EVALUATION OF EQUILIBRIUM PROPERTIES FOR SEMICLASSICAL STATISTICAL MECHANICAL THEORY FOR HARD SPHERE FLUID

Mukesh Kumar* and Sanjay Kumar

Department of Physics B. R. A. Bihar University Muzaffarpur-842001 (India)
email: mukbihar@yahoo.com; mukbihar@rediffmail.com

M.D.D.M. College, Muzaffarpur

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ABSTRACT

In this present paper an attempt has been made primarily concerned with the diffraction effects of quantum theory of liquids. The hard sphere system is treated as a reference in framing the theory of liquid. We are concerned with the evaluation of the radial distribution function of the hard sphere fluid in the semiclassical limit. When quantum effects are small, then the properties of fluid are analysed in power of Planck’s constant $h$. Some methods have been adopted to investigate the effects of quantum mechanics on the structural and thermodynamic properties of a dense hard sphere at higher temperature. It is found that the contribution of the higher order corrections increases with density. Other theoretical approach has been also taken to investigate the properties of simple fluids through an integral equation. We critically discuss the integral equation perturbation theory and the effective pair potential for the free energy and correlation function.

Key words: distribution function, fluid, perturbation theory, pair potential, correlation function

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1. INTRODUCTION

The purpose of the present work is to develop a theory for calculating the quantum effects as diffraction effects and symmetry effects. The simplest hard body fluids and hard convex body (HCB) fluids, such as hard ellipsoid of revolution (HER) fluids. Considerable progress has been made in recent years in understanding the equilibrium properties of the hard sphere fluid, because they can model the shape of real molecules, since it is treated as a reference in framing the theory of liquid, so the study of the hard sphere system is very important.

In the present paper we employ the simple method to investigate the quantum corrections to the thermodynamics properties of the HCB fluids as well as dense hard sphere fluid at high temperature. In section 2 we discuss the basic theory for calculating the equilibrium properties for semiclassical statistical theory. We derive expressions for the first order quantum correction to the free energy and correlation function the results are discussed there, the concluding remarks are given in section 4.

2. Basic Theory :

2.1 Density Matrix and Slater Sum :

In statistical mechanics, the state of the quantum ensemble is described by the
density operator (or statistical operator) \( \hat{\rho} \). Any matrix representing the operator is called a density matrix. Nature of the density operator \( \hat{\rho} \) depends on the choice of operator.

We consider a quantum mechanical fluid of \( N \) identical particles, each of mass \( 'm' \). The Hamiltonian operator of the system is

\[
\hat{H} = -\left( \frac{\hbar^2}{2m} \right) \sum_{i=1}^{N} \nabla_i^2 + U(1,2,\ldots,N) \tag{1}
\]

Where \( \nabla_i^2 \) is the Laplacian operator and \( U \) is the total interaction potential which is assumed to be pair-wise additive.

\[
U(1,2,\ldots,N) = \sum_{i<j} u(i,j) \tag{2}
\]

where \( u(i, j) \) is the pair potential between the particles \( i \) and \( j \).

For a closed system, the density operator \( \hat{\rho} \) is

\[
\hat{\rho} = \exp\left[-\beta \hat{H} \right]/Q_N \tag{3}
\]

where \( \beta = (kT)^{-1} \) (\( k \) is the Boltzmann constant and \( T \) the absolute temperature) and \( Q_N \) is the normalization factor, known as the quantum mechanical partition function. Since

\[
\text{Tr} = 1, \tag{4}
\]

where \( \text{Tr} \) (\( \equiv \text{Trace} \)) is the sum of the diagonal elements. Hence

\[
Q_N = \text{Tr}(\exp\left[-\beta \hat{u} \right]) = \sum_{\alpha} \exp\left[-\beta \hat{H}_N \right] (1,2,\ldots,N) \prod_{i=1}^{N} dr_i \tag{5}
\]

where \( \Psi_\alpha \) represents a complete set of orthogonal wave functions.

Now, we apply the Slater sum for a system, which can be defined as

\[
W_N = N! \sum_{\alpha} \Psi_\alpha^* \left( 1, \ldots, N \right) \exp\left[-\beta \hat{H}_N \right] (1,\ldots,N) \tag{6}
\]

Where

\[
\lambda = (2\pi \hbar^2 /m)^{1/2}
\]

is the thermal wavelength. The classical counterpart of the Slater sum is the Boltzmann factor

\[
W_N^C = \exp\left[-\beta U(1,2,\ldots,N) \right] \tag{7}
\]

In terms of the Slater sum, the canonical partition function is written as

\[
Q_N = (1/N!\lambda^3 N) \sum_{\alpha} W_N = \sum_{\alpha} W_N(1,2,\ldots,N) \prod_{i=1}^{N} dr_i \tag{8}
\]

The 1 - particle distribution function is defined as

\[
n_N(1,2,\ldots,1) = \rho \sum_{\alpha} g_N(1,2,\ldots,1) = [(N-1)!\lambda^3 N]^{-1} \sum_{\alpha} W_N(1,2,\ldots,N) \prod_{i=1}^{N} dr_i \tag{9}
\]

where \( g_N(1,2,\ldots,1) \) is the 1-particle canonical distribution function and \( \rho = N/V \) is the number density.

