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Correlation functions for estimating effects of the physical cluster formation

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Two correlation functions for estimating effects of the physical cluster formation on features of a fluid must satisfy a system of two integral equations which is equivalent to the Ornstein-Zernike equation and the sum of the two correlation functions is equivalent to the pair correlation function. A specific effect of the physical cluster formation persuades the dependence of their sum on the distance r between particular pair particles to develop a deviation from the dependence which is expressed as the product of the reciprocal of r and a particular function given as the Taylor series due to powers of r. The use of the two correlation functions allows the formation of extremely large physical clusters to be predicted at least near the triple point. The two correlation functions can contribute to examining a feature of a fluid in a specific situation where an effect of the physical cluster formation are considerable.

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I. INTRODUCTION

Physical clusters which are formed by attractive forces among particles can allow the density fluctuations to be enhanced in a fluid being at least in the gas state. The degree of the density fluctuations reaches the maximum at the liquid-vapor critical point of the fluid. A specific cause of generating the density fluctuations makes the dependence of the pair correlation function on the distance between particular pair particles near the liquid-vapor critical point [1,2] differ both from its dependence in the gas state being far from the critical point and from that in the liquid state being far from the critical point. Moreover, the density fluctuations can result in anomalies [3–7] with respect to various properties of fluids near their liquid-vapor critical points. If a fluid consists of metallic atoms, inhomogenieties of the fluid due to the physical cluster formation [8] can be observed as anomalies for electrical properties [3], the optical reflectivity [4], and the optical absorption [4,5]. The electrical conductivity of liquid mercury maintained at a temperature near the critical point decreases with a rather steep gradient as the density of mercury atoms decreases [3]. The real part of the dielectric constant determined using optical reflectivity and absorption measurements for a mercury fluid near the critical point increases sharply at a particular density as the density of mercury atoms increases [4]. The viscosities of fluids exhibit asymptotic divergence near the liquid-vapor critical points, and measuring the viscosities of carbon dioxide and xenon near their critical points allowed the critical exponent characterizing the asymptotic divergence to be determined [6]. The physical cluster formation can result in a characteristic increase in the viscosities of fluids near the critical points [7]. Various critical phenomena suggest that the formation of stable physical clusters, which is not expected in the gas phase, enables features of the fluid found in the liquid state to become different from its features found in the gas state, and this fact suggests that the physical cluster formation can cause the gas-liquid phase transition. A contribution of the physical cluster formation to the transition of a fluid from the liquid state into the solid state is suggested according to the fact that the development of physical clusters which are formed by attractive forces among colloidal particles allows a colloidal solution to generate a gel state [9]. A contribution of the physical cluster formation to the liquid-solid phase transition is also suggested according to the fact that a fluid composed of the liquid phase and the gas phase makes the liquid-vapor interface become smooth. The formation of the smooth liquid-vapor interface means that the situation where particles constituting the liquid phase are subjected is different from a state which is given by making particles dense in maintaining the situation where particles constituting the gas phase are subjected. At least in order to form the smooth liquid-vapor interface, the high-density fluid being in the liquid phase must generate a macroscopic force which contributes to minimizing its surface. Moreover, generating the clear smooth boundary between the high-density part being the liquid phase and the low-density part being the gas phase suggests that particles moving vigorously in the liquid phase have to be comparatively stably confined. The capability to confine particles moving vigorously can be generated by the formation of physical clusters. Besides, the capability to confine such particles allows for generating a macroscopic force which contributes to minimizing the surface of the high-density part. Such a macroscopic force should contribute to making particles in the liquid phase become close to each other, and as a result, the presence of the macroscopic force should aid in transforming the fluid of the liquid phase into the solid sate. On the other words, an effect of the physical cluster formation on the confinement of vigorously moving particles can contribute to the liquid-solid phase transition. The possibility that physical clusters influence a microscopic distribution pattern of particular atoms (or molecules) which are dissolved as solute particles in a fluid being in the liquid state makes another effect of the physical cluster formation realized, since a fluid being in the gas state where an effect of the physical cluster formation is not expected has a tendency to microscopically homogeneously mix with another fluid being in the gas state where an effect of the physical

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cluster formation is also not expected. Solute particles that cannot actively contribute to the physical cluster formation should have a tendency to distribute among physical clusters, and solute particles that can actively contribute to the physical cluster formation should have a tendency to distribute as a portion of the particle group which consists of particles forming physical clusters. Hence, physical clusters can make a microscopic distribution pattern of solute particles become inhomogeneous in a fluid mixture such as a liquid of metallic alloy and other solute-solvent mixtures. A specific effect of such a microscopic inhomogeneous distribution pattern of solute particles can be found as a macroscopic phenomenon called the osmotic pressure, since the osmotic pressure occurring by dissolving solute particles that cannot actively contribute to the physical cluster formation must be different from that occurring by dissolving solute particles that can actively contribute to the physical cluster formation. In addition, the dependence of the osmotic pressure on the density of solute particles in a situation where the stability of physical clusters is high should be considerably different from that in a situation where the stability of physical clusters is low. In a situation where the stability of physical clusters is low, both the formation of physical clusters and the decomposition of physical clusters can occur as very sensitive responses to slight variations in temperature. The anomalous behavior of the thermal conductivity of a fluid should be found in such a specific situation [10]. Then, physical clusters formed in the fluid do not have the capability to stably confine particles moving vigorously. Allowing both the confinement of such particle and the release of them easily to occur enables the fluid to be stirred. Hence, the thermal conductivity of the fluid should enhance in the situation where physical clusters loses the capability to stably confine particles moving vigorously. Although the physical cluster formation can contribute to the occurence of various phenomena, an effect of the physical cluster formation on the magnitude of the pair correlation function might not be sufficiently apparent. It is expected that the fraction of the contribution of the physical cluster formation to the pair correlation function can remain sufficiently small in comparison with the magnitude of the pair correlation function. Even if the pair correlation function which is determined by x-ray scattering measurements and neutron scattering measurements can expose the contribution of the physical cluster formation to the pair correlation function, its contribution may be found only as vague traces of peaks beside normal peaks.

Despite this fact, various phenomena found as effects of the physical cluster formation allow a procedure for simply estimating the physical cluster formation to become interesting in order to try examining their effects on features of a fluid. Each physical cluster which is formed in a fluid system is regarded as an ensemble of particles linked each other by bonds. Then, each bond is defined as a bound state in which a contribution of attractive forces between pair particles dominates a contribution of the relative kinetic energy between them, according to Hill [11]. A useful procedure for estimating the physical cluster formation due to such bonds can be found according to a concept of Coniglio and coworkers [12], and it results in an integral equation. The integral equation has played a role for examining the physical cluster formation. In fact, the use of the integral equation made it possible to examine the physical cluster formation caused by a contribution of a extremely short-ranged attractive force [13] and to examine the physical cluster formation caused by the Yukawa potential [14,15]. Moreover, a procedure for making corrections to the Percus-Yevick approximation [16] enabled an estimate of physical cluster formation due to the integral equation to be improved considerably [17]. Although the integral equation enables the physical cluster formation to be examined, it is not equivalent to the Ornstein-Zernike equation. The use of the Ornstein-Zernike equation has been successful for examining both a fluid being in the gas state and the fluid being in the liquid state, so that resulting from the Ornstein-Zernike equation must be considered indirectly to involve the contribution of the physical cluster formation. The Ornstein-Zernike equation should involve the contribution of the integral equation which enables the formation of physical clusters to be examined. This fact means that subtracting the contribution of the integral equation from the Ornstein-Zernike equation results in an additional integral equation which is equivalent to both an integral equation derived by Stell [16] and another one derived by Chiew and co-workers [18]. If this additional integral equation is coupled to the integral equation which enables the physical cluster formation to be examined, the two integral equations provide an integral equation system, which is equivalent to the Ornstein-Zernike equation. Estimating an effect of the physical cluster formation on a feature of a fluid can be allowed by the use of the integral equation system.

II. CORRELATION FUNCTIONS AND INTEGRAL EQUATIONS

A. Integral equations for correlation functions

The pair correlation function g_{ij} is useful for knowing whether particles in a fluid system can move easily or can be prevented from moving easily, and the use of g_{ij} allows for estimating the density fluctuations for the fluid system even near the critical point. If three-dimensional coordinates for a particle of species i and a particle of species j which constitute a fluid are denoted by $\mathbf{r}_1^{(i)}$ and $\mathbf{r}_2^{(j)}$, the use of the pair correlation function g_{ij} allows for expressing the probability that the i particle and the j particle is located in a volume element $d\mathbf{r}_1^{(i)}$ at $\mathbf{r}_1^{(i)}$ and in a volume element $d\mathbf{r}_2^{(j)}$ at $\mathbf{r}_2^{(j)}$, respectively. If the distance $|\mathbf{r}_1^{(i)}-\mathbf{r}_2^{(j)}|$ between the two particles is represented as r $(=|\mathbf{r}|)$, the probability is given as $\rho_i\rho_j g_{ij}(r)d\mathbf{r}_1^{(i)}d\mathbf{r}_2^{(j)}$ in which ρ_i and ρ_j are the densities of the i and j particles for a uniform distribution, respectively. The magnitude of $g_{ij}(r)$ is proportional to the probability that the i particle in the volume element $d\mathbf{r}_1^{(i)}$ is located at the distance r far from the j particle in the volume element $d\mathbf{r}_2^{(j)}$. This feature of the pair correlation function suggests that maximum values of $g_{ij}(r)$ should become larger when particles in a fluid system are prevented from moving easily than when they can move easily.

The i particle and the j particle have the possibility that both of them belong to the same physical cluster. Then, the use of the pair correlation function $\mathcal{P}_{ij}$ allows for expressing the probability that both the i particle in the volume element $d\mathbf{r}_1^{(i)}$ and the j particle in the volume element $d\mathbf{r}_2^{(j)}$ belong to the same physical cluster is expressed as $\rho_i\rho_j\mathcal{P}_{ij}(r)d\mathbf{r}_1^{(i)}d\mathbf{r}_2^{(j)}$. The pair connectedness $\mathcal{P}_{ij}(r)$ is important in order to estimate the mean size of physical clusters [12]. If the probability that the i particle in the volume element $d\mathbf{r}_1^{(i)}$ and the j particle in the volume element $d\mathbf{r}_2^{(j)}$ belong to a physical cluster and another physical cluster respectively is expressed as $\rho_i\rho_j\mathcal{D}_{ij}(r)d\mathbf{r}_1^{(i)}d\mathbf{r}_2^{(j)}$, the pair connectedness $\mathcal{P}_{ij}(r)$ is related to $g_{ij}(r)$ as

$$g_{ij}(r) = \mathcal{P}_{ij}(r) + \mathcal{D}_{ij}(r). \tag{2.1}$$

According to Kirkwood and Buff [19], the pair correlation function $g_{ij}(r)$ has the normalization given as

$$\frac{1}{V}\int_V g_{ij}(r)\mathrm{d}\mathbf{r} = \frac{\langle N_i\rangle - \delta_{ij}}{V\rho_i} + \frac{1}{V^2}\frac{1}{\rho_i\rho_j}[\langle N_iN_j\rangle - \langle N_i\rangle\langle N_j\rangle], \tag{2.2}$$

where $\langle N_i\rangle$ is the mean number of particles of species i within volume V [11]. The dependence of $g_{ij}(r)$ on V is negligible for macroscopic V, and the dependence of $\langle N_i\rangle/V$ on V and the dependence of $(\langle N_iN_j\rangle - \langle N_i\rangle\langle N_j\rangle)/V$ on V are also negligible. Thus, Eq. (2.2) results in $\int_V g_{ij}(r)\mathrm{d}\mathbf{r}/V = 1$ in the limit $V\to\infty$. This relation and Eq. (2.1) require $P_{ij}(r)$ and $\mathcal{D}_{ij}(r)$ to satisfy

$$\lim_{V\to\infty}\left[\frac{1}{V}\int_V \mathcal{P}_{ij}(r)\mathrm{d}\mathbf{r} + \frac{1}{V}\int_V \mathcal{D}_{ij}(r)\mathrm{d}\mathbf{r}\right] = 1. \tag{2.3}$$

