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Analytic Solution to Integral Equations of Liquid State Theories for Potentials with a Hard Core at Low Densities

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We present in this paper a general analytical solution to the integral equations of liquid state theories (Born–Green–Yvon, hyper-netted-chain, and Percus–Yevick Equations) at low-density limit for potentials with a hard core. For the specific case of the Lennard-Jones potential with a hard core, we have derived an analytical function for the radial distribution function at high temperature and low density. We have noted that this function has two humps which is the characteristic feature of the radial distribution function at low densities. In addition, this function has been used to calculate the third virial coefficient for such a fluid exactly. We see that for the especial case of Lennard-Jones fluid with a hard core, which its radial distribution function has explicitly been calculated at high temperatures, the correct behavior of the third virial coefficient with temperature is obtained. The magnitude of hard-core diameter has significant effect on the thermodynamic properties of fluid: for instance, when the diameter changes only by a few percent the third virial coefficient may change more than 100%. The hard-core diameter decreases when temperature increases. The reduction is less than 20%. For the supercritical fluid, the calculated compression factor and internal energy are in good agreement with those obtained from the simulation for the Lennard-Jones fluid.

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1. Introduction

Radial distribution function (RDF) is the main theme of fluid state theories. Using this function, one can calculate almost all thermodynamic properties of a fluid. For this reason various ways of obtaining the RDF has been introduced; including the integral equations theories, computer simulation methods (Molecular Dynamics and Monte Carlo), and neutron scattering experiments. However, in spite of all efforts, finding an exact analytical expression for the RDF has not yet been possible. Nevertheless, the semi-empirical expressions for some classes of simple fluids have been presented (including the hard sphere fluids,[1]) square-well fluids,[2]) and Lennard-Jones fluids.[3]) Also, via the RDF of a simple fluid one can study the role of the attractive and repulsive parts of the pair potential in the fluid structure.[2,4]) Thus obtaining an analytical expression for the RDF is of vital importance for the liquid state chemical physics.

It is well known that the various integral equations of classical simple liquid theory yield the approximate radial distribution functions.[5–8]) These approximate radial distribution functions in turn yield the correct second and third virial coefficients, but the incorrect fourth, fifth, and ..., virial coefficients, when substituted into either following equations which relates the pressure or the compressibility factor to the RDF respectively, i.e.;

$$p = \rho kT - \frac{2}{3}\pi\rho^2 \int_0^\infty g(r)\frac{\partial u}{\partial r} r^3 \mathrm{d}r \tag{1}$$

$$kT\left(\frac{\partial\rho}{\partial p}\right)_T = 1 + 4\pi\rho\int_0^\infty [g(r)-1]r^2\mathrm{d}r \tag{2}$$

where k is the Boltzmann constant, ρ is the average number density, p is the pressure, T is the absolute temperature, $u(r)$ is the interaction potential between two particles at distance r, and $g(r)$ is the RDF.

In this paper, we show that we can solve integral equations of liquid state theories (Percus–Yevick, hyper-netted-chain, and Born–Green–Yvon) for potentials with a hard core at low densities (i.e., densities at which the RDF has two humps only).

The integral equations that will be studied are the Percus–Yevick (PY):

$$\begin{aligned} &\mathrm{e}^{\beta u(r_{12})}g(r_{12}) \\ &\quad = 1 + \rho\int [g(r_{23})-1][1-\mathrm{e}^{\beta u(r_{13})}]g(r_{13})\mathrm{d}r_3 \end{aligned} \tag{3}$$

hyper-netted-chain (HNC):

$$\begin{aligned} \ln g(r_{12}) + \beta u(r_{12}) = \rho\int &[g(r_{23})-1][g(r_{13})-1 \\ &- \ln g(r_{13}) - \beta u(r_{13})]\mathrm{d}r_3 \end{aligned} \tag{4}$$

and Born–Green–Yvon (BGY):

$$\begin{aligned} &-kT\nabla_1 \ln g(r_{12}) \\ &\quad = \nabla_1 u(r_{12}) + \rho\int g(r_{13})g(r_{23})\nabla_1 u(r_{13})\mathrm{d}r_3 \end{aligned} \tag{5}$$

where $\beta = 1/kT$ and ∇_1 represents the gradient with respect to r_1.

These equations must be solved to give the approximate RDF, which in turn can be used to calculate other thermodynamic properties, and hence comparing them with one another and with the (computer) experiment values. In this way, one can decide on their range of validity. However, these equations have all been solved numerically except PY, which was solved analytically for the case of hard sphere potential.[9]) Although because of some approximations in deriving these equations, the obtained $g(r)$ are not exact,

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however the main features of this function may be reproduced in this way, and be used as a base for other theories. Although these equations can be solved numerically,[10–12] there are some interests to have $g(r)$ analytically for (reasonably) real potentials.[3,13] Nevertheless, there has been yet no analytical solution found even at low densities for the reasonable potentials. In this paper, we are going to derive an analytical solution to these equations for potentials with a hard core, at low densities. At zero density limit ($\rho \to 0$), one obtains from eqs. (3)–(5) that $g(r) = \mathrm{e}^{-\beta u(r)}$, which is the zeroth approximation to $g(r)$. Having this approximation, we can proceed to obtain low-density approximation for $g(r)$ as a first approximation; i.e., for densities not too high; $g(r)$ can be expanded in powers of the number density ρ[6–8] as:

$$g(r) = \mathrm{e}^{-\beta u(r)}[1 + G_1(r)\rho + G_2(r)\rho^2 + \cdots] \tag{6}$$

where the coefficients $G_1(r), G_2(r), \ldots$ are also functions of $u(r)$ and T. The exact expression for $G_1(r)$ is:[6–8]

$$G_1(r) = \int [1 - \mathrm{e}^{-\beta u(r_{23})}][1 - \mathrm{e}^{-\beta u(r_{13})}]\mathrm{d}r_3 \tag{7}$$