For the grand canonical ensemble, the density operator \( \hat{\rho} \) is defined as

\[
\hat{\rho} = \exp\left[-\beta \hat{H}_N - \mu \right] / Q_N \tag{10}
\]

Where \( \mu \) is the chemical potential. In the terms of the Slater sum, Eq.(11) can be written as

\[
(1/N!) \sum_{\alpha} \Psi_\alpha^* \left( 1, \ldots, N \right) \exp\left[-\beta \hat{H}_N \right] (1,\ldots,N) \prod_{i=1}^{N} dr_i = (Z_N/N!) \sum_{\alpha} \Psi_\alpha^* \left( 1, \ldots, N \right) \exp\left[-\beta \hat{H}_N \right] (1,\ldots,N) \prod_{i=1}^{N} dr_i \tag{12}
\]

The 1 - particle distribution function in this case is defined as

\[
n_N(1,2,\ldots,1) = \rho \gamma g_N(1,2,\ldots,1) = (Z_N/N!(N-1)!)^{-1} \sum_{\alpha} W_N(1,2,\ldots,1) \prod_{i=1}^{N} dr_i \tag{13}
\]
where
\[ z = \lambda^{-3} \exp [\beta \mu] \] (14)
is the quantum mechanical fugacity.

Thus, the quantity of central importance for constructing the theory of quantum liquid or semiclassical liquid is the Slater sum.

### 2.2. Expansion of Slater Sum in power of \( \eta \)

We consider a semiclassical fluid at a volume \( V \) and temperature \( T \). The molecules of the fluid are assumed to interact via hard sphere potential. The quantity of central importance for constructing the theory of the semiclassical fluid is the Slater sum \( W_N \).

In the semiclassical limit, the Slater sum for such a system can be written as\(^4,5\)
\[ W_N = W_N^c W_N^m \] (15)

Where \( W_N^c \) is the Boltzmann factor and \( W_N^m \) is the modified W-function which measures the deviation from the classical behaviour. If the pair potential has a hard-core, both \( W_N \) and \( W_N^c \) will vanish for the configuration in which hard-core overlap. In this case, \( W_N \) can be taken as zero also. Like \( W_N \) and \( W_N^c \), \( W_N^m \) will also possess the product property.

In usual treatment of a quantum gas\(^12\) \( W_N \) is expressed in terms of Ursell function \( U_1 \). In the same way, we express \( W_N^m \) in terms of "modified" Ursell function \( U_1^m \)\(^4,5\)

\[ W_N^m (1) = U_1^m (1) = 1 \] (16a)
\[ W_N^m (1,2) = 1 + U_2^m (1,2) \] (16b)
\[ W_N^m (1,2,3) = 1 + U_2^m (1,2) + U_3^m (1,3) + U_3^m (2,3) + U_3^m (1,2,3) \] (16c)
\[ W_N^m (1,2,\ldots,N) = 1 + \sum U_2^m (i,j) + \sum U_3^m (i,j,k) + \ldots \] (16d)

Since \( U_1^m \) possess the ‘product property’, it follows that \( U_1^m \) will possess the ‘Cluster property’.

From Eqs.(15) and (16d), we obtain an expression of \( W_N \)
\[ W_N^m (1,2,\ldots,N) = W_N^c (1,2,\ldots,N) [1 + \sum U_2^m (i,j) + \sum U_3^m (i,j,k) U_2^m (k,1) + \ldots] \] (17)

The function \( U_1^m \) appearing in Eq.(17) can be found from the solution of the quantum mechanical I - body problem. But the actual solution in general is not feasible. \( U_2^m \) and \( U_3^m \) have been evaluated for hard spheres\(^13\).

