# Kirkwood coupling-parameter expansion method for the distribution function in a fluid

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A general, formal structure of the Kirkwood coupling-parameter expansion method for the distribution function of a fluid is presented. In this method, no closure approximation, such as the superposition approximation, is required. Various properties of this method are discussed.

## I. INTRODUCTION

The interest in the two-particle distribution function in a classical fluid results not only from the fact that this quantity can be determined by numerical and experimental methods, but also from the fact that simple formulas exist which express thermodynamic quantities of fluid in terms of the two-particle distribution function.[1] In order to express the chemical potential of the fluid in terms of the two-particle distribution function, the dependence of this distribution function on the Kirkwood coupling parameter $\xi$ has to be determined. This $\xi$ dependence of the distribution function is not given in the conventional methods of determining the two-particle distribution function. In the conventional methods the two-particle distribution function is determined by solving an integral equation such as the Percus-Yevick or HNC (hypernetted-chain) equation which is obtained by essentially summing diagrams corresponding to different powers of the density up to infinite order. The other method is based on the superposition approximation for the three-particle distribution function, leading to the integral equation of Kirkwood and of Born, Green, and Yvon.[2]

In the Kirkwood coupling-parameter expansion method which we propose here, the $\xi$ dependence of the distribution function is determined by expanding the pair correlation function in powers of the coupling parameter $\xi$,

$$G(\vec{r}_1,\vec{r}_2;\xi)=\xi G_1(\vec{r}_1,\vec{r}_2)+\xi^2 G_2(\vec{r}_1,\vec{r}_2)+ \cdots \ , \quad (1)$$

where the pair correlation function $G(\vec{r}_1,\vec{r}_2;\xi)$ is defined by the Kirkwood decomposition of the two-particle distribution function

$$\rho^{(2)}(\vec{r}_1,\vec{r}_2;\xi)=\rho^{(1)}(\vec{r}_1;\xi)\rho^{(1)}(\vec{r}_2)$$
$$\times[1+G(\vec{r}_1,\vec{r}_2;\xi)] \ .$$

The triplet correlation function $H(\vec{r}_1,\vec{r}_2,\vec{r}_3;\xi)$ is defined and expanded in powers of $\xi$ in a similar manner. Thus the hierarchy of the two- and three-particle distribution functions is transformed into the hierarchy of the pair

and triplet correlation functions. The closure approximation, such as the superposition approximation of the hierarchy equations, is found unnecessary if the quantities of the same power of $\xi$ are taken to be equal in the hierarchy equations. In the lowest-order approximation which takes only terms linear in $\xi$, the equation for $G_1(\vec{r}_1,\vec{r}_2)$ does not include three-particle correlation effects. If one takes terms up to $\xi^2$, three coupled equations for $G_1$, $G_2$, and $H_1$ are obtained. In this case the quantity $G_1(\vec{r}_1,\vec{r}_2)$ includes three-particle correlation effects and differs from the similar quantity $G_1(\vec{r}_1,\vec{r}_2)$ which is derived as the lowest-order approximation. If one takes terms up to $\xi^3$, the quantity $G_1(\vec{r}_1,\vec{r}_2)$ includes four-particle correlation effects together with three-particle correlations. Thus the approximations associated with the Kirkwood coupling-parameter expansion method are quite different from the conventional approximations where the lowest-order quantity is used to determine the higher-order quantity in a successive manner. In Sec. II we show the formal structure of the Kirkwood coupling-parameter expansion method.

## II. KIRKWOOD COUPLING-PARAMETER EXPANSION METHOD

We consider a classical system of monatomic molecules in a volume $V$ at temperature $T$ and the chemical potential $\mu$. In the configuration $\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_N$, the potential energy $U_N$ of the system is given by

$$U_N(\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_N;\xi)=\xi \sum_{j=2}^{N} u(r_{1j})+ \sum_{i=2}^{N-1}\sum_{\substack{j=3 \\ j>i}}^{N} u(r_{ij}) \ , \quad (2)$$

where we assume only the pair interaction between molecules. The quantity $u(r_{ij})$ is the potential energy between the particles at $\vec{r}_i$ and $\vec{r}_j$ and is normalized by $k_B T$ where $k_B$ is the Boltzmann constant. The quantity $\xi$ is the Kirkwood coupling parameter. The $n$-particle distribution function $\rho^{(n)}(\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_n;\xi)$ in the grand-canonical ensemble is defined as

$$\rho^{(n)}(\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_n;\xi)= \frac{1}{\Xi(V,T,\mu;\xi)} \sum_{N \geq n} \frac{e^{\mu N/k_B T}}{(N-n)!\lambda_B^{3N}} \int \cdots \int e^{-U_N(\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_N;\xi)} d\vec{r}_{n+1} \cdots d\vec{r}_N \ , \quad (3)$$

where $\lambda_B$ is the thermal de Broglie wavelength and the quantity $\Xi(V,T,\mu;\xi)$ is given by

$$\Xi(V,T,\mu;\xi)=\sum_{N\geq 0}\frac{e^{\mu N/k_B T}}{N!\lambda_B^{3N}}\int\cdots\int e^{-U_N(\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_N;\xi)}d\vec{r}_1 d\vec{r}_2\cdots d\vec{r}_N . \tag{4}$$