Now in order to find $G_1(r)$ from each liquid state theory, $g(r)$ from eq. (6) is substituted into the integral equations and the coefficients of like powers of ρ on both sides are set equal to each other, from which one can show that $G_1(r)$ is given by the exact expression, eq. (7), in each case. However, the exact expressions for other G_is [for $i \geq 2$] obtained from these equations are different. Hence, to the first approximation eqs. (3)–(5) are equal, but yet their RDFs will be different.[6–8] At this first level of approximation we may obtain;

$$g(r) = \mathrm{e}^{-\beta u(r)}[1 + \rho G_1(r)] \tag{8}$$

from the PY equation at low densities, and

$$g(r) = \mathrm{e}^{-\beta u(r)}\mathrm{e}^{\rho G_1(r)} \tag{9}$$

from the HNC and BGY equations at low densities. So in order to find $g(r)$ at this first level of approximation we have to calculate $G_1(r)$. In order to calculate the $G_1(r)$, it is necessary to write it in bipolar coordinates[6–8] as:

$$G_1(r) = \frac{2\pi}{r}\int [1 - \mathrm{e}^{-\beta u(R)}][1 - \mathrm{e}^{-\beta u(r')}]Rr'\mathrm{d}R\mathrm{d}r' \tag{10}$$

Let us use a general potential with a hard core as;

$$u'(r) = \begin{cases} \infty & r < d \\ u(r) & r \geq d \end{cases} \tag{11}$$

where d is the hard core diameter. In the reduced form, the potential may be written in terms of the reduced distance $r^* = r/d$ as:

$$u'(r^*) = \begin{cases} \infty & r^* < 1 \\ u(r^*) & r^* \geq 1 \end{cases} \tag{12}$$

Then eq. (10) reduces to:

$$G_1(r^*) = \frac{2\pi d^3}{r^*}\int [1 - \mathrm{e}^{-\beta u'(R^*)}][1 - \mathrm{e}^{-\beta u'(r'^*)}] \times R^* r'^* \mathrm{d}R^* \mathrm{d}r'^* \tag{13}$$

For simplicity, we shall drop the stars on the reduced variables, and write $G_1(r)$ as:

$$G_1(r) = \frac{2\pi d^3}{r}\int_0^\infty \int_{|r-R|}^{r+R} [1 - \mathrm{e}^{-\beta u'(R)}][1 - \mathrm{e}^{-\beta u'(r')}] \times Rr'\mathrm{d}R\mathrm{d}r' \tag{14}$$

We shall show in the following section that an analytical expression for $G_1(r)$ may be derived if a hard-core potential is used.

2. General Analytical Expression for RDF at Low Densities

In order to solve eq. (14) for $G_1(r)$, we may note from eqs. (8), (9), and (12) that $g(r) = 0$ when $r < 1$; so we must have $r \geq 1$. But r' and R may either be more or less than 1. So the four following cases should be considered.

A) When we simultaneously have:

$$r \geq 1, \quad R < 1, \quad \text{and} \quad r' < 1. \tag{15}$$

In general we have $0 \leq R < \infty$, and $|r - R| \leq r' \leq r + R$; which in combination to eq. (15) will give: $r - R \leq r' < 1 \leq r + R$, which is equivalent to $r - 1 \leq R < 1$, hence $1 \leq r \leq 2$. So $G_1(r)$ in this case will equal to:

$$a = \frac{2\pi d^3}{r}\int_{r-1}^1 \int_{r-R}^1 Rr'\mathrm{d}R\mathrm{d}r' \quad (\text{with } 1 \leq r \leq 2) \tag{16}$$

B) When we simultaneously have:

$$r \geq 1, \quad R < 1, \quad \text{and} \quad r' \geq 1. \tag{17}$$

From eq. (17) we have $r \geq R$ and $|r - R| \leq r' \leq r + R$; from which one can deduce:

$$r - R \leq 1 \leq r' \leq r + R \tag{18}$$

and/or:

$$1 \leq r - R \leq r' \leq r + R \tag{19}$$

Equation (18) gives $R \geq r - 1$, which in combination to eq. (17) indicates:

$$0 \leq r - 1 < R < 1 \leq r \quad \text{that results in} \quad 1 \leq r \leq 2 \tag{20}$$

Equation (19) gives $R \leq r - 1$, which in combination to eq. (17) indicates:

$$0 \leq R \leq r - 1 \leq 1 \leq r \quad \text{that results in } 1 \leq r \leq 2 \tag{21}$$

and

$$0 \leq R \leq 1 \leq r - 1 \leq r \quad \text{that results in } r \geq 2 \tag{22}$$

Hence, the integration in this case will become as:

$$\int_{r-1}^1 \int_1^{r+R} (1 \leq r \leq 2) + \int_0^{r-1} \int_{r-R}^{r+R} (1 \leq r \leq 2) + \int_0^1 \int_{r-R}^{r+R} (r \geq 2) \tag{23}$$

which can easily be transformed to:

$$\int_0^1 \int_1^{r+R} (r \geq 1) + \int_0^{r-1} \int_{r-R}^1 (1 \leq r \leq 2) + \int_0^1 \int_{r-R}^1 (r \geq 2) \tag{24}$$

Hence, $G_1(r)$ in this case consists of three terms, namely b_1, b_2, and b_3:

$$b_1 = \frac{2\pi d^3}{r}\int_0^1\int_1^{r+R}[1-\mathrm{e}^{-\beta u(r')}]Rr'\mathrm{d}R\mathrm{d}r' \quad \text{(with } r \geq 1) \tag{25}$$

$$b_2 = \frac{2\pi d^3}{r}\int_0^{r-1}\int_{|r-R|}^{1}[1-\mathrm{e}^{-\beta u(r')}]Rr'\mathrm{d}R\mathrm{d}r' \quad \text{(with } 1 \leq r \leq 2) \tag{26}$$

$$b_3 = \frac{2\pi d^3}{r}\int_0^1\int_{r-R}^{1}[1-\mathrm{e}^{-\beta u(r')}]Rr'\mathrm{d}R\mathrm{d}r' \quad \text{(with } r \geq 2) \tag{27}$$

