Structures of Fluids

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(Dated: 4 January 2020)

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I. INTRODUCTION

In an ensemble of simple particles exemplifying atoms or molecules, which form a fluid, inhomogenieties can occur, because the particles can interact with each other via attractive forces and repulsive forces. At extremely low temperature, the particles can move even coherently. Certainly, the ensemble cannot be inhomogeneous, if the following two relations are satisfied:

(1) The distribution of particles in a microscopic volume δV located at $\mathbf{r}_a$ cannot differ from the distribution of particles in the microscopic volume δV located at $\mathbf{r}_b$ ($\neq \mathbf{r}_a$).

(2) The distribution of momenta of particles in a microscopic volume δV located at $\mathbf{r}_a$ cannot differ from the distribution of momenta of particles in the microscopic volume δV located at $\mathbf{r}_b$ ($\neq \mathbf{r}_a$).

If factors that prevent the ensemble from becoming homogeneous become apparent, the occurrence of interesting phenomena can be apparent. The factors can affect behaviors of fluids and configurations of particles. One of the factors is the formation of physical clusters.

For an ensemble of particles exemplifying atoms or molecules, the liquid phase coexists with the gas phase at the temperatures between the triple point and the critical point. At the temperatures, the density of particles in the liquid phase is much higher than that in the gas phase, even if the portion in the liquid phase and the other portion in the gas phase are in equilibrium. In necessity, the compressibility in the liquid phase is much smaller than that in the gas phase. Then, it is inevitable to consider a contribution of something that generates the difference between the portion in the liquid phase and the other portion in the gas phase. A contribution of the formation of physical clusters should be considered to allow the liquid phase to be distinguished from the gas phase.

Physical clusters can be formed even in the gas phase if the temperature of a system is near the liquid-vapor critical point. Particles constituting the system interact with each other via attractive forces between them. The system include particles that can freely individually move because the contribution of the relative kinetic energy between particles of each pair exceed the contribution of an attractive force acting between them. The system include also other particles that cannot freely move for each other because the contribution of the attractive force acting between particles of each pair exceed the contribution of the relative kinetic energy between them. The particles that cannot freely move for each other can contribute to the formation of physical clusters.

At least attractive forces between particles enable the particles to be located near each other. Repulsive forces between particles enable the particles to be excluded from each other. The strength of each of attractive forces and that of each of repulsive forces depend on the mean inter-particle distance. The formation of physical clusters depends at least on attractive forces between particles, repulsive forces between them, the mean inter-particle distance, and the degree of movements of particles. Their formation can affect features of a fluid system. If contributions of attractive forces between particles are sufficiently small, the formation of ensembles of particles being located near each other and moving coherently can allow generation of specific excitation states at extremely low temperatures. The formation of ensembles of particles moving coherently changes thermodynamic properties of a quantum fluid system.

For a classical fluid, a basic idea for estimating the formation of physical clusters was given by Hill[1]. A useful method for analyzing the formation of physical clusters via an integral equation was established by Coniglio at al[2]. The method allows the Ornstein-Zernike equation to be split into two integral equations. The method allows the pair correlation function also to be sprit into two correlation functions. One of the two correlation functions is called the pair connectedness. One of the two integral equations is the integral equation for the pair connectedness. The integral equation for the pair connectedness is an equation for analyzing physical clusters and it has enabled many studies on off-lattice percolation of physical clusters to proceed.

The mathematical structure of the integral equation connecting with physical clusters is the same as that of the Ornstein- Zernike equation. Hence, it is necessary to solve the integral equation with a specific closure. The closure was extracted from the Percus-Yevick approximation. The relation between the Percus-Yevick approximation and the mean spherical approximation allowed a simple closure to be obtained. The use of the simple closure allows the contribution of physical clusters to the structure of particle distribution to be revealed. Moreover, the use of the simple closure allows the contribution of physical cluster formation to thermodynamic properties to be simply known. Its use enables structures of physical clusters to to be revealed. The structure of the distribution of galaxies in the universe is known as the structure of physical clusters of galaxies. Then, it is revealed that the structure is fractal. In a specific medium, the distribution of charged particles has a fractal structure. The use of the pair connectedness allows the fractal structure to be revealed.

II. FLUID SYSTEMS INCLUDING PHYSICAL CLUSTERS

A. A Classical Fluid System of N Particles

For a classical fluid system of N particles with volume V, the partition fuction Q_N is defined as

$$Q_N = \frac{1}{N!(2\pi\hbar)^{3N}} \int_V d\mathbf{r}_1 \int_V d\mathbf{r}_2 \cdots \int_V d\mathbf{r}_N \int_{-\infty}^{\infty} d\mathbf{p}_1 \int_{-\infty}^{\infty} d\mathbf{p}_2 \cdots \int_{-\infty}^{\infty} d\mathbf{p}_N \exp[-\beta\mathcal{H}_N], \quad (1)$$

where a coefficient $\hbar$ is the ratio of the Planck's constant to 2π and another coefficient β is defined as $\beta \equiv 1/k_BT$ with Boltzmann's constant k_B and the temperature T of the system. In Eq. (1), $\mathcal{H}_N$ is given by

$$\mathcal{H}_N = \sum_{i=1}^{N} \frac{p_i^2}{2m} + V_N(\mathbf{r}_1, \mathbf{r}_2, \cdots, \mathbf{r}_N), \quad (2)$$

where m is the particle mass and p_i is defined by $p_i \equiv |\mathbf{p}_i|$ with the momentum $\mathbf{p}_i$ of i particle. For a fluid, $V_N(\mathbf{r}_1, \mathbf{r}_2, \cdots, \mathbf{r}_N)$ in Eq. (2) can be expressed by using a pair potential $u_{ij}(r_{ij})$ generating the attractive force between i particle located at $\mathbf{r}_i$ and j particle located at $\mathbf{r}_j$ and the repulsive force between them as

$$V_N(\mathbf{r}_1, \mathbf{r}_2, \cdots, \mathbf{r}_N) = \sum_{i<j}^{N} u_{ij}(r_{ij}), \quad (3)$$

where r_{ij} is expressed the three-dimensional distance between i particle and j particle as defined by

$$r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|. \quad (4)$$

The partition fuction Q_N allows the Helmholtz feer energy F to be given as

$$F = -k_B \ln Q_N. \quad (5)$$

For the classical fluid system, Q_N is estimated as

$$Q_N = \frac{1}{N!} \left(\frac{m}{2\pi\hbar^2\beta} \right)^{3N/2} Z_N, \quad (6)$$

where

$$Z_N = \int_V d\mathbf{r}_1 \int_V d\mathbf{r}_2 \cdots \int_V d\mathbf{r}_N \exp[-\beta V_N(\mathbf{r}_1, \mathbf{r}_2, \cdots, \mathbf{r}_N)]. \tag{7}$$

The use of Z_N can allow the probability density for particle 1 being at $\mathbf{r}_1$, particle 2 being at $\mathbf{r}_2$, $\cdots$, and particle N being at $\mathbf{r}_N$ to be estimated as

$$\frac{1}{Z_N} \exp[-\beta V_N(\mathbf{r}_1, \mathbf{r}_2, \cdots, \mathbf{r}_N)].$$

Because the possible ways for choosing one particle from N particles is given by $N!/(N-1)!1!$, $n^{(1)}1(\mathbf{r}_1)d\mathbf{r}_1$ being the probability that one of the N particles is located in a volume element $d\mathbf{r}_1$ at $\mathbf{r}_1$ is given as

$$n^{(1)}(\mathbf{r}_1)d\mathbf{r}_1 = \left(\frac{N!}{(N-1)!1!}\right) \frac{d\mathbf{r}_1}{Z_N} \int_V d\mathbf{r}_2 \int_V d\mathbf{r}_3 \cdots \int_V d\mathbf{r}_N \exp[-\beta V_N(\mathbf{r}_1, \mathbf{r}_2, \cdots, \mathbf{r}_N)]. \tag{8}$$

If a fluid satisfies a situation where the distribution of particles in a volume element does not depend on locations of the volume element,

$$n^{(1)}(\mathbf{r}_1) = \frac{N}{V} = \rho. \tag{9}$$

Similarly, if $n^{(2)}(\mathbf{r}_1, \mathbf{r}_2)d\mathbf{r}_1 d\mathbf{r}_2$ denotes the probability that a particle is located in a volume element $d\mathbf{r}_1$ at $\mathbf{r}_1$ and another particle is located in a volume element $d\mathbf{r}_2$ at $\mathbf{r}_2$is given as

$$n^{(2)}(\mathbf{r}_1, \mathbf{r}_2)d\mathbf{r}_1 d\mathbf{r}_2 = \left(\frac{N!}{(N-2)!2!}\right) \frac{d\mathbf{r}_1 d\mathbf{r}_2}{Z_N} \int_V d\mathbf{r}_3 \int_V d\mathbf{r}_4 \cdots \int_V d\mathbf{r}_N \exp[-\beta V_N(\mathbf{r}_1, \mathbf{r}_2, \cdots, \mathbf{r}_N)]. \tag{10}$$

If a fluid satisfies a situation where the distribution of particles in a volume element maintains independence of locations of the volume element on average,

$$n^{(2)}(\mathbf{r}_1, \mathbf{r}_2) = n^{(2)}(r_{12}). \tag{11}$$

The quantity $n^{(2)}(r_{12})$ corresponds to the radial distribution function for a fluid system. The pair correlation function $g(r_{12})$, which is related to $h(r_{12}) = g(r_{12}) - 1$ with the correlation function $h(r_{12})$ that satisfies the Ornstein-Zernike equation, is related to the radial distribution function as follows:

$$n^{(2)}(r_{12}) = n^{(1)} n^{(1)} g(r_{12}). \tag{12}$$

Z_N can be rewritten by using the Mayer f-function, which is useful for analyzing a fluid based on an aspect that allows a fluid to be considered as an ensemble of pairs of particles.

