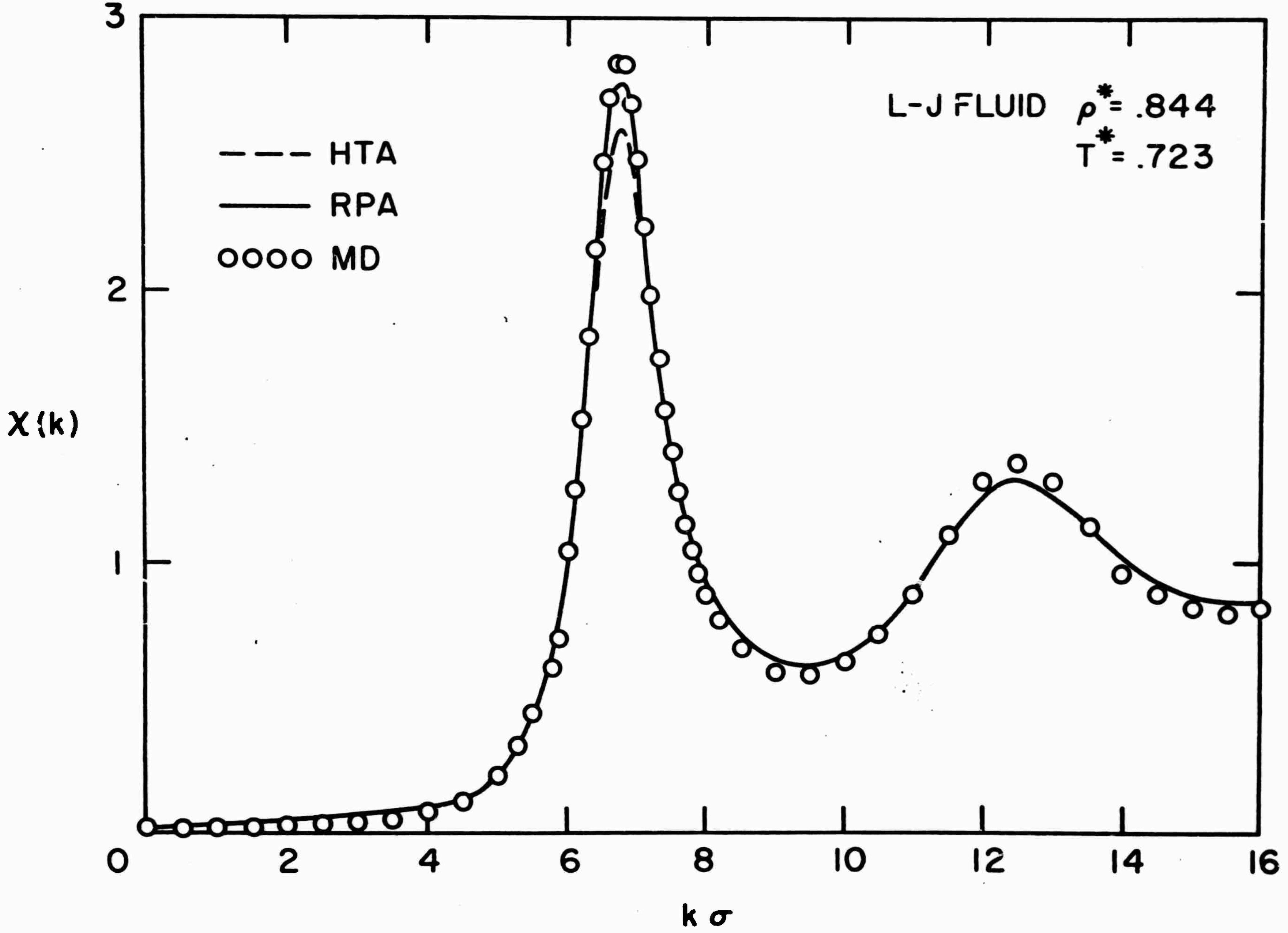

3
2
1
0
X(k)
0
2
4
6
8
10
12
14
16
kσ
HTA
RPA
0000 MD
L-J FLUID $\rho^* = .844$
$T^* = .723$

