The Born-Greeb Yvon 2 Theory at High Density Regions of Hard-Core Systems

by

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The Born-Green-Yvon 2 theory has been solved for the systems of hard core. The solution will be applicable to calculate the radial distribution function and the thermodynamic quantities at high-density regions of hard-core systems.

I. Introduction

The statistical studies about the radial distribution function, g(r) and the related thermodynamic quantities of classical fluids have been done by many approximation tl ories, such as Percus-Yevick(PY) theory[1-6] Born-Green-Yvon (BGY or BGY1) theory[2-7], Convolution-Hyper-Netted-chain (CHNC) theory[2-6] and Improved Born-Green-Yvon(BGY2) theory[4-6,8], and by computor simulation methods[9].

In the first stage of studies of fluids by statistical mechanics, BGY theory, which is obtained by applying the Kirkwood superposition approximation[10]

$$g(r_{12}, r_{13}, r_{23}) = g(r_{12})\, g(r_{13})\, g(r_{23}) \tag{1}$$

to BGY heirarchy[11], played an important part. Later, PY theory[12] and CHNC theory[13] were developed by the different method from the derivation of BGY theory (PY theory and CHNC theory are expressed in terms of the Mayer-Montroll rooted graph integrals[14]). In the calculations of g(r) and the thermodynamic quantities, PY theory and CHNC theory are superior to BGY theory[1,2,7]. Because of that, not too much attention seemed to have been paid to improve BGY theory.

Chae, et al.[3] introduced BGYM equation obtained by truncating BGY hierarchy with the approximation

$$g_{123} = g_{ij}\, g_{jk} \;; r_{ik} = \max(r_{12}, r_{13}, r_{23}) \tag{2}$$

instead of the Kirkwood superposition approximation, where $g_{123} = g(r_{12}, r_{13}, r_{23})$ and $g_{ij} = g(r_{ij})$. The BGYM theory improved BGY theory, but it is still much inferior to the PY theory. However, the trial to truncate the BGY hierarchy by using an approximation for higher order correlation function than triplet correlation function was not taken for long time because of the computational difficulty of the second equation of the BGY hierarchy (much more diffcult

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for the third equation of the hierarchy). The trial to truncate BGY heirarchy at the second equation was done by Ree, et al.[5-8] with the help of recent progress of computing technology. They applied the approximation for quadraplet correlation function, g_{1234}, proposed by Fisher and Kopeliovich[15],

$$g_{1234} = (g_{123}\, g_{124}\, g_{134}\, g_{234}) \big/ (g_{12}\, g_{13}\, g_{14}\, g_{23}\, g_{24}\, g_{34}) \tag{3}$$

to truncate the BGY hierarchy and obtained two simultanious integrodifferential equations. These two equations were called BGY2 equations, and the theory corresponding to BGY2 equations is called BGY2 theory. Ree, et al.[5] successfully applied the BGY2 theory to the system of hard spheres and evaluated the theory by calculating the radial distribution function and relating quantities at the densities of $\rho = 0.298\ \rho_0$ and $\rho = 0.372\rho_0$, where ρ_0 is a close-packed density. It was shown the BGY2 theory made much progress respect to unrefind BGY theory. The results obtained from BGY2 theory agree very well with those from Monte Carlo (MC) method which is considered to produce the exact data within a statistical error. For hard disks, BGY2 theory was evaluated by Uehara[6] at the medium densities (ρ : from 0.4 ρ_0 to 0.53 ρ_0) and shown it is superior to other approximation theories.

The study of the triplet correlation function, g_{123}, is much behind that of the radial distribution function. g_{123}, however, is also worth to study for liquids because of at least the following reasons: (1) g_{123} is a function which expresses the correlation between three particles. Consequently it gives more informations about the structure of fluids than g(r) does; (2) the knowledge of g_{123} leads to an estimate of the departure of g_{123} from the value given by the Kirkwood superposition approximation.

Several works have been done to evaluate g_{123} by machine simulation methods[16-20] But the approximate theories to calculate g_{123} have not been well established yet [21-23] Uehara[6] evaluated g_{123} obtained from BGY2 theory by comparing with g_{123} from MC method at the densities of $\rho = 0.298\ \rho_0$ and $\rho = 0.372\ \rho_0$ for hard spheres. It has been shown that BGY2 g_{123} has quite good agreement with MC g_{123}.

From above discussion, further evaluation of BGY2 theory is very curious to us. Here some device for current BGY2 equations is proposed to calculate g(r) and g_{123} at higher densities than that investigated above.