Moreover, the pair correlation function behaves as $g_{ij}(|\mathbf{r}_1^{(i)} - \mathbf{r}_2^{(j)}|) \approx 1$ when two particles located at $\mathbf{r}_1^{(i)}$ and $\mathbf{r}_2^{(j)}$ in a fluid system are widely separated. In the limit $V\to\infty$ and $r\to\infty$, it behaves as $g_{ij}(r) = 1$ [11]. According to this fact, Eq. (2.1) allows the physical meanings of $\mathcal{P}_{ij}(r)$ and those of $\mathcal{D}_{ij}(r)$ to result in

$$\lim_{r\to\infty}\mathcal{P}_{ij}(r) = 0 \quad \text{and} \quad \lim_{r\to\infty}\mathcal{D}_{ij}(r) = 1.$$

According to Eq. (2.1), the pair correlation function $g_{ij}(r)$ is expressed as the sum of the contribution of $\mathcal{P}_{ij}(r)$ and the contribution of $\mathcal{D}_{ij}(r)$. Owing to this fact, each term of the pair correlation function which is expressed in the form of a density expansion [20,21] should be divided into terms contributing to $\mathcal{P}_{ij}(r)$ and terms contributing to $\mathcal{D}_{ij}(r)$ [12]. Dividing into these two kinds of terms contribute to deriving an integral equation which should be satisfied by $\mathcal{P}_{ij}(r)$ and another integral equation which should be satisfied by $\mathcal{D}_{ij}(r)$.

The pair correlation function expressed in the form of a density expansion [20,21] is obtained from the use of the Mayer f function instead of the use of the factor $\exp[-\beta u_{ij}(r)]$. The Mayer f function is defined as $f_{ij}(r) \equiv e^{-\beta u_{ij}(r)} - 1$ in which $\beta u_{ij}(r)$ is a pair potential multiplied by β which is defined as $\beta \equiv 1/kT$. Here, k is Boltzmann's constant and T the temperature. The function $f_{ij}(r)$ becomes -1 in the region of the hard core in which $u_{ij}(r) = \infty$, and it becomes zero outside the range in which an attractive force between an i particle and a j particle retains effective strength. The function $f_{ij}(r)$, however, is positive within the range where the attractive force retains effective strength, and it expresses the strength of the attractive interaction in this range.

Each term found in the form of the density expansion of $g_{ij}(r)$ is formed by the integrals of a product of f functions, although the two coordinates corresponding to the root points labeled 1 and 2 in the present work are not integrated over in each term. The other coordinates which are integrated over in each term are field points, and they are labeled 3, 4, … in the present work. Both the root points and the field points correspond to particle coordinates.

An ensemble of particle pairs which are specified by the f functions forming a product in the density expansion is regarded as an ensemble of particle pairs linked by the f bonds defined as the f functions. Since this ensemble is a mathematical cluster [21], it cannot simply correspond to a physical cluster. The ensemble can be symbolized as a diagram having a structure which is formed from particle pairs linked by f bonds. Every diagram which is found in the density expansion has the same pair of root points. The density expansion corresponds to the sum of all the diagrams having specific structures which form f bonds' paths joining a root point to the other root point [20,21]. The paths of f bonds allow for propagating effects of the behavior of a particle corresponding to a root point to the other particle corresponding to the other root point.

On the other hand, pair particles which are specified by an f function have two possibilities. One is a possibility that a contribution of attractive forces between the pair particles exceeds a contribution E of their relative kinetic energy, and the other is a possibility that E exceeds a contribution of the attractive forces. If a pair of an i particle and a j particle which are specified by an f function are located at $\mathbf{r}_1^{(i)}$ and $\mathbf{r}_2^{(j)}$ in terms of the distance $r = |\mathbf{r}_1^{(i)} - \mathbf{r}_2^{(j)}|$, the probability $p_{ij}(r)$ that the pair satisfies the condition $E + u_{ij}(r) \leqslant 0$ [11] is given as

$$p_{ij}(r) = 2\pi^{-1/2}[\Gamma(3/2) - \Gamma(3/2, -\beta u_{ij})], \tag{2.4}$$

since the integral $\int_t^\infty e^{-y}y^{\tau-1}\mathrm{d}y$ due to the definition $y \equiv [\beta E]^{1/2}$ expresses the incomplete gamma function $\Gamma(\tau, t)$. This probability should behave as $p_{ij}(r) = 0$ if $u_{ij}(r)$ is a repulsive potential [i.e., $\beta u_{ij}(r) > 0$]. The use of $p_{ij}(r)$ enables $f_{ij}(r)$ to be given as the sum of the contribution $f_{ij}^{+}(r)$ of a bound state $E + u_{ij}(r) \leqslant 0$ and the contribution $f_{ij}^{*}(r)$ of an unbound state $E + u_{ij}(r) > 0$. Then, the relation $f_{ij}(r) = f_{ij}^{+}(r) + f_{ij}^{*}(r)$ allows the f^{+} function and the f^{*} function to be expressed as

$$f_{ij}^{+}(r) \equiv p_{ij}(r)e^{-\beta u_{ij}(r)}, \quad f_{ij}^{*}(r) \equiv [1 - p_{ij}(r)]e^{-\beta u_{ij}(r)} - 1. \tag{2.5}$$

If each f bond in a diagram which is found in the density expansion of $g_{ij}(r)$ is, according to Eq. (2.5), expressed as the sum of the f^{+} bond defined as the contribution of a bound state and the f^{*} bond defined as the contribution of an unbound state, the diagram is given as the sum of diagrams resulting from products of f^{+} functions and f^{*} functions.

Then, it is possible to find a diagram in which a root point is connected to the other root point through at least one path of all f^{+} bonds given as a product of f^{+} functions. This diagram can be regarded as a physical cluster, and it means that the two particles corresponding to the two root points are two of particles constituting the physical cluster according to Hill [11]. The second simplest diagram in the diagrams which are found in the density expansion of $g_{ij}(r)$ consists of three particles linked by two f bonds, and the three particles correspond to two root points $(\mathbf{r}_1^{(i)},\mathbf{r}_2^{(j)})$ and one field point $(\mathbf{r}_3^{(k)})$ which corresponds to a coordinates of particle of species k. According to Hill [11], the three particles are bound each other when the f bonds retain the three particles in a bound state characterized as the conditions $E_{(1,3)}+u_{ik}(|\mathbf{r}_1^{(i)}-\mathbf{r}_3^{(k)}|)\leqslant 0$ and $E_{(3,2)}+u_{kj}(|\mathbf{r}_3^{(k)}-\mathbf{r}_2^{(j)}|)\leqslant 0$ in which the suffix of E indicates a particle pair contributing to E. This situation corresponds to that represented as a diagram in which a root point is connected to the other root point through at least one path of all f^{+} bonds given as a product of f^{+} functions, and the two particles corresponding to the two root points are two of particles constituting the same physical cluster. This fact allows $\mathcal{P}_{ij}(r)$ to be given as the sum of contributions resulting from every diagram having at least one path of all f^{+} bonds between the root points.

The diagrams which are found in the density expansion of $g_{ij}(r)$ are divided into two categories. One group of diagrams corresponds to the group of nodal diagrams having nodal points, and the other group of diagrams corresponds to the group of non-nodal diagrams having no nodal point. A nodal point is a specific field point in a diagram, and missing the field point in the diagram means that the diagram is separated into a group including a root point and the other group including the other root point.

Similarly, the diagrams contributing to $\mathcal{P}_{ij}(r)$ should be separated into the group of nodal diagrams and the group of non-nodal diagrams. This fact means that $\mathcal{P}_{ij}(r)$ is expressed as $\mathcal{P}_{ij}(r)=N_{ij}^{+}(r)+C_{ij}^{+}(r)$, in which $N_{ij}^{+}(r)$ is the contribution of all nodal diagrams having at least one path of all f^{+} bonds between the two root points, and $C_{ij}^{+}(r)$ is the contribution of all non-nodal diagrams having at least one path of all f^{+} bonds between the two root points. In the Ornstein-Zernike equation [20], the contribution of all non-nodal diagrams consisting of paths of f bonds between the two root points corresponds to the direct correlation function $c_{ij}(r)$. According to the Ornstein-Zernike equation, $g_{ij}(r)-1$ is equal to $N_{ij}(r)+c_{ij}(r)$ in which $N_{ij}(r)$ represents the contribution of all nodal diagrams consisting of paths of f bonds between the two root points, and $N_{ij}(r)$ is given as the convolution integral $\sum_{k=1}^{\mathcal{L}}\rho_k\int c_{ik}(r_{ik})[g_{kj}(r_{kj})-1]\mathrm{d}\mathbf{r}_k$, which is simplified by using $r_{ik}\equiv|\mathbf{r}_1^{(i)}-\mathbf{r}_3^{(k)}|$, $r_{kj}\equiv|\mathbf{r}_3^{(k)}-\mathbf{r}_2^{(j)}|$, and $\mathrm{d}\mathbf{r}_k\equiv\mathrm{d}\mathbf{r}_3^{(k)}$. If an analogy with the Ornstein-Zernike equation is assumed, the convolution integral of the product of $C_{ik}^{+}(r)$ and $\mathcal{P}_{kj}(r)$ should result in $N_{ij}^{+}(r)=\sum_{k=1}^{\mathcal{L}}\rho_k\int C_{ik}^{+}(r_{ik})\mathcal{P}_{kj}(r_{kj})\mathrm{d}\mathbf{r}_k$. This fact and the relation $\mathcal{P}_{ij}(r)=C_{ij}^{+}(r)+N_{ij}^{+}(r)$ results in an integral equation which is required in order to estimate $\mathcal{P}_{ij}(r)$ [12]. Thus, the pair connectedness $\mathcal{P}_{ij}(r)$ is given as a solution of the integral equation expressed as

$$\mathcal{P}_{ij}(r_{ij})=C_{ij}^{+}(r_{ij})+\sum_{k=1}^{\mathcal{L}}\rho_k\int_V C_{ik}^{+}(r_{ik})\mathcal{P}_{kj}(r_{kj})\mathrm{d}\mathbf{r}_k, \quad (2.6)$$

where $\mathcal{L}$ is the number of constituents and $r_{ij}\equiv|\mathbf{r}_1^{(i)}-\mathbf{r}_2^{(j)}|=r$. This equation, which is used in the limit $V\to\infty$, has the same mathematical structure as the Ornstein-Zernike equation, and C_{ij}^{+} in Eq. (2.6) is an unknown function.

