PHYSICAL REVIEW E **66**, 051502 (2002)

Contribution of physical clusters to phase behavior

Tetsuo Kaneko*
Kurakenchikuzokeisha Company, Ltd., Shimo 1-27-22, Kita-ku, Tokyo 115-0042, Japan

(Received 20 January 2002; revised manuscript received 28 June 2002; published 18 November 2002)

In a multicomponent fluid mixture, each physical cluster generated as an ensemble consisting of particles joined by each particle pair characterized by a bound state $E_{ij}+u_{ij}\leqslant 0$ can contribute towards prohibiting a transition from its macroscopically homogeneous phase to its macroscopically inhomogeneous phase. Here, E_{ij} and u_{ij} represent the relative kinetic energy and the pair potential for the pair of *i* and *j* particles, respectively. Branches constructing such physical clusters can confine unbound particles (i.e., particles constituting pairs characterized by an unbound state $E_{ij}+u_{ij}>0$) within regions surrounded by the branches, and can prohibit the boundaries of the regions from expanding freely. Particles belonging to one of the two groups characterizing constituents of a multicomponent fluid mixture (particles of $\mathcal{A}$) should have a tendency to satisfy the condition $E_{ij}+u_{ij}\leqslant 0$; particles belonging to the other group (particles of $\mathcal{B}$) should have a tendency to satisfy the condition $E_{ij}+u_{ij}>0$. The pair connectedness $P_{ij}(\sigma)$ proportional to the probability that a particle of $\mathcal{A}$ is bound near another particle of $\mathcal{A}$ hardly varies as densities of particles of $\mathcal{A}$ increase, although the mean physical cluster size diverges to infinity as the densities approach values specified at the percolation threshold. Thus, each physical cluster should grow toward that having a larger span as densities of particles of $\mathcal{A}$ increase. According to this growth of physical clusters, the number of unbound particles confined by branches of the physical clusters is enhanced. The formation of physical clusters of particles of $\mathcal{A}$ can be considered as a primary phenomenon resulting in density fluctuations. Their formation results in the confinement of particles of $\mathcal{B}$ and $\mathcal{A}$ within regions surrounded by the branches of the physical clusters.

DOI: 10.1103/PhysRevE.66.051502 PACS number(s): 64.70.Fx, 64.60.Ak, 05.70.Jk, 61.20.Gy

I. INTRODUCTION

The statistics of cluster size diversity can contribute to the statistical description of a complex system. Such an aspect was demonstrated as the results of Monte Carlo simulations [1]. It is possible even for complicated phase behavior of a multicomponent fluid mixture [2] to be attributed to a contribution of physical clusters. The present interest is focused on examining a contribution of physical clusters to phase behavior of a multicomponent fluid mixture.

The transition of a fluid from its gas phase to its liquid phase can be driven by attractive forces among particles constituting the fluid. The attractive forces contribute to generating each physical cluster as an ensemble composed of particles bound to each other by it.

A bound state between *i* and *j* particles can, then, be defined by the condition $E_{ij}+u_{ij}\leqslant 0$ [3], if the relative kinetic energy E_{ij} and the pair potential u_{ij} for the pair of the *i* and *j* particles are used. Thus, every physical cluster mentioned in the present work is an ensemble of particles linked to each other by bonds defined as the condition $E_{ij}+u_{ij}\leqslant 0$.

In the present work, it is assumed that the potential βu_{ij} is given as the sum of $\mathcal{N}$ terms composed of $k_0^{(n)}d_i^{(n)}d_j^{(n)}\exp(-z_n r)/r$ $(n=1,2,\ldots,\mathcal{N})$ having the same feature as the Yukawa potential, since an estimate of phase behavior for a multicomponent fluid mixture can proceed analytically. Here, the coefficient β is defined as $\beta\equiv 1/k_BT$ with k_B the Boltzmann's constant and T the temperature. The product $k_0^{(n)}d_i^{(n)}d_j^{(n)}$ of coefficients is proportional to both the factor $1/k_BT$ and the strength of the attractive force. Hence, an increase in $k_0^{(n)}d_i^{(n)}d_j^{(n)}$ should stabilize branches of physical clusters. Similarly, an increase in $1/z_n$ corresponding to the effective range of the attractive force can stabilize them.

If physical clusters are formed with developed branches which densely surround particles constituting pairs characterized by an unbound state $E_{ij}+u_{ij}>0$, then, the physical clusters should restrict the particles to diffuse freely. It is, moreover, expected that the physical clusters can tend to prohibit the boundaries surrounding the particles from expanding freely.

If branches that are components of physical clusters have high stability in a fluid, particles constituting pairs specified by an unbound state $E_{ij}+u_{ij}>0$ can be confined within regions surrounded by the branches even at a high temperature. The physical clusters should be developed toward extremely large sizes as found in a percolation state related to the physical clusters, and can contribute towards preserving the liquid phase of the fluid at a high temperature.

In addition, particles within regions surrounded by branches of physical clusters are unbound particles (i.e., particles constituting pairs characterized by an unbound state $E_{ij}+u_{ij}>0$). Local densities of particles within the regions should, thus, be lower than the local particle densities of the physical clusters.

In a multicomponent fluid mixture, particles interacting with strongly attractive forces can effectively contribute to the formation of physical clusters. Such particles can contribute to phase behavior of the fluid mixture through promoting the growth of physical clusters.

Particles interacting with relatively weakly attractive forces in the fluid mixture can hardly effectively contribute to the formation of physical clusters. Almost all the particles

---

*Electronic address: kaneko@mailaps.org

should be categorized as unbound particles.

Therefore, constituents of the fluid mixture can be separated into at least two groups $\mathcal{A}$ and $\mathcal{B}$. The group $\mathcal{A}$ is categorized as constituents that specify particles interacting with strongly attractive forces between each other (i.e., the particles having a tendency to satisfy the condition $E_{ij}+u_{ij} \leqslant 0$). The other group $\mathcal{B}$ is categorized as constituents that specify particles interacting with weakly attractive forces either between each other or between a particle belonging to $\mathcal{A}$ and a particle belonging to $\mathcal{B}$ (i.e., the particles having a tendency to satisfy the condition $E_{ij}+u_{ij}>0$).

Although particles belonging to $\mathcal{B}$ can hardly effectively contribute to the formation of physical clusters, the particles should receive passively attractive forces generated from the cooperation between the exclusion of the particles due to the hard core potential and each attractive force between particles belonging to $\mathcal{A}$. The passively attractive forces should contribute to driving the phase separation of particles belonging to $\mathcal{B}$, although the features of the forces cannot be simple owing to a contribution of physical clusters.

The phase separation of particles belonging to $\mathcal{A}$ should be driven by the strongly attractive interaction forces among particles belonging to $\mathcal{A}$. The formation of physical clusters should be directly influenced by an increase in particles belonging to $\mathcal{A}$.

If particles added into a fluid interact with a sufficiently strongly attractive force between one of them and a particle composed of the fluid, the addition of the particles should increase the stabilization of the physical clusters in the fluid. If an interaction similar to the interaction caused by the added particles is done by atoms of bismuth added into a mercury fluid maintained at low density at a temperature near the critical point, bismuth atoms migrating into physical clusters of mercury atoms should increase the stabilization of the physical clusters. The stabilization of the physical clusters due to the addition of bismuth atoms should enhance the electrical conductivity of the mercury fluid, since the physical clusters can play a role as paths helping electrons to migrate. Furthermore, their stabilization should reduce the pressure of the mercury fluid, since branches of the stabilized physical clusters can confine unbound mercury atoms. Such phenomena due to the addition of bismuth atoms were experimentally demonstrated [4].

However, the stability of physical clusters in a fluid mixture should be reduced, if the temperature of the fluid mixture rises. It can, then, become difficult for branches of the physical clusters to stably confine particles belonging to the group $\mathcal{B}$, within regions surrounded by their branches. This phenomenon can disturb a macroscopically homogeneous phase of the fluid mixture.

Physical clusters not only contribute towards prohibiting a transition from a liquid phase of a fluid to its gas phase, but also towards prohibiting a transition from a macroscopically homogeneous phase of a multicomponent fluid mixture to its macroscopically inhomogeneous phase. Thus, a multicomponent fluid mixture can be considered as a good medium for examining a contribution of physical clusters to phase behavior. It is, moreover, expected that a distribution structure that is constructed from physical clusters and unbound particles surrounded by branches of the physical clusters can play a role microscopically to interpret phenomena found for a specific fluid mixture.

For a binary fluid mixture, the viscosity anomaly [5] can be induced near the consolute point corresponding to the critical transition point for demixing the two constituents macroscopically. It is considered for the distribution structure having physical clusters to contribute to the viscosity anomaly.

Particles belonging to the group $\mathcal{B}$ can be stably confined within regions surrounded by branches of physical clusters, if their particle sizes are small. If the particles have sizes larger than those of the regions, it is expected that the stable confinement of those particles becomes more difficult than that of the smaller particles.

Such size effect can contribute to phase behavior of a binary fluid mixture [6]. Similarly, the size effect can contribute to phase behavior of a binary fluid mixture of 2,6-lutidine and water near the consolute point also, since the size of a 2,6-lutidine molecule is much larger than that of a water molecule.

Nevertheless, 2,6-lutidine molecules should be considered as molecules belonging to the group $\mathcal{A}$ with water molecules. The attractive force between two 2,6-lutidine molecules, as well as that between a 2,6-lutidine molecule and a water molecule cannot be ignored, although these attractive forces are weaker than the attractive force between two water molecules. Thus, two kinds of physical clusters can be generated in a binary fluid mixture of 2,6-lutidine and water; those are water molecule clusters that are principally composed of water molecules, and the others are 2,6-lutidine molecule clusters that are principally composed of 2,6-lutidine molecules. A partial amount of 2,6-lutidine molecules can have a tendency to enter regions surrounded by branches of water molecule clusters. However, the size effect mentioned above should induce the phase separation of 2,6-lutidine molecules, when 2,6-lutidine molecules in the binary fluid mixture exceed a specific amount. Another partial amount of 2,6-lutidine molecules should participate in the formation of a water molecule cluster with water molecules. These 2,6-lutidine molecules can contribute towards cutting branches of the water molecule cluster, since the attractive force between two 2,6-lutidine molecules should be weaker than that between a water molecule and a 2,6-lutidine molecule. Thus, 2,6-lutidine molecules participating in the formation of water molecule clusters should contribute to expand sizes of the regions surrounded by branches of the water molecule clusters in cooperation with a temperature effect. If regions surrounded by branches of the water molecule clusters expand, 2,6-lutidine molecules can readily confine within the regions. Even 2,6-lutidine molecule clusters should, then, be found within the regions, if the regions are sufficiently large. Furthermore, the contribution of 2,6-lutidine molecules towards cutting branches of the water molecule cluster can decrease the average extent of water molecule clusters, and as a result, declining water molecule clusters should allow 2,6-lutidine molecule clusters to exist among them. It is, thus, expected that a macroscopically homogeneous mixture of 2,6-lutidine and water should be generated, although the microscopic distribution of water molecules and 2,6-lutidine molecules is nonuniform. In addition, the microscopically nonuniform distribution of 2,6-lutidine molecules occurring in binary fluid mixtures of 2,6-lutidine and water near the consolute point can be realized through the aggregation phenomena of colloidal particles [7].

Density fluctuations in a specific constituent in a multicomponent fluid mixture can induce density fluctuations for other constituents, as predicted from the aggregation of the colloidal particles. This phenomenon can be a factor complicating a phase diagram for a multicomponent fluid mixture. Monte Carlo simulation revealed such complicated phase diagrams even for a binary fluid mixture composed of particles interacting with the attractive force due to a square-well potential [2].

Even if colloidal particles having mesoscopic sizes are regarded as hard core spheres in the absence of attractive forces, it is possible for passively attractive forces to be generated among the colloidal particles immersed in a molecular fluid mixture. At a temperature near the consolute point of the fluid mixture, a distribution structure that is constructed from physical clusters and unbound molecules surrounded by branches of the physical clusters can vary considerably. If the average extent of the physical clusters increases beyond that comparable with the diameter of a colloidal particle, the passively attractive forces among the colloidal particles should be strengthened, since the surface of a colloidal particle cannot contribute to making a physical cluster grow. Thus, it is expected that such attractive forces can contribute to Casimir forces, which can act among colloidal particles (or between parallel plates) immersed within a binary fluid mixture near the consolute point (or a one-component fluid near the liquid-vapor critical transition point) [8].