C) When we simultaneously have:

$$r \geq 1, \quad R \geq 1, \quad \text{and} \quad r' < 1. \tag{28}$$

From eq. (28) we have $r+R \geq 2$ and also $|r-R| \leq r' \leq r+R$; from which one can deduce;

$$|r-R| \leq r' \leq 1 \tag{29}$$

for which we have two following cases:

1) When $R \geq r$; which in combination to eq. (29) yields:

$$0 < R-r \leq r' \leq 1 \tag{30}$$

and

$$1 \leq r \leq R < 1+r \tag{31}$$

2) When $R \leq r$; which in combination to eq. (29) yields:

$$0 < r-R \leq r' \leq 1 \tag{32}$$

But we have in this case $r' < 1$ which in combination to eq. (29) yields:

$$0 < 1 \leq r-1 \leq R < r \quad \text{that results in } r \geq 2 \tag{33}$$

and

$$0 \leq r-1 < 1 \leq R < r \quad \text{that results in } 1 \leq r \leq 2 \tag{34}$$

Hence, the integration in this case will become as:

$$\int_1^r\int_{r-R}^1(1 \leq r \leq 2) + \int_{r-1}^r\int_{r-R}^1(r \geq 2) + \int_r^{r+1}\int_{R-r}^1(r \geq 1) \tag{35}$$

which can easily be transformed to:

$$\int_1^{1+r}\int_{|r-R|}^1(1 \leq r \leq 2) + \int_{r-1}^{r+1}\int_{|r-R|}^1(1 \geq 2) \tag{36}$$

Hence $G_1(r)$ in this case consists of two following terms:

$$c_1 = \frac{2\pi d^3}{r}\int_1^{1+r}\int_{|r-R|}^1[1-\mathrm{e}^{-\beta u(R)}]Rr'\mathrm{d}R\mathrm{d}r' \quad \text{(with } 1 \leq r \leq 2) \tag{37}$$

$$c_2 = \frac{2\pi d^3}{r}\int_{r-1}^{r+1}\int_{|r-R|}^1[1-\mathrm{e}^{-\beta u(R)}]Rr'\mathrm{d}R\mathrm{d}r' \quad \text{(with } r \geq 2) \tag{38}$$

D) When we simultaneously have:

$$r \geq 1, \quad R \geq 1, \quad \text{and} \quad r' \geq 1. \tag{39}$$

Combination of eq. (39) with $|r-R| \leq r' \leq r+R$ yields two situations:

$$|r-R| \leq 1 \leq r' \leq r+R \tag{DI}$$

and/or

$$1 \leq |r-R| \leq r' \leq r+R \tag{DII}$$

Now we have two cases:

1) when $R \geq r$; which in combination to eqs. (DI) and (DII) yield:

$$\begin{aligned}\text{(DI)} &\longrightarrow R-r \leq 1 \leq r' \leq r+R\\ &\longrightarrow 1-r \leq 0 < 1 \leq r \leq R \leq 1+r \quad \text{(with } r \geq 1)\end{aligned} \tag{40}$$

$$\begin{aligned}\text{(DII)} &\longrightarrow 1 \leq R-r \leq r' \leq r+R\\ &\longrightarrow 1-r \leq 0 < 1 \leq r \leq 1+r \leq R \quad \text{(with } r \geq 1)\end{aligned} \tag{41}$$

2) when $R \leq r$; which in combination to eqs. (DI) and (DII) yield:

$$\begin{aligned}\text{(DI)} &\longrightarrow r-R \leq 1 \leq r' \leq r+R\\ &\longrightarrow 1-r \leq 0 < 1 \leq r-1 \leq R \leq r \quad \text{(with } r \geq 2)\end{aligned} \tag{42}$$

and/or

$$\begin{aligned}\text{(DI)} &\longrightarrow r-R \leq 1 \leq r' \leq r+R\\ &\longrightarrow 1-r \leq 0 < r-1 \leq 1 \leq R \leq r \quad \text{(with } 1 \leq r \leq 2)\end{aligned} \tag{43}$$

and

$$\begin{aligned}\text{(DII)} &\longrightarrow 1 \leq r-R \leq r' \leq r+R\\ &\longrightarrow 1-r \leq 0 < 1 \leq R \leq r-1 \quad \text{(with } r \geq 2)\end{aligned} \tag{44}$$

Hence, the integration in this case will become:

$$\int_r^{r+1}\int_1^{r+R}(r \geq 1) + \int_{1+r}^{\infty}\int_{R-r}^{R+r}(r \geq 1) + \int_{r-1}^{r}\int_1^{r+R}(r \geq 2) + \int_1^r\int_1^{r+R}(1 \leq r \leq 2) + \int_1^{r-1}\int_{r-R}^{r+R}(r \geq 2)$$

which can easily be transformed to:

$$\int_r^{\infty}\int_1^{r+R}(r \geq 1) + \int_{1+r}^{\infty}\int_{R-r}^{1}(r \geq 1) + \int_1^{r-1}\int_{r-R}^{1}(r \geq 2) \tag{45}$$