Finding an integral equation for the correlation function $\mathcal{D}_{ij}(r)$ is possible by considering the Ornstein-Zernike equation. Owing to Eq. (2.1), the Ornstein-Zernike equation is expressed as

$$\begin{aligned}\mathcal{P}_{ij}(r_{ij})+\mathcal{D}_{ij}(r_{ij})-1&=c_{ij}(r_{ij})+\sum_{k=1}^{\mathcal{L}}\rho_k\int_V c_{ik}(r_{ik})\mathcal{P}_{kj}(r_{kj})\mathrm{d}\mathbf{r}_k\\&\quad+\sum_{k=1}^{\mathcal{L}}\rho_k\int_V c_{ik}(r_{ik})[\mathcal{D}_{kj}(r_{kj})-1]\mathrm{d}\mathbf{r}_k.\end{aligned} \quad (2.7)$$

This equation must involve the contribution of the pair connectedness $\mathcal{P}_{ij}$ expressed by Eq. (2.6). If the contribution of non-nodal diagrams which do not include paths of all f^{+} bonds between i and j is expressed as $C^{*}(r_{ij})$, the direct correlation function $c_{ij}(r_{ij})$ which represents the contribution of all non-nodal diagrams consisting of paths of f bonds between the two root points must be equal to the sum of $C^{*}(r_{ij})$ and $C_{ij}^{+}(r_{ij})$ which is the contribution of all non-nodal diagrams having at least one path of all f^{+} bonds between the two root points. According to this fact, $c_{ij}(r_{ij})$ is expressed as

$$c_{ij}(r_{ij})=C_{ij}^{+}(r_{ij})+C_{ij}^{*}(r_{ij}). \quad (2.8)$$

If Eq. (2.6) is considered, the substitution of Eq. (2.8) into Eq. (2.7) results in an integral equation which is equivalent to both an integral equation derived by Stell [16] and another one derived by Chiew and co-workers [18]. This integral equation is expressed as

$$\begin{aligned}\mathcal{H}_{ij}(r_{ij})&=C_{ij}^{*}(r_{ij})+\sum_{k=1}^{\mathcal{L}}\rho_k\int_V C_{ik}^{*}(r_{ik})\mathcal{P}_{kj}(r_{kj})\mathrm{d}\mathbf{r}_k\\&\quad+\sum_{k=1}^{\mathcal{L}}\rho_k\int_V C_{ik}^{+}(r_{ik})\mathcal{H}_{kj}(r_{kj})\mathrm{d}\mathbf{r}_k\\&\quad+\sum_{k=1}^{\mathcal{L}}\rho_k\int_V C_{ik}^{*}(r_{ik})\mathcal{H}_{kj}(r_{kj})\mathrm{d}\mathbf{r}_k,\end{aligned} \quad (2.9)$$

where

$$\mathcal{H}_{ij}(r_{ij})\equiv\mathcal{D}_{ij}(r_{ij})-1. \quad (2.10)$$

According to the relation given by Eq. (2.8), an integral equation system consisting of Eqs. (2.6) and (2.9) is equivalent to the Ornstein-Zernike equation. Equation (2.6) contributes to estimating the formation of physical clusters, and Eq. (2.9) contributes to estimating an effect of the physical cluster formation. In fact, the second term and the third term on the right-hand side in Eq. (2.9) represent a way to have an effect of the formation of physical clusters on the correlation function $\mathcal{H}_{ij}$. An effect of these terms might play a role for explaining phenomena due to the formation of physical clusters.

B. Effects of the physical cluster formation

Representing the Ornstein-Zernike equation as an integral equation system which consists of Eq. (2.6) being relevant to $\mathcal{P}_{ij}(r)$ and Eq. (2.9) being relevant to $\mathcal{H}_{ij}(r)$ is equivalent to actively considering that a fluid consisting of particles interacting each other with attractive forces has a tendency to become inhomogeneous. Considering the two correlation functions $\mathcal{P}_{ij}(r)$ and $\mathcal{H}_{ij}(r)$ means that particle pairs constituting a fluid are divided into two groups. One is a group of particle pairs characterized as pair particles interacting in a specific situation where a contribution of an attractive force between the pair particles exceeds a contribution of their relative kinetic energy. The other is a group of particle pairs characterized as pair particles interacting in a specific situation where a contribution of the relative kinetic energy of the pair particles exceeds a contribution of the attractive force between them. Particle pairs belonging to the former group contribute to the magnitude of $\mathcal{P}_{ij}(r)$, and particle pairs belonging to the latter group contribute to the magnitude of $\mathcal{D}_{ij}(r)$. Since the particle pairs contributing to the magnitude of $\mathcal{P}_{ij}(r)$ form physical clusters, particle pairs contributing to the magnitude of $\mathcal{P}_{ij}(r)$ cannot homogeneously be mixed with particle pairs contributing to the magnitude of $\mathcal{D}_{ij}(r)$. In addition, it is possible for physical clusters to be made grow in shapes similar to branches [22].

The formation of physical clusters should be neglected in the gas state of a fluid being at least far from the critical point. This means that $\mathcal{P}_{ij}(r)$ should always remain much smaller in the gas phase of a fluid than $\mathcal{D}_{ij}(r)$. Then, it is possible to make an assumption as

$$\left|\sum_{k=1}^{\mathcal{L}} \rho_k \int_V C^{*}_{ik}(r_{ik})\mathcal{P}_{kj}(r_{kj})\mathrm{d}\mathbf{r}_k + \sum_{k=1}^{\mathcal{L}} \rho_k \int_V C^{+}_{ik}(r_{ik})\mathcal{H}_{kj}(r_{kj})\mathrm{d}\mathbf{r}_k\right| \ll \left|\mathcal{H}_{ij}(r_{ij})\right|. \tag{2.11}$$

Hence, the correlation function $\mathcal{H}_{ij}(r)$ being equal to $\mathcal{D}_{ij}(r) -1$ approximately satisfies an integral equation which has the same form as the Ornstein-Zernike equation and is given as

$$\mathcal{H}_{ij}(r_{ij}) \approx C^{*}_{ij}(r_{ij}) + \sum_{k=1}^{\mathcal{L}} \rho_k \int_V C^{*}_{ik}(r_{ik})\mathcal{H}_{kj}(r_{kj})\mathrm{d}\mathbf{r}_k. \tag{2.12}$$

When the gas phase of a fluid and the liquid phase of the fluid are in equilibrium, Eq. (2.12) is applicable to examining the behavior of this gas phase, and Eq. (2.9) should be applicable to examining the behavior of that liquid phase. In addition, Eq. (2.12) can be an appropriate approximation even for a fluid involving the formation of physical clusters, if the condition $|\mathcal{P}_{ij}(r)/\mathcal{D}_{ij}(r)| \ll 1$ is satisfied for the fluid.

In the case that the contribution of the formation of physical clusters is significant, the pair connectedness $\mathcal{P}_{ij}(r)$ should be estimated. Particle pairs contributing to the magnitude of $\mathcal{P}_{ij}(r)$ are characterized as pair particles interacting in a specific situation where a contribution of an attractive force between the pair particles exceeds a contribution of their relative kinetic energy. Owing to this fact, $\mathcal{P}_{ij}(r)$ might contribute to explaining the transition from the liquid sate of a fluid to its solid state as a phenomenon due to the growth of physical clusters. The growth of physical clusters can be known from the mean size S of physical clusters which can be estimated through the use of $\mathcal{P}_{ij}(r)$. The equilibrium number n_ν of physical clusters consisting of ν particles can be related to the pair connectedness $\mathcal{P}_{ij}$, and according to the formula given by Coniglio and co-workers [12], the relation between n_ν and $\mathcal{P}_{ij}$ is given as

$$\sum_{2\leqslant\nu} \nu(\nu-1)n_\nu = \sum_{i=1}^{\mathcal{L}}\sum_{j=1}^{\mathcal{L}} \rho_i\rho_j \int_V\int_V \mathcal{P}_{ij}(|\mathbf{r}_1^{(i)}-\mathbf{r}_2^{(j)}|)d\mathbf{r}_1^{(i)}d\mathbf{r}_2^{(j)}. \tag{2.13}$$

If the probability $p(i)$ that an i particle exists in a cluster is independent of ν, then the factor $\Sigma_\nu \nu n_\nu$ included in Eq. (2.13) can be related to the density ρ_i of the i particles in the volume V as $\rho_i = [p(i)/V]\Sigma_\nu \nu n_\nu$. If $\Sigma_{i=1}^{\mathcal{L}} p(i)=1$ is considered, the sum $\Sigma_\nu \nu n_\nu$ is estimated as

$$\sum_\nu \nu n_\nu = V\sum_{i=1}^{\mathcal{L}} \rho_i. \tag{2.14}$$

Since the mean physical cluster size S is given as $S = (\Sigma_\nu \nu^2 n_\nu)/(\Sigma_\nu \nu n_\nu)$, the substitution of Eqs. (2.13) and (2.14) into this formula results in

$$S = 1 + \left(\sum_{k=1}^{\mathcal{L}} \rho_k\right)^{-1} \sum_{i=1}^{\mathcal{L}}\sum_{j=1}^{\mathcal{L}} \rho_i\rho_j \int_V \mathcal{P}_{ij}(r)d\mathbf{r}. \tag{2.15}$$

If the percolation of physical clusters does not occur in macroscopic V found in a fluid system, S which is estimated for the fluid system by Eq. (2.15) should be sufficiently independent of V, and the limit $V \to \infty$ does not influence S. Then, the limit $V \to \infty$ allows Eq. (2.15) to result in $[(S-1)/V]\Sigma_{k=1}^{\mathcal{L}}\rho_k = 0$ and $(1/V)\int_V \mathcal{P}_{ij}(r)d\mathbf{r} = 0$. This fact allows Eq. (2.3) to result in the normalization condition which is given in the limit $V \to \infty$ as $(1/V)\int_V \mathcal{D}_{ij}(r)\mathrm{d}\mathbf{r} = 1$. If the percolation of physical clusters occurs in macroscopic V found in a fluid system, S which is estimated for the fluid system by Eq. (2.15) should be dependent on V. Then, the magnitude of $[(S-1)/V]\Sigma_{k=1}^{\mathcal{L}}\rho_k$ can have a finite value being different from zero. If a state of the fluid is in the immediate vicinity of the liquid-solid transition point where the relation $0 < \rho_i^{sd} - \rho_i^{lq} \ll 1$ (ρ_i^{sd} denotes ρ_i in a solid state, and ρ_i^{lq} denotes ρ_i in a liquid state which can be transformed into the solid state) is satisfied, the dependence of S on V might be estimated as $S/V \approx \Sigma_{i=1}^{\mathcal{L}}\rho_i^{sd}$. Then, Eq. (2.15) should result in $(1/V)\Sigma_{i=1}^{\mathcal{L}}\Sigma_{j=1}^{\mathcal{L}}\rho_i\rho_j\int_V \mathcal{P}_{ij}(r)d\mathbf{r} \approx \Sigma_{i=1}^{\mathcal{L}}\rho_i^{sd}\Sigma_{k=1}^{\mathcal{L}}\rho_k$ in the limit $V \to \infty$. This situation allows Eq. (2.3) to result in $(1/V)\int_V \mathcal{D}_{ij}(r)\mathrm{d}\mathbf{r} \approx 0$. Moreover, the state specified by $(1/V)\int_V \mathcal{D}_{ij}(r)\mathrm{d}\mathbf{r} \approx 0$ should extremely lack particle pairs characterized as pair particles interacting in a specific situation where a contribution of the relative kinetic energy of the pair particles exceeds a contribution of an attractive force between them. This fact means that the fluid might lose a feature found as liquid. Thus, the growth of physical clusters can aid the transition from the liquid state of a fluid to the solid state through the occurrence of the percolation of physical clusters in macroscopic V.

III. APPROXIMATE FEATURES OF CORRELATION FUNCTIONS

A. Approximate expressions of $\mathcal{P}_{ij}$ and $\mathcal{D}_{ij}$

The characterization of $\mathcal{P}_{ij}(r)$ due to a pair potential can be performed through an aid of the Percus-Yevick (PY) approximation. Simultaneously, the characterization of $\mathcal{D}_{ij}(r)$ due to a pair potential can be performed. Then, the PY approximation results in the approximate relation between $\mathcal{P}_{ij}(r)$ and $C^{+}_{ij}(r)$ [12] within the range where the contribution of $u_{ij}(r)$ to i and j particles is not neglected, and also it results in the approximate relation between $\mathcal{D}_{ij}(r)$ and $C^{*}_{ij}(r)$ within the range.