When physical clusters are formed in a fluid, particles constituting the fluid can be classified into two groups. One group is categorized as an ensemble of pair particles that belong to the same physical cluster. The other group is categorized as an ensemble of pair particles that do not belong to the same physical cluster. This categorization divides the pair correlation function $g_{ij}(r)$ into a correlation function $P_{ij}(r)$ and the other correlation function $\mathcal{D}_{ij}(r)$ [9].

According to the above categorization, particles belonging to the group $\mathcal{A}$ should significantly contribute to the magnitude of $P_{ij}(r)$, since these particles can actively contribute to the formation of physical clusters. Particles belonging to the group $\mathcal{B}$ should relatively contribute to the magnitude of $\mathcal{D}_{ij}(r)$, since these particles should have a tendency to distribute within regions surrounded by branches of physical clusters. Thus, a distribution structure of particles can be characterized by $P_{ij}(r)$ and $\mathcal{D}_{ij}(r)$ that are able to describe a multicomponent fluid mixture.

The correlation function $P_{ij}(r)$ called the pair connectedness should rapidly decay as r increases beyond the average extent of physical clusters. The decay of $\mathcal{D}_{ij}(r)$ for r should not depend on the average extent of physical clusters, if r is sufficiently large. Thus, the asymptotic behavior of $\mathcal{D}_{ij}(r)$ for $r \gg 1$ should be expressed as $\mathcal{D}_{ij}(r) \approx g_{ij}(r)$, since $g_{ij}(r)$ is given by the sum $P_{ij}(r) + \mathcal{D}_{ij}(r)$. The asymptotic behavior of $P_{ij}(r)$ for $r \gg 1$ can be approximately expressed as $P_{ij}(r) \sim [-\beta u_{ij}(r)]^{3/2}$ [10]. This asymptotic behavior suggests that if a physical cluster has a fractal structure, its structure can rely on a feature of $u_{ij}(r)$. If the asymptotic behavior of $u_{ij}(r)$ for $r \gg 1$ is expressed as $u_{ij}(r) \sim 1/r$, the asymptotic behavior of $P_{ij}(r)$ suggests a physical cluster to have a structure with a fractal dimension 1.5. The growth of a physical cluster of a particular constituent can result from the contact of small physical clusters. This growth process can be similar to that known as cluster-cluster aggregation. In addition, the distribution of particles resulting from cluster-cluster aggregation leads to a fractal structure, while the dimension d_f of the fractal structure is known as $d_f \sim 1.75$ [11].

The mean size of physical clusters can be estimated using the pair connectedness $P_{ij}(r)$ [9]. An equation for estimating their mean size is given in Sec. II C. Thus, a criterion for the growth of physical clusters into macroscopic size can be given as that for the growth of the mean size of the physical clusters. Using this measure, it is possible to estimate the percolation threshold at which the physical clusters can grow without bounds according to the contact between physical clusters. Such estimates on the percolation threshold proceeded analytically for single-component fluids composed of particles interacting via the Yukawa potential [10,12]. Moreover, such an estimate of the percolation threshold proceeded analytically for a multicomponent fluid composed of particles interacting via a potential having the same feature as the Yukawa potential [13].

According to the use of a specific Yukawa potential, an accurate and efficient estimation of the pair correlation function $g_{ij}(r)$ is possible for a binary fluid mixture over the entire r range [14]. In the present work, the pair correlation function $g_{ij}(r)$ at a specific point $(r = \sigma_{ij})$ will be estimated for the potential βu_{ij} having terms composed of $k_0^{(n)} d_i^{(n)} d_j^{(n)} \exp(-z_n r)/r$ $(n = 1, 2, \ldots, \mathcal{N})$, using an analytical solution [15,16] of the Ornstein-Zernike equation due to the mean spherical approximation (MSA). The pair correlation function derived from this analytical solution is shown in the Appendix. The pair connectedness $P_{ij}(r)$ can be obtained for that potential as summarized in Sec. II.

In order to estimate phase behavior for specific two-component fluids, $P_{ij}(r)$ and $g_{ij}(r)$ will be given in Sec. III. Each two-component fluid discussed in Sec. III is a mixture in which hard core spheres ($i = 1$ particles) interacting with an attractive force are mixed with hard core spheres ($i = 2$ particles) in the absence of attractive forces. In addition, the $i = 1$ particles correspond to particles belonging to the group $\mathcal{A}$, and the $i = 2$ particles correspond to particles belonging to the group $\mathcal{B}$.

II. PAIR CONNECTEDNESS

A. A closure scheme similar to the MSA

The pair connectedness $P_{ij}(r)$ is defined as the probability $\rho_i \rho_j P_{ij}(r) d\mathbf{r}_i d\mathbf{r}_j$ that both the i particle in a volume element $d\mathbf{r}_i$ and the j particle in a volume element $d\mathbf{r}_j$ belong to the same physical cluster. In the above, ρ_i and ρ_j are the densities of the i and j particles, respectively, for a uniform distribution. The probability that the i particle in $d\mathbf{r}_i$ and the j particle in $d\mathbf{r}_j$ do not belong to the same cluster is expressed as $\rho_i\rho_j\mathcal{D}_{ij}(r)d\mathbf{r}_i d\mathbf{r}_j$.

The pair connectedness $P_{ij}(r)$ should satisfy an integral equation derived from classifying Mayer's mathematical clusters (diagrams defined in terms of f bonds) which constitute g_{ij}. The Mayer f function $f_{ij}=e^{-\beta u_{ij}}-1$ is represented as the sum of two factors; one factor is expressed as f_{ij}^{+} contributing to the bound state, and the other factor is expressed as f_{ij}^{*} which does not contribute to the bound state. The factors f_{ij}^{+} and f_{ij}^{*} can be given as $f_{ij}^{+}\equiv p_{ij}(r)e^{-\beta u_{ij}}$ and $f_{ij}^{*}\equiv[1-p_{ij}(r)]e^{-\beta u_{ij}}-1$, respectively, using the probability, $p_{ij}(r)$, that a pair of i and j particles satisfies the condition $E_{ij}+u_{ij}\leqslant 0$. The probability $p_{ij}(r)$ should be given as

$$p_{ij}(r)=2\pi^{-1/2}\int_0^{-\beta u_{ij}} y^{1/2}e^{-y}dy,$$

where y is defined as $y=[\beta E_{ij}]^{1/2}$ [3]. Thus, Mayer's mathematical clusters constituting g_{ij} can be expressed as mathematical clusters consisting of f_{ij}^{+} and f_{ij}^{*}. If each f_{ij}^{+} is defined in terms of an f^{+} bond, the f^{+} bond corresponds to the pair of particles satisfying the condition $E_{ij}+u_{ij}(r)\leqslant 0$. Particles jointed by f^{+} bonds form a physical cluster. If the physical cluster includes i and j particles, the physical cluster includes the particles contributing to a diagram having at least one path of all the f^{+} bonds between the root points i and j, at which the i and j particles are located. Such diagrams are those that contribute to P_{ij}, according to the definition of P_{ij}. The collection of diagrams contributing to P_{ij} can, then, be separated into the sum of two parts, namely, C_{ij}^{+} and N_{ij}^{+}. The part C_{ij}^{+} is the contribution of non-nodal diagrams having at least one path of all f^{+} bonds between i and j. The part N_{ij}^{+} represents the contribution of nodal diagrams having at least one path of all f^{+} bonds between i and j. Hence, N_{ij}^{+} can be given by the convolution integral of the product of C_{ij}^{+} and P_{ij}. The convolution integral can result in an integral equation that should be satisfied by P_{ij}. Therefore, the pair connectedness P_{ij} can be given as a solution of the integral equation [9]. Such an integral equation can be expressed for $\mathcal{L}$ constituents as

$$P_{ij}(r)=C_{ij}^{+}(r)+\sum_{k=1}^{\mathcal{L}}\rho_k\int C_{ik}^{+}(|\mathbf{r}-\mathbf{r}_k|)P_{kj}(\mathbf{r}_k)d\mathbf{r}_k, \tag{2.1}$$

where $\mathcal{L}$ is the number of constituents.

The meaning of the correlation function C_{ij}^{+} can be revealed from Eq. (2.1), since Eq. (2.1) can be solved recursively for P_{ij} to give

$$P_{ij}=C_{ij}^{+}+\sum_{k_1=1}^{\mathcal{L}}\rho_{k_1}\int C_{ik_1}^{+}C_{k_1j}^{+}d\mathbf{r}_{k_1}+\sum_{k_1=1}^{\mathcal{L}}\sum_{k_2=1}^{\mathcal{L}}\rho_{k_1}\rho_{k_2}\int\int C_{ik_1}^{+}C_{k_1k_2}^{+}C_{k_2j}^{+}d\mathbf{r}_{k_1}d\mathbf{r}_{k_2}+\cdots. \tag{2.2}$$

Since P_{ij} is proportional to the probability that both i and j particles belong to the same physical cluster, each term on the right-hand side of Eq. (2.2) has a magnitude proportional to that probability. This fact means that each term on the right-hand side of Eq. (2.2) is proportional to the probability that both the i and j particles belong to the same physical cluster via the contribution of other particular particles $(k_1,k_2,\ldots)$, although the first term is proportional to the probability without the contribution of other particular particles. Thus, the correlation function C_{ij}^{+} is proportional to the probability that both the i and j particles belong to the same physical cluster without the contribution of other particular particles. Therefore, C_{ij}^{+} should be defined as a function proportional to the probability that both the i and j particles are found within the simplest bonding structure.

Equation (2.1) has the same mathematical structure as the Ornstein-Zernike equation. The Ornstein-Zernike equation can be solved analytically for some fluids, if the MSA is used. In the MSA, the direct correlation function c_{ij} is given as the sum of the short-ranged contribution (c_{ij}^{0}) and the long-ranged contribution $(-\beta u_{ij})$. If C_{ij}^{+} can be also given as such a sum, the procedure for solving Eq. (2.1) can be simplified, as can be found in the procedures concerning the MSA. Fortunately, a closure scheme similar to the MSA can be obtained for the integral equation as the sum of a short-ranged contribution and a long-ranged contribution [13], and can be given as

$$C_{ij}^{+}(r)=C_{ij}^{0+}(r)+\frac{4}{3\sqrt{\pi}}[-\beta u_{ij}(r)]^{3/2}\quad\text{for}\quad \beta u_{ij}(r)<0. \tag{2.3}$$

In the same manner as the assumption made about c_{ij}^{0} for the MSA, the short-ranged contribution $C_{ij}^{0+}(r)$ is assumed as

$$C_{ij}^{0+}(r)=0\quad\text{for}\quad r\geqslant\sigma_{ij}, \tag{2.4}$$

where σ_{ij} is given as $\sigma_{ij}=\frac{1}{2}(\sigma_i+\sigma_j)$ for the diameter σ_i of the hard core of particle i and the diameter σ_j of the hard core of particle j. The most completely short-ranged interaction between i and j particles should be attributed to hard core potentials. The hard core potentials do not directly contribute to the interaction between them for $r\geqslant\sigma_{ij}$. Thus, Eq. (2.4) should be justified as an approximate expression as found according to the MSA.

If it is assumed that the potential βu_{ij} is given as

$$-\beta u_{ij}(r)=\sum_{n=1}^{\mathcal{N}}k_0^{(n)}d_i^{(n)}d_j^{(n)}\frac{\exp(-z_n r)}{r}\quad\text{for}\quad r\geqslant\sigma_{ij}, \tag{2.5}$$

the closure scheme given by Eq. (2.3) can be expressed as

$$C_{ij}^{+}(r)=C_{ij}^{0+}(r)+\frac{4}{3\sqrt{\pi}}\left[\sum_{n=1}^{\mathcal{N}}k_0^{n}d_i^{n}d_j^{n}\exp(-z_n r)\right]^{3/2}\frac{1}{r^{3/2}}. \tag{2.6}$$

Here, $1/z_n$ represents a feature corresponding to the effective range of the attractive force between i and j particles. The factor $k_0^{(n)}$ is proportional to the factor $1/k_B T$, and is also proportional to the strength of a common effect contributing to every attractive force acting between particles of each particle pair. A factor $d_i^{(n)}$ represents a feature of an i particle, and the strength of a common effect contributing to every interaction occurring between the i particle and another particle. Moreover, the feature of the i particle does not influence the magnitude of $k_0^{(n)}$.