Then, Z_N is given by

$$\begin{aligned} Z_N =& \int_V d\mathbf{r}_1 \int_V d\mathbf{r}_2 \cdots \int_V d\mathbf{r}_N \prod_{i<j}^{N} (1+f_{ij}) \\ =& \int_V d\mathbf{r}_1 \int_V d\mathbf{r}_2 \cdots \int_V d\mathbf{r}_N \Big[1 + (f_{12} + f_{13} + \cdots + f_{1N}) \\ & +(f_{12}f_{13} + f_{12}f_{14} + \cdots + f_{12}f_{1N}) + \cdots \\ & +(f_{23}f_{12} + f_{23}f_{13} + \cdots + f_{23}f_{1N}) + \cdots \\ & +(f_{23}f_{12}f_{13} + f_{23}f_{12}f_{14} + \cdots + f_{23}f_{12}f_{1N}) + \cdots \\ & +(f_{34}f_{24}f_{12} + f_{34}f_{24}f_{13} + f_{34}f_{24}f_{14} + \cdots + f_{34}f_{24}f_{1N}) + \cdots \\ & +(f_{34}f_{23}f_{24}f_{12} + f_{34}f_{23}f_{24}f_{13} + f_{34}f_{23}f_{24}f_{14} + \cdots + f_{34}f_{23}f_{24}f_{1N}) + \cdots \Big], \end{aligned} \tag{13}$$

where the Mayer f-function f_{ij} is defined as

$$f_{ij}(r_{ij}) \equiv e^{-\beta u_{ij}(r_{ij})} - 1. \tag{14}$$

Hence, the f-function f_{ij} satisfies

$$\begin{aligned} f_{ij}(r_{ij}) &= f_{ji}(r_{ji}), \\ \lim_{r_{ij}\to 0} f_{ij}(r_{ij}) &= -1, \\ \lim_{r_{ij}\to \infty} f_{ij}(r_{ij}) &= 0. \end{aligned}$$

The minimum of $f_{ij}(r_{ij})$ is -1. if i particle and j particle have hard cores, $f_{ij}(r_{ij}) = -1$ is satisfied in the region where the hard cores contribute to their interaction characterized by $u_{ij}(r_{ij}) = \infty$. The function $f_{ij}(r_{ij})$, 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. The value of $f_{ij}(r_{ij})$ becomes zero outside the range in which an attractive force between an i particle and a j particle retains effective strength. If an ensemble of particles is a fluid, it is possible to assume $-1 < \beta u_{ij}(r_{ij})$ at temperatures of the system. The maximum of $f_{ij}(r_{ij})$ does not become a large value.

Eq. (13) indicates that Z_N is the sum of the integrals of products of f-functions. This means that the pair correlation function $g(r_{ij})$ also can be given as the sum of the integrals of products of f-functions although the two coordinates specified by r_{ij} are not integrated over.

Typical features of the integrals of products of f-functions are extracted from Eq. (13). The integrals of f_{ij} for i and j satisfying $i < j$ are identical. The integrals of $f_{12}f_{1j}$ for j

satisfying $3 < j$ are identical. The integrals of $f_{12}f_{1j}$ for j satisfying $3 < j$ are identical. However, the integral of $f_{23}f_{13}$ is not identical with each integral of $f_{23}f_{1j}$ for j except $j = 3$. Cases similar to the above can be found from integrals of other products of f-functions.

The integrals of products of f functions allow a specific image showing that two particles specified by each f-function are linked mathematically by the f function. This image enables an ensemble of particles to be considered as clusters that are formed from particle pairs linked mathematically by f functions. Then, each f function forms a f bond that mathematically links two particle.

In Eq. (13), $f_{23}f_{13}$, $f_{23}f_{12}f_{13}$, $f_{34}f_{24}f_{13}$, and $f_{34}f_{23}f_{24}f_{13}$, are found as specific products of f-functions. The first product, $f_{23}f_{13}$, denotes that two f bonds link particle 1 and particle 2 via particle 3, as shown by a diagram symbolized by $1 \leftrightarrow 3 \leftrightarrow 2$. The third product, $f_{34}f_{24}f_{13}$, denotes that particle 1 and particle 2 are linked via particle 3 and particle4 as shown by a diagram symbolized by $1 \leftrightarrow 3 \leftrightarrow 4 \leftrightarrow 2$, which forms one path of f bonds. The second product, $f_{23}f_{12}f_{13}$, denotes that particle 1 and particle 2 are linked through two paths of f bonds as shown by a diagram symbolized by $1 \leftrightarrow 2$ and $1 \leftrightarrow 3 \leftrightarrow 2$. The fourth, $f_{34}f_{23}f_{24}f_{13}$, denotes that particle 1 and particle 2 are linked through special two paths of f bonds that form a diagram symbolized by $1 \leftrightarrow 3 \leftrightarrow 2$ and $1 \leftrightarrow 3 \leftrightarrow 4 \leftrightarrow 2$. Then, all the paths of f bonds that connect particle 1 to particle 2 include particle 3 as a common particle.

In the case of the pair correlation function $g(r_{12})$ formed for the use of f functions, the two coordinates labeled with 1 and 2 are not integrated over. The coordinates $\mathbf{r}_1$ and $\mathbf{r}_2$ that are not integrated over are called the root points. The other coordinates that are integrated over are called field points, and they are labeled 3, 4, $\cdots$ for distinguishing them from the root points. Both the root points and the field points correspond to particle coordinates.

The pair correlation function $g(r_{12})$ includes the integrals of products of f-functions exemplified by the paths of f bonds corresponding to $f_{23}f_{13}$, $f_{34}f_{24}f_{13}$, and $f_{34}f_{23}f_{24}f_{13}$ although the two coordinates labeled with 1 and 2 are not integrated over. A diagram that is formed by all the paths of f bonds given for $f_{34}f_{23}f_{24}f_{13}$ include the coordinate corresponding to particle 3. A diagram that is each of the paths of f bonds given for $f_{23}f_{13}$, $f_{34}f_{24}f_{13}$ also includes the coordinate corresponding to particle 3. As exemplified by these cases, at least one common coordinate corresponding to a particle can be shared by each path of f bonds that connect particle 1 to particle 2 in a diagram of f bonds. Then, the diagram of f bonds is called a nodal diagram, and the common coordinate is a nodal point.

The pair correlation function $g(r_{12})$ includes also the integrals of products of f-functions exemplified by the paths of f bonds corresponding to $f_{23}f_{12}f_{13}$ although the coordinates 1 and 2 are not integrated over. In a diagram that is formed by all the paths of f bonds given for $f_{23}f_{12}f_{13}$, there is not a nodal point. As exemplified by this case, there is a diagram that does not include nodal points. Each diagram of f functions without including nodal points is a non-nodal diagram.

The pair correlation function $g(r_{12})$ can be expressed in the form of a density expansion.[22,23] Each term found in the form of the density expansion of $g(r_{12})$ is formed by the integrals of a product of f functions, although the two coordinates 1 and 2 corresponding to the root points are not integrated over in each term. The other coordinates are integrated over in each term. A diagram of f bonds which forms each term in the density expansion corresponds to either a nodal diagram or a non-nodal diagram. According to the density expansion, $g(r_{12})$ can be given by the sum of the contribution of all the nodal diagrams and the contribution of all the non-nodal diagrams.[22,23] This demonstrates that the Ornstein-Zernike equation being an integral equation, which should be satisfied by $g(r_{12})$, is expressed as the sum of the contribution $N(r_{12})$ of all the nodal diagrams and the contribution $c(r_{12})$ of all the non-nodal diagrams. Thus, the use of the direct correlation function $c(r_{12})$ being the contribution of all the non-nodal diagrams allows the Ornstein-Zernike equation to be expressed as

$$h(r_{12}) = c(r_{12}) + N(r_{12}), \tag{15}$$

where the contribution of all the nodal diagrams can be estimated by

$$N(r_{12}) = \rho \int_V c(r_{13})h(r_{32})\mathrm{d}\mathbf{r}_3 \tag{16}$$

with

$$h(r_{12}) = g(r_{12}) - 1. \tag{17}$$

The paths of f-bonds forming each nodal diagrams and the paths of f-bonds forming each non-nodal diagrams both 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.

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. Since this ensemble is a mathematical cluster,[23] it cannot simply correspond to a physical cluster.

B. Contributions of physical clusters

1. Phenomena dependent on the formation of physical clusters

A fluid system can include particle pairs of which each is characterized as a pair formed by two particles interacting in a situation in which the contribution of the mutually attractive force between them exceeds the contribution of their relative kinetic energy. Physical clusters are formed by these particle pairs.[1] Properties of the fluid system should be transformed by the development of physical clusters. If their development makes large physical clusters occur, it should participate in various phenomena involving phase behavior.

In a fluid system consisting of molecules, inhomogeneity that is generated as the density fluctuations[8,9] near the liquid-vapor critical points should be caused by the formation of large physical clusters. Physical clusters can allow the density fluctuations to be enhanced in a fluid being in the gas state. The degree of the density fluctuations reaches the maximum at the liquid-vapor critical point of the fluid. This allows the compressibility to diverge to the infinity at the liquid-vapor critical point. The compressibility equation allows the pair correlation function $g(r)$ to be related to the pressure P of a single component fluid as

$$\left[\beta\left(\frac{\partial P}{\partial \rho}\right)_{V,T}\right]^{-1} = 1 + \lim_{V\to\infty} \rho \int_V [g(r) - 1]\mathrm{d}\mathbf{r} \quad (r \equiv |\mathbf{r}|). \tag{18}$$

Even at the critical point, $g(r)$ maintains finite values in the range $0 \le r < \infty$, and the correlation between two particles disappears with an increase in the distance separating one of the two particles from the other.[16] These mean that Eq. (18) requires the divergence of the compressibility to be caused at least by the fact that the long-range behavior of $g(r)$ should be characterized near the critical point as follows:

$$g(r) - 1 \sim r^{-\mu} \quad (0 < \mu \le 3). \tag{19}$$

In fact, the long-range feature of the pair correlation function can be expressed in several particular conditions as the product of the factor r^{D-3} ($D = 2$) and a particular function

$\phi(r)$ which can be given as a Taylor series with respect to powers of r.[18,19]

$$g(r) - 1 \approx r^{D-3}\phi(r) \quad (D = 2). \tag{20}$$

Despite this fact, the physical cluster growth can allow the dependence of the pair correlation function $g(r)$ on the three-dimensional distance r between two particles[20] to deviate near the liquid-vapor critical point. The growth can alter the dependence that is expressed as the product of a negative power r^{-1} and a particular function given as the Taylor series with respect to positive powers of r.[9,17] The density fluctuations makes the behavior of the pair correlation function $g(r)$ at large r near the liquid-vapor critical point[9,17] differ from that in the gas state being far from the critical point.

Furthermore, the density fluctuations related to the formation of physical clusters can result in anomalies[11–15] with respect to various properties of fluids near their liquid-vapor critical points. Inhomogeneity that is generated in fluids consisting of metallic atoms near the liquid-vapor critical points[10] can cause anomalies in electrical properties,[11] optical reflectivity,[12] and optical absorption.[12,13] If a fluid consists of metallic atoms, inhomogenieties of the fluid due to the physical cluster formation[10] can be observed as anomalies for electrical properties,[11] the optical reflectivity,[12] and the optical absorption.[12,13] 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.[11] 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.[12]

The viscosities of fluids can become anomalous near the liquid-vapor critical points[14,15]. 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.[14] The physical cluster formation can result in a characteristic increase in the viscosities of fluids near the critical points.[15]

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 between colloidal particles allows a colloidal solution to generate a gel state.[3]

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 macroscopically 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 formation of physical clusters in multi-component fluids is interesting subjects that should be considered. 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 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.[43] 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 occurrence 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.[1] A useful procedure for estimating the physical cluster formation due to such bonds can be found according to a concept of Coniglio and co-workers,[2] 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-range attractive force[4] and to examine the physical cluster formation caused by the Yukawa potential.[5,75] Moreover, a procedure for making corrections to the Percus-Yevick approximation[28] enabled an estimate of physical cluster formation due to the integral equation to be improved considerably.[6] 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[28] and another one derived by Chiew and co-workers.[29] If this additional integral equation is coupled to the integral equation which enables the physical cluster formation to be examined, the two integral equations provides 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.