The pair correlation function $g^{\mathrm{PY}}_{ij}(r)$ due to the PY approximation is expressed as $g^{\mathrm{PY}}_{ij}(r)e^{\beta u_{ij}}=1+N_{ij}(r)$. If the relations $e^{-\beta u_{ij}(r)}=f^{+}_{ij}(r)+f^{*}_{ij}(r)+1$ and $N_{ij}(r)=N^{+}_{ij}(r)+N^{*}_{ij}(r)$ are considered, the PY approximation is rewritten as

$$g^{\mathrm{PY}}_{ij}(r) = f^{+}_{ij}(r)[1 + N^{+}_{ij}(r) + N^{*}_{ij}(r)] + [f^{*}_{ij}(r) + 1]N^{+}_{ij}(r) + [f^{*}_{ij}(r) + 1][1 + N^{*}_{ij}(r)], \tag{3.1}$$

where $N^{*}_{ij}(r)$ is all nodal diagrams which do not include any paths of all f^{+} bonds between i and j. The right-hand side of Eq. (3.1) should be the sum of the terms contributing to $\mathcal{P}_{ij}(r)$ and the terms contributing to $\mathcal{D}_{ij}(r)$ owing to Eq. (2.1). Considering this fact allows Eq. (3.1) to be divided into two formulas. Owing to $\mathcal{P}_{ij}(r)=C^{+}_{ij}(r)+N^{+}_{ij}(r)$, one of the two formulas is

$$\mathcal{P}_{ij}(r) = f^{+}_{ij}(r)g^{\mathrm{PY}}_{ij}(r)e^{\beta u_{ij}(r)} + [f^{*}_{ij}(r) + 1][\mathcal{P}_{ij}(r) - C^{+}_{ij}(r)], \tag{3.2a}$$

and owing to $1+N^{*}_{ij}(r)=g^{\mathrm{PY}}_{ij}(r)e^{\beta u_{ij}}-N^{+}_{ij}(r)$, the other is

$$\mathcal{D}_{ij}(r) = [f^{*}_{ij}(r) + 1][g^{\mathrm{PY}}_{ij}(r) - c^{\mathrm{PY}}_{ij}(r) - \mathcal{P}_{ij}(r) + C^{+}_{ij}(r)], \tag{3.2b}$$

where $c^{\mathrm{PY}}_{ij}(r)$ is the direct correlation function due to the PY approximation and is given as $c^{\mathrm{PY}}_{ij}(r)/(1-e^{\beta u_{ij}(r)})=g^{\mathrm{PY}}_{ij}(r)$. In addition, Eqs. (3.2a) and (3.2b) correspond to formulas having specific forms which can be derived from general forms given by Stell [16] and Chiew and co-workers [18].

By considering Eq. (2.4) and the relations expressed by Eq. (2.5), Eqs. (3.2a) can be rewritten as

$$\mathcal{P}_{ij}(r) + \frac{2\Gamma(3/2,-\beta u_{ij}(r))}{\pi^{1/2}e^{\beta u_{ij}(r)} - 2\Gamma(3/2,-\beta u_{ij}(r))}C^{+}_{ij}(r) = \frac{2\{\Gamma(3/2) - \Gamma(3/2,-\beta u_{ij}(r))\}e^{\beta u_{ij}(r)}}{\pi^{1/2}e^{\beta u_{ij}(r)} - 2\Gamma(3/2,-\beta u_{ij}(r))}\frac{c^{\mathrm{PY}}_{ij}(r)}{(1 - e^{\beta u_{ij}(r)})}. \tag{3.3a}$$

Similarly, Eq. (3.2b) can be rewritten as

$$\mathcal{D}_{ij}(r) = \frac{2\Gamma(3/2,-\beta u_{ij}(r))}{2\Gamma(3/2,-\beta u_{ij}(r)) - \pi^{1/2}e^{\beta u_{ij}(r)}}C^{*}_{ij}(r), \tag{3.3b}$$

although the relations expressed by Eqs. (2.1) and (2.8) have to be considered to obtain Eq. (3.3b). Equations (3.3a) and (3.3b) enable $\mathcal{P}_{ij}(r)$ and $\mathcal{D}_{ij}(r)$ to be characterized by a pair potential, if $c^{\mathrm{PY}}_{ij}(r)$, $C^{+}_{ij}(r)$, and $C^{*}_{ij}(r)$ are given. Moreover, Eq. (3.3a) can be used as a closure scheme for Eq. (2.6), if $c^{\mathrm{PY}}_{ij}(r)$ is given. If $\mathcal{P}_{ij}(r)$ is estimated with the use of Eq. (2.6), $\mathcal{H}_{ij}(r)$ can be obtained from solving Eq. (2.9) with the use of Eq. (3.3b). Moreover, Eqs. (3.3a) and (3.3b) suggest that separating $\mathcal{P}_{ij}(r)$ from $g_{ij}(r)$ allows a pair potential characterizing $\mathcal{P}_{ij}(r)$ to be made different from a pair potential characterizing $\mathcal{D}_{ij}(r)$. Even if a pair potential controlling the behavior of pair particles which interact in a situation where a contribution of an attractive force between them exceeds a contribution of their relative kinetic energy is different from a pair potential controlling the behavior of pair particles which interact in a situation where a contribution of their relative kinetic energy exceeds a contribution of the attractive force between them, the use of Eqs. (3.3a) and (3.3b) enables $\mathcal{P}_{ij}(r)$ and $\mathcal{D}_{ij}(r)$ to be estimated.

B. Behavior of C^{+}_{ij} and behavior of C^{*}_{ij}

The direct correlation function $c_{ij}(r)$ is the contribution of all non-nodal diagrams consisting of paths of f bonds between the two root points. Similarly, $C^{+}_{ij}(r)$ is the contribution of all non-nodal diagrams having at least one path of all f^{+} bonds between the two root points, and $C^{*}_{ij}(r)$ is the contribution of non-nodal diagrams which do not include paths of all f^{+} bonds between the two root points. The similarity among these diagram structures suggests that both the behavior of $C^{+}_{ij}(r)$ and the behavior of $C^{*}_{ij}(r)$ should be similar to the behavior of $c_{ij}(r)$. According to the mean spherical approximation (MSA) [23], the direct correlation function $c_{ij}(r)$ is given as the sum of the short-ranged contribution expressed as $c^{0}_{ij}(r)$ and the long-ranged contribution given as $-\beta u_{ij}(r)$, and the MSA shows that $c_{ij}(r)$ behaves as $c_{ij}(r)/[-\beta u_{ij}(r)]=1$ and $c^{0}_{ij}(r)=0$ outside the range of the hard-core potential. Thus, the similarity between $c_{ij}(r)$ and $C^{+}_{ij}(r)$ suggests that the behavior of $C^{+}_{ij}(r)$ should is given as the sum of the short-ranged contribution expressed as $C^{0+}_{ij}(r)$ and the long-ranged contribution to $C^{+}_{ij}(r)$. Moreover, the similarity between $c_{ij}(r)$ and $C^{*}_{ij}(r)$ suggests that the behavior of $C^{*}_{ij}(r)$ should is given as the sum of the short-ranged contribution expressed as $C^{0*}_{ij}(r)$ and the long-ranged contribution to $C^{*}_{ij}(r)$.

A long-ranged contribution to $C^{+}_{ij}(r)$ is obtained from Eq. (3.3a) by considering an assumption which is made as $\mathcal{P}_{ij}(r)\sim[-\beta u_{ij}(r)]^{\nu}$ and $1\leqslant\nu$ for $1\ll r/\sigma_{ij}$. Here, σ_{ij} is given as $\sigma_{ij}=\frac{1}{2}(\sigma_i+\sigma_j)$ for the diameter σ_i of the hard core of an i particle and the diameter σ_j of the hard core of a j particle. Since at least the condition $\mathcal{P}_{ij}(r)/[g_{ij}(r)-1]\leqslant 1$ is always satisfied, $\mathcal{P}_{ij}(r)$ for $1\ll r/\sigma_{ij}$ should satisfy $[g_{ij}(r)-1]/[-\beta u_{ij}(r)]\geqslant\mathcal{P}_{ij}(r)/[-\beta u_{ij}(r)]$. The MSA gives $c^{\mathrm{PY}}_{ij}(r)/[-\beta u_{ij}(r)]=1$ for $1\ll r/\sigma_{ij}$. By considering this fact, the relation $g_{ij}^{\mathrm{PY}}(r)=c_{ij}^{\mathrm{PY}}(r)/\{1-\exp[\beta u_{ij}(r)]\}$ due to the PY approximation results in $\lim_{r\to\infty}[g_{ij}(r)-1]/[-\beta u_{ij}(r)]=1/2$ owing to a general assumption $\lim_{r\to\infty}u_{ij}(r)=0$. This result suggests $1/2 \geqslant \mathcal{P}_{ij}(r)/[-\beta u_{ij}(r)]$ for $1 \ll r/\sigma_{ij}$, and the behavior of $\mathcal{P}_{ij}(r)$ for $1 \ll r/\sigma_{ij}$ is expressed as $\mathcal{P}_{ij}(r) \sim [-\beta u_{ij}(r)]^{\nu}$ and $1 \leqslant \nu$. Owing to this behavior of $\mathcal{P}_{ij}(r)$, a long-ranged contribution to $C_{ij}^{+}(r)$ is found from Eq. (3.3a) as $C_{ij}^{+}(r) \approx 4/(3\sqrt{\pi})[-\beta u_{ij}(r)]^{3/2}$ [14]. Therefore, this result and analogy with the MSA should allow the behavior of $C_{ij}^{+}(r)$ to be approximately expressed as

$$C_{ij}^{+}(r) = C_{ij}^{0+}(r) + \frac{4}{3\sqrt{\pi}}[-\beta u_{ij}(r)]^{3/2} \quad \text{for} \quad \beta u_{ij}(r) < 0 \tag{3.4}$$

and

$$C_{ij}^{0+}(r) = 0, \quad \text{for} \quad r > \sigma_{ij}. \tag{3.5}$$

Then, the expression of $C_{ij}^{+}(r)$ should enable Eq. (2.6) to be readily solved.

On the other hand, Eq. (2.1) and the relation $g_{ij}^{\mathrm{PY}}(r)=c_{ij}^{\mathrm{PY}}(r)/\{1-\exp[\beta u_{ij}(r)]\}$ result in $\mathcal{D}_{ij}(r)-1 \approx -(1/2)\beta u_{ij}(r)$ for $1 \ll r/\sigma_{ij}$ owing to the MSA and the behavior of $\mathcal{P}_{ij}(r)$. The behavior of $\mathcal{D}_{ij}(r)-1$ allows Eq. (3.3b) to lead to $C_{ij}^{*}(r) \approx -\beta u_{ij}(r)$ for $1 \ll r/\sigma_{ij}$. Therefore, this result and analogy with the MSA allow the behavior of $C_{ij}^{*}(r)$ to be approximately expressed as

$$C_{ij}^{*}(r) = C_{ij}^{0*}(r) - \beta u_{ij}(r) \quad \text{for} \quad \beta u_{ij}(r) < 0 \tag{3.6}$$

and

$$C_{ij}^{0*}(r) = 0, \quad \text{for} \quad r > \sigma_{ij}. \tag{3.7}$$

Moreover, Eqs. (3.4)–(3.7) are consistent with the MSA according to Eq. (2.8).