II. Formulation of BGY2 Theory

By truncating BGY hierarchy, two integro- differential equations[4,6]

$$-\nabla_1 \ln g_{12} = \nabla_1 u_{12} + \rho \int (\nabla_1 u_{13})(X_{1,23} - 1)\, g_{13}\, d\mathbf{r}_3 \tag{4}$$

and

$$-\nabla_1 (X_{1,23}\, g_{12}\, g_{13}) = \nabla_1 (u_{12} + u_{13}) + \rho \int (\nabla_1 u_{14}) \left(\frac{X_{1,34}\, X_{3,14}\, X_{1,24}}{g_{24}} - 1 \right) g_{14}\, d\mathbf{r}_4 \tag{5}$$

are obtained,

where

$$X_{i,jk} = \frac{g_{i,jk}}{g_{ij}\; g_{ik}} \tag{6}$$

Eqs. (4) and (5) are called BGY2 equations.

In the integration of eqs. (4) and (5), the conditions of Δr (the discripancy of r) $\rightarrow 0$ and $r_\infty \rightarrow \infty$ should be satisfied. But in the actual numerical computation of g(r) and the triplet correlation function, g_{123}, some finite values of Δr and r_∞ are taken. This causes the main deviation from the exact values. At low-density regions, this deviation will be succesfully negrected because of the short range ordering of fluids. At high-density regions, the deviation becomes significant. Especially the numerical data are very sensitive to Δr. But in present computational scheme, we have a district limitation for the choice of Δr, because of computer capacity. The necessary memories for the calculation of g(r) and g_{123} by BGY 2 theory in computer is proportional to $A(\Delta r/r_{max})^h$ because of two dimensional arrey of X(a, b, c=1), where A and h are some constants, and r_{max} is the maximum of r to which r can be extended.

Now,

$$A(\Delta r/r_{max})^h < \text{maximum memories of computer}$$

should be always satisfied. Therefore we have some limitations of Δr and r_{max}. r_{max} has some values at some density, which can not be reduce anymore. For example, in present comuputer program, $r_{max} > 6$ at $\rho = 0.4\ \rho_\circ$ and $r_{max} > 8$ at $\rho = 0.5\ \rho_\circ$ for hand-disk system. So $\Delta r > 0.04$ in investigated density rainge ($\rho = 0.4\ \rho_\circ$ to $0.53\ \rho_\circ$). At highdensity regions, obviously we have $r_{max} > 8$. Consequently Δr should be greater than 0.04. This gives much numerical errors.

To overcome this difficulty, some device is taken, that is, to find the range where $X_{i,jk}$ is approximately replaced by radial distribution function, such as

$$X_{i,jk} = \frac{g_{i,ik}}{g_{ij}\ g_{ik}} = g_{ik}\ \delta_{ijk} \tag{7}$$

where

$$g_{ijk} = g_{ij}\ g_{ik}\ g_{jk}\ \delta_{jk} \tag{8}$$

For Kirkwood superposition approximation, δ_{ijk} is an unity. In BGY2 calculation, $\delta_{ijk}(r_{ij}, r_{ik}, r_{jk})$ is very close to an unity at the configurations of $r_{ij} > r_{max}$ and $r_{jk} = 1$. But according to our investigation at low-density region of hard-core system[6],

$$\delta_{123}\,(r_{12} > \alpha\, r_{max},\ r_{13} > \beta\, r_{max},\ r_{23} = 1.0) \cong 1 \tag{9}$$

where $0 < \alpha < 1$ and $0 < \beta < 1$. For example, in the hard-sphere system at $\rho = 0.298\ \rho_\circ$ and $\rho = 0.372\ \rho_\circ$, $|1 - \delta_{123}|$ is less than 10^{-3} when $\alpha = 0.5$ and $\beta = 0.5$.

Accordingly, the necessary computer memories are reduced to $A(\Delta r\ /\ r(L))^h$, where $r(L) = \max(\alpha r_{max}, \beta r_{max})$, because $X_{i,jk}$ can be replaced by

$$X_{i,ik} = g_{ik} \tag{10}$$

at the configurations ot ($r_{ij} > \alpha r_{max}$, $r_{jk} > \beta r_{mak}$, $r_{jk} = 1.0$).