2. The pair connectedness for estimating the physical cluster formation

(a) *Correlation functions*

Three-dimensional coordinates for the positions of particles in a fluid system are denoted by $\mathbf{r}_i$ for particle i and $\mathbf{r}_j$ for particle j. A situation where these particle are included in the same physical cluster is allowed. A correlation function that can play a role instead of the pair correlation function is necessary to estimate the mean size of physical clusters. The pair connectedness $\mathcal{P}(|\mathbf{r}_i - \mathbf{r}_j|)$ is an important correlation unction[2] to estimate it. The probability that particle i and particle j are located in the volume elements $d\mathbf{r}_i$ at $\mathbf{r}_i$ and $d\mathbf{r}_j$ at $\mathbf{r}_j$, respectively, is $\rho\rho g(r_{ij})d\mathbf{r}_i d\mathbf{r}_j$. The probability increases when particles in the fluid system are prevented from moving easily. Here, r_{ij} is the distance $|\mathbf{r}_i - \mathbf{r}_j|$, and ρ is the density of particles for a uniform distribution, so that the mean number of particles within a macroscopic volume V is $V\rho$. The magnitude of $g(r_{ij})$ is proportional to the probability that particle i in a volume element $d\mathbf{r}_i$ is located at the distance r_{ij} far from particle j in a volume element $d\mathbf{r}_j$. This feature of the pair correlation function suggests that maximum values of $g(r_{ij})$ should become larger when particles in a fluid system are prevented from moving easily than when they can move easily. The pair correlation function g 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 allows for estimating the density fluctuations for the fluid system even near the critical point. A feature of a fluid near the liquid-vapor critical point appears as a characteristic behavior of the pair correlation function g, which can express the degree of preventing particles in a fluid system from moving easily.[9,16,17] Nevertheless, the pair correlation function g cannot simply aid in examining the physical cluster formation. Even if a fluid is a particle system consisting of hard-cores between which attractive forces do not exist, the pair correlation function $g(r_{ij})$ $(i \neq j)$ can express the degree of preventing particles from moving easily because increasing ρ increases the probability $\rho\rho g(r_{ij})d\mathbf{r}_i d\mathbf{r}_j$. Physical clusters are, however, not formed in the fluid.

If physical clusters are formed, the magnitude of $g(r_{ij})$ is affected by the physical cluster formation. The magnitude of $g(r_{ij})$ includes the contribution of physical cluster formation. If the contribution of physical cluster formation to the magnitude of $g(r_{ij})$ is divided, other contributions of physical cluster formation can be clearly estimated.

An f function based on the definition $f(r_{ij}) \equiv e^{-\beta u(r_{ij})} - 1$ specifies a particle pair that consists of particle i at $\mathbf{r}_i$ and particle j at $\mathbf{r}_j$. The use of f functions allows the pair correlation function $g(r_{ij})$ to be expressed in the form of a density expansion.[22,23] For an N particle fluid system, specific features of $g(r_{ij})$ are determined by $N(N-1)/2$ particle pairs. Then, the relation between two particles constituting each pair maintains one of the two possibilities. A possibility is a situation where the two particles are bound to each other. The other possibility is a situation where the two particles are not bound.

The Hamiltonian for describing the movements of the two particles is given as

$$H_2 = \frac{p_i^2}{2m_i} + \frac{p_j^2}{2m_j} + u(r_{ij}), \tag{21}$$

where the mass of particle i and that of particle j are m_i and m_j respectively. r_{ij} corresponds to the relative position between particle i and particle j. The center of mass $\mathbf{R}$ is given by $\mathbf{R} = (m_i\mathbf{r}_i + m_j\mathbf{r}_j)/(m_i + m_j)$. The total momentum $\mathbf{P}$ carried by the center of mass is given by $\mathbf{P} = \mathbf{p}_i + \mathbf{p}_j$. The relative velocity between particle i and particle j is given by dividing $\mathbf{p}_{\rm rel}$ by the reduced mass $\bar{m}$. $\mathbf{p}_{\rm rel}$ is given by $\mathbf{p}_{\rm rel} = (m_j\mathbf{p}_i - m_i\mathbf{p}_j)/(m_i + m_j)$, and $\bar{m}$ is given by $\bar{m} = m_i m_j/(m_i+m_j)$. If the total mass M estimated as $M = m_i + m_j$ is used, the Hamiltonian is expressed by the use of the kinetic energy of the center of mass $P^2/2M$ and the relative kinetic energy $p_{\rm rel}^2/2\bar{m}$ as follows:

$$H_2 = \frac{P^2}{2M} + \frac{p_{\rm rel}^2}{2\bar{m}} + u(r_{ij}), \tag{22}$$

where $P = |\mathbf{P}|$ and $p_{\rm rel} = |\mathbf{p}_{\rm rel}|$. Then, Eq. (22) means that the Hamiltonian is $H_2 = \bar{H}_2(\mathbf{P}, \mathbf{p}_{\rm rel}, \mathbf{r}_i, \mathbf{r}_j)$. Based on the assumption that particle i is located at the origin of a coordinate, the use of the relative kinetic energy that is expressed in the polar coordinate denoted by the parameters r, θ, ϕ allows H_2 to be given as

$$H_2 = \frac{P^2}{2M} + \frac{1}{2\bar{m}}\left(p_r^2 + \frac{p_\theta^2}{r^2} + \frac{p_\phi^2}{r^2\sin^2\theta}\right) + u(r), \tag{23}$$

Eq. (23) means that the Hamiltonian is $H_2 = \hat{H}_2(\mathbf{P}, p_r, p_\theta, p_\phi, r, \theta, \phi)$. In Eq. (23), the second term on the right hand side of the equation is the contribution of the relative kinetic energy of the two particles, and the third term is the contribution of the interactions between them. For the Hamiltonian given by Eq. (23), Q_2 is denoted as

$$Q_2 = \frac{1}{2!(2\pi\hbar)^6} V \int_V drd\theta d\phi \int_{-\infty}^{\infty} dp_r dp_\theta dp_\phi \int_{-\infty}^{\infty} d\mathbf{P} \exp[-\beta\hat{H}_2], \tag{24}$$

where D corresponds to the whole ranges for the parameters p_r, p_θ, and p_ϕ. If parameters $\bar{p}_r$, $\bar{p}_\theta$, and $\bar{p}_\phi$ are defined as $\bar{p}_r \equiv p_r(\beta/2\bar{m})^{1/2}$, $\bar{p}_\theta \equiv (p_\theta/r)(\beta/2\bar{m})^{1/2}$ $\bar{p}_\phi \equiv (p_\phi/r\sin\theta)(\beta/2\bar{m})^{1/2}$, βH_2 is expressed as

$$\beta H_2 = \beta\frac{P^2}{2M} + \bar{p}_r^2 + \bar{p}_\theta^2 + \bar{p}_\phi^2 + \beta u(r). \tag{25}$$

For the use of the parameters P_r, P_θ, and P_ϕ, Eq. (25) allows Eq. (24) to be rewritten as follows

$$Q_2 = \frac{V}{2\pi^{3/2}} \left(\frac{2\pi\sqrt{M\bar{m}}}{(2\pi\hbar)^2\beta} \right)^{3/2} \int_0^\infty 4\pi r^2 dr e^{-\beta u(r)} \int_{-\infty}^{\infty} d\bar{p}_r d\bar{p}_\theta d\bar{p}_\phi e^{-(\bar{p}_r^2+\bar{p}_\theta^2+\bar{p}_\phi^2)}, \tag{26}$$

According to Eq. (25), the contribution, $\mathcal{E}$, of the relative kinetic energy of the two particles is given as $\mathcal{E} = \bar{p}_r^2 + \bar{p}_\theta^2 + \bar{p}_\phi^2$, and $\beta u(r)$ denotes the contribution of the interactions between them at each r. At each r that allows $u(r)$ to be negative, the situation where the two particles are bound to each other for the attractive force requires a relation expressed by

$$\bar{p}_r^2 + \bar{p}_\theta^2 + \bar{p}_\phi^2 \leq -\beta u(r). \tag{27}$$

The probability $p(r)$ that the two particles are found in a bound state $\mathcal{E} + \beta u(r) \leq 0$ is estimated from the integration of $\exp[-(\bar{p}_r^2 + \bar{p}_\theta^2 + \bar{p}_\phi^2)]$ included in Eq. (26) as follows:

$$p(r) = \frac{1}{\pi^{3/2}} \int_{\bar{p}_r^2+\bar{p}_\theta^2+\bar{p}_\phi^2 \leq -\beta u(r)} d\bar{p}_r d\bar{p}_\theta d\bar{p}_\phi e^{-(\bar{p}_r^2+\bar{p}_\theta^2+\bar{p}_\phi^2)}. \tag{28}$$

Then, the integration of $\exp[-(\bar{p}_r^2 + \bar{p}_\theta^2 + \bar{p}_\phi^2)]$ is limited by $\bar{p}_r$, $\bar{p}_\theta$, and $\bar{p}_\phi$ that satisfy Eq. (27). If Eq. (28) is rewritten through the use of $\mathcal{E}$, the following equation is obtained for $p(r)$

$$\begin{aligned} p(r) =& \frac{2}{\pi^{1/2}} \int_0^{-\beta u(r)} e^{-\mathcal{E}} \mathcal{E}^{1/2} d\mathcal{E} \\ =& \frac{2}{\pi^{1/2}} \left[\Gamma\left(\frac{3}{2}\right) - \Gamma\left(\frac{3}{2}, -\beta u(r)\right) \right], \end{aligned} \tag{29}$$

where $\Gamma(\tau, t)$ is the incomplete gamma function expressed by $\Gamma(\tau, t) = \int_t^\infty e^{-y} y^{\tau-1} \mathrm{d}y$.[1]

At each r that allows $u(r)$ to be negative, the situation where the two particles are not bound requires a relation expressed by

$$\bar{p}_r^2 + \bar{p}_\theta^2 + \bar{p}_\phi^2 > -\beta u(r). \tag{30}$$

The probability $\bar{p}(r)$ that the two particles are found in an unbound state $\mathcal{E} + \beta u(r) > 0$ is estimated as follows:

$$\bar{p}(r) = \frac{1}{\pi^{3/2}} \int_{\bar{p}_r^2+\bar{p}_\theta^2+\bar{p}_\phi^2 > -\beta u(r)} d\bar{p}_r d\bar{p}_\theta d\bar{p}_\phi e^{-(\bar{p}_r^2+\bar{p}_\theta^2+\bar{p}_\phi^2)} \tag{31}$$

$$\begin{aligned} =& \frac{2}{\pi^{1/2}} \Gamma\left(\frac{3}{2}, -\beta u(r)\right) \\ =& 1 - p(r). \end{aligned} \tag{32}$$

At each r that allows $u(r)$ to be positive, Eq. (30) is always satisfied for arbitrary values of three parameters $\bar{p}_r$, $\bar{p}_\theta$, and $\bar{p}_\phi$. Then, $\bar{p}(r) = 1$ ($p(r) = 0$) is satisfied, and the two particles are not bound at each r that allows $u(r)$ to be positive.