Significant terms which should contribute to the long-ranged contribution of the closure scheme, can be extracted from the terms included in the factor $[\Sigma_n k_0^n d_i^n d_j^n \exp(-z_n r)]^{3/2}$ in Eq. (2.6) by considering an assumption made as

$$0<z_1 \leqslant z_2 \leqslant \cdots \leqslant z_{\mathcal{N}} < \infty. \tag{2.7a}$$

According to this assumption, the factor which should contribute to the long-ranged contribution of the closure scheme, should be modified as

$$\left[\sum_{n=1}^{\mathcal{N}} k_0^n d_i^n d_j^n \exp(-z_n r)\right]^{3/2} \approx [k_0^1 d_i^1 d_j^1 \exp(-z_1 r)]^{3/2} \left[1 + \frac{3}{2}\frac{\exp(z_1 r)}{k_0^1 d_i^1 d_j^1} \sum_{n=2}^{\mathcal{N}} k_0^n d_i^n d_j^n \exp(-z_n r)\right]. \tag{2.7b}$$

Thus, the significant terms which should be considered in the long-ranged contribution of the closure scheme, can be found from Eq. (2.7b).

Furthermore, two approximate expressions for the factor $(1/r)^{3/2}$ in Eq. (2.6) should be derived in order to avoid mathematical difficulty due to $(1/r)^{3/2}$ in solving Eq. (2.1) analytically. The decrease in $C_{ij}^{+}(r)$ due to each term of exponential function can be much more dominant than that due to the factor $(1/r)^{3/2}$, as r increases. By considering this effect, one of the approximate expressions is represented as $(1/\sqrt{a})(1/r)$ instead of $(1/r)^{3/2}$. The other can be derived by requiring the relation $(1/r)^{3/2} = e^{-z'r}/r$ for $0<r-a \ll 1$, and is represented as $(e^{1/2}/\sqrt{a})(1/r)\exp[-r/(2a)]$ instead of $(1/r)^{3/2}$. Here, the coefficient a is a constant.

By considering the above approximations with Eq. (2.7b), two approximate expressions for a long-ranged contribution of the closure scheme can be found, and can derive two approximate expressions for Eq. (2.6). These two approximate expressions are characterized by the parameter f_c, and can be expressed as

$$C_{ij}^{+}(r) = C_{ij}^{0+}(r) + \sum_{n=1}^{\mathcal{N}} \breve{k}_0^n \breve{d}_i^n \breve{d}_j^n \frac{\exp(-\breve{z}_n r)}{r}, \tag{2.7c}$$

where

$$0<\breve{z}_1 \leqslant \breve{z}_2 \leqslant \breve{z}_3 \leqslant \cdots, \tag{2.7d}$$

$$\breve{z}_n = \begin{cases} (3/2) z_1 + a^{-1}\ln(f_c) & (n=1,\ f_c=1,\ e^{1/2}) \\ z_n + (1/2) z_1 + a^{-1}\ln(f_c) & (n=2,3,\ldots,\mathcal{N},\ f_c=1,\ e^{1/2}), \end{cases} \tag{2.7e}$$

and

$$\breve{k}_0^n \breve{d}_i^n \breve{d}_j^n = \begin{cases} 4 f_c (3\sqrt{\pi}\sqrt{a})^{-1} (k_0^{(1)})^{3/2} (d_i^{(1)})^{3/2} (d_j^{(1)})^{3/2} & (n=1,\ f_c=1,\ e^{1/2}) \\ 2 f_c (\sqrt{\pi}\sqrt{a})^{-1} (k_0^{(1)})^{1/2} k_0^{(n)} (d_i^{(1)})^{1/2} d_i^{(n)} (d_j^{(1)})^{1/2} d_j^{(n)} & (n=2,3,\ldots,\mathcal{N},\ f_c=1,\ e^{1/2}). \end{cases} \tag{2.7f}$$

Here, the maximum hard sphere diameter of particles distributed in the fluid mixture is applied as the coefficient a. When the closure expressed as Eq. (2.7c) is used, the integral equation system given by Eqs. (2.1) and (2.7c) can be exactly solved as known from solving the Ornstein-Zernike equation system [15,16] which has the Yukawa closure due to the MSA.

In addition, the approximation given by Eq. (2.7c) for $f_c = 1$ somewhat overestimates the long-ranged contribution of $C_{ij}^{+}(r)$, since the approximation specified for $f_c = 1$ means that the long-ranged contribution described by the factor $(1/r)^{3/2}$ in Eq. (2.6) is approximated as $(1/\sqrt{a})(1/r)$. The alternative approximation given by Eq. (2.7c) for $f_c = e^{1/2}$ somewhat overestimates the decay of $C_{ij}^{+}(r)$ dependent on r, since the long-ranged contribution described by the factor $(1/r)^{3/2}$ in Eq. (2.6) is approximated as $(e^{1/2}/\sqrt{a})(1/r)\exp[-r/(2a)]$.

According to a previous study on Yukawa fluids [10], overestimation of the long-ranged contribution of $C_{ij}^{+}(r)$ can lead to an overestimation of $1/(\breve{k}_0^n \breve{d}_i^n \breve{d}_j^n)$ at the percolation threshold. The diagram of the percolation threshold for overestimating the long-ranged contribution, however, has the same pattern as that for overestimating the decay of $C^{+}_{ij}(r)$.

B. A solution of the integral equation

Based on a mathematical procedure similar to that for the Orstein-Zernike equation [15,17,18], the use of Baxter's Q function [17] gives $P_{ij}(r)$ and $C^{+}_{ij}(r)$ satisfying Eq. (2.1) for the $\mathcal{L}$-component fluid mixture. They are expressed as

$$2\pi r P_{ij}(r) = -\frac{d}{dr}Q_{ij}(r) + 2\pi \sum_{k=1}^{\mathcal{L}} \rho_k \times \int_{\lambda_{jk}}^{\infty} Q_{kj}(t)(r-t)P_{ik}(|r-t|)dt \quad \text{for } \lambda_{ji} \leqslant r < \infty, \tag{2.8a}$$

and

$$2\pi r C^{+}_{ij}(r) = -\frac{d}{dr}Q_{ij}(r) + \sum_{k=1}^{\mathcal{L}} \rho_k \times \int_{sup[\lambda_{kj},\lambda_{ki}-r]}^{\infty} Q_{jk}(t)\frac{d}{dr}Q_{ik}(r+t)dt \quad \text{for } \lambda_{ji} \leqslant r < \infty, \tag{2.8b}$$

where λ_{ji} is defined as $\lambda_{ji} \equiv \frac{1}{2}(\sigma_j - \sigma_i)$. The function $Q_{ij}(r)$ in Eqs. (2.8a) and (2.8b) is introduced as

$$\tilde{Q}_{ij}(k) = \delta_{ij} - (\rho_i \rho_j)^{1/2} \int_{\lambda_{ji}}^{\infty} e^{ikr} Q_{ij}(r) dr, \tag{2.8c}$$

where $\delta_{ij}=0\,(i \neq j)$ and $\delta_{ii}=1$. The function $Q_{ij}(r)$ may have a specific form that includes unknown coefficients X^{nm}_{j}/x and P^{m}_{j}, and can be expressed as

$$Q_{ij}(r) = Q^{0}_{ij}(r) + \sum_{n=1}^{\mathcal{N}} \sigma_i \sigma_j \frac{\breve{d}^{n}_{i}}{\sigma_i} \frac{1}{x} \sum_{m=1}^{2} X^{nm}_{j} P^{m}_{j} e^{\breve{z}_n \sigma_j/2} e^{-\breve{z}_n r} \quad (\lambda_{ji} < r,\ \mathcal{N}=2), \tag{2.8d}$$

$$Q^{0}_{ij}(r) = \sum_{n=1}^{\mathcal{N}} \left[-\sigma_i \sigma_j \frac{\breve{d}^{n}_{i}}{\sigma_i} \frac{1}{x} \sum_{m=1}^{2} X^{nm}_{j} P^{m}_{j} e^{\breve{z}_n \sigma_j/2} + \sigma_i \sigma_j P^{n}_{i} \frac{1}{\breve{z}_n \sigma_i} \frac{1}{x} \sum_{m=1}^{2} X^{nm}_{j} P^{m}_{j} e^{\breve{z}_n \sigma_j/2} \right] (e^{-\breve{z}_n r} - e^{-\breve{z}_n \sigma_{ij}}) \quad (\lambda_{ji} < r < \sigma_{ji},\ \mathcal{N}=2), \tag{2.8e}$$

and

$$Q^{0}_{ij}(r) = 0 \quad (\sigma_{ji} \leqslant r,\ \mathcal{N}=2). \tag{2.8f}$$

In addition, an unknown coefficient P^{n}_{j} is related to the pair connectedness and is expressed as

$$P^{n}_{j} \equiv 12 \sum_{l=1}^{\mathcal{L}} \phi_l \frac{\breve{d}^{n}_{l}}{\sigma_l} \frac{1}{(\breve{z}_n \sigma_l)^2} \left[\int_0^{\infty} P_{lj}(\tau/s) e^{-\tau} \tau d\tau \right]_{s=\breve{z}_n}, \tag{2.8g}$$

where ϕ_l represents the volume fraction defined as

$$\phi_l \equiv \frac{\pi}{6} \rho_l \sigma_l^3. \tag{2.8h}$$

The coefficient P^{n}_{j} defined by Eq. (2.8g) must always be positive, since $\breve{d}^{n}_{j}/\sigma_j$ should be positive for arbitrary values of j and n. According to Eq. (2.8g), this coefficient should be small, if the effective range characterized by $1/\breve{z}_n$ is short.

The correlation function $C^{+}_{ij}(r)$ given by Eq. (2.8b) must satisfy Eqs. (2.4) and (2.7c). The pair connectedness $P_{ij}(r)$ must satisfy $P_{ij}(r)=0$ for $r<\sigma_{ij}$, since hard core potentials contribute to the interaction between i and j particles. This relation must be also satisfied by the pair connectedness $P_{ij}(r)$ given by Eq. (2.8a). Thus, the behavior of $P_{ij}(r)$ given by Eq. (2.8a) and the behavior of $C^{+}_{ij}(r)$ given by Eq. (2.8b) are restricted. Unknown coefficients X^{nm}_{j}, x, and P^{m}_{j} can be exactly determined according to the restrictions mentioned above. As a result, unknown coefficients X^{nm}_{j} and x are given as

$$\begin{pmatrix} X^{11}_{j} & X^{12}_{j} \\ X^{21}_{j} & X^{22}_{j} \end{pmatrix} \equiv \frac{\pi}{6} \begin{pmatrix} e^{\breve{z}_1 \sigma_j/2}(\breve{z}_1 \sigma_j)^{-1} x^{22} & -e^{\breve{z}_2 \sigma_j/2}(\breve{z}_2 \sigma_j)^{-1} x^{12} \\ -e^{\breve{z}_1 \sigma_j/2}(\breve{z}_1 \sigma_j)^{-1} x^{21} & e^{\breve{z}_2 \sigma_j/2}(\breve{z}_2 \sigma_j)^{-1} x^{11} \end{pmatrix} \tag{2.9a}$$

and

$$x \equiv x^{11}x^{22} - x^{12}x^{21}, \tag{2.9b}$$

where

$$x^{nm} \equiv \sum_{l=1}^{\mathcal{L}} \frac{e^{\breve{z}_n \sigma_l/2} e^{-\breve{z}_m \sigma_l/2}}{\breve{z}_n \sigma_l (\breve{z}_n + \breve{z}_m) \sigma_l} \left[\breve{z}_m \sigma_l e^{-\breve{z}_n \sigma_l} \frac{\breve{d}^{n}_{l}}{\sigma_l} \left(\frac{\breve{d}^{m}_{l}}{\sigma_l} - \frac{1}{\breve{z}_m \sigma_l} P^{m}_{l} \right) + P^{n}_{l} \left(\frac{\breve{d}^{m}_{l}}{\sigma_l} Y^{mn}_{ll} + P^{m}_{l} Z^{mn}_{ll} \right) \right] \phi_l \quad (m=1,2;\ \ n=1,2), \tag{2.9c}$$

$$Y^{mn}_{jl} \equiv \frac{1}{\breve{z}_n \sigma_l} [(\breve{z}_n + \breve{z}_m)\sigma_l - \breve{z}_m \sigma_l e^{-\breve{z}_n \sigma_j}] \quad (m=1,2;\ \ n=1,2), \tag{2.9d}$$

and

$$Z_{jl}^{mn} \equiv \frac{1}{\breve{z}_m \sigma_j \breve{z}_n \sigma_l} [\breve{z}_n \sigma_l e^{\breve{z}_m \sigma_j} - (\breve{z}_n + \breve{z}_m) \sigma_l + \breve{z}_m \sigma_l e^{-\breve{z}_n \sigma_j}], \quad (m=1,2;\ \ n=1,2). \tag{2.9e}$$