The expression for \( U_2^m \) for the hard system is given as\(^1,13\)
\[ U_2^m (r) = \phi_0 + \phi_1 + \ldots \quad r > d \] (18)

where
\[ \phi_0 = -\exp (-Q^2) \] (19a)
\[ \phi_1 = \left( \frac{1}{\sqrt{2}} \right) \left( \frac{\lambda}{d} \right) Q^2 \text{erfc}(Q) \] (19b)

Here
\[ Q = \left( \sqrt{2\pi/(\lambda/d)} \right) \left[ (r/d - 1) \right] \]
and \text{erfc} \( Q \) is the complementary error function.

Instead of using the ‘modified’ Ursell function \( U_1^m \), Sinha and Singh\(^8\) have introduced the I-particle ‘modified’ Mayer function \( f_1,2,\ldots,1 \), which is defined in such a way that it reduces to zero. if any one of the particles 1,2,\ldots,1 becomes far from others. Thus
\[ W_N^m = \prod_{i<j} (1 + f_{ij}^{ll}) \prod_{i<j<k} (1 + f_{ijk}^{ll}) \] (20)

Comparing Eq.(16) and (20), we get
\[ U_2^{m}(1,2) = f_{ij} \]  
(21a)

\[ U_3^{m}(1,2,3) = f_{12}^{11} f_{13}^{11} f_{23}^{11} + f_{12}^{11} f_{13}^{11} + f_{12}^{11} f_{23}^{11} + f_{13}^{11} f_{23}^{11} \]  
(21b)

\[ U_1^{m}(1,2,...,1) = \sum_{C_1} \prod_{i<j} (1+f_{ij}) \]  
(21c)

where the sum of the product is carried out over all connected diagrams \( C_1 \) of 1 labeled points. Using Eqs.(15) and (20), we obtain.

Assuming the total potential as a pair-wise additive, and substituting Eq.(21), Ed.(17) can be written as

\[ W_N(1,2,...,N) = W^c_N \prod_{i<j} (1+f_{ij}) \]  
(22)

where

\[ W^c_N = \exp \left[-\beta \sum_{i<j} u(i,j) \right] = \sum_{i<j} (1 + f_{ij}^c) \]  
(23a)

and

\[ f_{ij}^c = \exp \left[-b u(i,j) \right] - 1 \]  
(23b)

\( W^c_N \) is the Boltzmann factor, \( f^{11} \) and \( f^{111} \) are, respectively, the two-and three-body ‘modified’ Mayer functions.

2.3 Theory:

The grand canonical partition function of the semiclassical fluid is defined as

\[ \Xi = \sum_{N=0}^{\infty} \frac{(1/N)!}{Z^N} \prod_{i=1}^{N} (1+f_{ij}) \prod_{i<j} (1+f_{ij}^{11}) \prod_{i=1}^{N} dr_i \]  
(24)

where

\[ z(i) = z \exp \left[-\beta u(i) \right] \]

\[ f_{ij} = f_{ij}^c + [1 + f_{ij}^c] f_{ij}^{11} \]

Here \( \beta = (kT)^{-1} \) and \( z \) is the fugacity. The Helmholtz free energy \( A \) of the uniform system is written as

\[ \beta A = N \ln(1 - 3\lambda) - H \{ \rho, f f^{111} \} \]  
(25)

Where

\[ \lambda = (2\rho \hbar^2 / m)^{1/2} \]

is the thermal wavelength, \( \rho = N/V \) is the number density and \( H \) is the excess Helmholtz free energy. The functional dependence of \( H \) on the density \( \rho \) and the Mayer functions \( f \) and \( f^{111} \) is indicated by the curly bracket \{ \}. The diagrammatic of expansion of 11 is given by

\[ H \{ \rho, f, f^{111} \} \]

Here a solid line and a curly line, respectively, represent the \( f \)- and \( (1+f) \)-link and a shared triangle denotes a \( f^{111} \) bond. Each black circle has a vertex function \( \rho \), which is integrated over.

The function \( H \) acts as a generating functional for the correlation functions14,15

\[ \frac{\partial H}{\rho(1)} = c(1) = h(1) \]  
(27a)

\[ \frac{2H}{\rho(1)\rho(2)} = c(1,2) \]  
(27b)

and

\[ H / \ln(1 + f) = (1/2) \rho^2 g(1,2) \]  
(27c)

where \( c(1,2) \) is the direct correlation function and \( g(1,2) \) is the pair correlation function.

2.4 Effective Pair Potentials:

In order to sum the diagrams appearing in the expansion of \( H \), we introduce an effective Mayer function \( F^H \) defined as

\[ E_{12}^H = f_{12} + (1 + f_{12}) E_{12}^H \]  
(28)

Where

\[ E_{12}^H = (1/3) \rho \int dr_3 \cdots \quad g_0(1,2,3) / g_0(1,2) \]  
(30)

where \( g_0(1,2,3) \) is the 1 body correlation function generated by \( f \)-bond only.