Thus, $p(r)\big|_{r=r_{ij}}$ given by the use of Eq. (29) denotes the probability that particle i at $\mathbf{r}_i$ and particle j at $\mathbf{r}_j$ that are specified by an f function $f(r_{ij})$ are bound to each other. The use of the probability $p(r_{ij})$ allows the f function $f(r_{ij})$ to be given as the sum of the f^+-function and the f^*-function, which are expressed as

$$f^+(r_{ij}) \equiv p(r_{ij})e^{-\beta u(r_{ij})} \tag{33}$$

$$f^*(r_{ij}) \equiv [1 - p(r_{ij})]e^{-\beta u(r_{ij})} - 1. \tag{34}$$

Each f-bond in each of diagrams found from the density expansion of $g(r_{12})$ corresponds to an f function. In its density expansion, each of the f functions is substituted with the sum of an f^+-function and an f^*-function, which is exemplified by $f(r_{ij}) = f^+(r_{ij}) + f^*(r_{ij})$. As the result, each diagram is expressed as the sum of diagrams that are formed by f^+ bonds specified by f^+-functions and f^* bonds specified by f^*-functions. The sum includes at least a diagram in which one root point $\mathbf{r}_1$ is connected to the other root point $\mathbf{r}_2$ through at least one path of all f^+-bonds given as a product of f^+-functions. According this diagram, the two particles corresponding to the two root points are part of the same physical cluster[1]. Based on these procedures, the pair connectedness $\mathcal{P}(r_{12})$, which is a correlation function related directly to the physical cluster formation can be extracted from the density expansion of $g(r_{12})$.[2]

The pair connectedness $\mathcal{P}(r_{12})$ is given by the sum of the contributions resulting from every diagram having at least one path of all f^+-bonds between the root points labeled 1 and 2. The use of $\mathcal{P}(r_{12})$ allows $\rho\rho\mathcal{P}(r_{12})d\mathbf{r}_1 d\mathbf{r}_2$ to express the probability that both particle 1 in $d\mathbf{r}_1$ located at $\mathbf{r}_1$ and particle 2 in $d\mathbf{r}_2$ located at $\mathbf{r}_2$ belong to the same physical cluster.[2] If the probability that particle 1 and particle 2 belong to different physical clusters is expressed as $\rho\rho\mathcal{D}(r_{12})d\mathbf{r}_1 d\mathbf{r}_2$,[2] the pair connectedness $\mathcal{P}(r_{12})$ is related to $g(r_{12})$ as

$$g(r_{12}) = \mathcal{P}(r_{12}) + \mathcal{D}(r_{12}), \quad (r_{12} \equiv |\mathbf{r}_1 - \mathbf{r}_2|). \tag{35}$$

This formula indicates that variations in the thermodynamic behavior of a fluid system due to variations in temperature are dominated by variations in a magnitude of $\mathcal{D}(r_{12})$ if a high temperature condition forbids physical clusters to be formed. The magnitude of $\mathcal{D}(r_{12})$

depends on the number of particles that are categorized as particles linked through each path that includes f^*-bonds. Particles linked through each path that includes f^*-bonds are either particles that do not participate in the physical cluster formation or particles that do not belong to the same physical cluster. On the other hand, the magnitude of $\mathcal{P}(r_{12})$ depends on the number of particles that participate in the physical cluster formation and are linked by paths of f^+-bonds. Near or below the liquid-vapor critical point, effects of the physical cluster formation on the thermodynamic behavior should not be ignored.

Then, unless particles contributing to the magnitude of $\mathcal{P}(r_{12})$ can microscopically and homogeneously mix with particles contributing to the magnitude of $\mathcal{D}(r_{12})$, a correlation between the behaviors of the former and latter particle groups must occur. Phenomena similar to the above correlation can be found from computer simulations of supercooled liquids. According to the computer simulations, particles having low mobility cannot microscopically and homogeneously mix with those having high mobility, so that particles participate in cooperative motion in structural relaxation.[24] Such cooperative motion can be observed also in colloidal suspensions.[25–27]

In every hard-sphere fluid system, cooperative motion similar to the above examples should not exist because every hard-sphere fluid system is characterized by the pair correlation function expressed by $g(r_{12}) = \mathcal{D}(r_{12})$ with $\mathcal{P}(r_{12}) = 0$. According to the equation of state resulting from the Percus-Yevick approximation,[22,23] the density fluctuations in a hard-sphere fluid system are simply reduced as the density of hard spheres increases, because an increase in their density limits their motion. If the contribution of attractive forces between particles to the formation of specific particle configurations is not ignored, then a fluid system should be characterized by the pair correlation function expressed by $g(r_{12}) = \mathcal{P}(r_{12}) + \mathcal{D}(r_{12})$ with $\mathcal{P}(r_{12}) \neq 0$. In this fluid system, attractive forces between particles cause the density fluctuations to reach a maximum at the critical point. After reaching a maximum, the density fluctuations are gradually reduced as the density of particles increases.[8,9] In a fluid system where attractive forces between particles is not ignored, the magnitude of $\mathcal{P}(r_{12})$ should not be ignored near the critical point. Then, the expression $g(r_{12}) = \mathcal{P}(r_{12}) + \mathcal{D}(r_{12})$ should allow the behavior of the pair correlation function to be given.

According to $g(r_{12})$, the probability that particle 1 in a volume element $d\mathbf{r}_1$ at $\mathbf{r}_1$ is located at the distance r_{12} from particle 2 located in a volume element $d\mathbf{r}_2$ at $\mathbf{r}_2$ is given by

$\rho\rho g(r_{12})d\mathbf{r}_1 d\mathbf{r}_2$ for a uniform fluid in which $\rho\delta V$ at $\mathbf{r}_1$ is equal to $\rho\delta V$ at $\mathbf{r}_2$ on average for a microscopic volume δV. Then, the probability that particle 1 and the particle 2 are in $d\mathbf{r}_1$ at $\mathbf{r}_1$ and in $d\mathbf{r}_2$ at $\mathbf{r}_2$, respectively is the sum of two contributions. One of the two contributions corresponds to the probability that both the particle 1 in the volume element $d\mathbf{r}_1$ at $\mathbf{r}_1$ and the particle 2 in the volume element $d\mathbf{r}_2$ at $\mathbf{r}_2$ belong to the same physical cluster. The other contribution corresponds to the probability that the particle 1 in the volume element $d\mathbf{r}_1$ at $\mathbf{r}_1$ and the particle 2 in the volume element $d\mathbf{r}_2$ at $\mathbf{r}_2$ belong to a physical cluster and another physical cluster respectively. The former is given by $\rho\rho\mathcal{P}(r_{12})d\mathbf{r}_1 d\mathbf{r}_2$ and the latter is given by $\rho\rho\mathcal{D}(r_{12})d\mathbf{r}_1 d\mathbf{r}_2$. Thus, the sum, $\rho\rho\mathcal{P}(r_{12})d\mathbf{r}_1 d\mathbf{r}_2 + \rho\rho\mathcal{D}(r_{12})d\mathbf{r}_1 d\mathbf{r}_2$, is required to be equal to $\rho\rho g(r_{12})d\mathbf{r}_1 d\mathbf{r}_2$.

(**b**) *The mean size* $\mathcal{S}$ *of physical clusters*

The microscopic fluid structure induced by the physical cluster formation persuades the behavior of the pair correlation function to be determined by the sum of the behavior of a correlation functions and the behavior of the other correlation function. The former correlation function corresponds to $\mathcal{D}$, and is a correlation function characterized by pairs of particles having highly relative kinetic abilities.[2] The magnitude of $\mathcal{D}_{ij}$ depends on the number of particles interacting in unbound states. The latter correlation function is the pair connectedness $\mathcal{P}$, and is a correlation function characterized by pairs of particles having low relative kinetic abilities.[1,2] The magnitude of $\mathcal{P}$ depends on the number of particles interacting in bound states. Particle pairs contributing to the magnitude of $\mathcal{P}$ 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, $\mathcal{P}$ should allow explaining the transition from the liquid sate of a fluid to its solid state as a phenomenon caused by macroscopically sized physical clusters caused by the growth of physical clusters. Knowing the growth of physical clusters is enabled from estimating the mean size S of physical clusters through the use of $\mathcal{P}$.