Taking the derivative of $\rho^{(n)}(\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_n;\xi)$ with respect to $\xi$, we find the following equation:

$$\frac{\partial\rho^{(n)}(\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_n;\xi)}{\partial\xi}=-\left[\sum_{j=2}^{n}u(r_{1j})+\frac{1}{N}\int u(r_{12})\rho^{(2)*}(\vec{r}_1,\vec{r}_2;\xi)d\vec{r}_1 d\vec{r}_2\right]\rho^{(n)}(\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_n;\xi)$$

$$-\int u(r_{1,n+1})\rho^{(n+1)}(\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_{n+1};\xi)d\vec{r}_{n+1} , \tag{5}$$

where

$$\bar{N}=\frac{1}{\Xi}\sum_{N\geq 0}\frac{Ne^{\mu N/k_B T}}{N!\lambda_B^{3N}}\int\cdots\int e^{-U_N(\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_N;\xi)}d\vec{r}_1 d\vec{r}_2\cdots d\vec{r}_N ,$$

$$\tag{6}$$

$$\rho^{(2)*}(\vec{r}_1,\vec{r}_2;\xi)=\frac{\bar{N}}{\Xi}\sum_{N\geq 0}\frac{N-1}{N!\lambda_B^{3N}}e^{\mu N/k_B T}\int\cdots\int e^{-U_N(\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_N;\xi)}d\vec{r}_3\cdots d\vec{r}_N .$$

Equation (5) is identical with Eq. (37.60) in Hill.[1] Conventionally, Eq. (5) is used as the basic equation for $\rho^{(n)}(\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_n;\xi)$. In this case the basic equation for $\rho^{(n)}(\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_n;\xi)$ in the grand-canonical ensemble is different from the similar equation derived in the canonical ensemble in which the quantity $\rho^{(2)*}(\vec{r}_1,\vec{r}_2;\xi)$ does not appear. Besides, the chemical potential of the system is expressed by the quantity $\rho^{(2)*}(\vec{r}_1,\vec{r}_2;\xi)$ in the grand-canonical ensemble, while in the canonical ensemble it is expressed by $\rho^{(2)}(\vec{r}_1,\vec{r}_2;\xi)$ as shown in Eq. (30.35) of Ref. 1. This inconvenience can be avoided if one uses the following equation to eliminate $\rho^{(2)*}(\vec{r}_1,\vec{r}_2;\xi)$ in Eq. (5):

$$\frac{1}{N}\int u(r_{12})\rho^{(2)*}(\vec{r}_1,\vec{r}_2;\xi)d\vec{r}_1 d\vec{r}_2=\frac{\partial}{\partial\xi}\ln\rho^{(1)}(\vec{r}_1;\xi)+\int u(r_{12})\frac{\rho^{(2)}(\vec{r}_1,\vec{r}_2;\xi)}{\rho^{(1)}(\vec{r}_1;\xi)}d\vec{r}_2 . \tag{7}$$

Equation (7) is obtained by setting $n=1$ in Eq. (5). Substituting Eq. (7) into Eq. (5), we find the basic equation of the $n$-particle distribution function

$$\frac{\partial}{\partial\xi}\frac{\rho^{(n)}(\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_n;\xi)}{\rho^{(1)}(\vec{r}_1;\xi)}=\left[-\sum_{j=2}^{n}u(r_{1j})+\int u(r_{12})\frac{\rho^{(2)}(\vec{r}_1,\vec{r}_2;\xi)}{\rho^{(1)}(\vec{r}_1;\xi)}d\vec{r}_2\right]\frac{\rho^{(n)}(\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_n;\xi)}{\rho^{(1)}(\vec{r}_1;\xi)}$$

$$-\int u(r_{1,n+1})\frac{\rho^{(n+1)}(\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_{n+1};\xi)}{\rho^{(1)}(\vec{r}_1;\xi)}d\vec{r}_{n+1} . \tag{8}$$

The identical equation to Eq. (8) is obtained in canonical and isothermal-isobaric ensembles. Thus the basic equation for the $n$-particle distribution function in different ensembles is found to be formally identical.

The Kirkwood decompositions of the two-, three-, and four-particle distribution functions are given by the following equations:

$$\rho^{(2)}(\vec{r}_1,\vec{r}_2;\xi)=\rho^{(1)}(\vec{r}_1;\xi)\rho^{(1)}(\vec{r}_2)[1+G(\vec{r}_1,\vec{r}_2;\xi)] , \tag{9}$$

$$\rho^{(3)}(\vec{r}_1,\vec{r}_2,\vec{r}_3;\xi)=\rho^{(1)}(\vec{r}_1;\xi)\rho^{(1)}(\vec{r}_2)\rho^{(1)}(\vec{r}_3)[1+(1+P_{23})G(\vec{r}_1,\vec{r}_2;\xi)+G(\vec{r}_2,\vec{r}_3)+H(\vec{r}_1,\vec{r}_2,\vec{r}_3;\xi)] , \tag{10}$$

$$\rho^{(4)}(\vec{r}_1,\vec{r}_2,\vec{r}_3,\vec{r}_4;\xi)=\rho^{(1)}(\vec{r}_1;\xi)\rho^{(1)}(\vec{r}_2)\rho^{(1)}(\vec{r}_3)\rho^{(1)}(\vec{r}_4)$$

$$\times[1+(1+P_{23}+P_{24})G(\vec{r}_1,\vec{r}_2;\xi)+(1+P_{34}+P_{24})G(\vec{r}_2,\vec{r}_3)$$

$$+(1+P_{23}+P_{24})G(\vec{r}_1,\vec{r}_2;\xi)G(\vec{r}_3,\vec{r}_4)+(1+P_{34}+P_{24})H(\vec{r}_1,\vec{r}_2,\vec{r}_3;\xi)$$

$$+H(\vec{r}_2,\vec{r}_3,\vec{r}_4)+I(\vec{r}_1,\vec{r}_2,\vec{r}_3,\vec{r}_4;\xi)] , \tag{11}$$