IV. CHARACTERIZATION OF CORRELATION FUNCTIONS

A. Recursive solutions of integral equations

According to the MSA, the direct correlation function $c_{ij}(r)$ can be effective within the range where the magnitude of $u_{ij}(r)$ cannot be neglected, and it decays to zero as rapidly as $-\beta u_{ij}(r)$, which expresses a microscopic feature. The correlation function $g_{ij}(r)-1$ can decay to zero much more slowly than $c_{ij}(r)$ [1,2]. Thus, the behavior of $g_{ij}(r)-1$ is different from the behavior of $c_{ij}(r)$, which has a tendency to maintain the microscopic feature. This fact can be suggested even by a solution which is obtained by solving the Ornstein-Zernike equation recursively, and the solution is given as

$$\begin{aligned} g_{ij} - 1 = c_{ij} &+ \sum_{k_1=1}^{\mathcal{L}} \rho_{k_1} \int_V c_{ik_1} c_{k_1 j} \mathrm{d}\mathbf{r}_3^{(k_1)} \\ &+ \sum_{k_1=1}^{\mathcal{L}} \sum_{k_2=1}^{\mathcal{L}} \rho_{k_1}\rho_{k_2} \int_V \int_V c_{ik_1} c_{k_1 k_2} c_{k_2 j} \mathrm{d}\mathbf{r}_3^{(k_1)} \mathrm{d}\mathbf{r}_4^{(k_2)} + \cdots . \end{aligned} \tag{4.1}$$

Particles $(k_1, k_2, \ldots)$ distributing around an i particle and a j particle cannot always be positively contribute to the probability that the i particle exists away from the j particle at the distance r. In the case of Eq. (4.1), every convolution integral must not always be positive for the reason that $c_{ij}(r)$ are negative for at least $0 < r/\sigma_{ij} \leqslant 1$ owing to $g_{ij}(r)-1 \approx -1$ $(0 < r/\sigma_{ij} \leqslant 1)$. This fact means that every convolution integral in Eq. (4.1) cannot always positively contribute to the magnitude of $g_{ij}(r)-1$. The magnitude of $g_{ij}(r)-1$ at large r where $c_{ij}(r) \approx 0$ can, however, remain a finite value which is not zero, in the case that convolution integrals which can positively contribute to the magnitude of $g_{ij}(r)-1$ are dominant in Eq. (4.1).

In a way being similar to that of solving the Ornstein-Zernike equation, solving Eq. (2.9) for $\mathcal{H}_{ij}$ recursively results in

$$\begin{aligned} \mathcal{H}_{ij} = C_{ij}^{*} &+ \sum_{k_1=1}^{\mathcal{L}} \rho_{k_1} \int_V c_{ik_1} C_{k_1 j}^{*} \mathrm{d}\mathbf{r}_3^{(k_1)} + \sum_{k_1=1}^{\mathcal{L}} \sum_{k_2=1}^{\mathcal{L}} \rho_{k_1}\rho_{k_2} \int_V \int_V c_{ik_1} c_{k_1 k_2} C_{k_2 j}^{*} \mathrm{d}\mathbf{r}_3^{(k_1)} \mathrm{d}\mathbf{r}_4^{(k_2)} + \sum_{k_1=1}^{\mathcal{L}} \rho_{k_1} \int C_{ik_1}^{*} \mathcal{P}_{k_1 j} \mathrm{d}\mathbf{r}_3^{(k_1)} \\ &+ \sum_{k_1=1}^{\mathcal{L}} \sum_{k_2=1}^{\mathcal{L}} \rho_{k_1}\rho_{k_2} \int_V \int_V c_{ik_1} C_{k_1 k_2}^{*} \mathcal{P}_{k_2 j} \mathrm{d}\mathbf{r}_3^{(k_1)} \mathrm{d}\mathbf{r}_4^{(k_2)} + \sum_{k_1=1}^{\mathcal{L}} \sum_{k_2=1}^{\mathcal{L}} \sum_{k_3=1}^{\mathcal{L}} \rho_{k_1}\rho_{k_2}\rho_{k_3} \int_V \int_V \int_V c_{ik_1} c_{k_1 k_2} C_{k_2 k_3}^{*} \mathcal{P}_{k_3 j} \mathrm{d}\mathbf{r}_3^{(k_1)} \mathrm{d}\mathbf{r}_4^{(k_2)} \mathbf{r}_5^{(k_3)} + \cdots . \end{aligned} \tag{4.2}$$

In the case of Eq. (4.2) also, every convolution integral must not always be positive for the reason that $C_{ij}^{*}(r)$ and $c_{ij}(r)$ are negative for at least $0 < r/\sigma_{ij} \leqslant 1$ owing to $\mathcal{H}_{ij}(r) \approx -1$ $(0 < r/\sigma_{ij} \leqslant 1)$ and $g_{ij}(r)-1 \approx -1$ $(0 < r/\sigma_{ij} \leqslant 1)$. This fact means that every convolution integral in Eq. (4.2) cannot always positively contribute to the magnitude of $\mathcal{H}_{ij}(r)$. However, it is possible that the magnitude of $\mathcal{H}_{ij}(r)$ at large r where $C_{ij}^{*}(r) \approx 0$ remains a finite value which is not zero, in the case that convolution integrals which can positively contribute to the magnitude of $\mathcal{H}_{ij}(r)$ are dominant in Eq. (4.2). Even if $C_{ij}^{*}(r)$, according to Eq. (3.6), decays to zero as rapidly as $-\beta u_{ij}(r)$, which expresses a microscopic feature, $\mathcal{H}_{ij}(r)$ might still have a finite value which is not zero in the specific situation.

Moreover, Eq. (2.6) can be solved recursively for $\mathcal{P}_{ij}$ to give as

$$\mathcal{P}_{ij} = C^+_{ij} + \sum_{k_1=1}^{\mathcal{L}} \rho_{k_1}\int_V C^+_{ik_1}C^+_{k_1 j}\mathrm{d}\mathbf{r}_3^{(k_1)} + \sum_{k_1=1}^{\mathcal{L}}\sum_{k_2=1}^{\mathcal{L}}\rho_{k_1}\rho_{k_2}\int_V\int_V C^+_{ik_1}C^+_{k_1k_2}C^+_{k_2j}\mathrm{d}\mathbf{r}_3^{(k_1)}\mathrm{d}\mathbf{r}_4^{(k_2)} + \cdots . \tag{4.3}$$

This equation means that the probability that both the i and j particles belong to the same physical cluster can enhance via the contribution of other particles $(k_1,k_2,\ldots)$. Even if $C^+_{ij}(r)$, according to Eq. (3.4), decays to zero as rapidly as $[-\beta u_{ij}(r)]^{3/2}$, which expresses a microscopic feature, $\mathcal{P}_{ij}(r)$ can have a finite value which is not zero. The convolution integrals on the right-hand side of Eq. (4.3) are positive for the reason that $C^+_{ij}(r)$ must everywhere be positive owing to $0<\mathcal{P}_{ij}(r)$ $(0<r)$. If the contributions of particles $(k_1,k_2,\ldots)$ distributing around the i particle and the j particle cannot be negligible, it is possible for $\mathcal{P}_{ij}(r)$ to remain not zero even out of the range where $C^+_{ij}(r)\neq 0$. Although the contributions of particles $(k_1,k_2,\ldots)$ distributing around the i particle and the j particle to $\mathcal{P}_{ij}(r)$ seems different from their contributions to $g_{ij}(r)$, according to Eq. (2.1), Eq. (4.1) resulting from the Ornstein-Zernike equation corresponds to the sum of the contribution of Eq. (4.2) and the contribution of Eq. (4.3). The contribution of Eq. (4.3) to $g_{ij}(r)$, which should be considered as the contribution of the formation of physical custers to $g_{ij}(r)$, is hidden in the expression of Eq. (4.1).

B. Expressions given as differential equations

The ranges within which the correlation functions $c_{ij}(r)$, $C^+_{ij}(r)$, and $C^*_{ij}(r)$ are not zero can remain microscopic sizes, according to the perspective of the MSA and the perspectives of the approximations given as Eqs. (3.4) and (3.6). These perspectives allow $\mathcal{P}_{ij}(r)$ and $\mathcal{H}_{ij}(r)$ in the convolution integrals in Eqs. (2.6) and (2.9) to be expressed as Taylor series expansions. One of the Taylor series expansions allows Eqs. (2.6) to be given as

$$\mathcal{P}_{ij}(r) = C^+_{ij}(r) + \sum_{k=1}^{\mathcal{L}}\rho_k\int_V C^+_{ik}(|\mathbf{r}_3^{(k)}|)\mathcal{P}_{kj}(|\mathbf{r}|)\mathrm{d}\mathbf{r}_3^{(k)} + \frac{1}{6}\sum_{k=1}^{\mathcal{L}}\rho_k\int_V C^+_{ik}(|\mathbf{r}_3^{(k)}|)|\mathbf{r}_3^{(k)}|^2\nabla^2\mathcal{P}_{kj}(|\mathbf{r}|)\mathrm{d}\mathbf{r}_3^{(k)} + \frac{1}{16}\sum_{k=1}^{\mathcal{L}}\rho_k\int_V C^+_{ik}(|\mathbf{r}_3^{(k)}|)|\mathbf{r}_3^{(k)}|^4\Delta_r\mathcal{P}_{kj}(|\mathbf{r}|)\mathrm{d}\mathbf{r}_3^{(k)} + \cdots , \tag{4.4}$$

where

$$\Delta_r \equiv -\frac{2}{r^3}\frac{\partial}{\partial r} + \frac{2}{r^2}\frac{\partial^2}{\partial r^2} + \frac{8}{15}\frac{1}{r}\frac{\partial^3}{\partial r^3} + \frac{1}{60}\frac{\partial^4}{\partial r^4}. \tag{4.5}$$

The other of the Taylor series expansions allow Eqs. (2.9) to be given as

$$\begin{aligned}\mathcal{H}_{ij}(r) = {}& C^*_{ij}(r) + \sum_{k=1}^{\mathcal{L}}\rho_k\int_V C^*_{ik}(|\mathbf{r}_3^{(k)}|)\mathcal{P}_{kj}(|\mathbf{r}|)\mathrm{d}\mathbf{r}_3^{(k)} + \frac{1}{6}\sum_{k=1}^{\mathcal{L}}\rho_k\int_V C^*_{ik}(|\mathbf{r}_3^{(k)}|)|\mathbf{r}_3^{(k)}|^2\nabla^2\mathcal{P}_{kj}(|\mathbf{r}|)\mathrm{d}\mathbf{r}_3^{(k)} + \frac{1}{16}\sum_{k=1}^{\mathcal{L}}\rho_k\int_V C^*_{ik}(|\mathbf{r}_3^{(k)}|)\\ &\times|\mathbf{r}_3^{(k)}|^4\Delta_r\mathcal{P}_{kj}(|\mathbf{r}|)\mathrm{d}\mathbf{r}_3^{(k)} + \cdots + \sum_{k=1}^{\mathcal{L}}\rho_k\int_V c_{ik}(|\mathbf{r}_3^{(k)}|)\mathcal{H}_{kj}(|\mathbf{r}|)\mathrm{d}\mathbf{r}_3^{(k)} + \frac{1}{6}\sum_{k=1}^{\mathcal{L}}\rho_k\int_V c_{ik}(|\mathbf{r}_3^{(k)}|)|\mathbf{r}_3^{(k)}|^2\nabla^2\mathcal{H}_{kj}(|\mathbf{r}|)\mathrm{d}\mathbf{r}_3^{(k)}\\ &+ \frac{1}{16}\sum_{k=1}^{\mathcal{L}}\rho_k\int_V c_{ik}(|\mathbf{r}_3^{(k)}|)|\mathbf{r}_3^{(k)}|^4\Delta_r\mathcal{H}_{kj}(|\mathbf{r}|)\mathrm{d}\mathbf{r}_3^{(k)} + \cdots .\end{aligned} \tag{4.6}$$