Effects of the physical cluster growth on the behavior of $g(r)$ should be estimated from the sum of the behaviors of $\mathcal{P}(r)$ and $\mathcal{D}(r)$. In accordance with Kirkwood and Buff,[30] the pair correlation function $g(r)$ has the normalization given as

$$\frac{1}{V}\int_V g(r)\mathrm{d}\mathbf{r} = \frac{\langle N\rangle - 1}{V\rho} + \frac{1}{V^2}\frac{1}{\rho^2}\Big[\langle NN\rangle - \langle N\rangle\langle N\rangle\Big], \tag{36}$$

where $\langle N\rangle$ is the mean number of particles within volume V. The dependence of $g(r)$ on V is negligible for macroscopic V, and the dependence of $\langle N\rangle/V$ on V and the dependence of $(\langle NN\rangle - \langle N\rangle\langle N\rangle)/V$ on V are also negligible. Thus, Eq. (36) results in $\int_V g(r)\mathrm{d}\mathbf{r}/V = 1$ in the limit $V \to \infty$. This relation, along with Eq. (35), requires the normalization for the pair correlation function to be expressed by

$$\lim_{V\to\infty}\left[\frac{1}{V}\int_V \mathcal{P}(r)\mathrm{d}\mathbf{r} + \frac{1}{V}\int_V \mathcal{D}(r)\mathrm{d}\mathbf{r}\right] = 1. \tag{37}$$

The mean size $\mathcal{S}$ of physical clusters can be estimated from the use of $\mathcal{P}(r_{12})$. The equilibrium number n_s of physical clusters consisting of s particles can be related to the pair connectedness $\mathcal{P}$. According to the formula given by Coniglio and co-workers[2], the relation between n_s and $\mathcal{P}$ is given as

$$\sum_{1\le s} s(s-1)n_s = \rho\rho\int_V\int_V \mathcal{P}(|\mathbf{r}_1 - \mathbf{r}_2|)d\mathbf{r}_1 d\mathbf{r}_2. \tag{38}$$

The factor $\sum_s sn_s$ included in Eq. (38) can be related to the density ρ of particles in the volume V as $\rho = [1/V]\sum_s sn_s$. The mean physical cluster size $\mathcal{S}$ is given as $\mathcal{S} = (\sum_s s^2 n_s)/(\sum_s sn_s)$. This formula and the relation $\sum_s sn_s = V\rho$ allow Eq. (38) to be rewritten as

$$\mathcal{S} = 1 + \rho\int_V \mathcal{P}(r)d\mathbf{r}. \tag{39}$$

The percolation of physical clusters occurs in a fluid system at the percolation threshold. The use of Eq. (39) allows examining the percolation of physical clusters. The critical condition at which the mean physical cluster size $\mathcal{S}$ given by Eq. (39) reaches infinity corresponds to the percolation threshold. The percolation of physical clusters in a macroscopic V maintained by a fluid system affects the dependence of $\mathcal{S}$ on V. If the percolation of physical clusters does not occur in V, $\mathcal{S}$ should be sufficiently independent of V. When percolated physical clusters exist in macroscopic sizes in V, $\mathcal{S}$ should depend on V.

3. Effects of the physical cluster growth

(**a**) *The occurrence of macroscopically sized physical clusters*

According to a formula given by Coniglio and co-workers[2], the integral of $\mathcal{P}(r)$ found in Eq. (37) can be related to the mean size S of physical clusters, because Eq. (39) resulting in the estimate of S can be rewritten as follows:

$$\frac{S-1}{V} = \rho\frac{1}{V}\int_V \mathcal{P}(r)d\mathbf{r}. \tag{40}$$

If the percolation of physical clusters does not occur in a macroscopic V maintained by a fluid system, $\mathcal{S}$ which is estimated for the fluid system by Eq. (39) should be sufficiently independent of V, and the limit $V \to \infty$ does not affect $\mathcal{S}$. Then, the limit $V \to \infty$ results in $(\mathcal{S}-1)/V = 0$. Therefore, Eq. (40) allows $(\rho/V)\int_V \mathcal{P}(r)d\mathbf{r} = 0$ to be satisfied. Moreover, Eq. (37) requires $(1/V)\int_V \mathcal{D}(r)\mathrm{d}\mathbf{r} = 1$ to be satisfied in the limit $V \to \infty$. Based on these consequences, the normalization conditions that are given in the limit $V \to \infty$ are described as

$$\begin{cases} \lim_{V\to\infty}(1/V)\int_V \mathcal{P}(r)d\mathbf{r} = 0, \\ \lim_{V\to\infty}(1/V)\int_V \mathcal{D}(r)\mathrm{d}\mathbf{r} = 1. \end{cases}$$

If the percolation of physical clusters occurs in a macroscopic V maintained by the fluid system, the mean size $\mathcal{S}$ that is estimated for the fluid system from the use of Eq. (39) should be dependent on V. Then, the magnitude of $[(\mathcal{S}-1)/V]$ can have a finite non-zero value. Then, Eq. (37) requires conditions given as

$$\begin{cases} 0 < \lim_{V\to\infty}(1/V)\int_V \mathcal{P}(r)d\mathbf{r} \le 1, \\ 0 \le \lim_{V\to\infty}(1/V)\int_V \mathcal{D}(r)\mathrm{d}\mathbf{r} < 1. \end{cases}$$

If a state of the fluid is in the immediate vicinity of the liquid-solid transition point where the relation $0 < \rho^{sd} - \rho^{lq} \ll 1$ (ρ^{sd} denotes ρ in a solid state, and ρ^{lq} denotes ρ in a liquid state which can be transformed into the solid state) is satisfied, almost all physical clusters should hold macroscopic sizes in V. Then, the dependence of $\mathcal{S}$ on V should be characterized by $\mathcal{S}/V \approx \rho^{sd}$, which corresponds to the situation where the growth of physical clusters reaches the limit. Also, Eq. (40) results in $(1/V)\rho\int_V \mathcal{P}(r)d\mathbf{r} \approx \rho^{sd}$ in the limit $V \to \infty$. According to this situation, Eq. (37) allows $(1/V)\int_V \mathcal{D}(r)\mathrm{d}\mathbf{r} \approx 0$ to be satisfied in the limit $V \to \infty$. Based on these consequences, the normalization conditions that are given in the limit $V \to \infty$ are described as

$$\begin{cases} \lim_{V\to\infty}(1/V)\int_V \mathcal{P}(r)d\mathbf{r} \approx 1, \\ \lim_{V\to\infty}(1/V)\int_V \mathcal{D}(r)\mathrm{d}\mathbf{r} \approx 0. \end{cases}$$

A state specified by $(1/V)\int_V \mathcal{D}(r)\mathrm{d}\mathbf{r} \approx 0$ 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 means that the fluid might lose a feature found as liquid. Thus, the growth of physical clusters that proceeds in macroscopic V beyond the percolation threshold can contribute to making the phase transition from the liquid state of a fluid to the solid state occur. A situation where $(1/V)\int_V \mathcal{D}(r)\mathrm{d}\mathbf{r} \approx 0$ is satisfied should be found at least near the triple point.

(**b**) *The behavior of correlation functions*

The pair correlation function behaves as $g(|\mathbf{r}_1 - \mathbf{r}_2|) \approx 1$ for large $|\mathbf{r}_1 - \mathbf{r}_2|$, which corresponds to a situation where one of two particles corresponding to the location at $\mathbf{r}_1$ in a fluid system are widely separated from the other corresponding to the location at $\mathbf{r}_2$. In the limit $V \to \infty$ and $r \to \infty$, it behaves as $g(r) = 1$.[1] This fact requires the behaviors of the two correlation functions to be restricted by the following relation:

$$\mathcal{P}(r) + \mathcal{D}(r) \approx 1, \quad (1 \ll r/\sigma), \tag{41}$$

where the repulsive force between two particles exceeds the attractive force between them at a position satisfying $r < \sigma$. Eq. (41) denotes that the behaviors of $\mathcal{P}(r)$ and $\mathcal{D}(r)$ are restricted for large r.

In a situation where no percolation of physical clusters occurs, the physical meanings of the two correlation functions and their behavior given by Eq. (41) require the behaviors of $\mathcal{P}(r)$ and $\mathcal{D}(r)$ at large r to be expressed by

$$\begin{cases} \lim_{r\to\infty} \mathcal{P}(r) = 0, \\ \lim_{r\to\infty} \mathcal{D}(r) = 1. \end{cases} \tag{42}$$

The relations given by Eq. (42) should be satisfied even at the percolation threshold, although they are not correct beyond that point.

The relations have to be modified correctly if macroscopically sized physical clusters in the fluid increase under a condition being beyond the percolation threshold. Then the magnitude of $\mathcal{P}(r)$ should have a non-zero finite value even for large r. Hence, while increasing extremely large physical clusters, the sum of the two correlation functions given by Eq. (41) should require $\mathcal{P}(r)$ and $\mathcal{D}(r)$ to behave as

$$\begin{cases} 0 < \lim_{r\to\infty} \mathcal{P}(r) \leq 1, \\ 0 \leq \lim_{r\to\infty} \mathcal{D}(r) < 1, \\ \lim_{r\to\infty}[\mathcal{P}(r) + \mathcal{D}(r)] = 1. \end{cases}$$

The relations have to be modified correctly if a fluid includes a number of macroscopically sized physical clusters developed under a condition being beyond the percolation threshold. The existence of a number of extremely large physical clusters allows the normalization condition that is given as $\lim_{V\to\infty}(1/V)\int_V \mathcal{P}(r)\mathrm{d}\mathbf{r} = 1$ and $\lim_{V\to\infty}(1/V)\int_V \mathcal{D}(r)\mathrm{d}\mathbf{r} \approx 0$. If the value of $\mathcal{D}(r)$ on the surface of volume V preserves a non-zero finite value, $\lim_{V\to\infty}(1/V)\int_V \mathcal{D}(r)\mathrm{d}\mathbf{r} \approx 0$ is not satisfied. Therefore, the relation given by Eq. (41) requires the two correlation functions to behave for the existence of a number of extremely large physical clusters as follows

$$\begin{cases} \lim_{r\to\infty} \mathcal{P}(r) \approx 1, \\ \lim_{r\to\infty} \mathcal{D}(r) \approx 0, \\ g(r) \approx \mathcal{P}(r). \end{cases}$$

The above relations are satisfied at least near the triple point, where the specific relation $(1/V)\int_V \mathcal{D}(r)\mathrm{d}\mathbf{r} \approx 0$ should be satisfied

In addition, the state specified by $(1/V)\int_V \mathcal{D}_{ij}(r)\mathrm{d}\mathbf{r} \approx 0$ extremely lacks particle pairs characterized as pair particles interacting in a specific situation where the relative kinetic energy of the pair particles exceeds a contribution of an attractive force between them. Then, the system should lose a feature found as liquid and should gain a feature found as solid. If the growth of physical clusters increases macroscopically sized physical clusters in macroscopic V, its growth should contribute to the transition from the liquid state of a fluid to the solid state.

(**c**) *Integral equations for correlation functions including the pair connectedness*

The pair connectedness $\mathcal{P}(r_{ij})$ ($r_{ij} \equiv |\mathbf{r}_i - \mathbf{r}_j|$) is given as the sum of contributions resulting from every diagram having at least one path of all f^+ bonds between the root points corresponding to the two coordinates $\mathbf{r}_i$ and $\mathbf{r}_j$. The pair correlation function $g(r_{ij})$ is given as the sum of contributions resulting from every diagram formed by paths of f bonds between the root points, according to the density expansion of $g(r_{ij})$. Moreover, Eq. (15) with Eq. (17) and (16) requires $g(r_{ij})$ to be given the sum of the two contributions that correspond to the contribution of the nodal diagrams having nodal points and the other contribution of the 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.