In terms of the effective Mayer function \( F^H \), we can write \( H \) as
H \{ρ, f, f^{111}\} = \hat{H}\{ρ, f^{*}\} + X \quad (31)

where \{ρ, f^{*}\} is H\{ρ, f\} with f-bond replaced by f^{*}-bond and X is a set of diagram belonging to \hat{H}, not included in H\{ρ, f^{*}\}. H\{ρ, f^{*}\} includes all diagram up to one f^{111}-bond and subsets of diagrams with n f^{111}-bonds (n≥2). Thus the diagrams, which are neglected through X contribute to the higher order quantum corrections.

The effective pair potential \(u_H\) is obtained from the effective Mayer function by the relation

\[ u_H(1,2) = u(1,2) - kT \ln \left[ 1 + f^{111}_{12} + (1 + f^{111}_{12})E_{12} \right] \]

where

\[ f^{111}_{12} = f^{111}_{12} + (1 + f^{111}_{12})E_{12} \]

We can formally expand \(u^e\) and \(f^{11e}\) as

\[ u^e(1,2) = u(1,2) + \eta v_1(1,2) + \eta^2 v_2(1,2) + ... \quad (39) \]

\[ F^{11e}_{12} = \eta F^1_{12} + \eta^2 F^{11}_{12} + ... \quad (40) \]

where \(\eta\) is the parameter representing the effect of quantum corrections. When \(\eta = 0\), Eq.(37) reduces to the classical Boltzmann factor while \(\eta = 1\) gives the effective potential in presence of quantum effect. The power on \(\eta\) denotes the order of quantum correction.

2.5. Integral Equation Perturbation Theory for Radial Distribution Function:

The radial distribution function (RDF) of a semiclassical fluid can be expanded about the classical value as

\[ g(1,2) = g^c(1,2) + \eta g^1(1,2) + \eta^2 g^{11}(1,2) + ... \quad (43) \]

where \(g^c(1,2)\) is the RDF of the classical fluid and \(g^c(1,2)\) is the nth order quantum correction. The usual expansion is not suitable to evaluate even \(g^1(1,2)\) because its expression involves three- and four- body classical distribution functions which are not known.
Singh and Sinha\textsuperscript{1} and Sainger et al.\textsuperscript{9} have already suggested the evaluation of the correction term by means of an approximate integral equation theory such as the hypernetted chain (HNC) and Percus - Yevick (PY) theories. Thus Eq.(43) becomes.

\[ g(\mathbf{i}, \mathbf{j}) \approx g^e(\mathbf{i}, \mathbf{j}) + \eta g_{1E}^{(1,2)} + \eta \eta g_{2E}^{(1,2)} + \cdots \] (44)

where \( g^e(\mathbf{i}, \mathbf{j}) \) is the ‘exact’ RDF for the classical system and \( g_{nE}^{(1,2)} \) is the nth order quantum correction obtained by an integral equation theory. One attractive feature of an integral equation for the RDF is that the higher order correction terms are evaluated in principle, as easily as the first order term.

2.6. The HNC Integral Equation Theory:

In the extended HNC approximation, the RDF of a semiclassical fluid is given\textsuperscript{1,9}

\[ \ln g(\mathbf{i}, \mathbf{j}) = -\beta u(\mathbf{i}, \mathbf{j}) + \rho Z_g(\mathbf{i}, \mathbf{j}) - 1 - \ln g(\mathbf{i}, \mathbf{j}) \]

This relation has been used to obtain expressions for the quantum corrections to the RDF. Thus, \( g_{\text{HNC}}(1,2) \), nth order quantum correction to the RDF, is given by

\[ g_{\text{HNC}}(1,2) = g^e(1,2) F_{12}^{1} + \rho (1 + f_{12}^{11}) g^e(1,2) \]

(46)

Thus, each correction term \( g_{\text{HNC}}(1,2) \) requires previous terms in the expansion and can be obtained by the ‘iterative’ process.

2.7 The PY - integral Equation Theory:

Singh and Sinha\textsuperscript{1} have obtained the extended PY integral equation for the RDF of a semiclassical fluid

\[ g(\mathbf{i}, \mathbf{j}) = \exp \{ -\beta u(\mathbf{i}, \mathbf{j}) \} [1 + \rho Z(\mathbf{i}, \mathbf{j}) \{1-\exp \{\beta u(\mathbf{i}, \mathbf{j})\}\} (g(2,3) - 1) \] (49)

This expression can be used to obtain expressions for the quantum corrections to the RDF. Thus expressions for \( g_{\text{PY}}(1,2) \) for the hard sphere fluid are given by

\[ g_{\text{PY}}(1,2) = g^e(1,2) F_{12}^{1} + \rho (1 + f_{12}^{11}) \exp \{ -\beta u(\mathbf{i}, \mathbf{j}) \}
\]

(50)

Thus the quantum correction terms in the PY theory are also obtained by the method of iteration.