Hence, $G_1(r)$ in this case consists of three terms, namely d_1, d_2, and d_3:

$$d_1 = \frac{2\pi d^3}{r}\int_1^{\infty}\int_1^{r+R}[1-\mathrm{e}^{-\beta u(R)}][1-\mathrm{e}^{-\beta u(r')}]Rr'\mathrm{d}R\mathrm{d}r' \quad \text{(with } r \geq 1) \tag{46}$$

$$d_2 = \frac{2\pi d^3}{r}\int_{r+1}^{\infty}\int_{r-R}^{1}[1-\mathrm{e}^{-\beta u(R)}][1-\mathrm{e}^{-\beta u(r')}]Rr'\mathrm{d}R\mathrm{d}r' \quad \text{(with } r \geq 1) \tag{47}$$

$$d_3 = \frac{2\pi d^3}{r}\int_1^{r-1}\int_{r-R}^{1}[1-\mathrm{e}^{-\beta u(R)}][1-\mathrm{e}^{-\beta u(r')}]Rr'\mathrm{d}R\mathrm{d}r' \quad \text{(with } r \geq 2) \tag{48}$$

Now with having expressions for a, b_1, b_2, b_3, c_1, c_2, d_1, d_2, d_3 we can write $G_1(r)$ as follows:

$$G_1(r) = a + b_1 + b_2 + c_1 + d_1 + d_2 \quad (\text{with } 1 \le r \le 2) \tag{49}$$

$$G_1(r) = b_1 + b_3 + c_2 + d_1 + d_2 + d_3 \quad (\text{with } r \ge 2) \tag{50}$$

which in combination to, for example eq. (9), gives us $g(r)$ at low densities. At this stage, we would like to write down the explicit expression for $g(r)$, which is:

$$g(r) = 0 \quad \text{when } 0 \le r < 1 \tag{51a}$$

and,

$$g(r) = \mathrm{e}^{-\beta u(r)} \exp\left\{ \frac{2\pi\rho d^3}{r} \left[\begin{array}{l} \int_{r-1}^{1}\int_{r-R}^{1} Rr'\mathrm{d}R\mathrm{d}r' \\ + \int_{0}^{1}\int_{1}^{r+R} [1-\mathrm{e}^{-\beta u(r')}]Rr'\mathrm{d}R\mathrm{d}r' \\ + \int_{0}^{r-1}\int_{|r-R|}^{1} [1-\mathrm{e}^{-\beta u(r')}]Rr'\mathrm{d}R\mathrm{d}r' \\ + \int_{1}^{r+1}\int_{|r-R|}^{1} [1-\mathrm{e}^{-\beta u(R)}]Rr'\mathrm{d}R\mathrm{d}r' \\ + \int_{1}^{\infty}\int_{1}^{r+R} [1-\mathrm{e}^{-\beta u(R)}][1-\mathrm{e}^{-\beta u(r')}]Rr'\mathrm{d}R\mathrm{d}r' \\ + \int_{r+1}^{\infty}\int_{r-R}^{1} [1-\mathrm{e}^{-\beta u(R)}][1-\mathrm{e}^{-\beta u(r')}]Rr'\mathrm{d}R\mathrm{d}r' \end{array} \right] \right\} \text{when } 1 \le r \le 2 \tag{51b}$$

and

$$g(r) = \mathrm{e}^{-\beta u(r)} \exp\left\{ \frac{2\pi\rho d^3}{r} \left[\begin{array}{l} \int_{0}^{1}\int_{1}^{r+R} [1-\mathrm{e}^{-\beta u(r')}]Rr'\mathrm{d}R\mathrm{d}r' \\ + \int_{0}^{1}\int_{r-R}^{1} [1-\mathrm{e}^{-\beta u(r')}]Rr'\mathrm{d}R\mathrm{d}r' \\ + \int_{r-1}^{r+1}\int_{|r-R|}^{1} [1-\mathrm{e}^{-\beta u(R)}]Rr'\mathrm{d}R\mathrm{d}r' \\ + \int_{1}^{\infty}\int_{1}^{r+R} [1-\mathrm{e}^{-\beta u(R)}][1-\mathrm{e}^{-\beta u(r')}]Rr'\mathrm{d}R\mathrm{d}r' \\ + \int_{r+1}^{\infty}\int_{r-R}^{1} [1-\mathrm{e}^{-\beta u(R)}][1-\mathrm{e}^{-\beta u(r')}]Rr'\mathrm{d}R\mathrm{d}r' \\ + \int_{1}^{r-1}\int_{r-R}^{1} [1-\mathrm{e}^{-\beta u(R)}][1-\mathrm{e}^{-\beta u(r')}]Rr'\mathrm{d}R\mathrm{d}r' \end{array} \right] \right\} \text{when } r \ge 2 \tag{51c}$$

The analytical expression given by eqs. (51) may be used to calculate $g(r)$ at any temperatures at low densities accurately, if the pair interaction potential is known. The above expression for $g(r)$ is based on the HNC and/or BGY equations; however, if eq. (8) is used for $g(r)$, one will obtain the $g(r)$ of the PY equation. Nevertheless, in order to obtain analytical expressions for these integrals, the mathematical form of the $u(r)$ must be known. If $u(r)$ is the inverse powers of r, it is possible to obtain an analytic expression for the $g(r)$ at this level of approximation (i.e., at low densities), at least for high temperatures. For example, we have derived the RDF for the Lennard-Jones fluid with a hard core; see the appendix. At any reduced temperature and density, the RDF may be calculated at that thermodynamic state for a hard-core Lennard-Jones fluid. As an example, the calculated RDF at $T^* = 3.5$ and $\rho^* = 0.25$ is shown in Fig. 1 when the hard-core diameter is taken to be $d = 0.96\sigma$ and $d = 0.92\sigma$. As expected, our RDF has only two humps which indicates that the function can only works at low densities. It is interesting to note that $g(r)$ for the Lennard-Jones potential at low densities was obtained numerically and plotted for some different temperatures and densities by de Boer.[14] His numerical results are essentially similar to ours, though we have included an arbitrary hard core in the Lennard-Jones potential. Based on the WCA theory,[15] one expects that the hard-core diameter has a significant effect

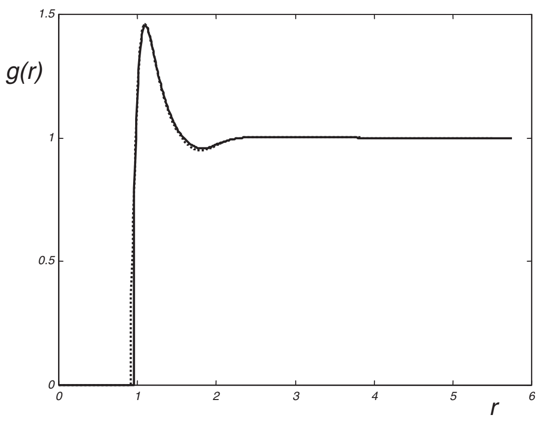

Fig. 1. The radial distribution function for the Lennard-Jones fluid with hard core when $d = 0.92\sigma$ (dotted line) and $d = 0.96\sigma$ (solid line).