Based on the example of $g(r_{ij})$, the diagrams contributing to $\mathcal{P}(r_{ij})$ are separated into two groups, i.e., a group consisting of the nodal diagrams of f^+-bonds and the other group consisting of the non-nodal diagrams of f^+-bonds. This means that $\mathcal{P}(r_{ij})$ is expressed as

$$\mathcal{P}(r_{ij}) = N^+(r_{ij}) + C^+(r_{ij}),$$

where $N^+(r_{ij})$ is the contribution of all nodal diagrams having at least one path of all f^+-bonds between the two root points, and $C^+(r_{ij})$ 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,[22] the contribution of all non-nodal diagrams consisting of paths of f-bonds between the two root points corresponds to the direct correlation function $c(r_{ij})$. According to the Ornstein-Zernike equation, $g(r_{ij}) - 1$ is equal to $N(r_{ij}) + c(r_{ij})$ in which $N(r_{ij})$ represents the contribution of all nodal diagrams consisting of paths of f-bonds between the two root points, and $N(r_{ij})$ is given as the convolution integral $\rho \int c(r_{ik})[g(r_{kj}) - 1]\mathrm{d}\mathbf{r}_k$, which is simplified by using $r_{ik} \equiv |\mathbf{r}_i - \mathbf{r}_k|$ and $r_{kj} \equiv |\mathbf{r}_k - \mathbf{r}_j|$.

If analogy with the Ornstein-Zernike equation are assumed, the convolution integral of the product of $C^+(r_{ik})$ and $\mathcal{P}(r_{kj})$ should result in $N^+(r_{ij}) = \rho \int C^+(r_{ik})\mathcal{P}(r_{kj})\mathrm{d}\mathbf{r}_k$. This consequence and the relation $\mathcal{P}(r_{ij}) = C^+(r_{ij}) + N^+(r_{ij})$ results in an integral equation which is required in order to estimate $\mathcal{P}(r_{ij})$.[2] Thus, the pair connectedness $\mathcal{P}(r_{ij})$ is given as a solution of the integral equation expressed as

$$\mathcal{P}(r_{ij}) = C^+(r_{ij}) + \rho \int_V C^+(r_{ik})\mathcal{P}(r_{kj})\mathrm{d}\mathbf{r}_k, \tag{43}$$

where $C^+(r_{ij})$ is an unknown function. Eq. (43) has the same mathematical structure as the Ornstein-Zernike equation, and it is used in the limit $V \to \infty$,

Finding an integral equation for the correlation function $\mathcal{D}(r_{ij})$ is possible by considering the Ornstein-Zernike equation. Owing to the relation given by Eq. (35), the Ornstein-Zernike equation is expressed as

$$\begin{aligned}\mathcal{P}(r_{ij})+\mathcal{D}(r_{ij})-1=&c(r_{ij})+\rho\int_V c(r_{ik})\mathcal{P}(r_{kj})\mathrm{d}\mathbf{r}_k\\&+\rho\int_V c(r_{ik})[\mathcal{D}(r_{kj})-1]\mathrm{d}\mathbf{r}_k.\end{aligned}\tag{44}$$

This equation must involve the contribution of the pair connectedness $\mathcal{P}$, which should be estimated by Eq. (43). 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 $c(r_{ij})$, 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 $C^+(r_{ij})$. Then, $C^+(r_{ij})$ is the contribution of all non-nodal diagrams having at least one path of all f^+-bonds between the two root points. Thus, $c(r_{ij})$ is expressed as

$$c(r_{ij})=C^+(r_{ij})+C^*(r_{ij}).\tag{45}$$

If Eq. (43) is considered, the substitution of Eq. (45) into Eq. (44) results in an integral equation which is equivalent to both an integral equation derived by Stell[28] and another one derived by Chiew and co-workers.[29] This integral equation is expressed as

$$\begin{aligned}\mathcal{H}(r_{ij})=&C^*(r_{ij})+\rho\int_V C^*(r_{ik})\mathcal{P}(r_{kj})\mathrm{d}\mathbf{r}_k\\&+\rho\int_V C^+(r_{ik})\mathcal{H}(r_{kj})\mathrm{d}\mathbf{r}_k+\rho\int_V C^*(r_{ik})\mathcal{H}(r_{kj})\mathrm{d}\mathbf{r}_k,\end{aligned}\tag{46}$$

where

$$\mathcal{H}(r_{ij})\equiv\mathcal{D}(r_{ij})-1.\tag{47}$$

In Eq. (46), $C^*(r_{ij})$ is an unknown function. According to the relation given by Eq. (45), an integral equation system consisting of Eqs. (43) and (46) is equivalent to the Ornstein-Zernike equation. Equation (43) contributes to estimating the formation of physical clusters, and Equation (46) contributes to estimating an effect of the physical cluster formation. In fact, the second term and the third term on its right hand side in Eq. (46) represent a way to have an effect of the formation of physical clusters on the correlation function $\mathcal{H}$. An effect of these terms should play a role for explaining phenomena due to the formation of physical clusters. For a specific fluid system in which no physical cluster formation is expected, Eq. (46) is simplified as

$$\mathcal{H}(r_{ij})=C^*(r_{ij})++\rho\int_V C^*(r_{ik})\mathcal{H}(r_{kj})\mathrm{d}\mathbf{r}_k.\tag{48}$$

The ensemble of particles that contribute to the magnitude of $C^{+}(r)$ is the same as that contributing to $\mathcal{P}(r)$. Similarly, the ensemble of particles that contribute to the magnitude of $C^{*}(r)$ is the same as that contributing to $\mathcal{D}(r)$.

The integral equation system composed of Eqs. (43) and (46) is equivalent to the Ornstein-Zernike equation, which has been successful for examining a fluid in both the gas and liquid states.

When the gas phase of a fluid and the liquid phase of the fluid are in equilibrium, Eq. (48) is applicable to examining the behavior of this gas phase, and Eq. (46) should be applicable to examining the behavior of that liquid phase. In addition, when $\Big|\mathcal{P}(r)/\mathcal{D}(r)\Big| \ll 1$ is satisfied, the following relation can occur

$$\Big|\rho\int_V C^{*}(r_{ik})\mathcal{P}(r_{kj})\mathrm{d}\mathbf{r}_k + \rho\int_V C^{+}(r_{ik})\mathcal{H}(r_{kj})\mathrm{d}\mathbf{r}_k\Big| \ll \Big|\mathcal{H}(r_{ij})\Big|. \tag{49}$$

Eq. (48) can be an appropriate approximation even for a fluid involving the formation of physical clusters, if the condition $|\mathcal{P}(r)/\mathcal{D}(r)| \ll 1$ is satisfied for the fluid.

4. Each closure scheme for solving each integral equation

(**a**) *Two closure schemes*

According to the Percus-Yevick (PY) approximation, an approximate relation between $\mathcal{P}(r_{ij})$ and $C^{+}(r_{ij})^{2}$ can be given within the effective range where the contribution of $u(r_{ij})$ to an attractive force, which makes particle i interact with particle j, cannot be neglected. An approximate relation between $\mathcal{D}(r_{ij})$ and $C^{*}(r_{ij})$ also can be given within the effective range. As a result, an aid of the PY approximation allows the characterization of $\mathcal{P}(r_{ij})$ due to a pair potential. Moreover, it allows the characterization of $\mathcal{D}(r_{ij})$ due to a pair potential.

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

$$\begin{aligned} g^{\mathrm{PY}}(r_{ij}) =& f^{+}(r_{ij})\Big[1 + N^{+}(r_{ij}) + N^{*}(r_{ij})\Big] + \Big[f^{*}(r_{ij}) + 1\Big]N^{+}(r_{ij}) \\ &+ \Big[f^{*}(r_{ij}) + 1\Big]\Big[1 + N^{*}(r_{ij})\Big]. \end{aligned} \tag{50}$$

The right hand side of Eq. (50) should be the sum of the terms contributing to $\mathcal{P}(r_{ij})$ and the terms contributing to $\mathcal{D}(r_{ij})$ owing to the relation given by Eq. (35). Considering this fact allows Eq. (50) to be divided into two formulae. Owing to $\mathcal{P}(r_{ij}) = C^{+}(r_{ij}) + N^{+}(r_{ij})$, one of the two formulae is

$$\mathcal{P}(r_{ij}) = f^{+}(r_{ij}) g^{\mathrm{PY}}(r_{ij}) e^{\beta u(r_{ij})} + [f^{*}(r_{ij}) + 1][\mathcal{P}(r_{ij}) - C^{+}(r_{ij})], \tag{51}$$

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

$$\mathcal{D}(r_{ij}) = [f^{*}(r_{ij}) + 1][g^{\mathrm{PY}}(r_{ij}) - c^{\mathrm{PY}}(r_{ij}) - \mathcal{P}(r_{ij}) + C^{+}(r_{ij})], \tag{52}$$

where $c^{\mathrm{PY}}(r_{ij})$ is the direct correlation function due to the PY approximation and is given as $c^{\mathrm{PY}}(r_{ij})/(1 - e^{\beta u(r_{ij})}) = g^{\mathrm{PY}}(r_{ij})$.

By considering the relations expressed by Eqs. (33) and (34) with Eq. (29), Eq. (51) can be rewritten as

$$\begin{aligned} \mathcal{P}(r_{ij}) &+ \frac{2\Gamma[3/2, w(r_{ij})]}{\pi^{1/2} e^{\beta u(r_{ij})} - 2\Gamma[3/2, w(r_{ij})]} C^{+}(r_{ij}) \\ &= \frac{2\{\Gamma(3/2) - \Gamma[3/2, w(r_{ij})]\} e^{\beta u(r_{ij})}}{\pi^{1/2} e^{\beta u(r_{ij})} - 2\Gamma[3/2, w(r_{ij})]} \frac{c^{\mathrm{PY}}(r_{ij})}{1 - e^{\beta u(r_{ij})}}, \end{aligned} \tag{53}$$

where $w(r_{ij}) \equiv -\beta u(r_{ij}) \theta[-\beta u(r_{ij})]$ $(\theta[x] = 1 \ (0 \leq x),\ \theta[x] = 0 \ (0 > x))$. Eq. (53) can be used as a closure scheme for Eq. (43), if $c_{ij}^{\mathrm{PY}}(r)$ is given.

If the relations expressed by Eqs. (35) and (45) are considered, Eq. (52) can be rewritten as

$$\mathcal{D}(r_{ij}) = \frac{2\Gamma[3/2, w(r_{ij})]}{2\Gamma[3/2, w(r_{ij})] - \pi^{1/2} e^{\beta u(r_{ij})}} C^{*}(r_{ij}). \tag{54}$$

An estimate of $\mathcal{D}(r_{ij})$ is allowed from considering Eq. (54) as a closure scheme for Eq. (46) if $\mathcal{P}_{ij}(r)$ is estimated with the use of Eq. (43). Although Eqs. (53) and (54) can be used when either $\beta u(r_{ij}) < 0$ or $\beta u(r_{ij}) > 0$, the relation $\beta u(r_{ij}) > 0$ requires $\mathcal{P}_{ij}(r) = 0$, $C^{+}(r_{ij}) = 0$, $\mathcal{D}(r_{ij}) \neq 0$, and $C^{*}(r_{ij}) \neq 0$.

