

Radial Distribution Function of Dense Quantum Fluids

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A new method is proposed for the calculation of the radial distribution of quantum fluids and its application to the liquid He is discussed.

1. Introduction

For the investigation of the structure of the quantum fluids such as liquid He⁴ and liquid He³, the detailed information for the two body distribution function, or the radial distribution function of the system is very important³⁾. A number of papers have been published concerning the theoretical calculation of the radial distribution of the quantum system³⁾. Severe requirements that the method must be effective at very low temperatures and at high density, however, force their results still to remain at quite insufficient level. Hence, new trials to overcome these difficulties may be allowed.

In this paper, we propose a method of calculation of the radial distribution function basing on the cluster expansion method. The cluster expansion method is essentially the method for the low density system. However, utilizing the partial summation technique which showed considerable success for the classical fluid, we introduce a method which enables us to take quantum effects into consideration in the case of high density.

2. General Formulation

We start from the formulae which have been

derived by the modified cluster expansion method¹⁾²⁾. In the followings, the single particle reduced density matrix is denoted by $\langle 1' | \rho_1 | 1 \rangle$, where $\langle 1' |$ ($| 1 \rangle$) stands for the bra-vector (ket-vector) $\langle \mathbf{r}_1 |$ ($| \mathbf{r}_1 \rangle$) in the coordinate representation. Similarly, the two particle reduced density matrix is denoted by $\langle 1' 2' | \rho_2 | 1 2 \rangle^*$, where $\langle 1' 2' |$ ($| 1 2 \rangle$) stands for the properly symmetrized bra-vector (ket-vector) for the system of particles 1 and 2. Of course the distribution function is the diagonal element of the corresponding reduced density matrix.

1) ρ_1

We have

$$\langle 1' | \rho_1 | 1 \rangle = \sum_{i=1}^{\infty} l(1' | \tilde{b}_i^{(1)} | 1) x^i \quad (2.1)$$

, where $\tilde{b}_i^{(1)}$ are modified cluster integrals²⁾ which are defined below.

$$\begin{aligned} \langle 1' | \tilde{b}_i^{(1)} | 1 \rangle &= \langle 1' | \rho_1^{(0)} | 1 \rangle \\ &= \sum_{\mathbf{k}} f_{\mathbf{k}} \langle 1' | \mathbf{k} \rangle \langle \mathbf{k} | 1 \rangle \end{aligned} \quad (2.2)$$

$$\langle \mathbf{k} | 1 \rangle = \frac{1}{\sqrt{V}} e^{i\mathbf{k} \cdot \mathbf{r}_1}$$

Here $\rho_1^{(0)}$ means the single particle reduced density matrix of the reference ideal system, $f_{\mathbf{k}}$ means the Fermi or the Bose distribution function and $\langle \mathbf{k} | 1 \rangle$ is the free particle wave function of momentum \mathbf{k} normalized in the volume V .

* We use similar notations throughout the paper.

$$\begin{aligned}
(1'|\tilde{b}_2^{(1)}|1) &= \frac{1}{2!} \int (\prod_2) (1'2'|\tilde{U}_2^{(1)}|12) \\
\tilde{U}_2^{(1)} &= U_2^{(1)} \rho_2^{(0)} \\
U_2^{(1)} &= (e^{-\beta H_2} e^{\beta H_2^{(0)}} - 1), \quad \beta = 1/kT
\end{aligned} \quad (2.3)$$

Here $\rho_2^{(0)}$ means the two particle reduced density matrix for the reference ideal system. $U_2^{(1)}$ is the two body cluster operator where H_2 is the Hamiltonian of the two particle system under consideration and $H_2^{(0)}$ is for the system in which the interaction is dropped. The integral means to take trace with respect to the coordinates specified there.