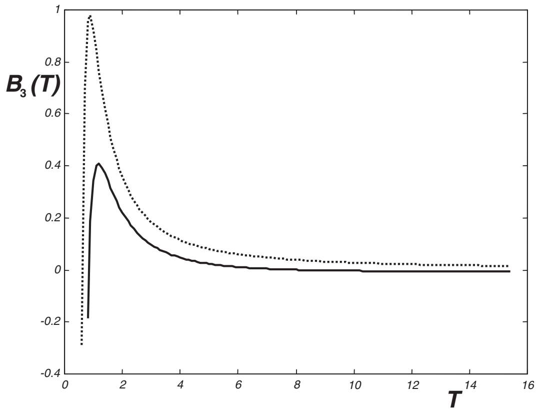

Fig. 2. The reduced third virial coefficients vs the reduced temperatures for the hard core Lennard-Jones fluid when $d = 0.92\sigma$ (dotted line) and $d = 0.96\sigma$ (solid line).

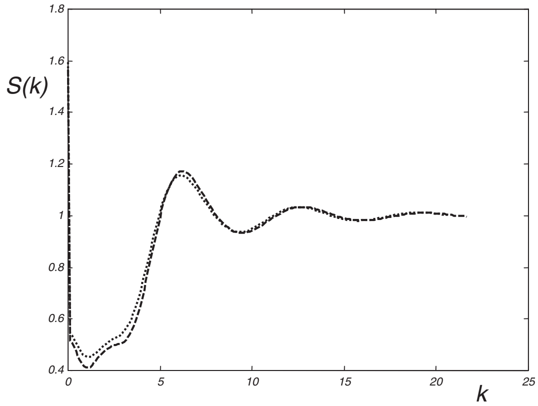

Fig. 3. The calculated structural factor from the obtained RDF for $\rho^* = 0.25$ and $T^* = 3.5$ when $d = 0.92\sigma$ (dashed line) and $d = 0.96\sigma$ (dotted line).

on the liquid state properties. For instance, hard-core diameter (or excluded volume) has significant contribution on the direct correlation function.[4] Therefore, we have decided to evaluate this expectation using the derived $g(r)$. For this purpose we have calculated the third virial coefficient, because one can *exactly* calculate this coefficient for fluids that their pair interaction potentials are given by eq. (11). Inserting eq. (6) into eq. (1), one obtains a general expression for the virial coefficients[8] as:

$$B_{i+2}(T) = \frac{-1}{6kT}\int_0^\infty ru'(r)\mathrm{e}^{-\beta u(r)}G_i(r,T)4\pi r^2\mathrm{d}r \quad (52)$$

where $G_i's$ are the same as those defined in eq. (6). As an especial case, the reduced third virial coefficient becomes as:

$$B_3(T) = \frac{-1}{6kT}\int_0^\infty ru'(r)\mathrm{e}^{-\beta u(r)}G_i(r,T)4\pi r^2\mathrm{d}r \quad (53)$$

Since we have obtained a general explicit expression for $G_1(r,T)$ for the hard core fluid, we are able to calculate the third virial coefficient *exactly*. As an example, we have used the calculated RDF along with eq. (53) to calculate $B_3(T)$ for the hard core Lennard-Jones potential with $d = 0.96\sigma$ and $d = 0.92\sigma$. The results are depicted in Fig. 2, which is seen that it predicts at least qualitatively the correct behavior of the third virial coefficient. As seen when the diameter of the hard core is changed only by a few percent, the third virial coefficient varies significantly. Such a conclusion is in accordance to the WCA theory; according to which it is assumed that the thermodynamic properties of fluids are strongly depend on the hard-core diameter.

To do another test for the derived RDF, we have calculated the structure factor, $S(k)$, from

$$S(k) = 1 + 4\pi\rho\int_0^\infty \mathrm{d}rr^2[g(r)-1]\frac{\sin(kr)}{kr} \quad (54)$$

where k is the wave vector. The results have been obtained for $\rho^* = 0.25$ and $T^* = 3.5$ with two hard core diameters. The calculated $S(k)$ looks like the experimental result obtained from scattering, for instance see Verlet.[16] Note that a minimum appears in $S(k)$ vs k when attraction exists, for instance there is no such a minimum for the hard sphere fluid, see for instance McQuarrie.[8] To see the effect of core size on the structure factor, we have calculated $S(k)$ for $d = 0.96\sigma$ and $d = 0.92\sigma$ both at $\rho^* = 0.25$ and $T^* = 3.5$, the results are shown in Fig. 3. Note that the effect of the core diameter on $S(k)$ becomes more significant for small values of k.

In order to find the range of applicability of the derived $g(r)$ of this work, we test it for the Lennard-Jones (LJ) fluid. Before doing that, we should note that our potential is a hard-core Lennard-Jones (HCLJ) potential with diameter d, to which all distances are reduced. Hence for a LJ potential we have to find an equivalent HCLJ potential. To follow Zwanzig[17] approach, we should note that the LJ potential has two parameters; namely, σ_{LJ}, $\varepsilon_{\mathrm{LJ}}$ whereas the HCLJ potential has three parameters; ε, σ, and $L = d/\sigma$.