Other unknown coefficients P_j^n are given as

$$2\pi e^{-\breve{z}_n \sigma_j/2} \frac{\breve{k}_0^n}{\breve{z}_n} \frac{\breve{d}_j^n}{\sigma_j} x^2 - x \sum_{r=1}^{2} X_j^{nr} P_j^r + \frac{6}{\pi} \sum_{m=1}^{2} \sum_{r=1}^{2} \sum_{s=1}^{2} \sum_{l=1}^{\mathcal{L}} \left[\phi_l X_l^{nr} X_l^{ms} P_l^r P_l^s \frac{e^{-\breve{z}_m \sigma_j/2}}{(\breve{z}_n + \breve{z}_m)\sigma_l} \times \left(\frac{\breve{d}_j^m}{\sigma_j} Y_{jl}^{mn} + P_j^m Z_{jl}^{mn} \right) \right] = 0. \tag{2.9f}$$

In addition, Eqs. (2.9a)–(2.9f) are results obtained for $\mathcal{N}=2$.

The behavior of the pair connectedness $P_{ij}(r)$ can be readily estimated at the particular distance $r=\sigma_{ij}$ where the hard spheres of an i particle and a j particle contact each other, if it is considered for Eq. (2.8a) to be given as a continuous function of r. By considering the relation $P_{ij}(r)=0$ for $r<\sigma_{ij}$, Eq. (2.8a) given as a continuous function of r can lead to the magnitude of $P_{ij}(r)$ given at $r=\sigma_{ij}$ as

$$P_{ij}(\sigma_{ij}) = \frac{1}{2\pi} \frac{\sigma_j}{\sigma_{ij}} \frac{1}{x} \sum_{m=1}^{2} \sum_{n=1}^{2} \left(\breve{z}_n \sigma_i \frac{\breve{d}_i^n}{\sigma_i} - P_i^n \right) \times e^{-\breve{z}_n \sigma_i/2} X_j^{nm} P_j^m. \tag{2.10}$$

In addition, Eq. (2.10) is a result obtained for $\mathcal{N}=2$.

C. Mean size of physical clusters

The equilibrium number n_ν of physical clusters consisting of ν particles can be related to the pair connectedness P_{ij}, according to the formula given by Coniglio, DeAngelis, and Foriani [9]. The mean physical cluster size S is given by $S=(\Sigma_\nu \nu^2 n_\nu)/(\Sigma_\nu \nu n_\nu)$. Thus, the mean physical cluster size S is the mean number of particles per physical cluster. The mean physical cluster size S can be related to the pair connectedness P_{ij} as

$$S = 1 + \left(\sum_{k=1}^{\mathcal{L}} \rho_k \right)^{-1} \sum_{i=1}^{\mathcal{L}} \sum_{j=1}^{\mathcal{L}} \rho_i \rho_j \int P_{ij}(r) d\mathbf{r}. \tag{2.11}$$

The mean physical cluster size S given by Eq. (2.11) can be rewritten as

$$S = \sum_{i=1}^{\mathcal{L}} \left\{ \sum_{j=1}^{\mathcal{L}} \left[\sum_{k=1}^{\mathcal{L}} \frac{\phi_k}{\phi_i} \left(\frac{\sigma_i}{\sigma_k} \right)^3 \right]^{-1/2} \tilde{Q}_{ij}^{-1}(0) \right\}^2, \tag{2.12a}$$

since the relation between $\tilde{Q}_{kj}^{-1}(0)$ and P_{ij} is given owing to Eq. (2.1) as

$$\sum_{k=1}^{\mathcal{L}} \tilde{Q}_{ki}^{-1}(0) \tilde{Q}_{kj}^{-1}(0) = \delta_{ij} + (\rho_i \rho_j)^{1/2} \int P_{ij}(r) d\mathbf{r}, \tag{2.12b}$$

where $\tilde{Q}_{ij}(0)$ for $\mathcal{N}=2$ can be given as

$$\tilde{Q}_{ij}(0) = \delta_{ij} + \frac{1}{x} \sum_{m=1}^{2} \sum_{n=1}^{2} \left(\frac{6}{\pi} \phi_i \sigma_i \right)^{1/2} Q_i^n \left(\frac{6}{\pi} \phi_j \frac{1}{\sigma_j} \right)^{1/2} X_j^{nm} P_j^m \tag{2.12c}$$

with

$$Q_i^n \equiv \frac{e^{-\breve{z}_n \sigma_i/2}}{\breve{z}_n \sigma_i} \left[- \frac{e^{z_n \sigma_i} - 1 - \breve{z}_n \sigma_i}{\breve{z}_n \sigma_i} P_i^n - \frac{\breve{d}_i^n}{\sigma_i} (\breve{z}_n \sigma_i + 1) \right]. \tag{2.12d}$$

Therefore, the mean physical cluster size diverges to infinity if $\tilde{Q}_{ij}^{-1}(0)$ reaches infinity. The percolation due to the contact of physical clusters can be generated under a condition satisfying $\tilde{Q}_{ij}^{-1}(0)=\infty$.

For a two-component mixture ($\mathcal{L}=2$), Eq. (2.12a) with the use of Eqs. (2.9a), (2.9c), and (2.12c) results in

$$\begin{aligned}
S = {} & \left[1 + \frac{\phi_2}{\phi_1} \left(\frac{\sigma_1}{\sigma_2} \right)^3 \right]^{-1} \Bigg\{ 1 + \sum_{l=1}^{2} \breve{z}_n \sigma_l e^{\breve{z}_n \sigma_l} x^{-1} \phi_l \Bigg[Q_l^1 \left(\frac{e^{\breve{z}_1 \sigma_l/2}}{\breve{z}_1 \sigma_l} (\breve{z}_n \sigma_l e^{\breve{z}_n \sigma_l})^{-1} x^{22} P_l^1 - \frac{e^{\breve{z}_2 \sigma_l/2}}{\breve{z}_2 \sigma_l} (\breve{z}_n \sigma_l e^{\breve{z}_n \sigma_l})^{-1} x^{12} P_l^2 \right) + e^{\breve{z}_2 \sigma_l/2} \\
& \times Q_l^2 \left(- \frac{e^{\breve{z}_1 \sigma_l/2}}{\breve{z}_1 \sigma_l} e^{-\breve{z}_2 \sigma_l/2} (\breve{z}_n \sigma_l e^{\breve{z}_n \sigma_l})^{-1} x^{21} P_l^1 + \frac{1}{\breve{z}_2 \sigma_l} (\breve{z}_n \sigma_l e^{\breve{z}_n \sigma_l})^{-1} x^{11} P_l^2 \right) \Bigg] + \phi_1 \phi_2 (Q_1^1 e^{\breve{z}_2 \sigma_2/2} Q_2^2 - e^{\breve{z}_2 \sigma_1/2} Q_1^2 Q_2^1 e^{-\breve{z}_2 \lambda_{12}}) \\
& \times \left(\breve{z}_n \sigma_2 e^{\breve{z}_n \sigma_2} x^{-1} \frac{e^{\breve{z}_1 \sigma_1/2}}{\breve{z}_1 \sigma_1} \frac{1}{\breve{z}_2 \sigma_2} (\breve{z}_n \sigma_2 e^{\breve{z}_n \sigma_2})^{-1} P_1^1 P_2^2 - \breve{z}_n \sigma_1 e^{\breve{z} \sigma_1} x^{-1} \frac{e^{\breve{z}_1 \sigma_2/2}}{\breve{z}_1 \sigma_2} \frac{e^{\breve{z}_2 \lambda_{12}}}{\breve{z}_2 \sigma_1} (\breve{z}_n \sigma_1 e^{\breve{z}_n \sigma_1})^{-1} P_2^1 P_1^2 \right) \Bigg\}^{-1} \\
& \times \Bigg\{ \Bigg\{ 1 - \frac{6}{\pi} \frac{\breve{z}_n \sigma_2 e^{\breve{z}_n \sigma_2}}{x} \sum_{m=1}^{2} \sum_{r=1}^{2} \left[\left(\phi_1 \phi_2 \frac{\breve{z}_m \sigma_1}{\breve{z}_m \sigma_2} \right)^{1/2} e^{\breve{z}_m \sigma_1/2} Q_1^m e^{-\breve{z}_m \lambda_{12}} - \phi_2 e^{\breve{z}_m \sigma_2/2} Q_2^m \right] e^{-\breve{z}_m \sigma_2/2} (\breve{z}_n \sigma_2 e^{\breve{z}_n \sigma_2})^{-1} X_2^{mr} P_2^r \Bigg\}^2 \\
& + \left(\frac{\sigma_1}{\sigma_2} \right)^2 \Bigg\{ \left(\frac{\phi_2}{\phi_1} \frac{\sigma_1}{\sigma_2} \right)^{1/2} + \frac{6}{\pi} \frac{\breve{z}_n \sigma_1 e^{\breve{z}_n \sigma_1}}{x} \sum_{m=1}^{2} \sum_{r=1}^{2} \Bigg[\left(\phi_1 \phi_2 \frac{\breve{z}_m \sigma_1}{\breve{z}_m \sigma_2} \right)^{1/2} e^{\breve{z}_m \sigma_1/2} Q_1^m \\
& - \phi_2 e^{\breve{z}_m \sigma_2/2} Q_2^m e^{-\breve{z}_m \lambda_{21}} \Bigg] e^{-\breve{z}_m \sigma_1/2} (\breve{z}_n \sigma_1 e^{\breve{z}_n \sigma_1})^{-1} X_1^{mr} P_1^r \Bigg\}^2 \Bigg\}.
\end{aligned} \tag{2.13}$$

If each physical cluster is formed as an ensemble of particles bound to each other satisfying the condition $E_{ij}+u_{ij}\leqslant 0$, then, the mean physical cluster size is S given as Eq. (2.13). Therefore, the percolation threshold can be readily estimated for a two-component mixture system ($\mathcal{L}=2$) composed of particles interacting with attractive forces due to the two-term potential ($\mathcal{N}=2$), using Eq. (2.13).