Eqs. (53) and (54) enable $\mathcal{P}(r_{ij})$ and $\mathcal{D}(r_{ij})$ to be characterized by a pair potential, if $c^{\mathrm{PY}}(r_{ij})$, $C^{+}(r_{ij})$, and $C^{*}(r_{ij})$ are given. Moreover, Eqs. (53) and (54) suggest that separating $\mathcal{P}(r_{ij})$ from $g(r_{ij})$ allows a pair potential characterizing $\mathcal{P}(r_{ij})$ to be made different from a pair potential characterizing $\mathcal{D}(r_{ij})$. Even if a pair potential controlling the behavior of pair particles which interact in a situation I 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 II where a contribution of their relative kinetic energy exceeds a contribution of the attractive force between them, the use of Eqs. (53) and (54) enables $\mathcal{P}(r_{ij})$ and $\mathcal{D}(r_{ij})$ to be estimated. The difference between a pair potential in the situation I and that in the situation II may occur in a fluid system consisting of molecules that can form hydrogen bonds between them.

When the integral equation system given by Eqs. (43) and (46) is solved, the characteristics of attractive forces which act between particles contributing to the magnitude of $\mathcal{P}(r_{ij})$ are permitted to differ from the characteristics of attractive forces which act among particles contributing to the magnitude of $\mathcal{D}(r_{ij})$. A pair potential $u^{+}(r_{ij})$ which can characterize the former attractive forces may differ from a pair potential $u^{*}(r_{ij})$ which can characterize the latter attractive forces. Attractive forces among particles can depend on bond angles, torsional angles and coordination number of particles.[48,49] Many-body effects which are generated as the dependence of attractive forces on bond angles, torsional angles and coordination number of particles should influence the features of pair potentials if the pair potentials are made function as models for simulating effects of the attractive forces. Then, the simplest model which can involve the mean features of the many-body effects as spherically symmetric contributions should be a pair potential which can characterize the mean features of attractive forces acting among particles. If a fluid has a temperature at which a locally ordered structure cannot be maintained, the many-body effects should be ignored even in a dense gas state. The many-body effects can depend on the degree of the kinetic energies of particles. Thus, attractive forces which depend on bond angles, torsional angles and atomic coordination number should make $u^{+}(r_{ij})$ differ from $u^{*}(r_{ij})$.

(**b**) *The simple closure scheme for the MSA*

The closure scheme given by Eq. (53) is not a practicable way to solve Eq. (43) analytically. Fortunately, Eq. (43) has the same mathematical structure as the Ornstein-Zernike equation. The Ornstein-Zernike equation can be solved analytically for some fluids, if the mean spherical approximation (MSA)[31] is used. In the MSA, the direct correlation function $c(r)$ is given as the sum of the short-range contribution $c^{0}(r)$ and the long-range contribution

$-\beta u(r)$. This means that $c(r)$ is expressed as

$$c(r) = c^0(r) - \beta u(r) \tag{55}$$

$$c^0(r) = 0, \qquad \text{for } \ r > \sigma, \tag{56}$$

where σ is the hard-core of a particle. If $C^+(r)$ is given in the same form as $c(r)$ given in the MSA, the procedure for solving Eq. (43) can be simplified, as is found in the procedures concerning the MSA.

According to the MSA,[23,31] the direct correlation function $c(r)$ out of the contribution of the hard-core interaction is effective within the range where the magnitude of $u(r)$ is not neglected. $c(r)$ decays to zero as rapidly as $-\beta u(r)$, which expresses a microscopic feature. This means that the ranges within which the correlation functions $C^+(r)$ and $C^*(r)$ are not zero remain microscopic sizes because of Eq. (45). The correlation function $g(r) - 1$ decays to zero much more slowly than $c(r)$[9,17]. Thus, the behavior of $g(r) - 1$ is different from the behavior of $c(r)$, which has a tendency to maintain the microscopic feature.

This fact is demonstrated by the solution that is obtained by solving the Ornstein-Zernike equation recursively. The solution is given as

$$\begin{aligned} g(r) - 1 =& c(r) + \rho \int_V c(r_{13}) c(r_{32}) \mathrm{d}\mathbf{r}_3 \\ &+ \rho\rho \int_V \int_V c(r_{13}) c(r_{34}) c(r_{42}) \mathrm{d}\mathbf{r}_3 \mathrm{d}\mathbf{r}_4 + \cdots , \end{aligned} \tag{57}$$

where the convolution integrals denote contributions from particle 3, particle 4, $\cdots$, which distribute around particle 1 and particle 2 that exist away from each other at the distance r. Contributions from particle 3, particle 4, $\cdots$, make the behavior of $g(r) - 1$ differ from the behavior of $c(r)$

When the relation between the distance r and the hard core diameter σ of each particle satisfies $r \leq \sigma$, the relation $g(r) - 1 = -1$ should be satisfied. Hence, Eq. (57) requires $c(r)$ to be negative even for $r/\sigma \approx 1$ if $0 < r/\sigma < 1$ is satisfied. Every convolution integral in Eq. (57) cannot always positively contribute to the magnitude of $g(r) - 1$. Nevertheless, the magnitude of $g(r) - 1$ can remain a positive finite value at large r that is out of the effective range where $c(r) \neq 0$. This means that convolution integrals which positively contribute to the magnitude of $g(r) - 1$ are dominant in Eq. (57). Thus, the manner in which the direct correlation function contributes to the magnitude of $g(r) - 1$ denotes that the long-range contribution characterized for $\sigma < r$ differs from the short-range contribution characterized for $r \leq \sigma$. This behavior agrees with the concept for the MSA, i.e., the concept that $c(r)$ is given as the sum of the short-range contribution and the long-range contribution.

The direct correlation function $c(r)$ is the contribution of all non-nodal diagrams consisting of paths of f-bonds between the two root points. Similarly, $C^+(r)$ is the contribution of all non-nodal diagrams having at least one path of all f^+-bonds between the two root points, and $C^*(r)$ 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 $C^+(r)$ and the behavior of $C^*(r)$ should be similar to the behavior of $c(r)$. According to the MSA,[31] the direct correlation function $c(r)$ is given by Eq. (56), and the MSA shows that $c(r)$ behaves as $c(r)/(-\beta u(r)) = 1$ and $c^0(r) = 0$ outside the effective range of the hard core potential. Thus, the similarity between $c(r)$ and $C^+(r)$ suggests that the behavior of $C^+(r)$ should is given as the sum of the short-range contribution expressed as $C^{0+}(r)$ and the long-range contribution to $C^+(r)$. Moreover, the similarity between $c(r)$ and $C^*(r)$ suggests that the behavior of $C^*(r)$ should is given as the sum of the short-range contribution expressed as $C^{0*}(r)$ and the long-range contribution to $C^*(r)$.

(**c**) *Behavior of* $C^+(r)$ *for* $0 < -\beta u(r) \ll 1$ *at large* r.

The behavior of $C^+(r)$ at large r can be readily determined. When the distance between particle 1 and particle 2 is sufficiently large, $|\beta u(r)|$ should be sufficiently small. Equation (29) can then be approximated as

$$\begin{aligned} p(r) = & \frac{4}{3\sqrt{\pi}}\left(-\beta u(r)\right)^{3/2} - \frac{4}{5\sqrt{\pi}}\left(-\beta u(r)\right)^{5/2} \\ & + \frac{2}{7\sqrt{\pi}}\left(-\beta u(r)\right)^{7/2} + \cdots . \end{aligned} \tag{58}$$

If $p(r)$ given by Eq. (58) is substituted into Eq. (53), the following formula is obtained:

$$\begin{aligned} C^+_{ij} = & \frac{c^{\mathrm{PY}}_{ij}}{-\beta u_{ij}}\left[\frac{4}{3\sqrt{\pi}}(-\beta u_{ij})^{3/2} - \frac{22}{15\sqrt{\pi}}(-\beta u_{ij})^{5/2} + \cdots\right] \\ & + P_{ij}\Big[-\beta u_{ij} - \frac{4}{3\sqrt{\pi}}(-\beta u_{ij})^{3/2} - \frac{1}{2}(-\beta u_{ij})^2 + \frac{32}{15\sqrt{\pi}}(-\beta u_{ij})^{5/2} + \cdots\Big]. \end{aligned} \tag{59}$$

A long-range contribution to $C^+(r)$ is obtained from Eq. (59) by considering an assumption which is made as $\mathcal{P}(r) \sim [-\beta u(r)]^\nu$ and $1 \leq \nu$ for $1 \ll r/\sigma$ and $\beta u(r) < 0$. Here, σ is the diameter of the hard core of each particle. At least the condition

$\mathcal{P}(r)/[g(r)-1] \leq 1$ is always satisfied. This is not inconsistent with Eq. (42) that is satisfied without percolation of physical clusters. Thus, $\mathcal{P}(r)$ for $1 \ll r/\sigma$ should satisfy $[g(r)-1]/[-\beta u(r)] \geq \mathcal{P}(r)/[-\beta u(r)]$. The MSA gives $c^{\mathrm{PY}}(r)/[-\beta u(r)] = 1$ for $1 \ll r/\sigma$, so that the relation $g^{\mathrm{PY}}(r) = c^{\mathrm{PY}}(r)/\{1-\exp[\beta u(r)]\}$ due to the PY approximation results in $\lim_{r\to\infty}[g(r)-1]/[-\beta u(r)] = 1/2$ owing to a general assumption $\lim_{r\to\infty} u(r) = 0$. This result suggests $1/2 \geq \mathcal{P}(r)/[-\beta u(r)]$ for $1 \ll r/\sigma$, and the behavior of $\mathcal{P}(r)$ for $1 \ll r/\sigma$ is expressed as $\mathcal{P}(r) \sim [-\beta u(r)]^{\nu}$ and $1 \leq \nu$. Owing to this behavior of $\mathcal{P}(r)$, a long-range contribution to $C^{+}(r)$[38] is found from Eq. (59) as

$$C^{+}(r) \approx \frac{4}{3\sqrt{\pi}}\big[-\beta u(r)\big]^{3/2}, \quad (\text{for } 1 \ll r/\sigma). \tag{60}$$

(**d**) *Behavior of* $\mathcal{P}(r)$ *for* $0 < -\beta u(r) \ll 1$ *at large* r.