where $P_{ij}$ is the exchange operator between $i$ and $j$. Substituting Eqs. (9), (10), and (11) into Eq. (8), we find the following equations for $G$, $H$, and $I$:

$$\frac{\partial G(\vec{r}_{21};\xi)}{\partial\xi}=-u(r_{12})[1+G(\vec{r}_{21};\xi)]+\rho_0\int d\vec{r}_3 u(r_{13})[G(\vec{r}_{31};\xi)G(\vec{r}_{21};\xi)-G(\vec{r}_{32})-H(\vec{r}_{21},\vec{r}_{31};\xi)] , \tag{12}$$

$$\frac{\partial H(\vec{r}_{21},\vec{r}_{31};\xi)}{\partial \xi} = -(1+P_{23})u(r_{12})[G(\vec{r}_{31};\xi)+G(\vec{r}_{32})+H(\vec{r}_{21},\vec{r}_{31};\xi)]$$

$$+\rho_0 \int d\vec{r}_4 u(r_{14})[G(\vec{r}_{41};\xi)H(\vec{r}_{21},\vec{r}_{31};\xi)-(1+P_{23})G(\vec{r}_{21};\xi)G(\vec{r}_{43})-H(\vec{r}_{32},\vec{r}_{42})-I(\vec{r}_{21},\vec{r}_{31},\vec{r}_{41};\xi)] ,$$

$$(13)$$

$$\frac{\partial I(\vec{r}_{21},\vec{r}_{31},\vec{r}_{41};\xi)}{\partial \xi} = -(1+P_{23}+P_{24})u(r_{12})[G(\vec{r}_{31};\xi)G(\vec{r}_{42})+G(\vec{r}_{41};\xi)G(\vec{r}_{32})+H(\vec{r}_{31},\vec{r}_{41};\xi)$$

$$+H(\vec{r}_{32},\vec{r}_{42})+I(\vec{r}_{21},\vec{r}_{31},\vec{r}_{41};\xi)]$$

$$+\rho_0 \int d\vec{r}_5 u(r_{15})\{G(\vec{r}_{51};\xi)I(\vec{r}_{21},\vec{r}_{31},\vec{r}_{41};\xi)$$

$$-(1+P_{23}+P_{34})[G(\vec{r}_{31};\xi)H(\vec{r}_{42},\vec{r}_{52})+G(\vec{r}_{53})H(\vec{r}_{21},\vec{r}_{41};\xi)]$$

$$-I(\vec{r}_{32},\vec{r}_{42},\vec{r}_{52})-J(\vec{r}_{21},\vec{r}_{31},\vec{r}_{41},\vec{r}_{51};\xi)\} ,$$

$$(14)$$

where we have assumed the uniform fluid with the density $\rho_0$ for simplicity.

Making use of the definition of the $n$-particle distribution function, we find the following relation:

$$\frac{\rho^{(n)}(\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_n;0)}{\rho^{(1)}(\vec{r}_1;0)}=\rho^{(n-1)}(\vec{r}_2,\vec{r}_3,\ldots,\vec{r}_n) . \quad (15)$$

Comparing Eq. (15) and Eqs. (9)—(11), we can easily obtain the equation

$$G(\vec{r}_{21};0)=H(\vec{r}_{21},\vec{r}_{31};0)$$

$$=I(\vec{r}_{21},\vec{r}_{31},\vec{r}_{41};0)=0 . \quad (16)$$

Thus it is quite reasonable to expand these quantities $G$, $H$, and $I$ in terms of power series of $\xi$ as follows:

$$G(\vec{r}_{21};\xi)=\xi G_1(\vec{r}_{21})+\xi^2 G_2(\vec{r}_{21})+\cdots , \quad (17)$$

$$H(\vec{r}_{21},\vec{r}_{31};\xi)=\xi H_1(\vec{r}_{21},\vec{r}_{31})$$

$$+\xi^2 H_2(\vec{r}_{21},\vec{r}_{31})+\cdots , \quad (18)$$

$$I(\vec{r}_{21},\vec{r}_{31},\vec{r}_{41};\xi)=\xi I_1(\vec{r}_{21},\vec{r}_{31},\vec{r}_{41})$$

$$+\xi^2 I_2(\vec{r}_{21},\vec{r}_{31},\vec{r}_{41})+\cdots , \quad (19)$$

Substituting Eqs. (17)—(19) into Eqs. (12)—(14) and taking terms of equal power of $\xi$ to be equal, we find the following:

$$G_1(\vec{r}_{21})=-u(r_{12})-\rho_0 \int d\vec{r}_3 u(r_{13})G(\vec{r}_{32}) , \quad (20)$$

$$2G_2(\vec{r}_{21})=-u(r_{12})G_1(\vec{r}_{21})-\rho_0 \int d\vec{r}_3 u(r_{13})H_1(\vec{r}_{21},\vec{r}_{31}) , \quad (21)$$

$$3G_3(\vec{r}_{21})=-u(r_{12})G_2(\vec{r}_{21})+\rho_0 \int d\vec{r}_3 u(r_{13})[G_1(\vec{r}_{31})G_1(\vec{r}_{21})-H_2(\vec{r}_{21},\vec{r}_{31})] , \quad (22)$$

$$H_1(\vec{r}_{21},\vec{r}_{31})=-[u(\vec{r}_{12})+u(r_{13})]G(\vec{r}_{32})-\rho_0 \int d\vec{r}_4 u(r_{14})H(\vec{r}_{32},\vec{r}_{42}) , \quad (23)$$