III. SPECIFIC FLUIDS

A. Formulas for evaluating correlation functions

1. A specific fluid

All the coefficients expressed as P_j^n in Eq. (2.9f) must be assessed to evaluate the percolation threshold for a fluid mixture composed of particles interacting through the two-term potential ($\mathcal{N}=2$). Their evaluation can be simplified for a specific two-component fluid mixture. This fluid mixture is specified as

$$\sigma_1=\sigma_2=\sigma, \tag{3.1}$$

$$z_1=z, \quad 0<z\sigma<z_2\sigma, \quad z_2\sigma\gg 1, \tag{3.2a}$$

$$\frac{d_1^{(1)}}{\sigma_1}=\frac{d}{\sigma}, \quad 0\leqslant\frac{d_2^{(1)}}{\sigma_2}\ll 1, \quad \frac{d_1^{(2)}}{\sigma_1}=\frac{d_2^{(2)}}{\sigma_2}=\frac{\delta}{\sigma}, \quad 0\leqslant\frac{\delta}{\sigma}, \tag{3.2b}$$

$$k_0^{(1)}=k, \text{ and } 0\leqslant k_0^{(2)}\ll 1. \tag{3.2c}$$

Then, Eqs. (2.7e) and (2.7f) for $n=1$ result in

$$\breve{z}_1\sigma=\frac{3}{2}z_1\sigma+\ln(f_c), \tag{3.3a}$$

$$\frac{\breve{z}_1}{z_1}\frac{\breve{k}_0^1}{\breve{z}_1}\frac{\breve{d}_i^1}{\sigma}\frac{\breve{d}_j^1}{\sigma}=\frac{4}{3\sqrt{\pi}}f_c\sqrt{z_1\sigma}\left(\frac{k_0^{(1)}}{z_1}\right)^{3/2}\left(\frac{d_i^{(1)}}{\sigma}\frac{d_j^{(1)}}{\sigma}\right)^{3/2}. \tag{3.3b}$$

Thus, Eq. (3.3b) leads to the simplest assumption made as

$$\frac{\breve{d}_i^1}{\sigma}=\left(\frac{d_i^{(1)}}{\sigma}\right)^{3/2}. \tag{3.3c}$$

Therefore, the parameters for estimating the pair connectedness, according to Eqs. (2.7e)–(2.7f), Eqs. (3.1)–(3.2c), and Eq. (3.3c), can be expressed as

$$\breve{z}_1\equiv\breve{z}, \quad 0<\breve{z}\sigma<\breve{z}_2\sigma, \quad \breve{z}_2\sigma\gg 1, \tag{3.4a}$$

$$\frac{\breve{d}_1^1}{\sigma_1}=\frac{\breve{d}}{\sigma}, \quad 0\leqslant\frac{\breve{d}_2^1}{\sigma_2}\ll 1, \quad \frac{\breve{d}_1^2}{\sigma_1}=\frac{\breve{d}_2^2}{\sigma_2}=\frac{\breve{\delta}}{\sigma}, \quad 0\leqslant\frac{\breve{\delta}}{\sigma}, \tag{3.4b}$$

$$\breve{k}_0^1=\breve{k}, \text{ and } 0\leqslant\breve{k}_0^2\ll 1. \tag{3.4c}$$

In addition, it can become somewhat easy to assess the pair connectedness $P_{ij}(\sigma)$ and the pair correlation function $g_{ij}(\sigma)$, if a specific condition given as $\breve{d}/\sigma=1$ is considered. For this condition, the relation $d/\sigma=1$ is satisfied owing to Eq. (3.3c). Moreover, Eqs. (3.3a) and (3.3b) result in

$$\frac{\breve{k}}{\breve{z}}=\frac{8}{9\sqrt{\pi}}f_c\left[z\sigma+\frac{2}{3}\ln(f_c)\right]^{-1}\left(\frac{kd^2}{\sigma}\right)^{3/2} \qquad (f_c=1,\ e^{1/2}). \tag{3.5}$$

A specific fluid mixture described by Eqs. (3.1)–(3.2c) is a two-component fluid mixture composed of a constituent ($i=1$ particles) and the other constituent ($i=2$ particles). $i=1$ particles interact between each other through the hard core potential ($r<\sigma$) and an attractive force ($zr>z\sigma$) and $i=2$ particles only through the hard core potential ($r<\sigma$). The fluid mixture is that in which hard core spheres interacting with the attractive force are mixed with hard core spheres in the absence of attractive forces.

2. The pair connectedness $P_{ij}(\sigma)$

According to Eq. (2.10), the pair connectedness $P_{ij}(\sigma)$ for *i* and *j* particles distributed in the fluid mixture characterized by Eqs. (3.4a)–(3.4c) can be found as

$$\begin{aligned}P_{11}(\sigma)={}&\frac{\breve{z}\sigma}{6}e^{-\breve{z}\sigma}\left(\frac{\breve{d}}{\sigma}-\frac{1}{\breve{z}\sigma}P_1^1\right)\frac{P_1^1}{\phi_1}\left[\frac{1}{2}\left(\frac{\breve{d}}{\sigma}\right)^2e^{-\breve{z}\sigma}+\frac{1}{\breve{z}\sigma}\frac{\breve{d}}{\sigma}\right.\\&\left.\times(1-e^{-\breve{z}\sigma})P_1^1+\frac{1}{2}(e^{\breve{z}\sigma}-2+e^{-\breve{z}\sigma})(P_1^1)^2\right]^{-1},\end{aligned} \tag{3.6a}$$

$$P_{12}(\sigma)=0, \quad P_{21}(\sigma)=0, \text{ and } P_{22}(\sigma)=0. \tag{3.6b}$$

Equation (3.6a) can be derived for $\phi_2\neq 0$. It does not, however, include ϕ_2. Therefore, $P_{11}(\sigma)$ is independent of ϕ_2. This effect is caused by the behavior of P_2^1 ($0<P_2^1\ll 1$ for $0<\breve{d}_2^1/\sigma\ll 1$).

In order to evaluate Eq. (3.6a), the coefficient P_1^1 must be estimated. The coefficients P_i^n satisfying the relations given by Eqs. (3.4a)–(3.4c) can be derived from Eq. (2.9f), and are expressed as

$$\begin{aligned}&12e^{-\breve{z}\sigma}\frac{\breve{k}}{\breve{z}}\frac{\breve{d}}{\sigma}\phi_1\left[\frac{1}{2}\left(\frac{\breve{d}}{\sigma}\right)^2e^{-\breve{z}\sigma}+\frac{1}{\breve{z}\sigma}\frac{\breve{d}}{\sigma}(1-e^{-\breve{z}\sigma})P_1^1\right.\\&\left.+\frac{1}{2}(e^{\breve{z}\sigma}-2+e^{-\breve{z}\sigma})(P_1^1)^2\right]^2-\left[\frac{1}{2}\left(\frac{\breve{d}}{\sigma}\right)^2e^{-\breve{z}\sigma}+\frac{1}{\breve{z}\sigma}\frac{\breve{d}}{\sigma}\right.\\&\left.\times(1-e^{-\breve{z}\sigma})P_1^1+\frac{1}{2}(e^{\breve{z}\sigma}-2+e^{-\breve{z}\sigma})(P_1^1)^2\right]P_1^1\\&+\frac{e^{-\breve{z}\sigma/2}(P_1^1)^2}{2\breve{z}\sigma}\left[(e^{\breve{z}\sigma}-2+e^{-\breve{z}\sigma})P_1^1+\breve{z}\sigma\frac{\breve{d}}{\sigma}(2-e^{-\breve{z}\sigma})\right]=0,\end{aligned} \tag{3.7a}$$

$$P_2^1\approx 0,\quad P_1^2\approx 0,\ \text{and}\ P_2^2\approx 0. \tag{3.7b}$$

The coefficient P_2^1 can be ignored for $0<\breve{d}_2^1/\sigma\ll 1$ as known from Eq. (3.7b). As a result, Eq. (3.7a) does not include ϕ_2, although it is a formula derived for $\phi_2\neq 0$. Therefore, P_1^1 is independent of ϕ_2.

In addition, P_1^2 and P_2^2 for $\breve{z}_2\sigma\gg 1$ can behave as

$$\frac{\breve{z}_2\sigma}{(\breve{\delta}/\sigma)}e^{\breve{z}_2\sigma}P_1^2\approx\breve{z}\sigma P_1^1\left[\frac{\breve{d}}{\sigma}-\frac{1}{\breve{z}\sigma}P_1^1\right]\left[\frac{1}{2}\left(\frac{\breve{d}}{\sigma}\right)^2e^{-\breve{z}\sigma}\right.$$
$$+\frac{1}{\breve{z}\sigma}\frac{\breve{d}}{\sigma}(1-e^{-\breve{z}\sigma})P_1^1$$
$$\left.+\frac{1}{2}(e^{\breve{z}\sigma}-2+e^{-\breve{z}\sigma})(P_1^1)^2\right]^{-1}, \tag{3.8}$$

3. The percolation threshold

The percolation threshold for the fluid mixture characterized by Eqs. (3.4a)–(3.4c) is determined as a particular state at which the mean physical cluster size S expressed by Eq. (2.13) diverges to infinity. The magnitude of P_1^1 at the percolation threshold can be given as

$$P_1^1=\breve{z}\sigma\frac{\breve{d}}{\sigma}[(\breve{z}\sigma)^2(e^{\breve{z}\sigma}-2+e^{-\breve{z}\sigma})-2e^{\breve{z}\sigma}+2\breve{z}\sigma+2]^{-1}$$
$$\times\{\breve{z}\sigma+e^{-\breve{z}\sigma}-\{[1-(\breve{z}\sigma)^2](e^{-\breve{z}\sigma}-2)e^{-\breve{z}\sigma}+2\}^{1/2}\}. \tag{3.9}$$

Equation (3.9) is derived for $\phi_2\neq 0$. It does not, however, include ϕ_2, since terms with P_2^1 can be ignored owing to $0<P_2^1\ll 1$ for $0<\breve{d}_2^1/\sigma\ll 1$. Therefore, the percolation threshold determined by Eqs. (3.7a) and (3.9) is independent of ϕ_2.

4. The pair correlation function $g_{ij}(\sigma)$

For a two-component fluid mixture specified by Eqs. (3.1)–(3.2c), Eq. (A1) can be simplified as

$$g_{ij}(\sigma)\approx\frac{1}{\Delta}+\frac{3}{2}\frac{\phi_1+\phi_2}{\Delta^2}-\frac{1}{6}\left\{-\frac{12}{\Delta}\left[\frac{3}{\Delta}(\phi_1+\phi_2)\frac{1}{z\sigma}+\frac{1}{z\sigma}-\frac{1}{2}\right]\left[\frac{1}{z\sigma}\left(-\frac{1}{2}+\frac{1}{z\sigma}-\frac{e^{-z\sigma}}{2}-\frac{e^{-z\sigma}}{z\sigma}\right)\sum_{k=1}^{2}\phi_ke^{z\sigma}B_k^{(1)}\right.\right.$$
$$\left.\left.+\left(\frac{1}{2}+\frac{1}{z\sigma}\right)\frac{d}{\sigma}\phi_1\right]+\frac{3}{\Delta}\Phi_0(z\sigma)\sum_{k=1}^{2}\phi_ke^{z\sigma}B_k^{(1)}+\frac{3}{\Delta}\phi_1\frac{d}{\sigma}-\left(\frac{d_i^{(1)}}{\sigma}-\frac{e^{-z\sigma}}{z\sigma}e^{z\sigma}B_i^{(1)}\right)z\sigma\right\}\left\{e^{z\sigma}B_j^{(1)}-\frac{12}{\Delta}\left(1+\frac{1}{2}z\sigma\right.\right.$$
$$\left.\left.+\frac{3}{\Delta}(\phi_1+\phi_2)\right)\frac{1+z\sigma/2}{(z\sigma)^2}\phi_1\frac{d}{\sigma}+\frac{3}{\Delta}\phi_1\frac{d}{\sigma}-\frac{3}{\Delta}\left[4\left(1+\frac{1}{2}z\sigma+\frac{3}{\Delta}(\phi_1+\phi_2)\right)\Psi_1(z\sigma)+\Phi_0(z\sigma)\right]\sum_{k=1}^{2}\phi_ke^{z\sigma}B_k^{(1)}\right\}$$
$$\times\left\{\sum_{l=1}^{2}\phi_l\left[\frac{d_l^{(1)}}{\sigma}-\frac{12(1+z\sigma/2)}{\Delta(z\sigma)^2}\phi_1\frac{d}{\sigma}+\Phi_0(z\sigma)e^{z\sigma}B_l^{(1)}-\frac{12}{\Delta}\Psi_1(z\sigma)\sum_{k=1}^{2}\phi_ke^{z\sigma}B_k^{(1)}\right]^2\right\}^{-1}, \tag{3.10}$$

where $\Delta\equiv 1-\Sigma_{l=1}^{\mathcal{L}}\phi_l$, $(\mathcal{L}=2)$, $\Psi_1(z\sigma)\equiv(z\sigma)^{-3}[1-z\sigma/2-(1+z\sigma/2)e^{-z\sigma}]$, and $\Phi_0(z\sigma)\equiv(z\sigma)^{-1}(1-e^{-z\sigma})$.