2.8 Hard Sphere Model:

We consider a fluid, whose molecules interact via a hard sphere potential

\[ U(r) = \infty \quad r < d \]
where

\[ r^* = r/d \]

and three-particle ‘modified’ Mayer function is

\[ F_{123}^{11} = U_{1}^{m}(1,2,3) - U_{1}^{m}(1,2) U_{2}^{m}(1,3) - U_{2}^{m}(1,3) U_{2}^{m}(2,3) \]

(56)

where \( U_{1}^{m} \) is the 1-particle ‘modified Ursell function. Thus Eq.(29) can be written as

\[ E_{1}(1,2) = \rho z dr_{3} gc(1,3) gc(2,3) \]

(57)

In the region \( r > d + \lambda \), \( U_{2}^{m}(r) \sim 0 \). The leading contribution to \( E_{1} \), which is of the order of \( \lambda^2 \), comes from the Cluster formation, in which two distance of a triangle formed by 1,2,3 lic within \( d \) and \( d + \lambda \) if \( r_{12} > d + \lambda \), thus \( E_{1}(1,2) \) may be evaluated following the method of jancovici. Thus the result is

\[ E_{1}(1,2) = (2\pi / r_{12} / d) (\lambda / d^2) (pd^3) \left[ \frac{g^m(\lambda)}{\sqrt{2\pi}} \right] \]

(58)

where

\[ \theta = \pi \cos^{-1}\left[(1/2)(1-r_{12}^2/2d^2)\right] \]

for \( d + \lambda \leq r_{12} \leq 2d \).

For the contribution in which \( d \leq r_{12} \leq d + \lambda \), \( E_{1}(1,2) \) is solved numerically.

\[ F_{11}(r) = \phi_{0}(r) + \phi_{1}(r) + \ldots \]

(53)

where

\[ \phi_{0} = -\exp(-Q^2) \]

(54a)

\[ \phi_{1} = \left( \frac{1}{\sqrt{2}} \right) \left( \frac{\lambda}{d} \right) Q^2 \text{erfc}(Q) \]

(54b)

with

\[ Q = \left( \frac{2\pi}{12} \right)^{1/2} \frac{(r^* - 1)}{(\lambda/d)} \]

(55)

\[ r^* = r/d \]

and three-particle ‘modified’ Mayer functions are given by

\[ F_{123}^{11} = U_{3}^{m}(1,2,3) - U_{2}^{m}(1,2) U_{2}^{m}(1,3) - U_{2}^{m}(1,3) U_{2}^{m}(2,3) \]

(56)

2.9 The HNC Approximation:

Equation (46) can be written as

\[ g_{\text{HNC}}(r_{12}) = A_{\text{HNC}}^{1}(r_{12}) + (2\pi / r_{12})(\rho d^3) \]

\[ (1+f^{11}(r_{12})) A_{\text{HNC}}^{1}(r_{12}) \]

(59)

where

\[ A_{\text{HNC}}^{1}(r_{12}) = g^{m}(r_{12}) \exp[-Q_{12}^2 (\pi/2)^2 \rho(r_{12}^* - 1)/(\lambda/d)] \]

\[ \{ r_{12} + (1+f^{11}(r_{12})) g^{m}(r_{12}) r_{12} + 1 \} \]

\[ r_{12} + 1 \]

(60)

\[ B_{\text{HNC}}^{1}(r_{12}) = g^{m}(r_{12}) \left[ r_{12} + (1+f^{11}(r_{12})) g^{m}(r_{12}) + 1 \right] \]

\[ r_{12} + 1 \]

(61)

Here \( r_{ij}^* = r_{ij} / d \) and \( Q_{12} = \sqrt{2\pi}(r_{12}^* - 1)/(\lambda/d) \).

Values of \( g_{\text{HNC}}^{m}(r_{12}) \) are obtained from Eqn.(59) by the method of iteration.