Even when the distance between an i particle and a j particle is much farther beyond the range where the magnitude of $u_{ij}(r)$ cannot be neglected, if the correlation between the i and j particles can be found, then $\mathcal{P}_{ij}(r_{ij})$ and $\mathcal{H}_{ij}(r_{ij})$ can be estimated from differential equations resulting from Eqs. (4.4) and (4.6). A differential equation resulting from Eq. (4.4) is expressed as

$$\frac{1}{6}\sum_{k=1}^{\mathcal{L}}\rho_k\int_V C^+_{ik}(|\mathbf{r}_3^{(k)}|)|\mathbf{r}_3^{(k)}|^2\mathrm{d}\mathbf{r}_3^{(k)}\nabla^2\mathcal{P}_{kj}(r) - \sum_{k=1}^{\mathcal{L}}\left[\delta_{ik} - \rho_k\int_V C^+_{ik}(|\mathbf{r}_3^{(k)}|)\mathrm{d}\mathbf{r}_3^{(k)}\right]\mathcal{P}_{kj}(r) \approx -C^+_{ij}(r), \tag{4.7}$$

where $C^+_{ij}(r)$ on the right-hand side should be given as $C^+_{ij}(r)=4/(3\sqrt{\pi})[-\beta u_{ij}(r)]^{3/2}$. According to Eq, (4.7), $\mathcal{P}_{ij}(r)$ is generated from $C^+_{ij}(r)$ regarded as a source. Thus, the relation between $\mathcal{P}_{ij}(r)$ and $C^+_{ij}(r)$ in Eq. (4.7) is similar to that in Eq. (4.3) since Eq. (4.3) represents that $\mathcal{P}_{ij}(r)$ is composed of contributions of quantities $C^+_{ik_1}C^+_{ik_2},\ldots,C^+_{k_lj}$ $(l=1,2,\ldots)$. The behavior of $\mathcal{P}_{ij}(r)$ out of the range in which the magnitude of $u_{ij}(r)$ can effectively contribute to the attractive force between an i particle and a j particle expresses a long-ranged feature of $\mathcal{P}_{ij}(r)$ which involves contributions of a number of particles. In the case of Eq. (4.3), the contributions of $C^{0+}_{ik_1},C^{0+}_{ik_2},\ldots,C^{0+}_{k_lj}$ $(l=1,2,\ldots)$ are required to estimate the long-ranged feature of $\mathcal{P}_{ij}(r)$. In the case of Eq. (4.7), it is possible to estimate the long-ranged feature of $\mathcal{P}_{ij}(r)$ without knowing the contribution of $C^{0+}_{ij}(r)$. This is an advantage of Eq. (4.7).

A differential equation resulting from Eq. (4.6) is expressed as

$$\begin{aligned}\frac{1}{6}\sum_{k=1}^{\mathcal{L}}\rho_k\int_V C^*_{ik}(|\mathbf{r}_3^{(k)}|)|\mathbf{r}_3^{(k)}|^2\mathrm{d}\mathbf{r}_3^{(k)}\nabla^2\mathcal{P}_{kj}(r)\\ +\sum_{k=1}^{\mathcal{L}}\rho_k\int_V C^*_{ik}(|\mathbf{r}_3^{(k)}|)\mathrm{d}\mathbf{r}_3^{(k)}\mathcal{P}_{kj}(r)\\ +\frac{1}{6}\sum_{k=1}^{\mathcal{L}}\rho_k\int_V c_{ik}(|\mathbf{r}_3^{(k)}|)|\mathbf{r}_3^{(k)}|^2\mathrm{d}\mathbf{r}_3^{(k)}\nabla^2\mathcal{H}_{kj}(r)\\ -\sum_{k=1}^{\mathcal{L}}\left[\delta_{ik}-\rho_k\int_V c_{ik}(|\mathbf{r}_3^{(k)}|)\mathrm{d}\mathbf{r}_3^{(k)}\right]\mathcal{H}_{kj}(r)\approx -C^*_{ij}(r),\end{aligned} \tag{4.8}$$

where $C^*_{ij}(r)$ on the right-hand side should be given as $C^*_{ij}(r)=-\beta u_{ij}(r)$. If a fluid exists as the gas state without physical clusters, the first term and the second term on the left-hand side of Eq. (4.8) should be completely neglected. If physical clusters contribute to features of a fluid, $\mathcal{P}_{ij}(r)$ should be estimated as a solution of Eq. (4.7). Next, using the solution, $\mathcal{H}_{ij}(r)$ should be estimated as a solution of Eq. (4.8). In the case that the first term and the second term on the left-hand side of Eq. (4.8) can be regarded as more important sources than $C^*_{ij}(r)$, the formation of physical clusters should considerably influences a feature of a fluid.

V. SPECIFIC BEHAVIOR OF CORRELATION FUCTIONS

A. Features found near the triple point

The behavior of the pressure P at the triple point enables specific features of correlation functions to be revealed. According to the compressibility equation, the relations given by Eq. (2.1) and (A4) allow the pressure P of a single component fluid to be expressed as

$$\left[\beta\left(\frac{\partial P}{\partial\rho}\right)_{V,T}\right]^{-1}=\widetilde{\mathcal{P}}(0)+\widetilde{\mathcal{H}}(0)+1. \tag{5.1}$$

In addition, suffixes added to quantities such as $\mathcal{P}_{ij}(r)$ and $\mathcal{H}_{ij}(r)$ are omitted owing to considering a single-component fluid in this section. If $\widetilde{\mathcal{P}}(0)$ being found from Eq. (A2) and $\widetilde{\mathcal{H}}(0)$ being found from Eq. (A3) are substituted into Eq. (5.1), Eq. (5.1) is rewritten as

$$\frac{1}{\beta}\left(\frac{\partial\rho}{\partial P}\right)_{V,T}=\frac{\widetilde{C}^+(0)}{1-\widetilde{C}^+(0)}+\frac{\widetilde{C}^*(0)+\widetilde{C}^*(0)\widetilde{\mathcal{P}}(0)}{1-\widetilde{C}^+(0)-\widetilde{C}^*(0)}+1. \tag{5.2}$$

According to Eq. (2.15), the mean physical cluster size S is given as $S=1+\widetilde{\mathcal{P}}(0)$, in which the relation $0<\widetilde{\mathcal{P}}(0)$ is always satisfied. If a relation given by Eq. (A2) is considered, it is expressed as $S=1/[1-\widetilde{C}^+(0)]$. Since the relation $1\leqslant S$ is always satisfied, the value of $\widetilde{C}^+(0)$ must satisfy the relation given as

$$0\leqslant\widetilde{C}^+(0)\leqslant 1. \tag{5.3}$$

If the relation $(\partial\rho/\partial P)_{V,T}\approx 0$ is generally satisfied at the triple point, Eq. (5.2) and the relation $\widetilde{\mathcal{P}}(0)=1/(1-\widetilde{C}^+(0))-1$ require that the relation $1\ll-\widetilde{C}^*(0)$ be satisfied at the triple point owing to the relation given by Eq. (5.3).

The relation $(\partial\rho/\partial P)_{V,T}\approx 0$ makes Eq. (5.1) require $\langle(N/V)^2\rangle-\langle N/V\rangle^2\approx 0$, since the density fluctuations are expressed as $\langle(N/V)^2\rangle-\langle N/V\rangle^2=(\langle N/V\rangle/V)[\mathcal{P}(0)+\widetilde{\mathcal{H}}(0)+1]$ if the number of particles in volume V is expressed as N. The relation $(\partial\rho/\partial P)_{V,T}\approx 0$ shows that the density fluctuations are prevented at the triple point. This fact suggests the occurrence of two phenomena. One of the two phenomena represents that particular particle pairs contributing to the magnitude of $\mathcal{D}(r)$ are confined among branches of physical clusters. The other represents that the percolation of physical clusters occurs at least near the triple point. If the percolation of physical clusters occurs near the triple point, the relation $1\ll\widetilde{\mathcal{P}}(0)$ should be satisfied according to Eq. (2.15). Then, the relation $1\ll\widetilde{\mathcal{P}}(0)$ requires $1\ll-\widetilde{\mathcal{H}}(0)$ at the triple point. The relation $1\ll-\widetilde{\mathcal{H}}(0)$ is equivalent to $(1/V)\int_V\mathcal{D}(r)\mathrm{d}\mathbf{r}\approx 0$ owing to $\mathcal{D}(r)=\mathcal{H}(r)+1$, and decreasing the magnitude of $\mathcal{D}(r)$ toward zero means that the magnitude of $-\widetilde{\mathcal{H}}(0)$ is made diverge. Each particle pair which contributes to the magnitude of $\mathcal{D}(r)$ corresponds to a specific particle pair characterized as pair particles interacting in a situation where a contribution of the relative kinetic energy of the pair particles exceeds a contribution of the attractive force acting between them, and such particle pairs should contribute to maintaining the density fluctuations. This fact suggests the assumption that particle pairs which contribute to the magnitude of $\mathcal{D}(r)$ are confined among branches of physical clusters formed by particle pairs which contribute to the magnitude of $\mathcal{P}(r)$. The more densely branches of physical clusters are developed, the more frequently particle pairs which contribute to the magnitude of $\mathcal{D}(r)$ and which are confined among the branches of physical clusters can be exchanged for particle pairs which contribute to the magnitude of $\mathcal{P}(r)$. This effect allows for decreasing the magnitude of $D(r)$ and allows $1\ll-\widetilde{\mathcal{H}}(0)$ to be caused. This fact, which results in $(1/V)\int_V\mathcal{D}(r)\mathrm{d}\mathbf{r}\approx 0$, allows a fluid to be transformed from the liquid state into the solid state. It can become consistent with the behavior which is found from the discussion of Sec. II B since the behavior is expressed near a liquid-solid transition point as $(1/V)\int_V\mathcal{D}(r)\mathrm{d}\mathbf{r}\approx 0$. If the percolation of physical clusters does not occur even at the triple point, the magnitude of $\widetilde{\mathcal{P}}(0)$ should not be large according to Eq. (2.15). Then, the magnitude of $-\widetilde{\mathcal{H}}(0)$ also should not be large, since the relation $(\partial\rho/\partial P)_{V,T}\approx 0$ requires $\widetilde{\mathcal{H}}(0)\approx-1-\widetilde{\mathcal{P}}(0)$. This fact means that the magnitude of $\mathcal{D}(r)$ can decrease not toward zero as the density ρ increases toward a specific value being given at the triple point. It is somewhat unreasonable to allow a fluid to be transformed from the liquid state into the solid state under the condition that the magnitude of $\mathcal{D}(r)$ does not become sufficiently small. Therefore, the condition

$1 \ll \tilde{\mathcal{P}}(0)$ corresponding to the occurrence of the percolation should be satisfied near the triple point. Ultimately, the assumption of $1 \ll \tilde{\mathcal{P}}(0)$ means that branches of physical clusters which develop densely over the whole of V can confine particle pairs contributing to the magnitude of $\mathcal{D}(r)$ among them, and the assumption of $1 \ll \tilde{\mathcal{P}}(0)$ near the triple point is effective for explaining the reason that the density fluctuations decease toward vanishing as ρ increases toward a specific value being given at the triple point.

B. Features found near the critical point and far from that

According to the magnitude of $\beta^{-1}(\partial\rho/\partial P)_{V,T}$ estimated by differentiating the equation of state of the hard-sphere fluid [21] with respect to ρ, the density fluctuations in a hard-sphere fluid system are simply reduced as the density of hard spheres increases. However, the presence of an attractive force acting between particles enables the density fluctuations to become extremely large as ρ increases toward the critical point. If a contribution of the hard-core potential to maintaining the average distance between particles in a fluid system is less important than a contribution of an attractive force to minimizing the average distance, the attractive force acting between particles can contribute to developing the density fluctuations. If particle pairs which correspond to particle pairs contributing to the magnitude of $\mathcal{D}(r)$ start to be confined among branches of physical clusters, then the occurrence of dense regions due to confining the particle pairs among the branches can considerably develop the density fluctuations since the occurrence of such dense regions in the fluid system makes the other regions rare [22].