By setting the second virial coefficient of the two potentials equal to each other, we find a set of values for the parameters of the HCLJ potential, among which we choose the set which gives the correct value for the third virial coefficient of the Lennard-Jones fluid at the same temperature. Also in the numerical calculations, one should notice that for the LJ fluid T and ρ are reduced as $T_{\mathrm{LJ}}{}^* = kT/\varepsilon_{\mathrm{LJ}}$ and $\rho_{\mathrm{LJ}}{}^* = \rho\sigma_{\mathrm{LJ}}^3$, whereas for the HCLJ potential the reduced variables are $T^* = kT/\varepsilon$ and $\rho^* = \rho d^3$. Now if we define the reduced energy $(e = \varepsilon/\varepsilon_{\mathrm{LJ}})$ and the reduced distance $(f = d/\sigma_{\mathrm{LJ}})$, we find that $T^* = T^*_{\mathrm{LJ}}/e$ and $\rho^* = \rho^*_{\mathrm{LJ}}f^3$. Therefore for the LJ fluid at a given T^*_{LJ} we may calculate L, e, and f parameters. The results are presented in Table I for some given temperatures. It is interesting to note that L decreases when T^*_{LJ} increases; which is in accordance with our expectation. Due to the fact that the penetration of two molecules into each other increases with temperature, therefore the core diameter decreases.

We may find the range of applicability of the derived $g(r)$ for the LJ fluid, as follows. At a given T^*_{LJ} and ρ^*_{LJ} for the LJ fluid we first find the equivalent HCLJ potential parameters and then T^* and ρ^*. By having the potential parameters, the $g(r)$ and hence the thermodynamic properties may be calculated. The results of such calculations are summarized in Table II, for different thermodynamic states.

From the calculated results given in this table, we may conclude that the calculated $g(r)$ in this work is reasonable for the supercritical state; at least for the LJ fluid for which $\rho^*_{\mathrm{LJ,critical}} = 0.35$ and $T^*_{\mathrm{LJ,critical}} = 1.35$.

It seems that the HCLJ potential model, along with the

Table I. The parameters, which make two potentials (the LJ and HCLJ) equivalent at given reduced temperatures.

T^*	L	e	f
1	0.9000	1.0078	0.8863
1.2	0.87033	1.0026	0.8652
1.35	0.86301	1.0019	0.8592
1.4	0.86143	1.0017	0.8579
1.6	0.85698	1.0014	0.8541
1.8	0.85402	1.0012	0.8515
2	0.85167	1.0011	0.8494
2.2	0.84953	1.0009	0.8475
2.4	0.84749	1.0008	0.8457
2.6	0.84551	1.0008	0.8439
2.74	0.84415	1.0007	0.8426
2.8	0.84357	1.0007	0.8421
3	0.84168	1.0006	0.8404
3.2	0.83983	1.0005	0.8386
3.4	0.83803	1.0005	0.8370
3.6	0.83628	1.0004	0.8353
3.8	0.834585	1.0004	0.8337
4	0.83294	1.0004	0.8322

derived expression for $g(r)$ can be used as an appropriate reference system in perturbation theory for the subcritical liquid states as well.

3. Conclusion

We have presented in this paper a general solution to integral equations of liquid state theories at low densities for potentials with a hard core, which is indeed one step forward to obtain analytical solution to the integral equations.

As an especial case, we have derived an explicit expression for the RDF of the Lennard-Jones potential with a hard core. One may use this expression to calculate the fluid properties at low densities. The calculated structural factor is shown in Fig. 3. At least qualitatively, the obtained analytical expression for the RDF gives correct behavior of $S(k)$ for the supercritical states, for instance see Fig. 3 for $\rho^* = 0.25$ and $T^* = 3.5$.

The fact that two molecules in touch become harder and harder when penetrate into each other, the hard core potential models seems to be more realistic than the hard sphere model (HSM), physically. Therefore, regarding the perturbation theories, one expects that the present model is more appropriate than the HSM as the reference system.

To investigate the importance of the hard-core diameter, we have calculated the reduced third virial coefficient at different reduced temperatures, which is qualitatively in agreement with the experiment. As it is obvious from Fig. 2, the hard-core diameter has an important effect on the exactly calculated third virial coefficient. The fact that all thermodynamic properties are strongly dependent on the hard-core diameter has already been confirmed by the WCA theory.[15)]

In order to calculate the thermodynamic properties of a fluid, one should therefore know the three parameters of the potential, namely ε, σ, and L, which is obtained and tabulated for a Lennard-Jones fluid from which one can easily calculated these properties. The calculated results show that the derived $g(r)$ works well for the supercritical states, see Table II.

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Table II. The calculated thermodynamic properties of the Lennard-Jones fluid obtained in this work and those obtained from the perturbation theories in the high temperature approximation (HTA) and optimized random phase approximation (ORPA) and Monte Carlo (MC).

		$\beta P/\rho$				$-\Delta E/N\varepsilon$			
T^*	ρ^*	HTA[a)]	ORPA[a)]	This work	MC[a)]	HTA[a)]	ORPA[a)]	This work	MC[a)]
1.35	0.1	0.77	0.73	0.98	0.72	0.55	0.71	0.76	0.78
1.35	0.2	0.53	0.51	0.96	0.50	1.16	1.39	1.54	1.51
1.35	0.3	0.31	0.34	0.95	0.35	1.67	1.77	2.32	1.78
1.35	0.4	1.18	1.19	0.98	1.20	2.28	2.36	3.14	2.37
2.74	0.1	0.98	0.97	0.99	0.97	0.52	0.60	0.63	0.78
2.74	0.2	0.99	0.99	1.00	0.99	1.08	1.19	1.28	1.21
2.74	0.3	1.04	1.05	1.05	1.04	1.67	1.77	1.96	1.78
2.74	0.4	1.18	1.19	1.14	1.20	2.28	2.36	2.68	2.37

a) The HTA, ORPA, and MC values are taken from ref. 18.