A coefficient expressed as $B_i^{(n)}$ in Eq. (3.10) is defined as

$$z_n\sigma_ie^{z_n\sigma_i}B_i^{(n)}\equiv 12\sum_{l=1}^{\mathcal{L}}\phi_l\frac{d_l^{(n)}}{\sigma_l}\frac{z_n\sigma_i}{(z_n\sigma_l)^2}e^{2z_n\lambda_{il}}e^{z_n\sigma_l}\left[\int_0^\infty e^{-\tau}g_{il}(\tau/s)\tau d\tau\right]_{s=z_n}. \tag{3.11a}$$

The coefficient $B_i^{(n)}$ defined by Eq. (3.11a) must always be positive, since $d_i^{(n)}/\sigma_i$ should be positive for arbitrary values of i and n.

According to Eq. (3.11a), this coefficient should be small, if the effective range characterized by $1/z_n$ is short. In fact, Eqs. (A2a) and (A3a) for $n=2$ result in

$$\lim_{z_2\to\infty}e^{z_2\sigma}B_j^{(2)}=0. \tag{3.11b}$$

Thus, the coefficients $B_1^{(2)}$ and $B_2^{(2)}$ are not included in Eq. (3.10). The above relation helps readily to derive Eq. (3.10) from Eq. (A1). In addition, even a product $z_2\sigma e^{z_2\sigma}B_j^{(2)}$ has a finite value as $\lim_{z_2\sigma\to\infty}[z_2\sigma e^{z_2\sigma}B_j^{(2)}]<\infty$, according to Eqs. (A2a) and (A3a).

Equation (A2a) for $n=1$ and $j=1$ and Eq. (A2a) for $n=1$ and $j=2$ can result in two equations given as

$$
\begin{aligned}
0 \approx {} & 6\frac{k}{z}\frac{d}{\sigma}e^{-z\sigma}\Biggl[\sum_{l=1}^{2}\phi_l\biggl(\frac{d_l^{(1)}}{\sigma}-\frac{12(1+z\sigma/2)}{\Delta(z\sigma)^2}\phi_1\frac{d}{\sigma}+\Phi_0(z\sigma)e^{z\sigma}B_l^{(1)}-\frac{12}{\Delta}\Psi_1(z\sigma)\sum_{k=1}^{2}\phi_k e^{z\sigma}B_k^{(1)}\biggr)^2\Biggr]^2 \\
& +\sum_{h=1}^{2}(-1)^h e^{z\sigma}B_h^{(1)}\sum_{l=1}^{2}\phi_l\biggl(\frac{d_l^{(1)}}{\sigma}-\frac{12(1+z\sigma/2)}{\Delta(z\sigma)^2}\phi_1\frac{d}{\sigma}+\Phi_0(z\sigma)e^{z\sigma}B_l^{(1)}-\frac{12}{\Delta}\Psi_1(z\sigma)\sum_{k=1}^{2}\phi_k e^{z\sigma}B_k^{(1)}\biggr)^2 \\
& +\frac{1}{z\sigma}\sum_{l=1}^{2}\phi_l\biggl\{e^{z\sigma}B_l^{(1)}-\frac{12}{\Delta}\biggl(1+\frac{1}{2}z\sigma+\frac{3}{\Delta}(\phi_1+\phi_2)\biggr)\frac{1+z\sigma/2}{(z\sigma)^2}\phi_1\frac{d}{\sigma}+\frac{3}{\Delta}\phi_1\frac{d}{\sigma}-\frac{3}{\Delta}\biggl[4\biggl(1+\frac{1}{2}z\sigma+\frac{3}{\Delta}(\phi_1+\phi_2)\biggr) \\
& \times\Psi_1(z\sigma)+\Phi_0(z\sigma)\biggr]\sum_{k=1}^{2}\phi_k e^{z\sigma}B_k^{(1)}\biggr\}^2\biggl\{\frac{d}{\sigma}+z\sigma\Phi_0(z\sigma)\frac{d}{\sigma}-z\sigma[\Phi_0(z\sigma)]^2\sum_{h=1}^{2}(-1)^h e^{z\sigma}B_h^{(1)}\biggr\},
\end{aligned}
\tag{3.12a}
$$

$$
\begin{aligned}
0 \approx {} & \sum_{k=1}^{2}\phi_k\biggl(\frac{d_k^{(1)}}{\sigma}-\frac{12(1+z\sigma/2)}{\Delta(z\sigma)^2}\phi_1\frac{d}{\sigma}+\Phi_0(z\sigma)e^{z\sigma}B_k^{(1)}-\frac{12}{\Delta}\Psi_1(z\sigma)\sum_{h=1}^{2}\phi_h e^{z\sigma}B_h^{(1)}\biggr)^2\sum_{l=1}^{2}\biggl[\delta_{l2}+\frac{3}{\Delta}\phi_l\Phi_0(z\sigma)-\frac{12}{\Delta}\phi_l\Psi_1(z\sigma) \\
& \times\biggl(1+\frac{1}{2}z\sigma+\frac{3}{\Delta}(\phi_1+\phi_2)\biggr)\biggr]\biggl\{e^{z\sigma}B_l^{(1)}-\frac{12}{\Delta}\biggl(1+\frac{1}{2}z\sigma+\frac{3}{\Delta}(\phi_1+\phi_2)\biggr)\frac{1+z\sigma/2}{(z\sigma)^2}\phi_1\frac{d}{\sigma}+\frac{3}{\Delta}\phi_1\frac{d}{\sigma} \\
& -\frac{3}{\Delta}\biggl[4\biggl(1+\frac{1}{2}z\sigma+\frac{3}{\Delta}(\phi_1+\phi_2)\biggr)\Psi_1(z\sigma)+\Phi_0(z\sigma)\biggr]\sum_{h=1}^{2}\phi_h e^{z\sigma}B_h^{(1)}\biggr\}+\frac{1}{z\sigma}\sum_{k=1}^{2}\phi_k\biggl\{e^{z\sigma}B_k^{(1)}-\frac{12}{\Delta}\biggl(1+\frac{1}{2}z\sigma \\
& +\frac{3}{\Delta}(\phi_1+\phi_2)\biggr)\frac{1+z\sigma/2}{(z\sigma)^2}\phi_1\frac{d}{\sigma}+\frac{3}{\Delta}\phi_1\frac{d}{\sigma}-\frac{3}{\Delta}\biggl[4\biggl(1+\frac{1}{2}z\sigma+\frac{3}{\Delta}(\phi_1+\phi_2)\biggr)\Psi_1(z\sigma)+\Phi_0(z\sigma)\biggr]\sum_{h=1}^{2}\phi_h e^{z\sigma}B_h^{(1)}\biggr\}^2 \\
& \times\biggl\{\sum_{l=1}^{2}\biggl(\frac{12}{\Delta}\Psi_1(z\sigma)\phi_l-\Phi_0(z\sigma)\delta_{l2}\biggr)\biggl\{e^{z\sigma}B_l^{(1)}-z\sigma\frac{d}{\sigma}\delta_{l1}+\frac{3}{\Delta}\frac{d}{\sigma}\phi_1\biggl(3+\frac{4}{z\sigma}\biggr)-\frac{12}{\Delta}\biggl(1+\frac{1}{2}z\sigma+\frac{3}{\Delta}(\phi_1+\phi_2)\biggr)\biggl(\frac{2+z\sigma}{2(z\sigma)^2}\phi_1\frac{d}{\sigma} \\
& +\Psi_1(z\sigma)\sum_{h=1}^{2}\phi_h e^{z\sigma}B_h^{(1)}\biggr)+\sum_{h=1}^{2}\biggl[-z\sigma\Phi_0(z\sigma)\delta_{lh}+\frac{3}{\Delta}[\Phi_0(z\sigma)+4z\sigma\Psi_1(z\sigma)]\phi_h\biggr]e^{z\sigma}B_h^{(1)}\biggr\} \\
& +\sum_{l=1}^{2}\biggl[\biggl(\delta_{l1}-\frac{12}{\Delta}\phi_1\frac{2+z\sigma}{2(z\sigma)^2}\biggr)\frac{d}{\sigma}+\sum_{h=1}^{2}\biggl(\Phi_0(z\sigma)\delta_{lh}-\frac{12}{\Delta}\phi_h\Psi_1(z\sigma)\biggr)e^{z\sigma}B_h^{(1)}\biggr]\biggl[\delta_{l2}+\frac{3}{\Delta}\phi_l\Phi_0(z\sigma)-\frac{12}{\Delta}\phi_l\Psi_1(z\sigma) \\
& \times\biggl(1+\frac{1}{2}z\sigma+\frac{3}{\Delta}(\phi_1+\phi_2)\biggr)\biggr]\biggr\},
\end{aligned}
\tag{3.12b}
$$

Another restriction due to a relation $g_{ij}(\sigma)=g_{ji}(\sigma)$ leads to a relation given as

$$
\begin{aligned}
0 \approx {} & -\biggl(4-2z\sigma+\frac{12}{\Delta}(\phi_1+\phi_2)\biggr)\sum_{l=1}^{2}(-1)^l e^{z\sigma}B_l^{(1)}\biggl[-(z\sigma)^2\Psi_1(z\sigma)\sum_{l=1}^{2}\phi_l e^{z\sigma}B_l^{(1)}-\biggl(1+\frac{1}{2}z\sigma\biggr)\frac{d}{\sigma}\phi_1\biggr] \\
& +\biggl(4+2z\sigma+\frac{12}{\Delta}(\phi_1+\phi_2)\biggr)\biggl(\sum_{l=1}^{2}(-1)^l B_l^{(1)}+z\sigma\frac{d}{\sigma}\biggr)\biggl[\biggl(\frac{2}{z\sigma}-(z\sigma)^2\Psi_1(z\sigma)\biggr)\sum_{l=1}^{2}\phi_l e^{z\sigma}B_l^{(1)}-\biggl(1+\frac{1}{2}z\sigma\biggr)\frac{d}{\sigma}\phi_1\biggr] \\
& +\biggl(-(1-e^{-z\sigma})\sum_{l=1}^{2}(-1)^l e^{z\sigma}B_l^{(1)}+z\sigma\frac{d}{\sigma}\biggr)\biggl[(1-e^{-z\sigma})\sum_{l=1}^{2}\phi_l e^{z\sigma}B_l^{(1)}+z\sigma\frac{d}{\sigma}\phi_1\biggr]z\sigma+(z\sigma)^3\frac{\Delta}{3}\frac{d}{\sigma}e^{z\sigma}B_2^{(1)}.
\end{aligned}
\tag{3.12c}
$$

Thus, the coefficients $B_1^{(1)}$ and $B_2^{(1)}$ in Eq. (3.10) can be assessed using Eqs. (3.12a), (3.12b), and (3.12c).

However, values being suitable for $B_1^{(1)}$ and $B_2^{(1)}$ should be selected. The correlation function $g_{12}(r)$ should be proportional to the probability that an $i=2$ particle exists in a volume element $d\mathbf{r}_2$ located at a particular place specified by a distance r from an $i=1$ particle. Hence, $g_{12}(r)$ should become zero, when $i=2$ particles separate from a macroscopically homogeneous phase mixed with $i=1$ particles. Near a point at which this phase separation occurs, $g_{12}(r)$ should extremely rapidly decay to zero as r increases. The coefficient $B_2^{(1)}$ is an integral involving $g_{12}(r)$ as an integrand, as known from Eq. (3.11a) with coefficients given by Eq. (3.2b). The coefficient $B_1^{(1)}$ is an integral involving $g_{11}(r)$ as an integrand, as known from Eq. (3.11a) with coefficients given by Eq. (3.2b). Therefore, $B_2^{(1)}$ should be much smaller than $B_1^{(1)}$, when the phase separation of $i=2$ particles occurs.