$$2H_2(\vec{r}_{21},\vec{r}_{31})=-u(r_{12})[G_1(\vec{r}_{31})+H_1(\vec{r}_{21},\vec{r}_{31})]-u(r_{13})[G_1(\vec{r}_{21})+H_1(\vec{r}_{21},\vec{r}_{31})]$$

$$-\rho_0 \int d\vec{r}_4 u(r_{14})[G_1(\vec{r}_{21})G(\vec{r}_{43})+G_1(\vec{r}_{31})G(\vec{r}_{42})+I_1(\vec{r}_{21},\vec{r}_{31},\vec{r}_{41})] , \quad (24)$$

$$I_1(\vec{r}_{21},\vec{r}_{31},\vec{r}_{41})=-[u(r_{12})+u(r_{13})+u(r_{14})]H(\vec{r}_{32},\vec{r}_{42})-\rho_0 \int d\vec{r}_5 u(r_{15})I(\vec{r}_{32},\vec{r}_{42},\vec{r}_{52}) . \quad (25)$$

The second term on the right-hand side (rhs) of Eq. (20) implies the following:

$$-\rho_0 \int d\vec{r}_3 u(r_{13})G(\vec{r}_{32})$$

$$=-\rho_0 \int d\vec{r}_3 u(r_{13})[G_1(\vec{r}_{32})+G_2(\vec{r}_{32})+\cdots] . \quad (26)$$

Similar care has to be exercised for the quantities $G$, $H$, and $I$ in Eqs. (23), (24), and (25).

In the lowest approximation, we set $G=G_1$ in Eq. (20) and the following equation is obtained which determines the quantity $G_1(\vec{r}_{21})$:

$$G_1(\vec{r}_{21})=-u(r_{12})-\rho_0 \int d\vec{r}_3 u(r_{13})G_1(\vec{r}_{32}) . \quad (27)$$

When the Fourier integral of the interaction potential $u(r_{12})$ exists, Eq. (27) can be easily solved in the following:

$$G_1(q) = -\frac{u(q)}{1+\rho_0 u(q)} ,\tag{28}$$

where the Fourier and the inverse Fourier transforms are defined as

$$u(\vec{q}) = \int d\vec{r}_{21} e^{-i\vec{q}\cdot\vec{r}_{21}} u(\vec{r}_{21}) ,$$

$$u(\vec{r}_{21}) = \int \frac{d\vec{q}}{(2\pi)^3} e^{i\vec{q}\cdot\vec{r}_{21}} u(\vec{q}) .\tag{29}$$

In the second approximation, we write $G$ and $H$ as follows:

$$G = G_1 + G_2, \quad H = H_1 .\tag{30}$$

Substituting Eq. (30) into Eqs. (20), (21), and (23), we find the following coupled equations of the quantities $G_1$, $G_2$, and $H_1$:

$$G_1(\vec{r}_{21}) = -u(r_{12})$$
$$-\rho_0 \int d\vec{r}_3 u(r_{13})[G_1(\vec{r}_{32})+G_2(\vec{r}_{32})] ,\tag{31}$$

$$2G_2(\vec{r}_{21}) = -u(r_{12})G_1(\vec{r}_{21})$$
$$-\rho_0 \int d\vec{r}_3 u(r_{13})H_1(\vec{r}_{21},\vec{r}_{31}) ,\tag{32}$$

$$H_1(\vec{r}_{21},\vec{r}_{31}) = -[u(r_{12})+u(r_{13})][G_1(\vec{r}_{32})+G_2(\vec{r}_{32})]$$
$$-\rho_0 \int d\vec{r}_3 u(r_{13})H_1(\vec{r}_{21},\vec{r}_{31}) ,\tag{33}$$

These coupled equations (31), (32), and (33) can be reduced to the linear integral equation for the quantity $G_1(\vec{q})$ in the following:

$$\left[1 - \frac{1}{2\rho_0}\frac{1}{1+\rho_0 u(\vec{q})}\int \frac{d\vec{q}'}{(2\pi)^3}\frac{\rho_0^2 u(\vec{q}')u(\vec{q}'-\vec{q})}{1+\rho_0^3 u(\vec{q}'-\vec{q})u(\vec{q}')u(\vec{q})}[1+\rho_0^2 u(\vec{q})u(\vec{q}')]\right]G_1(\vec{q})$$

$$= -\frac{\rho_0 u(\vec{q})}{\rho_0[1+\rho_0 u(\vec{q})]} + \frac{\rho_0 u(\vec{q})}{\rho_0^2[1+\rho_0 u(\vec{q})]}\int \frac{d\vec{q}'}{(2\pi)^3}\frac{\rho_0^2 u(\vec{q}')u(\vec{q}'-\vec{q})}{1+\rho_0^3 u(\vec{q}'-\vec{q})u(\vec{q}')u(\vec{q})}[1-\rho_0 u(\vec{q})+\rho_0^2 u(\vec{q})u(\vec{q}')]$$

$$+ \frac{\rho_0 u(\vec{q})}{2\rho_0[1+\rho_0 u(\vec{q})]}\int \frac{d\vec{q}'}{(2\pi)^3}\left[\rho_0 u(\vec{q}'+\vec{q}) - \rho_0^2 u(\vec{q})u(\vec{q}'+\vec{q})\frac{1-\rho_0 u(\vec{q}'+\vec{q})}{1+\rho_0^3 u(\vec{q}')u(\vec{q})u(\vec{q}'+\vec{q})}\right.$$

$$\left. + \frac{\rho_0 u(\vec{q}'-\vec{q})[1-\rho_0 u(\vec{q})]}{1+\rho_0^3 u(\vec{q}')u(\vec{q})u(\vec{q}'-\vec{q})}\right]G_1(\vec{q}') .\tag{34}$$