$$\begin{aligned}
(1'|\tilde{b}_3^{(1)}|1) &= \frac{1}{3!} \int (\prod_3) (1'2'3'|\tilde{U}_3^{(1)}|123) \\
\tilde{U}_3^{(1)} &= U_3^{(1)} \rho_3^{(0)} \\
&\quad + (U_1^{(1)} U_2 \rho_3^{(0)} - U_1^{(1)} \rho_1^{(0)} U_2 \rho_2^{(0)})
\end{aligned} \quad (2.4)$$

where U_1, U_2 are the cluster operators which appear in the formula for the partition function.¹⁾

The selector variable x satisfies the relation

$$1 = \prod_{l=1} l \tilde{b}_l x^l, \quad (2.5)$$

where

$$\tilde{b}_l = \frac{1}{\rho} \int (\prod_1) (1'|\rho_1^{(1)}|1), \quad \rho = \frac{N}{V}$$

Here we introduce a new selector variable y through the relations

$$y = \sum_{l=1} l \tilde{b}_l x^l, \quad (2.6)$$

$$x = y e^{-\sum_k \tilde{b}_k y^k} \quad (2.7)$$

where \tilde{b}_k are defined by

$$\tilde{b}_2 = 2\tilde{b}_2, \quad \tilde{b}_3 = 3\tilde{b}_3 - 6(\tilde{b}_2)^2, \quad \dots \quad (2.8)$$

These procedures are completely analogous to the techniques which are well known in the theory of the imperfect gas.

2) ρ_2

We have²⁾

$$(1'2'|\rho_2|12) = \sum_{l=1} l (1'2'|\tilde{b}_l^{(2)}|12) x^{l+1} \quad (2.9)$$

where

$$\tilde{b}_1^{(2)} = W_2 \rho_2^{(0)}, \quad W_2 = e^{-\beta H_2} e^{\beta H_2^{(0)}} \quad (2.10)$$

$$2! (1'2'|\tilde{b}_2^{(2)}|12) = \int (\prod_3) (1'2'3'|\tilde{U}_3^{(2)}|123)$$

$$\begin{aligned}
\tilde{U}_3^{(2)} &= w_3^{(2)} \rho_3^{(0)} \\
w_3^{(2)} &= e^{-\beta H_3} e^{\beta H_3^{(0)}} - e^{-\beta H_2} e^{\beta H_2^{(0)}} (12)
\end{aligned}$$

Using the relation (2.6) and (2.7), we can transform (2.9) into the expansion in terms of y . We have

$$(1'2'|\rho_2|12) = \sum_{k=2} (1'2'|\gamma_k^{(2)}|12) y^k \quad (2.11)$$

where $\gamma_k^{(2)}$ are defined successively as follows.

$$\gamma_2^{(2)} = \tilde{b}_1^{(2)}, \quad (2.12)$$

$$\gamma_3^{(2)} = 2\tilde{b}_2^{(2)} - 2\tilde{b}_2 \cdot 2\tilde{b}_1^{(2)},$$

$$\begin{aligned}
\gamma_4^{(2)} &= 3\tilde{b}_3^{(2)} - 12\tilde{b}_2 \tilde{b}_2^{(2)} \\
&\quad - (6\tilde{b}_3 - 20\tilde{b}_2^{(2)}) \tilde{b}_1^{(2)}
\end{aligned}$$

$$3\tilde{b}_3^{(2)} = \frac{1}{2} \int (\prod_4) (1'2'3'4'|\tilde{U}_4^{(2)}|1234)$$

$$\begin{aligned}
\tilde{U}_4^{(2)} &= U_4^{(2)} \rho_4^{(0)} \\
&\quad + (U_2^{(2)} U_2 \rho_4^{(0)} - U_2^{(2)} \rho_2^{(0)} U_2^{(2)} \rho_2^{(0)}) \\
U_4^{(2)} &= W_4 - W_3(123) - W_3(124) \\
&\quad - W_2(12) W_2(34) + 2 W_2(12)
\end{aligned}$$

Further we rearrange this into the following form. From now on we suppress the explicit matrix notation and write down only the relation between operators.