Figure 4

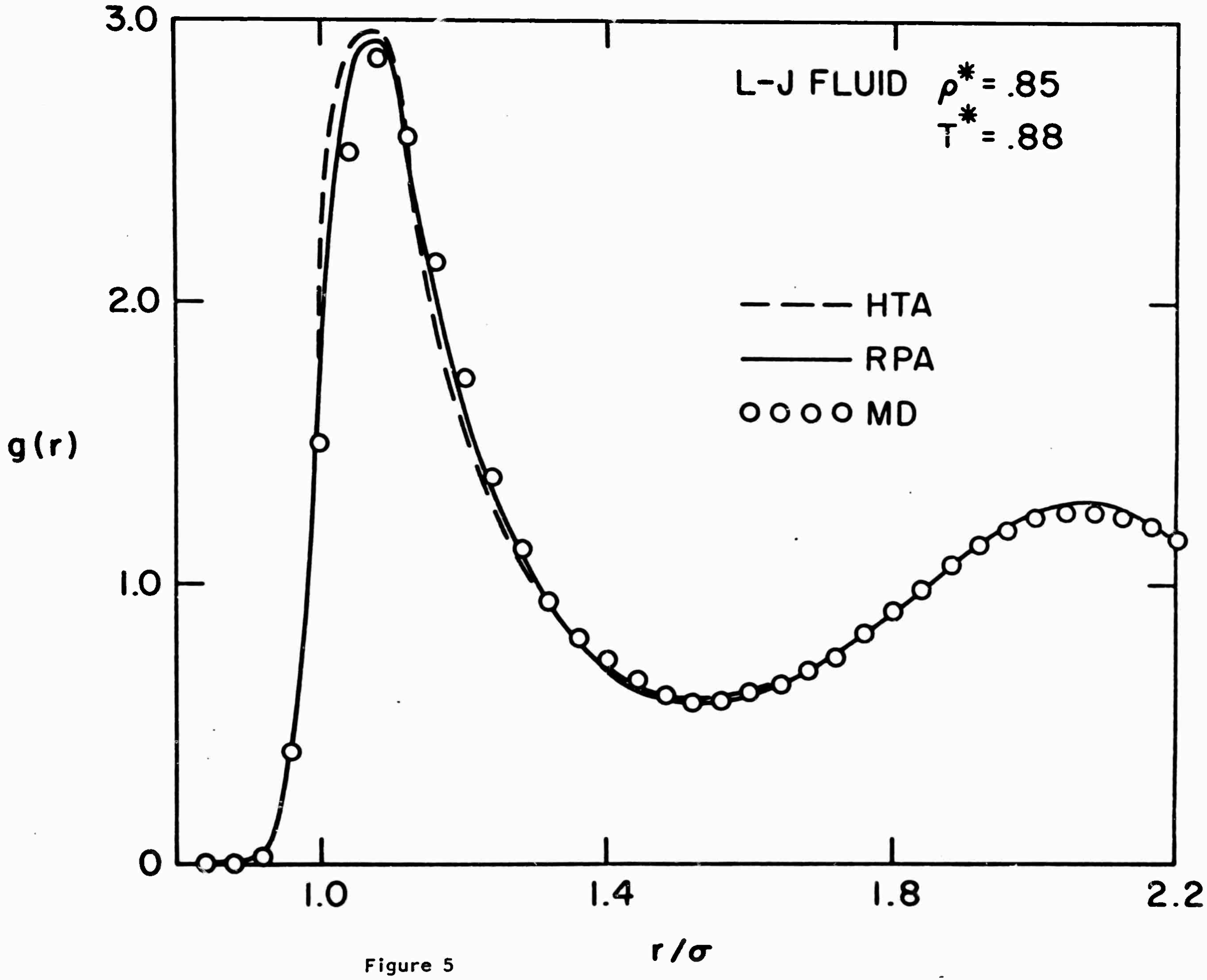


Figure 5

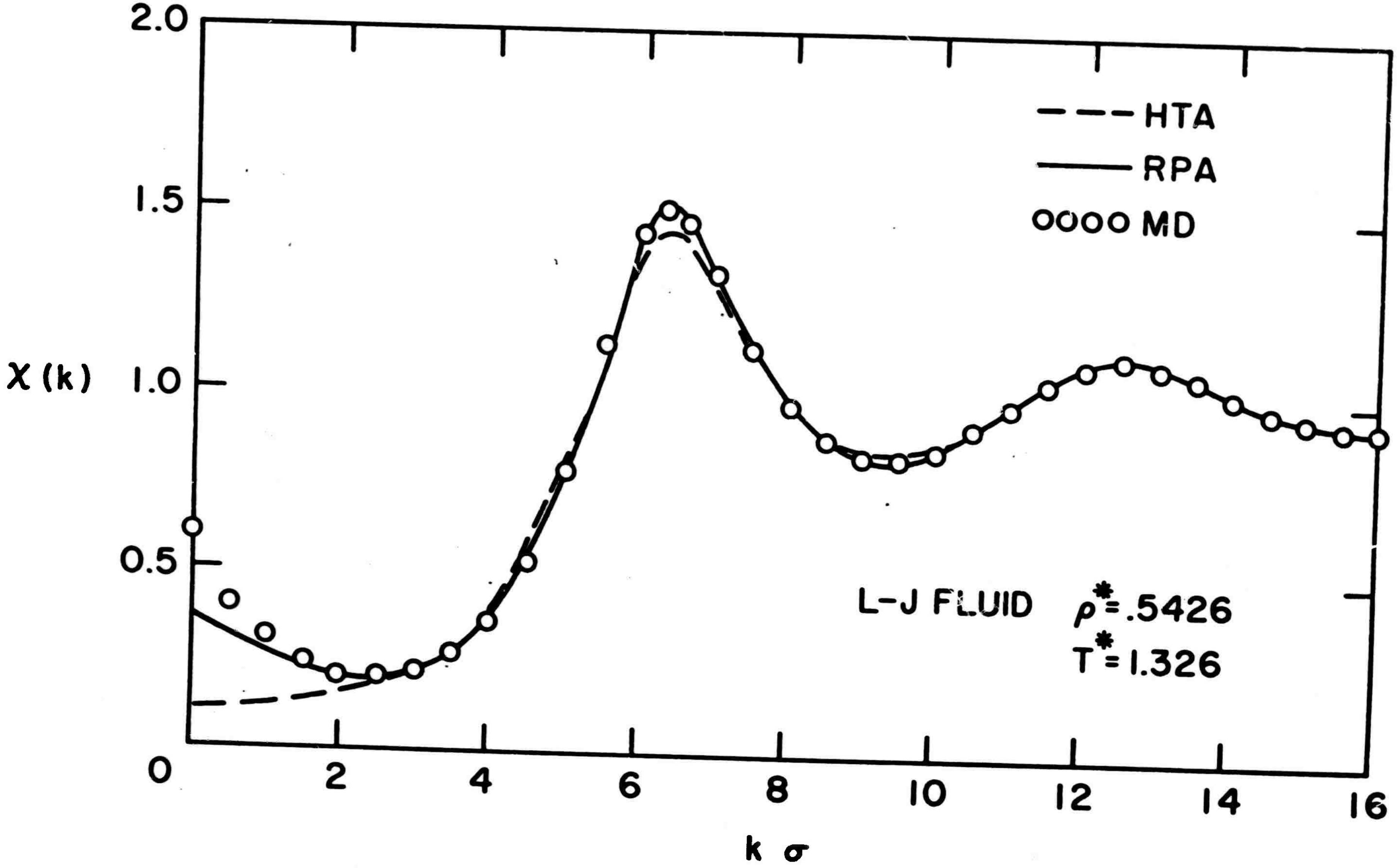

2.0
1.5
1.0
0.5
0
X (k)
2
4
6
8
10
12
14
16
k σ
HTA
RPA
0000 MD
L-J FLUID
$\rho^* = .5426$
$T^* = 1.326$