The quantities $G_2(\vec{q})$ and $H_1(\vec{q}_2,\vec{q}_3)$ are related with the solution of Eq. (34) as follows:

$$G_2(\vec{q}) = -\frac{1}{\rho_0} - \frac{1+\rho_0 u(\vec{q})}{\rho_0 u(\vec{q})}G_1(\vec{q}) ,\tag{35}$$

$$H_1(\vec{q}_2,\vec{q}_3) = \frac{u(\vec{q}_1)}{1+\rho_0^3 u(\vec{q}_1)u(\vec{q}_2)u(\vec{q}_3)}$$

$$\times \left\{\frac{1}{\rho_0}\left[2+\frac{G_1(\vec{q}_2)}{u(\vec{q}_2)}+\frac{G_1(\vec{q}_3)}{u(\vec{q}_3)}\right] - u(\vec{q}_2)\left[2+\frac{G_1(\vec{q}_3)}{u(\vec{q}_3)}+\frac{G_1(\vec{q}_1)}{u(\vec{q}_1)}\right]\right.$$

$$\left. + \rho_0 u(\vec{q}_2)u(\vec{q}_3)\left[2+\frac{G_1(\vec{q}_1)}{u(\vec{q}_1)}+\frac{G_1(\vec{q}_2)}{u(\vec{q}_2)}\right]\right\} ,\tag{36}$$

where $\vec{q}_1 = -(\vec{q}_2 + \vec{q}_3)$. In this approximation the coupled equations (31), (32), and (33) can be regarded as linear approximations for the basic equations (12) and (13).

In the next-order approximation, the nonlinear term on the rhs of Eq. (12) is included and the six coupled equations for the quantities $G_1$, $G_2$, $G_3$, $H_1$, $H_2$, and $I_1$ are obtained by the following substitution of the quantities $G$,

$H$, and $I$:

$$G = G_1 + G_2 + G_3 , \tag{37}$$

$$H = H_1 + H_2 , \tag{38}$$

$$I = I_1 . \tag{39}$$

In this approximation the six coupled equations are

$$G_1(\vec{r}_{21}) = -u(r_{12}) - \rho_0 \int d\vec{r}_3 u(r_{13}) G(\vec{r}_{32}) , \tag{40}$$

$$2G_2(\vec{r}_{21}) = -u(r_{12}) G_1(\vec{r}_{21}) - \rho_0 \int d\vec{r}_3 u(r_{13}) H_1(\vec{r}_{21}, \vec{r}_{31}) , \tag{41}$$

$$3G_3(\vec{r}_{21}) = -u(r_{12}) G_2(\vec{r}_{21}) + \rho_0 \int d\vec{r}_3 u(r_{13})[G_1(\vec{r}_{31}) G_1(\vec{r}_{21}) - H_2(\vec{r}_{21}, \vec{r}_{31})] , \tag{42}$$

$$H_1(\vec{r}_{21}, \vec{r}_{31}) = -[u(r_{12}) + u(r_{13})] G(\vec{r}_{32}) - \rho_0 \int d\vec{r}_4 u(r_{14}) H(\vec{r}_{32}, \vec{r}_{42}) , \tag{43}$$

$$2H_2(\vec{r}_{21}, \vec{r}_{31}) = -u(r_{12})[G_1(\vec{r}_{31}) + H_1(\vec{r}_{21}, \vec{r}_{31})] - u(r_{13})[G_1(\vec{r}_{21}) + H_1(\vec{r}_{21}, \vec{r}_{31})]$$

$$-\rho_0 \int d\vec{r}_4 u(r_{14})[G_1(\vec{r}_{21}) G(\vec{r}_{43}) + G_1(\vec{r}_{31}) G(\vec{r}_{42}) + I_1(\vec{r}_{21}, \vec{r}_{31}, \vec{r}_{41})] , \tag{44}$$

$$I_1(\vec{r}_{21}, \vec{r}_{31}, \vec{r}_{41}) = -[u(r_{12}) + u(r_{13}) + u(r_{14})] H(\vec{r}_{32}, \vec{r}_{42},) - \rho_0 \int d\vec{r}_5 u(r_{15}) I_1(\vec{r}_{32}, \vec{r}_{42}, \vec{r}_{52}) . \tag{45}$$

Solving these coupled equations is a lengthy process, however, the approximation scheme is systematic and it has the advantage that no closure assumption such as a superposition approximation for the three-particle distribution function is required. For completeness we have derived the Born-Green-Yvon type of equation based on the present method in the Appendix.

## III. DISCUSSION

Various thermodynamic quantities and the pair correlation functions are related in the following equations:

$$\frac{E}{Nk_B T} = \frac{3}{2} + \frac{\rho_0}{2} \int u(r_{12})[1 + G(\vec{r}_{21})] d\vec{r}_{21} , \tag{46}$$

$$\frac{PV}{Nk_B T} = 1 - \frac{\rho_0}{6} \int r_{12} \frac{du(r_{12})}{dr_{12}} [1 + G(\vec{r}_{21})] d\vec{r}_{21} , \tag{47}$$

$$\frac{\mu}{k_B T} = \ln \rho_0 \lambda_B^3$$

$$+ \rho_0 \int_0^1 d\xi \int u(r_{12})[1 + G(\vec{r}_{21}; \xi)] d\vec{r}_{21} , \tag{48}$$

$$k_B T \left[ \frac{\partial \rho_0}{\partial P} \right]_T = 1 + \rho_0 \int G(\vec{r}_{21}) d\vec{r}_{21} , \tag{49}$$

where the quantities $E$ and $P$ are the total energy and the pressure of the fluid. The entropy $S$ of the fluid can be obtained by making use of the thermodynamic relation $S = E/T + PV/T - \mu N/T$.