3.0 The PY Approximation:

Ed. (50) for the hard sphere fluid can be written as

\[ g_{\text{PY}}(r_{12}) = A_{\text{PY}}^{1}(r_{12}) + (2\pi / r_{12})(\rho d^3) \]

\[ (1+f^{11}(r_{12})) A_{\text{PY}}^{1}(r_{12}) \]

(62)

where

\[ A_{\text{PY}}^{1}(r_{12}) = -g^{m}(r_{12}) \exp[-Q_{12}^2 (\pi/2)^2 \rho(r_{12}^* - 1)/(\lambda/d)] \]

\[ \{ r_{12} + (1+f^{11}(r_{12})) g^{m}(r_{12}) + 1 \} \]

\[ r_{12} + 1 \]

(63)

\[ B_{\text{PY}}^{1}(r_{12}) = g^{m}(r_{12}) \left[ r_{12} + (1+f^{11}(r_{12})) g^{m}(r_{12}) + 1 \right] \]

\[ r_{12} + 1 \]

(64)

Here \( r_{ij}^* = r_{ij} / d \) and \( Q_{12} = \sqrt{2\pi}(r_{12}^* - 1)/(\lambda/d) \).

Values of \( g_{\text{PY}}^{m}(r_{12}) \) are obtained from Eqn.(59) by the method of iteration.
Table 1. Values of $\Delta g^1(r^*)$ for hard sphere fluid

| $r^*$ | $\lambda / d = 0.1$ | $\lambda / d = 0.2$ | $\lambda / d = 0.1$ | $\lambda / d = 0.1$ |
|-------|---------------------|---------------------|---------------------|---------------------|
| 1.00  | 0.0                 | 0.0                 | 0.0                 | 0.0                 |
| 1.05  | -0.00196            | -0.00161            | -0.00982            | -0.00806            |
| 1.10  | -0.00381            | -0.00604            | -0.02327            | -0.03694            |
| 1.15  | -0.00516            | -0.01002            | -0.03110            | -0.06039            |
| 1.20  | -0.00632            | -0.01262            | -0.03598            | -0.07182            |
| 1.25  | 0.00735             | -0.01469            | -0.03854            | -0.07708            |
| 1.30  | -0.00773            | -0.01547            | -0.03906            | -0.07811            |
| 1.35  | -0.00840            | -0.01681            | -0.03803            | -0.07606            |
| 1.40  | -0.00833            | -0.01666            | -0.03560            | -0.07119            |
| 1.45  | -0.00832            | -0.01663            | -0.03223            | -0.06447            |
| 1.50  | -0.00805            | -0.01609            | -0.02813            | -0.05662            |
| 1.55  | -0.00732            | -0.01464            | -0.02319            | -0.04637            |
| 1.60  | -0.00655            | -0.01309            | -0.01751            | -0.03502            |
| 1.65  | -0.00566            | -0.01132            | -0.01122            | -0.02243            |
| 1.70  | -0.00444            | -0.00888            | -0.00433            | -0.00865            |
| 1.75  | -0.00310            | -0.00621            | 0.00312             | 0.00624             |
| 1.80  | -0.00162            | -0.00325            | 0.01104             | 0.02208             |
| 1.85  | -0.00001            | -0.00001            | 0.01932             | 0.03854             |
| 1.90  | 0.00169             | 0.00338             | 0.02798             | 0.05597             |
| 1.95  | 0.00347             | 0.00693             | 0.03675             | 0.07350             |
| 2.00  | 0.00479             | 0.00959             | 0.04136             | 0.08272             |
| 2.10  | 0.00286             | 0.00571             | 0.01429             | 0.02857             |
| 2.20  | 0.00142             | 0.00284             | -0.00131            | -0.00262            |
| 2.30  | 0.00040             | 0.00179             | -0.00939            | -0.01879            |
| 2.40  | -0.00028            | 0.00056             | -0.01222            | -0.02445            |
| 2.50  | -0.00067            | -0.00134            | -0.01126            | -0.02251            |
| 2.60  | -0.00081            | -0.00162            | -0.00753            | -0.01506            |
| 2.70  | -0.00073            | -0.00146            | -0.00264            | -0.00528            |
| 2.80  | -0.00052            | -0.00105            | 0.00217             | 0.00435             |
| 2.90  | -0.00027            | -0.00053            | 0.00567             | 0.01134             |
| 3.00  | -0.00003            | -0.00006            | 0.00644             | 0.01288             |

In this case also, Eq.(62) can be solved by the method of iteration.

In both the HNC and PY approximations, the main contribution comes from $A^1(r^*)$. The second terms of Eqs.(59) and (62) is a correction over $A^1(r^*)$ to $g^1(r^*)$.