Figure 6

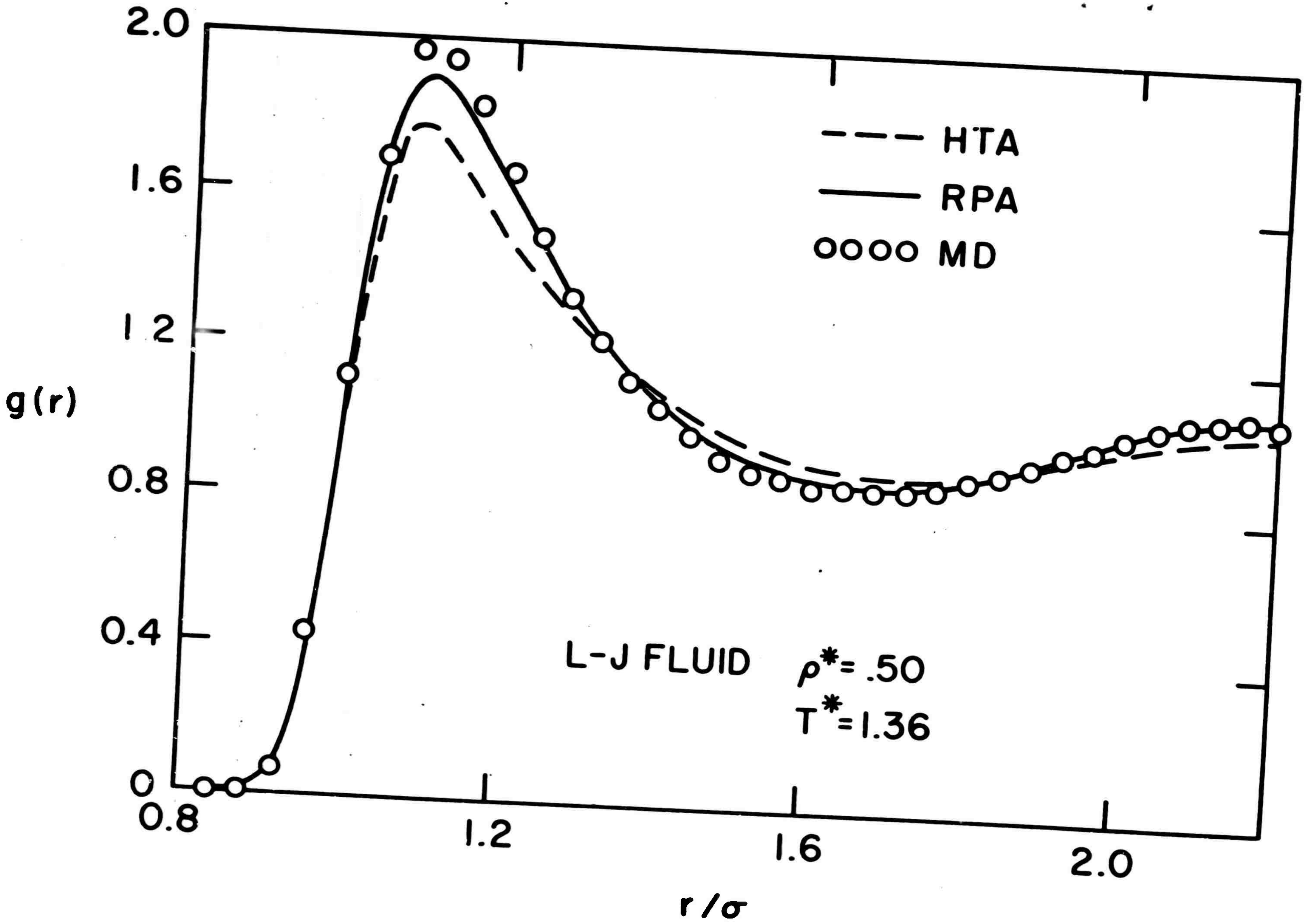


Figure 7