In the conventional method of deriving the two-particle distribution function, the $\xi$ dependence of this distribution

function is not obtained and other formulas to determine the entropy in terms of the two-particle distribution function are available.[3-6] In these methods, one starts from the following expression of the entropy $S$ of the fluid:

$$S = -\frac{k_B}{N!} \int \cdots \int f_N \ln f_N d(1) d(2) \cdots d(N) \tag{50}$$

or its variations, where $f_N$ is the $N$-particle distribution function and $d(1)d(2) \cdots d(N)$ represents a volume element of $6N$-dimensional phase space. The final expression of the entropy includes not only two-particle distribution functions, but also $n$-particle distribution functions. Besides, these expressions must be shown to be equivalent in the thermodynamic limit. Although one could presumably prove the equivalence between the expressions of the entropy in the canonical[3] and grand-canonical ensembles[4,5] it seems to the author, at least, that an easier problem is to determine the $\xi$ dependence of the pair correlation function.

Let us discuss the structure of Kirkwood coupling-parameter expansion method. If one uses Eq. (7) in the grand-canonical ensemble and similar equations in the canonical or isothermal-isobaric ensembles, one can easily find that the basic equation (8) of the $n$-particle distribution function becomes identical to the different ensembles. We use this integral equation (8) as the definition of the $n$-particle distribution function, rather than its defining formula as suggested by Kirkwood.[7] This is specifically mentioned by Green.[8] The basic equation (8) is transformed into the basic equations for $n$-particle correlation functions $G, H, I, \ldots$, making use of the Kirkwood decomposition of the $n$-particle distribution function. If one wants to include in the pair correlation function $G(\vec{r}_{21}; \xi)$ the effects of up to $n$-particle correlations, one simply expands the quantities $G, H, I, \ldots$ in terms of the Kirkwood coupling parameter $\xi$ as follows:

$$G(\vec{r}_{21};\xi)=\xi G_1(\vec{r}_{21})+\xi^2 G_2(\vec{r}_{21})+\cdots+\xi^{n-1}G_{n-1}(\vec{r}_{21}) ,$$

$$H(\vec{r}_{21},\vec{r}_{31};\xi)=\xi H_1(\vec{r}_{21},\vec{r}_{31})+\xi^2 H_2(\vec{r}_{21},\vec{r}_{31})$$

$$+\cdots+\xi^{n-2}H_{n-2}(\vec{r}_{21},\vec{r}_{31}) , \qquad (51)$$

$$I(\vec{r}_{21},\vec{r}_{31},\vec{r}_{41};\xi)=\xi I_1(\vec{r}_{21},\vec{r}_{31},\vec{r}_{41})+\xi^2 I_2(\vec{r}_{21},\vec{r}_{31},\vec{r}_{41})$$

$$+\cdots+\xi^{n-3}I_{n-3}(\vec{r}_{21},\vec{r}_{31},\vec{r}_{41}) ,$$

etc., and constructs the coupled equations of $(n-1)n/2$ dependent variables from these basic equations of $G,H,I,\ldots$ in the manner described in Sec. II. These coupled equations can be solved for $G_1,G_2,\ldots,G_{n-1}$ and substituted into Eqs. (46), (47), and (48) to obtain thermodynamic quantities of the fluid. The following equation is obtained from Eq. (47):

$$\frac{PV}{Nk_B T}=1-\frac{\rho_0}{6}\int r_{12}\frac{du}{dr_{12}}[1+G_1(\vec{r}_{21})+G_2(\vec{r}_{21})$$

$$+\cdots+G_{n-1}(\vec{r}_{21})]d\vec{r}_{21} .$$

$$(52)$$

This equation can be compared to the well-known expression of J. E. Mayer:[9]

$$\frac{PV}{Nk_B T}=1-\sum_{k\geq 1}^{\infty}\frac{k}{k+1}\beta_k\rho_0^k , \qquad (53)$$

where $\beta_k$ is the irreducible cluster integral. Equation (52) is based on the Kirkwood coupling-parameter expansion of the correlation function, while Eq. (53) is the conventional density expansion. In the low-density limit of the uniform fluid, the two-particle distribution function is known to be

$$\rho^{(2)}(r_1,r_2)=\rho_0^2 e^{-u(r_{12})} . \qquad (54)$$

In order to find this equation in the present method, we have to take an infinite number of terms in the expansion of $G(\vec{r}_{21};\xi)$ with respect to $\xi$, and the quantities $G_1,G_2,\ldots$ correspond to the Taylor series of the factor $e^{-u(r_{12})}$ shown in Eq. (54). Thus our method is quite different from the conventional density expansion.

We now apply the present method to the classical electron plasma. The Fourier transform of the interaction potential $u(\vec{q})$ can be expressed as

$$\rho_0 u(\vec{q})=\frac{1}{q^2} , \qquad (55)$$

where all lengths are normalized by the Debye length $\lambda_D=(k_B T/4\pi\rho_0 e^2)^{1/2}$. The quantities $\rho_0$ and $T$ are the density and temperature of the electron plasma, respectively, and $e$ is the electronic charge. Substitution of Eq. (55) into Eq. (28) yields the Debye-Hückel pair correlation function[10] as follows:

$$G_1(\vec{q})=-\frac{4\pi\epsilon}{q^2+1}, \quad G_1(\vec{r})=-\frac{\epsilon}{r}e^{-r} , \qquad (56)$$

where $\epsilon=[4\pi\rho_0(e^2/k_B T)^3]^{1/2}$ is the plasma parameter and the condition $\epsilon\ll 1$ is assumed. In the next-order approximation, $G_1(\vec{q})$ can be derived by solving the integral equation