Let us now discuss the contribution of $g^1(r^*)$ at different Values of $r^*$.

\[
-H^1(\max\{1, |r^*_1 - r^*_3| \})|r^*_1 - r^*_3| d|r^*_1 - r^*_3| \tag{64}
\]

\[
H^1(X) = \int_0^{\max\{X, |r^*_1 - r^*_3| \}} d|r^*_1 - r^*_3| \tag{65}
\]

Now we consider $A^1(r^*)$ under both approximations. They differ in the second term only. The values of $A^1_{\text{HNC}}$ are less than the values of $A^1_{\text{PY}}$ except at $r^* = 1$ where $A^1_{\text{HNC}}(1) = A^1_{\text{PY}}(1)$.

Let us now discuss the contribution of $g^1(r^*)$ at different Values of $r^*_1 - r^*_2$.

At the hard core ($r^*_1 - r^*_2 = d$), where $f^1(r^*_1 - r^*_2) = -1$, we have...
### Table 2. Values of $g_1(r^*)$ for hard sphere fluid using the HNC approximation at $\lambda/d_1 = 0.1$

| $\rho d_3$ | $r^*$ | 0.1 | 0.2 | 0.3 | 0.4 | 0.5 | 0.6 | 0.7 |
|------------|-------|-----|-----|-----|-----|-----|-----|-----|
| 1.00       | -1.1445 | -1.3390 | -1.5480 | -1.8110 | -2.1160 | -2.5610 | -3.1570 |
| 1.04       | -0.3915 | -0.4146 | -0.4308 | -0.4495 | -0.4437 | -0.4109 | -0.3047 |
| 1.08       | 0.0127 | 0.0577 | 0.1161 | 0.195G | 0.3065 | 0.4649 | 0.824 |
| 1.12       | 0.0321 | 0.0772 | 0.1357 | 0.2118 | 0.3149 | 0.4644 | 0.6759 |
| 1.16       | 0.0295 | 0.0690 | 0.1171 | 0.1817 | 0.2498 | 0.3427 | 0.4548 |
| 1.20       | 0.0283 | 0.0654 | 0.1097 | 0.1643 | 0.2276 | 0.3135 | 0.4248 |
| 1.24       | 0.0257 | 0.0581 | 0.0929 | 0.1378 | 0.1762 | 0.2265 | 0.2806 |
| 1.28       | 0.0246 | 0.0546 | 0.0880 | 0.1242 | 0.1625 | 0.2103 | 0.2677 |
| 1.32       | 0.0221 | 0.0479 | 0.0737 | 0.1029 | 0.1242 | 0.1473 | 0.1681 |
| 1.36       | 0.0210 | 0.0447 | 0.0683 | 0.0919 | 0.1137 | 0.1377 | 0.1653 |
| 1.40       | 0.0187 | 0.0381 | 0.0567 | 0.0746 | 0.0834 | 0.0911 | 0.0936 |
| 1.44       | 0.0176 | 0.0359 | 0.0521 | 0.0661 | 0.0765 | 0.0871 | 0.0975 |
| 1.48       | 0.0154 | 0.0302 | 0.0415 | 0.0513 | 0.0519 | 0.0499 | 0.0429 |
| 1.52       | 0.0144 | 0.0279 | 0.0379 | 0.0445 | 0.0475 | 0.0486 | 0.0496 |
| 1.56       | 0.0123 | 0.0225 | 0.0289 | 0.0317 | 0.0266 | 0.0185 | 0.0049 |
| 1.60       | 0.0113 | 0.0203 | 0.0256 | 0.0263 | 0.0241 | 0.0192 | 0.0133 |
| 1.64       | 0.0093 | 0.0156 | 0.0170 | 0.0151 | 0.0061 | -0.0071 | -0.0267 |
| 1.68       | 0.0083 | 0.0136 | 0.0142 | 0.0105 | 0.0042 | -0.0057 | -0.0180 |
| 1.72       | 0.0064 | 0.0090 | 0.0066 | 0.0006 | -0.0122 | -0.0301 | -0.0567 |
| 1.76       | 0.0054 | 0.0070 | 0.0041 | -0.0036 | -0.0137 | -0.0287 | -0.0483 |
| 1.80       | 0.0036 | 0.0028 | -0.0031 | -0.0129 | -0.0290 | -0.0529 | -0.0886 |
| 1.84       | 0.0027 | 0.0009 | -0.0054 | -0.0168 | -0.0309 | -0.0518 | -0.0812 |
| 1.88       | 0.0009 | -0.0031 | -0.0124 | -0.0256 | -0.0463 | -0.0767 | -0.1244 |
| 1.92       | -0.0001 | -0.0052 | -0.0145 | -0.0296 | -0.0480 | -0.0761 | -0.1176 |
| 1.96       | -0.0018 | -0.0089 | -0.0212 | -0.0385 | -0.0641 | -0.1025 | -0.1632 |
| 2.00       | -0.0023 | -0.0094 | -0.0207 | -0.0376 | -0.0573 | -0.0852 | -0.1231 |
| 2.08       | -0.0017 | -0.0064 | -0.0123 | -0.0187 | -0.0200 | -0.0121 | 0.0190 |
| 2.16       | -0.0012 | -0.0039 | -0.0058 | -0.0053 | 0.0037 | -0.0268 | 0.0755 |
| 2.24       | -0.0008 | -0.0020 | -0.0014 | 0.0026 | 0.0153 | 0.0394 | 0.0805 |
| 2.32       | -0.0005 | -0.0007 | 0.0014 | 0.0067 | 0.0189 | 0.0381 | 0.0637 |
| 2.40       | -0.0003 | 0.0001 | 0.0028 | 0.0080 | 0.0178 | 0.0298 | 0.0414 |
| 2.48       | -0.0001 | 0.0006 | 0.0034 | 0.0076 | 0.0141 | 0.0195 | 0.0205 |
| 2.56       | 0.0000 | 0.0009 | 0.0032 | 0.0061 | 0.0093 | 0.0082 | 0.0025 |
| 2.64       | 0.0001 | 0.0009 | 0.0026 | 0.0041 | 0.0043 | 0.0000 | 0.0021 |
| 2.72       | 0.0001 | 0.0007 | 0.0017 | 0.0019 | -0.0002 | -0.0074 | -0.0234 |
| 2.80       | 0.0001 | 0.0005 | 0.0008 | -0.0002 | -0.0040 | -0.0128 | -0.0303 |
| 2.88       | 0.0001 | 0.0003 | 0.0001 | -0.0017 | -0.0064 | -0.0153 | -0.0303 |
| 2.96       | 0.0000 | -0.0003 | -0.0007 | -0.0016 | -0.0067 | -0.0118 | -0.0152 |