The growth of physical clusters, which is important for confining particle pairs among their branches, cannot, however, simply develop the density fluctuations. The percolation of physical clusters cannot result in developing the density fluctuations. Although the percolation of physical clusters occurs at the condition given as $1-\tilde{C}^{+}(0)=0$, the relation $\tilde{\mathcal{P}}(0)=1/[1-\tilde{C}^{+}(0)]-1$ prevents the magnitude of $\beta^{-1}(\partial\rho/\partial P)_{V,T}$ given as Eq. (5.2) from diverging to the infinity at the condition $1-\tilde{C}^{+}(0)=0$. This fact and Eq. (5.1) suggest that the occurrence of the extremely large density fluctuations must be interpreted through the behavior of $\tilde{\mathcal{H}}(0)$. The magnitude of $\tilde{\mathcal{H}}(0)$ is given as the contribution of particle pairs characterized as pair particles interacting in a specific situation where a contribution of the relative kinetic energy of the pair particles exceeds a contribution of the attractive force between them. If particles belonging to the group of particle pairs which contribute to the magnitude of $\tilde{\mathcal{H}}(0)$ are confined among branches of physical clusters, the movements of the particles belonging to the group are restricted. The movement restriction of the particles should enhance maximum values of $\mathcal{D}(r)$, and then, an increase in maximum values of $\mathcal{H}(r)$ defined as $\mathcal{H}(r) \equiv \mathcal{D}(r)-1$ should increase the magnitude of $\tilde{\mathcal{H}}(0)$. On the other hand, the probability that particle pairs contributing to the magnitude of $\mathcal{D}(r)$ are exchanged for particle pairs contributing to the magnitude of $\mathcal{P}(r)$ should be raised when the particle pairs contributing to the magnitude of $\mathcal{D}(r)$ are confined among the branches of physical clusters. Raising this probability should contribute to a decrease in the magnitude of $\mathcal{D}(r)$. The effect of raising the probability should, however, be less dominant than the effect of the movement restriction if branches of physical clusters are not dense. Then, the occurrence of confining particles among branches of the physical clusters can efficiently enhance the magnitude of $\tilde{\mathcal{H}}(0)$. This means that the critical point should correspond to a specific situation where branches of physical clusters do not become dense yet even if large physical clusters beyond semimicro sizes might be included in a fluid. Owing to such a specific situation, the occurrence of confining particles among branches of the physical clusters allows the magnitude of $\tilde{\mathcal{H}}(0)$, which should behave as $\tilde{\mathcal{H}}(0) \approx 0$ at $\rho \approx 0$, to increase toward an extremely large positive value as ρ increases toward the critical point.

The behavior of $\tilde{\mathcal{H}}(0)$ must be changed when the value of ρ exceeds that at the critical point. An increase in the value of ρ allows the contribution of attractive forces to the growth of physical clusters to become more effective since the increase decreases the average distance between particles. The development of branches of physical clusters should raise the probability that particle pairs contributing to the magnitude of $\mathcal{D}(r)$ are exchanged for particle pairs contributing to the magnitude of $\mathcal{P}(r)$. These effects should decrease the magnitude of $\mathcal{D}(r)$ as ρ increases. This suggests that after $\tilde{\mathcal{H}}(0)$ reaches the maximum, $\tilde{\mathcal{H}}(0)$ must decrease as ρ increases. If an increase in the value of ρ allows a condition of a fluid to reach the triple point, then the magnitude of $\tilde{\mathcal{H}}(0)$ must reach an extremely large negative value as discussed in Sec. V A.

For a fluid consisting of particles interacting without attractive forces, the sum $\tilde{C}^{+}(0)+\tilde{C}^{*}(0)$ being equal to $\tilde{c}(0)$ always behaves as a negative quantity according to the magnitude of $\beta^{-1}(\partial\rho/\partial P)_{V,T}$ estimated by differentiating the equation of state of the hard-sphere fluid [21] with respect to ρ, although the magnitude of $\tilde{C}^{+}(0)+\tilde{C}^{*}(0)$ approaches zero as the density of hard spheres approaches zero. As the density of hard spheres increases, the negative value of $\tilde{C}^{+}(0)+\tilde{C}^{*}(0)$ decreases simply. If a solution given by Cummings and Smith [24] is used, it is, however, shown that a contribution of attractive forces among particles allows the magnitude of $\tilde{C}^{+}(0)+\tilde{C}^{*}(0)$ to increase toward the maximum as ρ increases. After reaching the maximum, the magnitude of $\tilde{C}^{+}(0)+\tilde{C}^{*}(0)$ decreases toward a large negative value as ρ increases. This fact means that the presence of an attractive force acting between particles enables the magnitude of $\tilde{C}^{*}(0)$ to reach the maximum at a particular value of ρ, since the magnitude of $\tilde{C}^{+}(0)$ is maintained within the range $0 \leqslant \tilde{C}^{+}(0) \leqslant 1$. Moreover, the aid of confining particular particles among branches of physical clusters should make the maximum value of $\tilde{C}^{+}(0)+\tilde{C}^{*}(0)-1$ approach zero near the critical point. If the relation $0 < \tilde{C}^{+}(0) \leqslant 1$ is expected even near the critical point, then the maximum value of $\tilde{C}^{*}(0)$

reaches a particular value given as $\widetilde{C}^*(0)\approx 1$ at the critical point. Therefore, the magnitude of $\widetilde{C}^*(0)$ should always satisfy the relation $\widetilde{C}^*(0)<1$.

Owing to Eq. (5.1) and a relation due to Eq. (A4), the quantity $\widetilde{C}^+(0)+\widetilde{C}^*(0)-1$ can be related to the pressure P as $\beta(\partial P/\partial\rho)_{V,T}=1-\widetilde{C}^+(0)-\widetilde{C}^*(0)$. If the pressure P which is given for a single component fluid by the pressure equation $\beta P=\rho-(\rho^2/6)\beta\int_V r[\mathrm{d}u(r)/\mathrm{d}r][\mathcal{P}(r)+\mathcal{D}(r)]\mathrm{d}\mathbf{r}$ is differentiated with respect to ρ, considering $\beta(\partial P/\partial\rho)_{V,T}=1-\widetilde{C}^+(0)-\widetilde{C}^*(0)$ allows the pressure to be expressed as

$$\beta P=\rho-\frac{\rho}{2}\widetilde{C}^+(0)+\frac{1}{12}\beta\rho^3\int_V r\frac{\mathrm{d}u(r)}{\mathrm{d}r}\left(\frac{\partial\mathcal{P}(r)}{\partial\rho}\right)_{V,T}\mathrm{d}\mathbf{r}-\frac{\rho}{2}\widetilde{C}^*(0)+\frac{1}{12}\beta\rho^3\int_V r\frac{\mathrm{d}u(r)}{\mathrm{d}r}\left(\frac{\partial\mathcal{D}(r)}{\partial\rho}\right)_{V,T}\mathrm{d}\mathbf{r}.\quad(5.4)$$

If the relation $0<\widetilde{C}^+(0)\ll 1$ is satisfied for a fluid, then it is expected that both the second and third terms on the right-hand side of Eq. (5.4) are negligible owing to the relation $0<\widetilde{\mathcal{P}}(0)\ll 1$ due to $\widetilde{\mathcal{P}}(0)=1/[1-\widetilde{C}^+(0)]-1$. Moreover, the relation, the relation $|[\partial\mathcal{P}(r)/\partial\rho]_{V,T}|\ll 1$ might be expected according to the behavior of the pair connectedness found from the previous work [22]. The fact that the second and third terms on the right-hand side of Eq. (5.4) can be neglected suggests that particles contributing dominantly to the pressure P are those which belong to a group of particle pairs characterized as pair particles interacting in a specific situation where a contribution of the relative kinetic energy of the pair particles exceeds a contribution of the attractive force between them. Moreover, the fact that the pressure at the critical point is given as $P\approx(\rho/2\beta)+(\rho^3/12)\int_V r[\mathrm{d}u(r)/\mathrm{d}r]\times[\partial\mathcal{D}(r)/\partial\rho]_{V,T}\mathrm{d}\mathbf{r}$ owing to Eq. (5.4) persuades the relation $1>-(\beta\rho^2/6)\int_V r[\mathrm{d}u(r)/\mathrm{d}r][\partial\mathcal{D}(r)/\partial\rho]_{V,T}\mathrm{d}\mathbf{r}$ to be found at the critical point. The factor $(\rho^3/12)\int_V r[\mathrm{d}u(r)/\mathrm{d}r]\times[\partial\mathcal{D}(r)/\partial\rho]_{V,T}\mathrm{d}\mathbf{r}$ should, however, have a large negative value in a situation being far from the critical point since $\widetilde{C}^*(0)$ has a large negative value in the situation. Thus, Eq. (5.4) requires the relation $0>\int_V r[\mathrm{d}u(r)/\mathrm{d}r][\partial\mathcal{D}(r)/\partial\rho]\mathrm{d}\mathbf{r}$, although the pressure equation requires the relation $0<\int_V r[\mathrm{d}u(r)/\mathrm{d}r]\mathcal{D}(r)\mathrm{d}\mathbf{r}$. This fact means that a contribution of $\int_V r[\mathrm{d}u(r)/\mathrm{d}r]\mathcal{D}(r)\mathrm{d}\mathbf{r}$ to the pressure decreases at least in a situation being far from the critical point, as ρ increases. Since the factor $\int_V r[\mathrm{d}u(r)/\mathrm{d}r]\mathcal{D}(r)\mathrm{d}\mathbf{r}$ corresponds to the contribution of particle pairs characterized as pair particles interacting in a specific situation where a contribution of the relative kinetic energy of the pair particles exceeds a contribution of the attractive force between them, a decrease in the magnitude of $\int_V r[\mathrm{d}u(r)/\mathrm{d}r]\mathcal{D}(r)\mathrm{d}\mathbf{r}$ due to an increase in the value of ρ is reasonable.

C. Long-ranged features of correlation functions

The use of Eqs. (4.7) and (4.8) allows long-ranged features of the correlation functions $\mathcal{P}(r)$ and $\mathcal{H}(r)$ to be estimated. Their long-ranged features should aid in interpreting a particular feature of a fluid which is caused in a specific situation by the formation of physical clusters. According to Eq. (4.7), a differential equation which $\mathcal{P}(r)$ should satisfy in the region specified by $1\ll r/\sigma$ is given as

$$\nabla^2\mathcal{P}(r)-[1-\widetilde{C}^+(0)]\frac{1}{\zeta^+}\mathcal{P}(r)=-\frac{4}{3\sqrt{\pi}\zeta^+}[-\beta u(r)]^{3/2},\quad(5.5)$$

where

$$\zeta^+\equiv\frac{\rho}{6}\int_V C^+(t)t^2\mathrm{d}\mathbf{t}.\quad(5.6)$$

Equation (5.6) expresses that at least $\widetilde{C}^+(0)<6\zeta^+$ is always satisfied. Equation (5.5) represents a contribution of a microscopic quantity $\beta u(r)$ to $\mathcal{P}(r)$, and Eq. (5.5) shows that a long-ranged feature of $\mathcal{P}(r)$ can be found as the behavior of $\mathcal{P}(r)$ out of the range within which the magnitude of $u(r)$ can effectively generate the attractive force between two particles. This means that the long-ranged feature of $\mathcal{P}(r)$ which is estimated by solving Eq. (5.5) is caused by involving contributions of a number of particles.