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Appendix

In this appendix, we shall derive an analytical expression for the RDF for the following potential at low densities.

$$u'(r) = \begin{cases} \infty & r < d \\ u(r) & r \geq d \end{cases}$$

where $u(r)$ is the Lennard-Jones potential, i.e.,

$$u(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$

Defining $r^* = r/d$, $T^* = kT/\varepsilon$, $\rho^* = \rho d^3$ and $L = d/\sigma$, one may write:

$$u(r^*) = 4\left[\left(\frac{1}{Lr^*}\right)^{12} - \left(\frac{1}{Lr^*}\right)^{6}\right]$$

At high temperatures, we assume that $1 - \mathrm{e}^{-\beta u} \cong \beta u$, and then perform all integrals of eq. (51). By using the MAPLE, we find that (just for simplicity we have dropped all stars):

$$\frac{a}{2\pi d^3} = \frac{1}{24}r^3 - \frac{1}{2}r + \frac{2}{3}$$

$$\frac{b_1}{2\pi d^3} = 4\left(\frac{1}{2}\frac{\frac{1}{10}\frac{1}{L^{12}} - \frac{1}{4}\frac{1}{L^6}}{r} + \frac{\frac{1}{24}(1+3r)}{L^6 r^3 (1+r)^3} - \frac{1}{720}\frac{36r^2 + 84r^3 + 1 + 36r^7 + 84r^6 + 126r^5 + 126r^4 + 9r}{L^{12} r^9 (1+r)^9}\right)\Big/ T$$

$$\frac{b_2}{2\pi d^3} = 4\,\frac{\frac{1}{2}\frac{\left(\frac{1}{4}\frac{1}{L^6} - \frac{1}{10}\frac{1}{L^{12}}\right)(r-1)^2}{r} - \frac{1}{4}\frac{\frac{1}{3}r^3 - \frac{1}{2}r^3 + \frac{1}{6}}{L^6 r^3} + \frac{\frac{1}{10}\left(\frac{1}{72} + \frac{1}{9}r^9 - \frac{1}{8}r^8\right)}{L^{12} r^9}}{T}$$

$$\frac{b_3}{2\pi d^3} = 4\left(\frac{1}{2}\frac{\frac{1}{4}\frac{1}{L^6} - \frac{1}{10}\frac{1}{L^{12}}}{r} - \frac{1}{24}\frac{-1+3r}{L^6 r^3 (r-1)^3} + \frac{\frac{1}{720}(-36r^2 + 84r^3 - 1 + 36r^7 - 84r^6 + 126r^5 - 126r^4 + 9r)}{L^{12} r^9 (r-1)^9}\right)\Big/ T$$

Similarly, the other integrals of eqs. (51) can be performed to obtain analytical expressions for c_1, c_2, d_1, d_2 and d_3 as well. Hence, by having analytical expressions for all terms of eqs. (49) and (50), may be obtained from eqs. (51) for the RDF.

For instance for $1 \leq r \leq 2$, we find that

$$\begin{aligned}
g(r) = {} & \exp\left(-\frac{4\left(\frac{1}{L^{12}r^{12}} - \frac{1}{L^6 r^6}\right)}{T}\right)\exp\left(2\pi\rho\left(\frac{r^3}{24} - \frac{r}{2} + 2/3 + \frac{4\left(\frac{\frac{1}{10L^{12}} - \frac{1}{4L^6}}{2r} + \frac{1+3r}{24L^6 r^3 (1+r)^3} - \frac{36r^2+9r+84r^3+126r^4+126r^5+84r^6+36r^7+1}{720L^{12}r^9(1+r)^9}\right)}{T}\right.\right. \\
& + \frac{4\left(\frac{\left(\frac{1}{4L^6} - \frac{1}{10L^{12}}\right)(r-1)^2}{2r} - \frac{1/3r^3 - 1/2r^2 + 1/6}{4L^6 r^3} + \frac{-1/8r^8 + 1/9r^9 + 1/72}{10L^{12}r^9}\right)}{T} + r(360 + 1800r - 2520L^6 r + 4290r^2 + 5922r^3 + 4788r^4 \\
& + 1860r^5 - 225r^6 - 585r^7 - 360L^6 - 7530L^6 r^2 - 12330L^6 r^3 - 11610L^6 r^4 - 5610L^6 r^5 - 270L^6 r^6 \\
& + 1170L^6 r^7 + 570L^6 r^8 + 90L^6 r^9 - 244r^8 - 36r^9)\Big/(180(1+r)^9 L^{12} T) + 16\left(\frac{\left(\frac{1}{4L^6} - \frac{1}{10L^{12}}\right)^2}{r}\right. \\
& + \left(\frac{1}{4L^6} - \frac{1}{10L^{12}}\right)\left(\frac{1}{10L^{12}r(1+r)^{10}} - \frac{1}{4L^6 r(1+r)^4}\right) + 1/5040\left(-2110966r^{10} + 360360\ln(1+r)\right. \\
& - 360360\ln\left(\frac{1}{1+r}\right) + 126r^{20} + 2070r^{17} + 1645r^{18} + 700r^{19} + 180r^{14} + 540r^{15} + 1485r^{16} - 840r^{13} - 65520r^{11} \\
& + 5460r^{12} - 3603600\ln\left(\frac{1}{1+r}\right)r^9 - 360360\ln\left(\frac{1}{1+r}\right)r^{10} - 16216200\ln\left(\frac{1}{1+r}\right)r^2 - 43243200\ln\left(\frac{1}{1+r}\right)r^3 \\
& - 75675600\ln\left(\frac{1}{1+r}\right)r^4 - 90810720\ln\left(\frac{1}{1+r}\right)r^5 - 75675600\ln\left(\frac{1}{1+r}\right)r^6 - 43243200\ln\left(\frac{1}{1+r}\right)r^7 \\
& - 16216200\ln\left(\frac{1}{1+r}\right)r^8 + 43243200\ln(1+r)r^7 + 75675600\ln(1+r)r^6 + 3603600\ln(1+r)r \\
& + 16216200\ln(1+r)r^2 + 43243200\ln(1+r)r^3 + 75675600\ln(1+r)r^4 - 3603600\ln\left(\frac{1}{1+r}\right)r \\
& + 16216200\ln(1+r)r^8 + 3603600\ln(1+r)r^9 + 360360\ln(1+r)r^{10} + 90810720\ln(1+r)r^5 - 6846840r^3 \\
& - 720720r - 29069040r^3 - 72492420r^4 - 117261144r^5 - 127987860r^6 - 94757520r^7 - 46344870r^8
\end{aligned}$$