\[ g_{HNC}^{(1)}(1) = g_{PY}^{(1)}(1) = g_{C}^{(1)} \]

and hence
\[ g_{HNC}(1) = g_{PY}(1) = 0 \]

In the region $1 < r_{12} < 1 + \lambda/d$, where $f_{11}^{(1)}(r_{12})$ \neq 0, $g_{HNC}^{(1)}(r_{12})$ and $g_{PY}^{(1)}(r_{12})$ are evaluated numerically from Eqs.(59) and (62).
In the region \( r_{12}^* > 1 + \frac{\lambda}{d}, f^{11}(r_{12}^*) = 0 \), we have
\[
\tilde{g}^{\text{hnc}}(r_{12}^*) = A_{\text{hnc}}^1(r_{12}^*) + \frac{(2\pi/r_{12}^*)}{(\lambda/d)} B_{\text{hnc}}^1(r_{12}^*)
\]
where
\[
A_{\text{hnc}}^1(r_{12}^*) = -g^c(r_{12}^*) \exp \left[ -\frac{Q^c_{12}}{\lambda} \right] f^{11}(r_{12}^*)
\]
\[
B_{\text{hnc}}^1(r_{12}^*) = \frac{r_{12}^* + 1}{r_{12}^* + 1} [ g^c(r_{12}^*) - 1 ] d_{13} d_{13}^* \quad (66)
\]
and
\[
A_{\text{py}}^1(r_{12}^*) = A_{\text{hnc}}^1(r_{12}^*) + \frac{(2\pi/r_{12}^*)}{(\lambda/d)} B_{\text{py}}^1(r_{12}^*)
\]
where
\[
A_{\text{py}}^1(r_{12}^*) = -g^c(r_{12}^*) \exp \left[ -\frac{Q^c_{12}}{\lambda} \right] f^{11}(r_{12}^*)
\]
\[
B_{\text{py}}^1(r_{12}^*) = \frac{r_{12}^* + 1}{r_{12}^* + 1} [ g^c(r_{12}^*) - 1 ] d_{13} d_{13}^* \quad (66)
\]

4. CONCLUDING REMARKS

We have developed a simple theory to calculate the first order quantum corrections to the free energy, pressure and quantum corrections of the HCB fluid and applied it to the HER and HDB fluids. The quantum corrections depend on \( K \) for the HER and \( 1^* \) for the HDB. The value \( \Delta g'(r^*) \) is oscillatory about zero. The magnitude of \( \Delta g'(r^*) \) increases with increasing of density \( \rho d^3 \) and increase of \( \lambda/d \). The peak value is \( g_{\text{hnc}}' \) occurs at about \( r^* = 1 + \frac{\lambda}{d} \) and increases with density.

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