Then eqs. (4) and (5) are rewritten by applying eq. (10) as

$$-\nabla_1 \ln g_{12} = \nabla_1 u_{12} + \rho \int_{r_{12} < r(L)\ \text{or}\ r_{13} < r(L)} (\nabla_1 u_{13})(X_{1,23} - 1)\, g_{13}\, dr$$

$$= \nabla_1 u_{12} + \rho \int (\nabla_1 u_{13})(X_{1,23} - 1)\, g_{13}\, dr$$

$$+ \quad \rho \int (\nabla_1 u_{13})(g_{23} - 1)\, g_{13}\, dr$$
$$r_{12} > r(L) \text{ and } r_{13} > r(L) \qquad (11)$$

and

$$-\nabla_1 (\ln X_{1,23}\, g_{12}\, g_{13}) = \nabla_1 (u_{12} + u_{13}) + \Sigma Q_i$$
$$+ \quad \rho \int (\nabla_1 u_{14})\, F(X_{i,jk}, g_{24})\, g_{14}\, dr \qquad (12)$$

where

$$F(X_{i,jk}, g_{24}) = \frac{X_{1,34}\ X_{3,24}\ X_{1,24}}{g_{24}} - 1 \qquad (13)$$

and Q_i is an integro-differential equation in which at least one of $X_{1,34}$ $X_{3,24}$ and $X_{1,24}$ is replaced by a radial distribution function.
Eqs. (11) and (12) will be applied to calculate g(r), g_{123} and the related thermodynamic quentities at the high-density regions of a system with any pair-wise potential.

III. BGY2 Equations for Hard-Core Systems

For hard-core systems, the potential function, u(r), is expressed by

$$u(r) = 0 \quad \text{at } r > \sigma$$
$$u(r) = \infty \quad \text{at } r < \sigma \qquad (14)$$

where σ is the radius of a particle. Substituting eq. (14) to eqs. (11) and (12), and rearranging the resulted eqations, we obtain the following BGY2 equations:
for hard disks

$$\ln g_{12} = -2\rho g(1) \left[\int_{r_{12}}^{r(L)} dr_{12} \int_{|r_{12}-1|}^{\min(r_{12}+1,\ r(L))} (X_{1,23} - 1) \cos\theta_{213}\ r_{23}\ dr_{23} \right.$$
$$\left. + \int_{r(L)}^{r_{max}} dr_{12} \int_{r(L)}^{\min(r_{max},\ r_{12}+L)} (g_{23} - 1) \cos\theta_{213}\ r_{23}\ dr_{23} \right] \qquad (15)$$

and

$$\ln \left(X_{1,23} \frac{g_{12}\ g_{13}}{g_{23}}\right) = -2\pi\ g(1)\rho \left[\int_{r_{12}}^{r(L)} d\xi \int_{|r_{12}-1|}^{\min(r_{12}+1,\ r(L))} \cos\theta_{214}\ F(X_{i,ik}, g_{24}) \right.$$
$$\cdot\ r_{24}\ dr_{24} + \sum_i QQ_i$$
$$\left. + \int_{r(L)}^{r_{max}} d\xi \int^{\min(r_{12}+1,\ r(L)} (g_{24}g_{34} - 1) \cos\theta_{214}\ r_{24}\ dr_{24} \right]$$

(16)

and for hard spheres

$$\ln g_{12} = -2\pi\rho g(1)\left[\int_{r_{12}}^{r(L)} \frac{dr_{12}}{r_{12}} \int_{|r_{12}-1|}^{\min(r_{12}+1,\ r(L))} dr_{23}\ r_{23}\ (x_{1,23}-1)\cos\theta_{213}\right.$$

$$\left.\int_{r(L)}^{r_{max}} \frac{dr_{12}}{r_{12}} \int_{r(L)}^{\min(r_{max},\ r_{12}+1)} dr_{23}\ r_{23}\ (g_{23}-1)\cos\theta_{213}\right] \tag{17}$$

and

$$\ln\left(X_{1,23}\ \frac{g_{12}\ g_{13}}{g_{23}}\right) = -2\rho g(1)\left[\int_{r_{12}}^{r(L)} \frac{d\xi}{\xi} \int_{|r_{12}-1|}^{\min(r_{12}+1,\ r(L))} dr_{24}\ r_{24}\ \cos\theta_{214}\ \cdot\right.$$

$$\int_0^{\pi} d\Phi\ F(X_{i,jk},\ g_{24}) + \sum_i QQ_i\ *$$

$$\left.+\int_{r(L)}^{r_{max}} \frac{d\xi}{\xi} \int_{r(L),\ r_{34}-r(L)}^{\min(r_{12}+1,\ r_{max})} dr_{24}\ r_{24}\ \cos\theta_{214} \int_0^{\pi} d\Phi\,(g_{24}\ g_{34}-1)\right] \tag{18}$$

were g(1) is the radial distribution function at r = 1, and QQ_i and $QQ_i{}^*$ are the integral equations in which at least one of $X_{1,24}$, $X_{1,34}$ and $X_{3,24}$ is replaced by a radial distribution function.

This device will save much computer memories and computing time. Therfore, it will make us possible to calculate g(r) and the related quantities by BGY2 theory at high-density regions of the systems of hard core.

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