$$\left[1-2\pi\epsilon\frac{q^2}{1+q^2}\int\frac{d\vec{q}'}{(2\pi)^3}\frac{1}{1+(\vec{q}'-\vec{q})^2 q^2 q'^2}\frac{1+q^2 q'^2}{q'^2}\right]G_1(\vec{q})$$

$$=-\frac{4\pi\epsilon}{1+q^2}+\frac{(4\pi\epsilon)^2}{1+q^2}\int\frac{d\vec{q}'}{(2\pi)^3}\frac{1}{1+(\vec{q}'-\vec{q})^2 q^2 q'^2}\frac{1+q'^2(q^2-1)}{q'^2}$$

$$+\frac{2\pi\epsilon}{1+q^2}\int\frac{d\vec{q}'}{(2\pi)^3}\left[\frac{1}{(\vec{q}'+\vec{q})^2}+\frac{1}{(\vec{q}'+\vec{q})^2}\frac{q'^2[1-(\vec{q}'+\vec{q})^2]}{1+q'^2 q^2(\vec{q}'+\vec{q})^2}+\frac{q'^2(q^2-1)}{1+(\vec{q}'-\vec{q})^2 q^2 q'^2}\right]G_1(\vec{q}') , \qquad (57)$$

which is obtained from Eq. (34). In any method of deriving the pair correlation function of the classical electron plasma,[11] the Debye-Hückel pair correlation function shown in Eq. (56) is obtained in the lowest order. However, Eq. (57) tells us that the Debye-Hückel pair correlation function itself has to be modified in the second-order approximation of the present method. We now check the validity of the Debye-Hückel pair correlation function by deriving and comparing the isothermal compressibility obtained from the pressure and the compressibility equation of state shown in Eqs. (47) and (49), respectively,

$$k_B T\left[\frac{\partial\rho_0}{\partial P}\right]_T=1+\frac{\epsilon}{4} , \qquad (58)$$

$$k_B T\left[\frac{\partial\rho_0}{\partial P}\right]_T=1-\int_0^{\infty}re^{-r}dr=0 . \qquad (59)$$

The discrepancy of these two equations occurs at order $O(1)$. One may argue that this discrepancy is either due to the well-known fact that the Debye-Hückel pair correlation function is not good for short distances or the lack of three-particle correlation effects. Such a modification was done by O'Neil and Rostoker.[12] They defined that the pair correlation function $G(\vec{r}_{21})$ consists of the sum of the short-range correlation function $\phi_{II}(r_{21})$ and the long-range correlation function $\phi_I(r_{21})$. The quantity $\phi_{II}(r_{21})$ is the so-called nonlinear Debye-Hückel pair correlation function. The long-range correlation function $\phi_I(r_{21})$ consists of the Debye-Hückel pair correlation function $\phi_I^{(1)}(r_{21})$ and the higher-order quantity $\phi_I^{(2)}(r_{21})$ which includes three-particle effects. Making use of these functions, Eq. (49) can be calculated as follows:

$$k_B T \left[ \frac{\partial \rho_0}{\partial P} \right]_T = 1 + 4\pi\rho_0\lambda_D^3 \left[ \int_0^{\rho_0^{-1/3}/\lambda_D} \phi_{\mathrm{II}}(r)r^2 dr + \int_{\rho_0^{-1/3}/\lambda_D}^{\infty} [\phi_{\mathrm{I}}^{(1)}(r) + \phi_{\mathrm{I}}^{(2)}(r)]r^2 dr \right]$$

$$= 1 + \frac{1}{\epsilon} \int_0^{(4\pi\epsilon)^{1/3}} (-1 + e^{-(\epsilon/r)e^{-r}})r^2 dr$$

$$+ \frac{1}{\epsilon} \int_{(4\pi\epsilon)^{1/3}}^{\infty} r^2 \left[ -\frac{\epsilon}{r}e^{-r} \right] dr + \frac{1}{\epsilon} \int_{(4\pi\epsilon)^{1/3}}^{\infty} r^2 \phi_{\mathrm{I}}^{(2)}(r) dr$$

$$= \epsilon \left[ \frac{7}{12} - \frac{\gamma + \ln(4\pi\epsilon)^{1/3}}{4} \right] , \tag{60}$$

where $\gamma$ is Euler's constant and all the lengths are normalized by the Debye length $\lambda_D$. The rhs of Eq. (60) is due to the contribution associated with the quantity $\phi_{\mathrm{I}}^{(2)}(r)$. By comparing Eqs. (58) and (60), it is clear that thermodynamic consistency is still not recovered at $O(1)$. Basically, the cause of this discrepancy can be traced to the idea of the conventional successive approximation, i.e., the Debye-Hückel pair correlation function is assumed to be unchanged even when the short-range and three-particle correlation effects are taken into account. In other words, if these two effects are taken account of, the Debye-Hückel pair correlation function itself has to be modified. We have already pointed out such a modification in the present method in Eq. (57). In the rhs of Eq. (57), the term associated with the quantity $1/(\vec{q}\,' + \vec{q}\,)^2$ represents the short-range effect, while terms associated with the quantity $1/[1 + (\vec{q}\,' \pm \vec{q}\,)^2 q^2 q'^2]$ represents three-particle effects. Although we are unable to solve Eq. (57), we have shown that the Kirkwood coupling-parameter expansion method has various advantages over the conventional method of deriving the pair correlation function in fluids.