In addition, numerical pairs of $B_1^{(1)}$ and $B_2^{(1)}$ assessed from Eqs. (3.12a)–(3.12c) for a parameter such as k can be separated into at least two groups. A group includes a numerical pair satisfying $B_2^{(1)}/B_1^{(1)} \ll 1$ for a specific value of k. The other does not include such a numerical pair: numerical pairs of $B_1^{(1)}$ and $B_2^{(1)}$ assessed for all the values of k do not include special pairs satisfying $B_2^{(1)}/B_1^{(1)} \ll 1$. These facts mean that the former can describe the phase separation of $i=2$ particles although the latter cannot. Therefore, numerical pairs belonging to the former group can be valid.

B. Evaluations of correlation functions

1. The pair connectedness evaluated from Eq. (3.6a)

The pair connectedness $P_{ij}(r)$ is proportional to the probability that an i particle and a j particle belong to the same physical cluster. Hence, the pair connectedness $P_{ij}(\sigma)$ given by Eq. (3.6a) is proportional to the probability that an i particle is bound near a j particle.

The pair connectedness $P_{ij}(\sigma)$ at the percolation threshold can be assessed from Eqs. (3.6a), (3.7a), and (3.9) which are formulas obtained by exactly solving the integral equation system constructed from Eq. (2.1) and the closure represented by Eq. (2.7c). The pair connectedness $P_{ij}(\sigma)$ assessed from Eqs. (3.6a), (3.7a), and (3.9) can depend on a parameter f_c that expresses the characteristics of the closure represented by Eq. (2.7c) with Eqs. (2.7e) and (2.7f). When the closure represented by Eq. (2.7c) is specified for $f_c=1$, the closure somewhat overestimates the long-ranged contribution of $C_{ij}^{+}(r)$ given by Eq. (2.6). When the closure is specified for $f_c=e^{1/2}$, it somewhat overestimates the decay of $C_{ij}^{+}(r)$ dependent on r. Fortunately, values of $P_{ij}(\sigma)$ assessed from Eqs. (3.6a), (3.7a), and (3.9) for $f_c=1$ can hardly differ from those for $f_c=e^{1/2}$, unless $z\sigma$ is too small. This is demonstrated by diagrams of Fig. 1 drawn from values of $P_{ij}(\sigma)$ assessed at the percolation threshold of each fluid mixture. Therefore, the pair connectedness $P_{ij}(\sigma)$ derived from the use of the closure represented by Eq. (2.7c) can well approximate that derived from the use of the closure given by Eq. (2.6), unless $z\sigma$ is too small.

In addition, if the magnitudes of $\phi_1, kd^2/\sigma$, and $z\sigma$ satisfy either Eqs. (3.7a) or (3.9), then, the magnitudes are expressed as $(\phi_1)_p, (kd^2/\sigma)_p$, and $(z\sigma)_p$. Thus, they represent the values of ϕ_1, kd^2/σ, and $z\sigma$ at the percolation threshold. Similarly, quantities and coefficients given at the percolation threshold are expressed as those having the suffix p.

2. A contribution of physical clusters to phase behavior

A physical cluster composed of particles bound to each other satisfying the condition $E_{ij}+u_{ij} \leqslant 0$ should be a dense region of $i=1$ particles. Moreover, it is possible for each physical cluster to have a fractal structure, since an approximate behavior of $P_{ij}(r)$ for $r \gg 1$ can be expressed as $P_{ij}(r) \sim [-\beta u_{ij}(r)]^{3/2}$ [10]. Branches constructing such physical clusters should be developed in a fluid mixture as ϕ_1 increases, since they should stabilize for the increase in ϕ_1.

The development of the branches suggests that the branches confine unbound particles (i.e., particles constituting pairs characterized by an unbound state $E_{ij}+u_{ij}>0$) within regions surrounded by them. This view is realized through using Eqs. (3.6a) and (3.7a). Values of P_1^1 evaluated by Eq. (3.7a) can satisfy the relation $0<P_1^1 \ll 1$ under various conditions. If this relation is considered, Eq. (3.7a) can be approximated as

$$6\frac{\breve{k}}{\breve{z}}\left(\frac{\breve{d}}{\sigma}\right)^3 \phi_1 \approx \frac{1}{2}e^{2\breve{z}\sigma}P_1^1 + \frac{e^{3\breve{z}\sigma}}{2\breve{z}\sigma}\left(\frac{\breve{d}}{\sigma}\right)^{-1}[2(1-e^{-\breve{z}\sigma}) + \breve{z}\sigma e^{-\breve{z}\sigma/2}(2-e^{-\breve{z}\sigma})](P_1^1)^2. \tag{3.13}$$

If the relation $0<P_1^1 \ll 1$ is considered with Eqs. (2.7e) and (2.7f), the substitution of Eq. (3.13) to Eq. (3.6a) leads to

$$P_{11}(\sigma) \approx \frac{8}{3\sqrt{\pi}}\left(\frac{kd^2}{\sigma}\right)^{3/2} e^{-3z\sigma} f_c^{-1}[1+W(f_c)\phi_1], \tag{3.14a}$$

where

$$W(f_c) \equiv \frac{48}{3\sqrt{\pi}}\left(\frac{kd^2}{\sigma}\right)^{3/2} \frac{f_c^{-1/2}\exp[-(9/4)z\sigma]}{(3/2)z\sigma+\ln f_c} \times \left\{1 - \frac{1}{2}\frac{f_c^{-1/2}\exp[-(3/4)z\sigma]}{(3/2)z\sigma+\ln f_c} - \frac{1}{2}f_c^{-1}\exp[-(3/2)z\sigma]\right\}. \tag{3.14b}$$

In Eq. (3.14a), the product $W(f_c)\phi_1$ can satisfy the relation $0<W(f_c)\phi_1 \ll 1$ under various conditions. Thus, the pair connectedness $P_{ij}(\sigma)$ hardly varies as ϕ_1 increases, although the mean physical cluster size diverges to infinity at the percolation threshold. Hence, each physical cluster should grow toward that having a larger span as ϕ_1 increases. Such growth of physical clusters means that an increase in ϕ_1 enhances the number of unbound particles confined by branches of the physical clusters. In addition, every diagram expressing $P_{ij}(\sigma)$ in Figs. 2(1a)–2(4b) demonstrates that $P_{ij}(\sigma)$ hardly varies as ϕ_1 increases.

The parameter f_c found in Eq. (3.14a) specifies the characteristics of the closure given as Eq. (2.7c). The closure specified for $f_c=1$ somewhat overestimates the long-ranged contribution of $C_{ij}^{+}(r)$ given by Eq. (2.6), and the closure specified for $f_c=e^{1/2}$ somewhat overestimates the decay of $C_{ij}^{+}(r)$ dependent on r. Nevertheless, Eq. (3.14a) shows that a change in magnitude of $P_{11}(\sigma)$ can approximately correspond to only a variation resulting from f_c^{-1} owing to the relation $0<W(f_c)\phi_1 \ll 1$. This means that the pair connect-

edness $P_{ij}(\sigma)$ derived from the use of the closure represented by Eq. (2.7c) leads to the same behavior as that derived from the use of the closure given by Eq. (2.6). Therefore, it should be inferred that the growth of physical clusters due to an increase in ϕ_1 enhances the number of unbound particles confined by branches of the physical clusters, even if the closure given by Eq. (2.6) is used.

Unbound $i=1$ particles within regions surrounded by branches of physical clusters should become denser than those outside of the regions, if their branches prohibit the boundaries of the regions from expanding freely. This means that densities of unbound $i=1$ particles in the regions should be enhanced, and as a result, their densities outside of the regions should be reduced. If a contribution of the latter to a decrease in $g_{11}(\sigma)$ is more dominant than that of the former to an increase in $g_{11}(\sigma)$, the value of $g_{11}(\sigma)$ should decrease as ϕ_1 increases. Such behavior can be realized from diagrams of Figs. 2(1a)–2(4b). Therefore, it is inferred that the branches of the physical clusters should prohibit the boundaries of the regions from expanding freely.

In addition, values of $(\phi_1)_p$ assessed from Eqs. (3.7a) and (3.9) for $f_c=1$ can differ from those assessed for $f_c=e^{1/2}$. Fortunately, these differences can become small, if $z\sigma$ is large. If Eqs. (2.7e) and (2.7f) are considered with the relations $0<P_1^1\ll 1$ and $1\ll z\sigma$, the substitution of Eq. (3.9) to Eq. (3.13) leads to

$$(\phi_1)_p \approx \frac{3\sqrt{\pi}}{16}\left(\frac{kd^2}{\sigma}\right)^{-3/2} z\sigma \exp[(3/2)z\sigma] \times\left\{1-\frac{2}{3}(2+\sqrt{2}-\ln f_c)\frac{1}{z\sigma}+\cdots\right\}. \quad (3.15)$$

This equation demonstrates that the difference between values of $(\phi_1)_p$ evaluated for $f_c=1$ and for $f_c=e^{1/2}$ decreases, as $z\sigma$ increases. This behavior can also be realized from the comparison between diagrams of Figs. 2(1a) and 2(2b). Therefore, if $z\sigma$ is large, values of $(\phi_1)_p$ derived from the use of the closure given by Eq. (2.6) can be well approximated by values of $(\phi_1)_p$ derived from the use of the closure given by Eq. (2.7c).

The formation of physical clusters cannot directly be helped by $i=2$ particles. There is no attractive force between two of the $i=2$ particles, and they also behave as hard cores in the absence of an attractive force between an $i=1$ particle and an $i=2$ particle. Hence, $i=2$ particles should distribute with unbound $i=1$ particles among branches of physical clusters. The $i=2$ particles can, then, be confined with the unbound $i=1$ particles within regions surrounded by their branches and their distribution should contribute to the magnitude of $\mathcal{D}_{ij}(r)$.

An increase in ϕ_2 should enhance local densities of $i=1$ particles in microscopically local areas surrounded by branches of physical clusters. This effect can increase the value of $\mathcal{D}_{11}(\sigma)$, so that this increase can result in an increase in $g_{11}(\sigma)$. Such behavior can be realized from comparisons between diagrams of Figs. 2(1a) and 2(1b) and between those of Figs. 2(2a) and 2(2b). In addition, diagrams of Fig. 2(1b) demonstrate that even the phase separation of $i=1$ particles from the fluid mixture can occur owing to the increase in ϕ_2.

In a fluid mixture, $i=2$ particles can always receive a passively attractive force generated from the cooperation between the exclusion of $i=2$ particles due to the hard core potential $(r<\sigma)$ and an attractive force between $i=1$ particles. Such passively attractive force should contribute to stuffing many $i=2$ particles within a region surrounded by branches of physical clusters. However, $i=2$ particles in the region should have a tendency to get larger values of the sum $E_{ij}+u_{ij}$ when comparing with $i=1$ particles, since there is no attractive force among $i=2$ particles. Hence, it is difficult for a large number of $i=2$ particles to be retained in the region. Then, the stability of physical clusters disturbed for an increase in ϕ_2 must be regained by redistributing $i=2$ particles into a large number of regions surrounded by branches of physical clusters. Such behavior can lead to a decrease in $g_{22}(\sigma)$, and can be realized from a comparison between diagrams of Figs. 2(2a) and 2(2b) since the values of $g_{22}(\sigma)$ at $\phi_1=0.4$ are given as $g_{22}(\sigma)\doteqdot 5.94$ for $\phi_2=0.025$ and $g_{22}(\sigma)\doteqdot 5.43$ for $\phi_2=0.05$.

A passively attractive force generated from the cooperation between the exclusion of $i=2$ particles due to the hard core potential and an attractive force between $i=1$ particles should depend on the diameter of the hard core of an $i=2$ particle and the effective range of the attractive force. Hence, it is expected that particles contributing principally to the magnitude of $\mathcal{D}_{ij}(r)$ can contribute to phase behavior of a fluid mixture through their particle sizes. If such particles are small, they can be relatively stably confined within regions surrounded by branches of physical clusters. If the particles have larger sizes than those of the regions, it is expected that the addition of the particles into the fluid mixture can increase the unstabilization of a macroscopically homogeneous phase.