We have

$$\rho_2 = e^{-\beta H_2} e^{\beta H_2^{(0)}} y^2 \Gamma(\beta, y) \rho_2^{(0)} \quad (2.13)$$

$$\Gamma(\beta, y) = \sum_{k=1} \gamma_{k+1}^{(2)*} y^{k-1}$$

$$\begin{aligned}
\gamma_2^{(2)*} &= e^{-\beta H_2^{(0)}} e^{\beta H_2} e^{\beta H_2^{(0)}} \rho_2^{(0)} (\rho_2^{(0)})^{-1} \\
&= 1
\end{aligned}$$

$$\gamma_2^{(2)*} = 2\tilde{b}_2^{(2)*} - 2(2\tilde{b}_2)$$

$$\tilde{b}_2^{(2)*} = e^{-\beta H_2^{(0)}} e^{\beta H_2} \tilde{b}_2^{(2)} (\rho_2^{(0)})^{-1},$$

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Finally we cast $\Gamma(\beta, y)$ in a form analogous to

the order exponential, that is,

$$\begin{aligned}
 \Gamma(\beta, y) &= \exp^* \left(\sum_{\lambda=1} \beta_{\lambda}^{(2)} y_{\lambda} \right) \\
 &= 1 + (\beta_1^{(2)} y + \beta_2^{(2)} y^2 + \dots) \\
 &\quad + \frac{1}{2!} (\beta_1^{(2)} y + \beta_2^{(2)} y^2 + \dots)^2 \\
 &\quad + \dots \\
 &= 1 + \beta_1^{(2)} y + y^2 \left(\beta_2^{(2)} + \frac{1}{2!} (\beta_1^{(2)})^2 \right) \\
 &\quad + \dots
 \end{aligned} \tag{2.14}$$

Here new operators $\beta_{\lambda}^{(2)}$ are defined in connection with the operators $\gamma_k^{(2)*}$ successively keeping the order of the operators in each product unchanged.

Putting $y=1$ we arrive at the formula

$$\rho_2 = e^{-\beta H_2} e^{\beta H_2^{(0)}} \exp^* \left(\sum_{\lambda=1} \beta_{\lambda}^{(2)} \right) \rho_2^{(0)} \tag{2.15}$$

3. Discussions.

From our general formula (2.15), we can derive various approximate formulae which show how the quantum effects come into the calculation. Cutting all quantum effects except final $\rho_2^{(2)}$ we obtain

$$\rho_2(12) = \exp(-\beta \phi(12) + S(12) + B(12)) \cdot \rho_2^{(0)}(12)$$

where the exponential factor coincide with the radial distribution function of the classical system³⁾. $\phi(12)$ is the interaction potential between the particles, $S(12)$ is the contribution

from the series diagram and $B(12)$ is that of the bridge diagram. Specifying the approximation for the classical system, we may use, for example, the form

$$g(r) = \rho_2 \rho^2 = g^{PY}(r) g^{(0)}(r), \quad r = |\mathbf{r}_1 - \mathbf{r}_2| \tag{3.2}$$

where $g^{(0)}(r)$ is the radial distribution function of the ideal quantum system and $g^{PY}(r)$ is the one in Percus-Yevick approximation for the classical hard-sphere system at the liquid density. The effect of the quantum statistics, that is, the effect of the Fermi hole for the case of the liquid He^3 and the effect of the Bose attraction for the case of the liquid He^4 are taken into consideration through this $g^{(0)}(r)$.

Further consideration of the quantum effects can be made through the detailed analysis of the cluster terms. For that purpose the use of the Mayer-type bond diagram generalized for the case of the quantum statistics will be quite helpful. The results of such consideration will be given in the near future.

References

- 1) H. Ichimura; Prog. Theor. Phys. 31; 538 (1964)
- 2) H. Ichimura; Prog. Theor. Phys. 37; 484 (1967)
- 3) B. J. Berne; Modern Theoretical Chemistry Vol.5 Plenum Press New York (1976)