$$- 13902460r^{9}\Bigg)\Bigg/(L^{18}r^{15}(1+r)^{10}) - 1/12600\Bigg(- 681842018r^{10} + 116396280\ln(1+r) - 116396280\ln\left(\frac{1}{1+r}\right)$$
$$+ 126r^{20} - 1710r^{17} + 665r^{18} - 280r^{19} + 58140r^{14} - 15504r^{15} + 4845r^{16} - 271320r^{13} - 21162960r^{11}$$
$$+ 1763580r^{12} - 1163962800\ln\left(\frac{1}{1+r}\right)r^{9} - 116396280\ln\left(\frac{1}{1+r}\right)r^{10} - 5237832600\ln\left(\frac{1}{1+r}\right)r^{2}$$
$$- 13967553600\ln\left(\frac{1}{1+r}\right)r^{3} - 24443218800\ln\left(\frac{1}{1+r}\right)r^{4} - 29331862560\ln\left(\frac{1}{1+r}\right)r^{5}$$
$$- 24443218800\ln\left(\frac{1}{1+r}\right)r^{6} - 13967553600\ln\left(\frac{1}{1+r}\right)r^{7} - 5237832600\ln\left(\frac{1}{1+r}\right)r^{8}$$
$$+ 13967553600\ln(1+r)r^{7} + 24443218800\ln(1+r)r^{6} + 1163962800\ln(1+r)r$$
$$+ 5237832600\ln(1+r)r^{2} + 13967553600\ln(1+r)r^{3} + 24443218800\ln(1+r)r^{4}$$
$$- 1163962800\ln\left(\frac{1}{1+r}\right)r + 5237832600\ln(1+r)r^{8} + 1163962800\ln(1+r)r^{9} + 116396280\ln(1+r)r^{10}$$
$$+ 29331862560\ln(1+r)r^{5} - 2211529320r^{2} - 232792560r - 9389299920r^{3} - 23415051660r^{4}$$
$$- 37875349512r^{6} - 41340078780r^{6} - 30606678960r^{7} - 14969393010r^{8} - 4490494580r^{9}\Bigg)\Bigg/$$
$$(L^{24}r^{21}(1+r)^{10}) - 1/48\Bigg(420\ln(1+r) - 420\ln\left(\frac{1}{1+r}\right) + 1680\ln(1+r)r + 2520\ln(1+r)r^{2}$$
$$+ 1680\ln(1+r)r^{3} + 420\ln(1+r)r^{4} - 1680\ln\left(\frac{1}{1+r}\right)r - 2520\ln\left(\frac{1}{1+r}\right)r^{2} - 1680\ln\left(\frac{1}{1+r}\right)r^{3}$$
$$- 420\ln\left(\frac{1}{1+r}\right)r^{4} - 2940r^{2} - 840r - 3640r^{3} - 1750r^{4} - 168r^{5} + 28r^{6} - 8r^{7} + 3r^{9}\Bigg)\Bigg/$$
$$(L^{12}r^{9}(1+r)^{4}) + 1/5040\Bigg(- 72072r^{10} + 360360\ln(1+r) - 360360\ln\left(\frac{1}{1+r}\right) - 189r^{17} - 56r^{18} - 72r^{14} - 144r^{15}$$
$$- 261r^{16} + 252r^{13} + 6552r^{11} - 1092r^{12} - 360360\ln\left(\frac{1}{1+r}\right)r^{9} - 12972960\ln\left(\frac{1}{1+r}\right)r^{2} - 30270240\ln\left(\frac{1}{1+r}\right)r^{3}$$
$$- 45405360\ln\left(\frac{1}{1+r}\right)r^{4} - 45405360\ln\left(\frac{1}{1+r}\right)r^{5} - 30270240\ln\left(\frac{1}{1+r}\right)r^{6} - 12972960\ln\left(\frac{1}{1+r}\right)r^{7}$$
$$- 3243240\ln\left(\frac{1}{1+r}\right)r^{8} + 12972960\ln(1+r)r^{7} + 30270240\ln(1+r)r^{6} + 3243240\ln(1+r)r$$
$$+ 12972960\ln(1+r)r^{2} + 30270240\ln(1+r)r^{3} + 45405360\ln(1+r)r^{4} - 3243240\ln\left(\frac{1}{1+r}\right)r$$
$$+ 3243240\ln(1+r)r^{8} + 360360\ln(1+r)r^{9} + 45405360\ln(1+r)r^{5} - 6126120r^{2} - 720720r - 22942920r^{3}$$
$$- 49549500r^{4} - 67711644r^{5} - 60276216r^{6} - 34481304r^{7} - 11863566r^{8} - 2038894r^{9}\Bigg)\Bigg/$$
$$(L^{18}r^{15}(1+r)^{9})\Bigg)\Bigg/T^{2}\Bigg)\Bigg).$$