The expansion of Eq. (53), which is obtained in powers of $-\beta u(r)$ for $|\beta u(r)| \ll 1$ and $1 \ll r/\sigma$ based on the substitution of $p(r)$ expressed by Eq. (58), can be given instead of Eq. (59) as follows

$$\begin{aligned}\mathcal{P}(r) =& -\frac{c^{\mathrm{PY}}(r)}{-\beta u(r)}\Big[\frac{4}{3\sqrt{\pi}}(-\beta u(r))^{1/2} + \frac{16}{9\pi}(-\beta u(r)) + \Big(\frac{64}{27\pi^{3/2}} - \frac{4}{5\sqrt{\pi}}\Big)(-\beta u(r))^{3/2} + \cdots\Big] \\ &+ \frac{C^{+}(r)}{-\beta u(r)}\Big[1 + \frac{4}{3\sqrt{\pi}}(-\beta u(r))^{1/2} + \Big(\frac{1}{2} + \frac{16}{9\pi}\Big)(-\beta u(r)) + \cdots\Big].\end{aligned} \tag{61}$$

The use of Eq. (60) obtained under the condition that no percolation of physical clusters occurs enables Eq. (61) to reveal the behavior of $P(r)$ for $1 \ll r/\sigma$. If the relation $c^{\mathrm{PY}}(r)/(-\beta u(r)) = 1$ given for the MSA at large r are considered in Eq. (61), the behavior of $P(r)$ at large r ($1 \ll r/\sigma$) is expressed as

$$\mathcal{P}(r) = \frac{22}{15\sqrt{\pi}}(-\beta u(r))^{3/2} \quad \text{for} \quad u(r) < 0. \tag{62}$$

If each physical cluster formed in a fluid where no percolation occurs has a fractal structure, then $P(r)$ given by Eq. (62) should represents the characteristics of the fractal structure.[38]

(**e**) *A simple closure scheme for Eq. (43)*

The similarity between the behavior of $c(r)$ and the behavior of $C^{+}(r)$ for variations in r should allow the behavior of $C^{+}(r)$ to be given as the sum of the short-range contribution expressed as $C^{0+}(r)$ and the long-range contribution to $C^{+}(r)$. An approximate $C^{+}(r)$ given by the sum becomes a simple closure scheme for the integral equation given by Eq. (43).

Since the long-range contribution to $C^{+}(r)$ is given by Eq. (60), the simple closure scheme similar to the MSA is expressed as

$$C^{+}(r) = C^{0+}(r) + \frac{4}{3\sqrt{\pi}}(-\beta u(r))^{3/2} \quad \text{for} \quad \beta u(r) < 0, \tag{63}$$

where for the short-range contribution $C^{0+}(r)$, the behavior similar to $c(r)^{0}$ is required according to analogy with the MSA. Thus, $C^{0+}(r)$ should be given as

$$C^{0+}(r) = 0, \qquad \text{for} \quad r \geq \sigma. \tag{64}$$

For the diameter σ of the hard core of each particle, the most completely short-range interaction between pair particles should be attributed to a hard core potential. The hard core potential does not directly contribute to the interaction between them for $r \geq \sigma$. Thus, Eq. (64) should be justified as an approximate expression as found according to the MSA.

According to the MSA, $c(r)$ decay to zero as rapidly as $-\beta u(r)$, which expresses a microscopic feature. Eq. (63) demonstrates that $C^{+}(r)$ behave in a way similar to $c(r)$, although Eq. (62) requires it to decay to zero more rapidly than $-\beta u(r)$. Despite this fact, $\mathcal{P}(r)$ can still have a finite value being no zero even out of the effective range in which the microscopic feature is subject. This can be explained via the solution that is obtained from solving Eq. (43) recursively in the same manner as the mathematical procedure for solving the Ornstein-Zernike equation. Thus, the integral equation expressed by Eq. (43) has the recursive solution given as

$$\begin{aligned} \mathcal{P}(r) =& C^{+}(r) + \rho \int_V C^{+}(r_{13})C^{+}(r_{32})\mathrm{d}\mathbf{r}_3 \\ &+ \rho\rho \int_V \int_V C^{+}(r_{13})C^{+}(r_{34})C^{+}(r_{42})\mathrm{d}\mathbf{r}_3\mathrm{d}\mathbf{r}_4 + \cdots . \end{aligned} \tag{65}$$

This equation denotes that the probability that both particle 1 and particle 2 being at the distance r from particle 1 belong to the same physical cluster can enhance via the contribution of other particles $(3, 4, \cdots)$. Then, each term on the right-hand side of Eq. (65) has the magnitude proportional to that probability, while depending on the contribution of other particular particles $(3, 4, \cdots)$. Although the first term without the contribution of other particular particles is the exception, the first term being $C^{+}(r)$ is also proportional to the probability that both the particle 1 and the particle 2 belong to the same physical cluster. If the contributions of particles $(3, 4, \cdots)$ distributing around the particle 1 and the particle 2 cannot be negligible, it is possible for $\mathcal{P}(r)$ to remain not zero even out of the effective range in which $C^{+}(r) \neq 0$.

Each convolution integral on the right hand side of Eq. (65) is positive for the reason that $C^{+}(r)$ must everywhere be positive because of $0 \leq \mathcal{P}(r) \ \ (0 < r)$. In Eq. (57), every convolution integral must not always be positive for the reason that $c(r)$ is negative for $0 < r/\sigma \leq 1$ because $g(r) - 1 \approx -1 \ (0 < r/\sigma \leq 1)$ is satisfied under the condition that no percolation of physical clusters occurs. The contributions of particles $(3, 4, \cdots)$ distributing around the particle 1 and the particle 2 to $\mathcal{P}(r)$ seems different from their contributions to $g(r)$. Despite this, Eq. (57) resulting from the Ornstein-Zernike equation corresponds to the sum of the contribution from $\mathcal{D}$ and the contribution from $\mathcal{P}$, according to Eq. (35). The contribution of Eq. (65) to $g(r)$, which should be considered as the contribution of the physical cluster formation to $g(r)$, is hidden in the expression of Eq. (57).

In addition, the pair connectedness $\mathcal{P}(r)$, which must satisfy an integral equation given by Eq. (43), involves contributions of many particles, which are expressed as convolution integrals found in Eq. (65). This fact means that the pair connectedness $\mathcal{P}(r)$ derived from the use of an approximate $C^{+}(r)$ involves contributions of many particles, even when the approximate $C^{+}(r)$ results from contributions of limited principal particles. Even without the use of an accurate $C^{+}(r)$ resulting from the contributions of all particles which should be considered, making $\mathcal{P}(r)$ satisfy the integral equation given by Eq. (43) makes it possible to succeed in replying to the necessity of considering contributions of many particles.

(**f**) *A simple closure scheme for Eq. (46).*

If $\beta u(r_{ij})$ is positive, every particle pair contributes to the magnitude of $C^{*}(r_{ij})$. Even if $\beta u(r_{ij})$ is negative, particle pairs contributing to the magnitude of $C^{*}(r_{ij})$ exist. The magnitude of $C^{*}(r_{ij})$ results from the contribution of non-nodal diagrams that do not include paths of all f^{+}-bonds between i and j. Particle pairs contributing to its magnitude include specific 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 between them.

If the MSA and the behavior of $\mathcal{P}(r_{ij})$ given by Eq. (62) are considered, the relation given by Eq. (35) and the PY approximation $g^{\mathrm{PY}}(r_{ij}) = c^{\mathrm{PY}}(r_{ij})/\{1 - \exp[\beta u(r_{ij})]\}$ result in

$$\mathcal{D}(r_{ij}) - 1 \approx -\frac{1}{2}\beta u(r_{ij}) \ \ \text{for} \ \ 1 \ll r_{ij}/\sigma. \tag{66}$$

Eq. (66) denotes the behavior of $\mathcal{D}(r)$ for $0 < |-\beta u(r)| \ll 1$ at large r.

The behavior of $\mathcal{D}_{ij}(r) - 1$ at large r allows Eq. (54) to lead to

$$C^*(r_{ij}) \approx -\beta u(r_{ij}) \;\text{ for }\; 1 \ll r_{ij}/\sigma. \tag{67}$$

This is the long-range contribution to $C^*(r_{ij})$. Thus, the use of Eq. (67) allows the behavior of $C^*(r_{ij})$ to be approximately given as the sum of the short-range contribution expressed as $C^{0*}(r)$ and the long- range contribution to $C^*(r_{ij})$ according to analogy with the MSA. This means that an approximation of $C^*(r_{ij})$ is expressed for either $\beta u(r_{ij}) < 0$ or $\beta u(r_{ij}) > 0$ by

$$C^*(r_{ij}) = C^{0*}(r_{ij}) - \beta u(r_{ij}), \tag{68}$$

$$C^{0*}(r_{ij}) = 0, \qquad \text{for } r > \sigma. \tag{69}$$

The hard core potential does not directly contribute to the interaction between them for $r \geq \sigma$. Thus, Eq. (69) should be justified as an approximate expression as found according to the MSA.

Eq. (69) demonstrates that $C^*(r)$ behave in a way similar to $c(r)$, and it decays to zero as rapidly as $-\beta u(r)$, which expresses a microscopic feature. Despite this fact, $\mathcal{H}(r)$ can still have a finite value being no zero even out of the effective range in which the microscopic feature is subject. This can be explained via the solution that is obtained from solving Eq. (46) recursively. The integral equation expressed by Eq. (46) has the recursive solution given as

$$\begin{aligned}\mathcal{H}(r) =& C^*(r) + \rho \int_V c(r_{13})C^*(r_{32})\mathrm{d}\mathbf{r}_3 + \rho\rho \int_V \int_V c(r_{13})c(r_{34})C^*(r_{42})\mathrm{d}\mathbf{r}_3\mathrm{d}\mathbf{r}_4 + \\ &+\rho \int C^*(r_{13})\mathcal{P}(r_{32})\mathrm{d}\mathbf{r}_3 + \rho\rho \int_V \int_V c(r_{13})C^*(r_{34})\mathcal{P}(r_{42})\mathrm{d}\mathbf{r}_3\mathrm{d}\mathbf{r}_4 \\ &+\rho\rho\rho \int_V \int_V \int_V c(r_{13})c(r_{34})C^*(r_{45})\mathcal{P}(r_{52})\mathrm{d}\mathbf{r}_3\mathrm{d}\mathbf{r}_4\mathrm{d}\mathbf{r}_5 + \cdots .\end{aligned} \tag{70}$$

In Eq. (70), every convolution integral must not always be positive for the reason that $C^*(r)$ and $c(r)$ are negative for at least $0 < r/\sigma \leq 1$ because $\mathcal{H}(r) \approx -1$ $(0 < r/\sigma \leq 1)$ and $g(r) - 1 \approx -1$ $(0 < r/\sigma \leq 1)$ are satisfied for no percolation of physical clusters. This denotes that every convolution integral in Eq. (70) cannot always positively contribute to the magnitude of $\mathcal{H}(r)$. However, it is possible that the magnitude of $\mathcal{H}(r)$ at large r out of the effective range, in which $C^*(r) \neq 0$, remains a finite value being no zero, in the case that convolution integrals which can positively contribute to the magnitude of $\mathcal{H}(r)$ are dominant in Eq. (70).