If a form of $\beta u(r)$ is assumed as $\beta u(r)=-\phi(r)/r\times[\lim_{r\to\infty}\phi(r)<\infty]$, a solution of Eq. (5.5), which represents the long-ranged feature of $\mathcal{P}(r)$, is given as

$$\mathcal{P}(r)=\frac{1}{3\pi^{3/2}\zeta^+}\int_V\frac{1}{t}\exp\left\{-\frac{1}{(\zeta^+)^{1/2}}[1-\widetilde{C}^+(0)]^{1/2}t\right\}\times\left[\frac{\phi(|\mathbf{r}-\mathbf{t}|)}{|\mathbf{r}-\mathbf{t}|}\right]^{3/2}\mathrm{d}\mathbf{t}\quad(t\equiv|\mathbf{t}|).\quad(5.7)$$

If the value of r is larger than the value of t for which $0<t^{-1}\exp\{-(\zeta^+)^{-1/2}[1-\widetilde{C}^+(0)]^{1/2}t\}\ll 1$ is satisfied, Eq. (5.7) can be rewritten as

$$\mathcal{P}(r)=\frac{1}{3\pi^{3/2}\zeta^+}\frac{1}{r^{3/2}}\int_V\frac{1}{t}\exp\left\{-\frac{1}{(\zeta^+)^{1/2}}[1-\widetilde{C}^+(0)]^{1/2}t\right\}\times[\phi(|\mathbf{r}-\mathbf{t}|)]^{3/2}\times\left[\sum_{n=0}^{\infty}\frac{1}{r^n}\sum_{m=-n}^{n}\frac{(n-m)!}{(n+m)!}P_n^m(\cos\vartheta)\times e^{im\varphi}t^nP_n^m(\cos\vartheta')e^{-im\varphi'}\right]^{3/2}\mathrm{d}\mathbf{t},\quad(5.8)$$

where $P_n^m(\cos\vartheta)$ are the Legendre functions, and the spherical coordinates of $\mathbf{r}$ and $\mathbf{t}$ are expressed as (r,ϑ,φ) and (t,ϑ',φ'), respectively. If $\phi(r)$ is expressed as the Taylor series, which is a power-series expansion of $\phi(r)$ in powers of r, Eq. (5.8) shows that the dependence of $\mathcal{P}(r)$ on r can be dominated at least by the term including $r^{-3/2}$.

According to Eq. (4.8), a differential equation which $\mathcal{H}(r)$ should satisfy in the region specified by $1\ll r/\sigma$ is given as

$$\nabla^2\mathcal{H}(r) - \frac{1}{\zeta}[1 - \tilde{c}(0)]\mathcal{H}(r)$$
$$= \frac{1}{\zeta}\beta u(r) - \frac{1}{\zeta}\left\{\frac{\zeta^*}{\zeta^+}[1 - \tilde{C}^{+}(0)] + \tilde{C}^{*}(0)\right\}\mathcal{P}(r)$$
$$+ \frac{3}{4\sqrt{\pi}}\frac{\zeta^*}{\zeta}[-\beta u(r)]^{3/2}, \qquad (5.9)$$

where

$$\zeta^* \equiv \frac{\rho}{6}\int_V C^*(t)t^2\mathrm{d}\mathbf{t}, \quad \zeta \equiv \frac{\rho}{6}\int_V c(t)t^2\mathrm{d}\mathbf{t}. \qquad (5.10)$$

The magnitudes of ζ^* and ζ subjects the dependence of a solution of Eq. (5.9) on r. The value of $c(t)$ is negative in a specific range $0<t<t_0$ and positive out of the range. Moreover, the value of $C^*(t)$ is negative in a specific range $0<t<t_0'$ and positive out of the range, since the behavior of $C^*(t)$ is similar to that of $c(t)$. Despite this fact, if $4\pi\rho\int_0^{t_0'}C^*(t)\mathrm{d}t+4\pi\rho\int_{t_0'}^{\infty}C^*(t)\mathrm{d}t$ is positive, $4\pi\rho\int_0^{t_0'}C^*(t)t^2\mathrm{d}t+4\pi\rho\int_{t_0'}^{\infty}C^*(t)t^2\mathrm{d}t$ should be positive. Then, the relation $\tilde{C}^*(0)<6\zeta^*$ should be satisfied. Similarly, if $4\pi\rho\int_0^{t_0}c(t)\mathrm{d}t+4\pi\rho\int_{t_0}^{\infty}c(t)\mathrm{d}t$ is positive, $4\pi\rho\int_0^{t_0}c(t)t^2\mathrm{d}t+4\pi\rho\int_{t_0}^{\infty}c(t)t^2\mathrm{d}t$ is positive. Then, the relation $\tilde{c}(0)<6\zeta$ should be satisfied. In addition, the value of $\tilde{c}(0)$ is the maximum at the critical point, and the value of $\tilde{C}^*(0)$ should be the maximum near the critical point. This fact allows for making the assumption that both ζ^* and ζ reach the maximum near the critical point. Owing to the contribution of the power t^2 to the integrals being estimated from Eq. (5.10), it is assumed that $\tilde{C}^*(0)\ll 6\zeta^*$ and $\tilde{c}(0)\ll 6\zeta$ are satisfied near the critical point where the maximum values of $\tilde{C}^*(0)$ and $\tilde{c}(0)$ are given as $\tilde{C}^*(0)\approx 1$ and $\tilde{c}(0)=1$, respectively.

If a form of $\beta u(r)$ is assumed as $\beta u(r)=-\phi(r)/r\times[\lim_{r\to\infty}\phi(r)<\infty]$, a solution of Eq. (5.9), which represents the long-ranged feature of $\mathcal{H}(r)$, is given as

$$\mathcal{H}(r) = \frac{1}{4\pi\zeta}\int_V \frac{1}{t}\exp\left[-\frac{1}{\zeta^{1/2}}[1-\tilde{c}(0)]^{1/2}t\right]$$
$$\times\left\{-\frac{\phi(|\mathbf{r}-\mathbf{t}|)}{|\mathbf{r}-\mathbf{t}|} - \left[\frac{\zeta^*}{\zeta^+}[1-\tilde{C}^{+}(0)] + \tilde{C}^{*}(0)\right]\right.$$
$$\left.\times\mathcal{P}(|\mathbf{r}-\mathbf{t}|) + \frac{3}{4\sqrt{\pi}}\zeta^*\left[\frac{\phi(|\mathbf{r}-\mathbf{t}|)}{|\mathbf{r}-\mathbf{t}|}\right]^{3/2}\right\}\mathrm{d}\mathbf{t} \quad (t\equiv|\mathbf{t}|). \qquad (5.11)$$

Equation (5.11) shows that the dependence of $\mathcal{H}(r)$ on r depends on the magnitude of ζ^*. If the magnitude of ζ^* is sufficiently small, a contribution of $\phi(|\mathbf{r}-\mathbf{t}|)/|\mathbf{r}-\mathbf{t}|$ can dominate the dependence of $\mathcal{H}(r)$ on r, and then its dependence can be expressed as the product of the factor r^{-1} and a particular function given as the Taylor series due to powers of r. If the magnitude of ζ^* is sufficiently large, both a contribution of $\mathcal{P}(|\mathbf{r}-\mathbf{t}|)$ and a contribution of $[\phi(|\mathbf{r}-\mathbf{t}|)/|\mathbf{r}-\mathbf{t}|]^{-3/2}$ can make the dependence of $\mathcal{H}(r)$ on r behave at least as $r^{-3/2}$. This fact means that the dependence of the sum $\mathcal{P}(r)+\mathcal{D}(r)$ on r develops the deviation from the dependence expressed as the product of the factor r^{-1} and a particular function given as the Taylor series due to powers of r, as the magnitude of ζ^* increases. This means that an effect of the physical cluster formation on a specific feature of a fluid is made become apparent when ζ^* is large. Both the factor $\mathcal{P}(|\mathbf{r}-\mathbf{t}|)$ and the factor $[\phi(|\mathbf{r}-\mathbf{t}|)/|\mathbf{r}-\mathbf{t}|]^{-3/2}$ in Eq. (5.11) are directly relevant to the formation of physical clusters, and the terms including these factors should be neglected if the influence of their formation on features of a fluid are negligible. If the dependence of $g(r)$ on r deviates from the dependence expressed as the product of the factor r^{-1} and a particular function which can be given as the Taylor series [2], then it is suggested that its dependence on r can be represented as a specific series including integer powers of r and half integer powers of r. This means that it should be effective to consider the possibility that the dependence of $\mathcal{P}(r)$ on r and the dependence of $\mathcal{H}(r)$ on r are expressed by Eqs. (5.8) and (5.11), respectively. If this possibility is true for a specific gas-liquid critical phenomenon, it is inferred that the formation of physical clusters plays a role for driving the critical phenomenon and for characterizing the fluid as liquid. Then, the possibility should demonstrate the value of separating the Ornstein-Zernike equation into the two integral equations given by Eqs. (2.6) and (2.9).

VI. CONCLUSIONS

A system of two integral equations corresponding to the Ornstein-Zernike equation should make it possible to show the contribution of the physical cluster formation to the pair correlation function and should aid in estimating an effect of the physical cluster formation on a feature of a fluid. Here, each physical cluster is regarded as an ensemble of particles linked each other by every bond which is defined as a bound state in which a contribution of attractive forces between pair particles dominates a contribution of the relative kinetic energy between them. The system of two integral equations makes the pair correlation function represented as the sum of two correlation functions. One of the two correlation functions is the pair connectedness, which contributes to estimating the formation of physical clusters. The other is a correlation function expressing the correlation between particles interacting in a specific situation where a contribution of the relative kinetic energy between pair particles exceeds a contribution of attractive forces between them. Representing the pair correlation function as the sum of the two correlation functions might contribute to explaining phase transitions and critical phenomena due to the formation of physical clusters.

APPENDIX: FOURIER TRANSFORMS OF INTEGRAL EQUATIONS

If each correlation function is expressed as $F_{ij}(r)$ which satisfies $\lim_{r\to 0} rF_{ij}(r)=0$, then a Fourier transform of $F_{ij}(r)$ is given as

$$\begin{aligned}\widetilde{F}_{ij}(k) &\equiv \lim_{V\to\infty}(\rho_i\rho_j)^{1/2}\int_V F_{ij}(r)\exp[i\mathbf{k}\cdot\mathbf{r}]\mathrm{d}\mathbf{r}\\ &= 4\pi(\rho_i\rho_j)^{1/2}\int_0^\infty \cos kr\mathrm{d}r\int_r^\infty t\mathrm{d}tF_{ij}(t)\\ &\quad\times(r\equiv|\mathbf{r}|,\ k\equiv|\mathbf{k}|).\end{aligned}\tag{A1}$$

If V is macroscopic, the integral $\sqrt{\rho_i\rho_j}\int_V F_{ij}(r)e^{i\mathbf{k}\cdot\mathbf{r}}\mathrm{d}\mathbf{r}$ can be expressed as $\widetilde{F_{ij}}(k)$ given by Eq. (A1). According to the expression of Eq. (A1), a Fourier transform of Eq. (2.6) is given as

$$\sum_{k=1}^{\mathcal{L}}[\delta_{ik}-\widetilde{C}^{+}_{ik}(k)]\widetilde{P}_{kj}(k)=\widetilde{C}^{+}_{ij}(k).\tag{A2}$$

Similarly, a Fourier transform of Eq. (2.9) is given as

$$\sum_{k=1}^{\mathcal{L}}[\delta_{ik}-\widetilde{C}^{*}_{ik}(k)-\widetilde{C}^{+}_{ik}(k)]\widetilde{\mathcal{H}}_{kj}(k)=\widetilde{C}^{*}_{ij}(k)+\sum_{k=1}^{\mathcal{L}}\widetilde{C}^{*}_{ik}(k)\widetilde{\mathcal{P}}_{kj}(k).\tag{A3}$$

Moreover, a Fourier transform of the Ornstein-Zernike equation expressed as Eq. (2.7) is given as

$$\sum_{k=1}^{\mathcal{L}}[\delta_{ik}-\tilde{c}_{ik}(k)][\widetilde{\mathcal{P}}_{kj}(k)+\widetilde{\mathcal{H}}_{kj}(k)]=\tilde{c}_{ij}(k),\tag{A4}$$

where, owing to Eq. (2.8),

$$\tilde{c}_{ij}(k)=\widetilde{C}^{+}_{ij}(k)+\widetilde{C}^{*}_{ij}(k).\tag{A5}$$

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