## ACKNOWLEDGMENTS

## APPENDIX

Taking the derivative of Eq. (3) with respect to $\vec{r}$, we find the Born-Green-Yvon integral equation for the $n$-particle distribution function:

$$\vec{\nabla}_1 \rho^{(n)}(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_n; \xi) = -\xi \sum_{j=2}^{n} [\vec{\nabla}_1 u(r_{1j})]\rho^{(n)}(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_n; \xi) - \xi \int [\vec{\nabla}_1 u(r_{1,n+1})]\rho^{(n+1)}(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_{n+1}; \xi) d\vec{r}_{n+1} .$$

$$\tag{A1}$$

Substituting Eqs. (9) and (10) into Eq. (A1), we find the basic equations for $G(\vec{r}_{21}; \xi)$ and $H(\vec{r}_{21}, \vec{r}_{31}; \xi)$ in the following:

$$\vec{\nabla}_1 G(\vec{r}_{21}; \xi) = -\xi[\vec{\nabla}_1 u(r_{12})][1 + G(\vec{r}_{21}; \xi)]$$

$$+ \xi\rho_0 \int [\vec{\nabla}_1 u(r_{13})][G_1(\vec{r}_{21}; \xi)G(\vec{r}_{31}; \xi) - G(\vec{r}_{32}) - H(\vec{r}_{21}, \vec{r}_{31}; \xi)]d\vec{r}_3 , \tag{A2}$$

$$\vec{\nabla}_1 H(\vec{r}_{21}, \vec{r}_{31}; \xi) = -\xi[\vec{\nabla}_1 u(r_{12})][G(\vec{r}_{31}; \xi) + G(\vec{r}_{32}) + H(\vec{r}_{21}, \vec{r}_{31}; \xi)]$$

$$- \xi[\vec{\nabla}_1 u(r_{13})][G(\vec{r}_{21}; \xi) + G(\vec{r}_{32}) + H(\vec{r}_{21}, \vec{r}_{31}; \xi)]$$

$$+ \xi\rho_0 \int [\vec{\nabla}_1 u(r_{14})][G(\vec{r}_{41}; \xi)H(\vec{r}_{21}, \vec{r}_{31}; \xi) - H(\vec{r}_{32}, \vec{r}_{42})$$

$$- G(\vec{r}_{21}; \xi)G(\vec{r}_{43}) - G(\vec{r}_{31}; \xi)G(\vec{r}_{42}) - I(\vec{r}_{21}, \vec{r}_{31}, \vec{r}_{41}; \xi)]d\vec{r}_4 . \tag{A3}$$

Expanding the quantities $G(\vec{r}_{21}; \xi)$ and $H(\vec{r}_{21}, \vec{r}_{31}; \xi)$ in powers of $\xi$ and taking terms of equal power of $\xi$ to be equal in Eqs. (A2) and (A3), we find the following equations:

$$\vec{\nabla}_1 G_1(\vec{r}_{21}) = -\vec{\nabla}_1 u(r_{12}) - \rho_0 \int d\vec{r}_3 [\vec{\nabla}_1 u(r_{13})]G(\vec{r}_{32}) , \tag{A4}$$

$$\vec{\nabla}_1 G_2(\vec{r}_{21}) = -[\vec{\nabla}_1 u(r_{12})]G_1(\vec{r}_{21}) - \rho_0 \int d\vec{r}_3 [\vec{\nabla}_1 u(r_{13})]H_1(\vec{r}_{21}, \vec{r}_{31}) , \tag{A5}$$

$$\vec{\nabla}_1 H_1(\vec{r}_{21}, \vec{r}_{31}) = -[\vec{\nabla}_1 u(r_{12}) + \vec{\nabla}_1 u(r_{13})]G(\vec{r}_{32}) - \rho_0 \int d\vec{r}_4 [\vec{\nabla}_1 u(r_{14})]H(\vec{r}_{32}, \vec{r}_{42}) . \tag{A6}$$

In the lowest-order approximation which takes only terms of $\xi$, the quantity $G(\vec{r}_{21})$ is assumed to be $G(\vec{r}_{21}) = G_1(\vec{r}_{21})$ and the equation which determines $G_1$ is given as

$$\vec{\nabla}_1 G_1(\vec{r}_{21}) = -\vec{\nabla}_1 u(r_{12}) - \rho_0 \int d\vec{r}_3 [\vec{\nabla}_1 u(r_{13})] G_1(\vec{r}_{32}) . \tag{A7}$$

In the second-order approximation we take terms up to $\xi^2$ and we have three coupled equations for $G_1$, $G_2$, and $H_1$:

$$\vec{\nabla}_1 G_1(\vec{r}_{21}) = -\vec{\nabla}_1 u(r_{12}) - \rho_0 \int d\vec{r}_3 [\vec{\nabla}_1 u(r_{13})][G_1(\vec{r}_{32}) + G_2(\vec{r}_{32})] , \tag{A8}$$

$$\vec{\nabla}_1 G_2(\vec{r}_{21}) = -[\vec{\nabla}_1 u(r_{12})] G_1(\vec{r}_{21}) - \rho_0 \int d\vec{r}_3 [\vec{\nabla}_1 u(r_{13})] H_1(\vec{r}_{21}, \vec{r}_{31}) , \tag{A9}$$

$$\vec{\nabla}_1 H_1(\vec{r}_{21}, \vec{r}_{31}) = -[\vec{\nabla}_1 u(r_{12}) + \vec{\nabla}_1 u(r_{13})][G_1(\vec{r}_{32}) + G_2(\vec{r}_{32})] - \rho_0 \int d\vec{r}_4 [\vec{\nabla}_1 u(r_{14})] H_1(\vec{r}_{32}, \vec{r}_{42})] . \tag{A10}$$

These coupled equations correspond to Eqs. (31), (32), and (33), respectively.

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