If specific particles interacting through only their hard core potentials are much larger than regions surrounded by branches of physical clusters, it is difficult for these particles to be stably retained in the regions. Despite this fact, it is expected that the particles can form a macroscopically homogeneous phase owing to their diffusion into areas among the physical clusters, if the average extent of the physical clusters is smaller than the sizes of the particles. Colloidal particles have mesoscopic sizes. Although the colloidal particles are hard core spheres in the absence of attractive forces, it is expected that they can be distributed into a molecular fluid mixture. Then, the average extent of physical clusters formed in the molecular fluid mixture must be smaller than the sizes of the colloidal particles. If the physical clusters develop near a specific temperature, then, passively attractive forces generated between two of the colloidal particles should be strengthened. Such attractive forces may contribute to Casimir forces that can act between colloidal particles immersed within a binary fluid mixture near the consolute point [8].

If branches of physical clusters have sufficiently high stability and make the physical clusters large, it is expected that $i=2$ particles being the same size as $i=1$ particles can be stably retained in regions surrounded by the branches. Then, the phase separation of $i=2$ particles from a mixture fluid should be prevented.

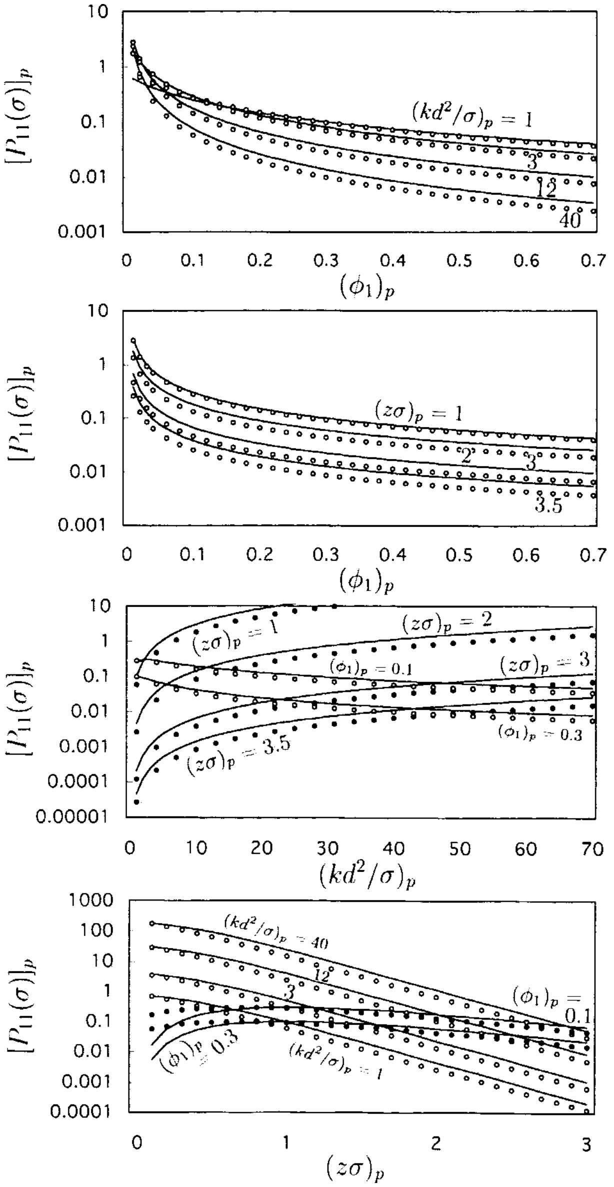

FIG. 1. The pair connectedness $[P_{11}(\sigma)]_p$ for the two component mixture fluids characterized by Eqs. (3.1)–(3.2c). To assess $[P_{11}(\sigma)]_p$, Eq. (3.6a) is used with Eqs. (3.7a) and (3.9). The values of $[P_{11}(\sigma)]_p$ should be considered as those assessed for ϕ_2 having an arbitrary value different from zero. Here, ϕ_2 is the volume fractions of $i=2$ particles. Solid lines represent $f_c=1$; open circles and solid circles $f_c=e^{1/2}$. In addition, ϕ_1, $z\sigma$, $P_{11}(\sigma)$, and kd^2/σ are dimensionless.

Even at a high temperature, the stabilized branches can stably confine unbound particles of $i=1$ particles with $i=2$ particles within regions surrounded by the branches. Physical clusters with the stabilized branches can grow toward macroscopic sizes. Thus, it is expected that a fluid including physical clusters of a percolation state should preserve its liquid phase even at a high temperature.

The stability of branches of physical clusters should increase, as the volume fraction (ϕ_1) of $i=1$ particles, the strength of the attractive force (proportional to kd^2/σ), and its effective range [proportional to $(z\sigma)^{-1}$] increase. Therefore, a macroscopically homogeneous phase can be stabilized, if $\phi_1, kd^2/\sigma$, and $(z\sigma)^{-1}$ have large values. Such phenomenon is suggested by diagrams of Figs. 2(3a) and 2(3b).

If the effective range of an attractive force between two of $i=1$ particles is decreased, the stability of branches of physical clusters is reduced. If kd^2/σ is large, then, it is possible to raise the probability that the $i=1$ particles which have approached each other satisfy a bound state $E_{ij}+u_{ij}\leqslant 0$. A percolation state of a fluid mixture due to the $i=1$ particles can be generated, although the effective range of an attractive force between two of the $i=1$ particles is considerably narrow in comparison with their hard core diameter.

In addition, the attractive force acting between two of the $i=1$ particles is sharply strengthened near the surface of each $i=1$ particle. This means that the movement of the $i=1$ particles which have approached each other should be rapidly strongly restricted by the attractive force. This effect due to the attractive force can be derived from a slight increase in ϕ_1. The characteristic of the attractive force can make the fluid mixture undergo a change from a macroscopically inhomogeneous phase to a macroscopically homogeneous phase and the phase separation of $i=1$ particles after the change, as ϕ_1 increases slightly. Thus, a macroscopically homogeneous phase of the fluid mixture can be sensitively influenced by a small change in ϕ_1. Moreover, the attractive force can make the percolation threshold approach to a particular point at which the phase separation of $i=1$ particles from the fluid mixture takes place. When the density of $i=1$ particles is low, the contribution of the attractive force towards making an $i=1$ particle approach another $i=1$ particle is more important than that when their density is high. Therefore, those characteristic effects due to the attractive force should be revealed from phase behavior occurring at a low density of $i=1$ particles, as is demonstrated by diagrams of Figs. 2(4a) and 2(4b).

3. A macroscopically homogeneous phase of $i=2$ particles induced at the percolation threshold

Values of $B_1^{(1)}$ and $B_2^{(1)}$ assessed from Eqs. (3.12a)–(3.12c) for a specific attractive force can satisfy $B_2^{(1)}/B_1^{(1)}\ll 1$ at the percolation threshold. A specific attractive force resulting in $B_2^{(1)}/B_1^{(1)}\ll 1$ at the percolation threshold can be given by coefficients having values found from Fig. 3(1). When a fluid composed of $i=1$ particles interacting with the specific attractive force reaches the percolation threshold, branches of physical clusters can retain a specific amount of $i=2$ particles in the fluid. It is expected that such a phenomenon can contribute to hydrodynamical transport phenomena such as the viscosity anomaly found from a fluid mixtureincluding particles similar to $i=2$ particles. In addition, diagrams of Fig. 3(2) express the magnitudes of correlation functions for each fluid in which a specific amount $(\phi_2=0.05)$ of $i=2$ particles can be macroscopically homogeneously mixed just at the percolation threshold.

Although the number of $i=1$ particles bound to each other satisfying the condition $E_{ij}+u_{ij}\leqslant 0$ should decrease as ϕ_1 is reduced, it is possible to maintain a percolation state, if

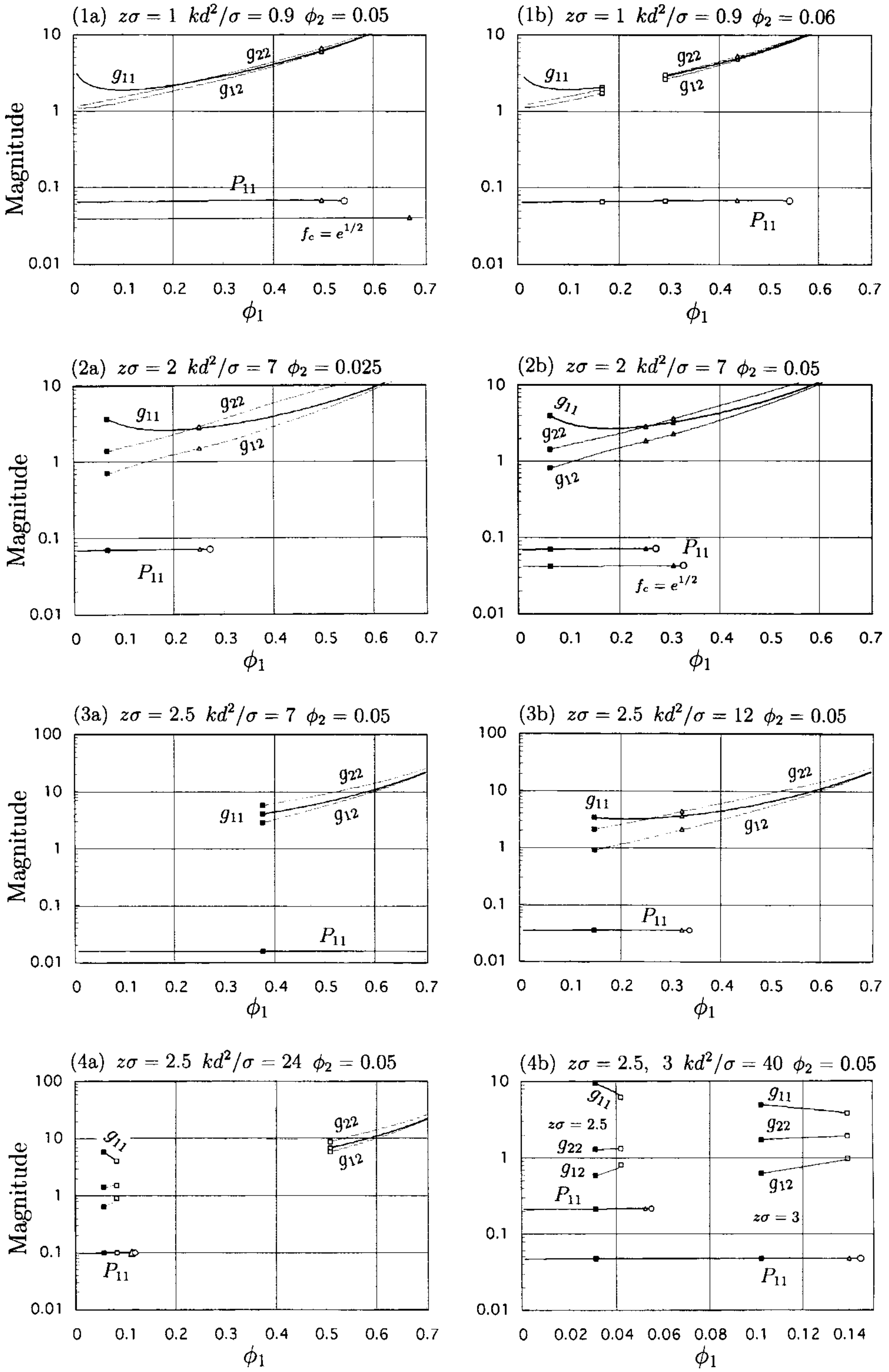

FIG. 2. Correlation functions $P_{11}(\sigma)$, $g_{11}(\sigma)$, $g_{12}(\sigma)$, and $g_{22}(\sigma)$ for the two component mixture fluids characterized by Eqs. (3.1)–(3.2c). The values of $P_{11}(\sigma)$ are those assessed for $f_c = 1$ (except for two thin lines) and ϕ_2 having an arbitrary value different from zero. The values of $P_{11}(\sigma)$ and $g_{ij}(\sigma)$ are those assessed through using Eqs. (3.6a) and (3.10) with Eqs. (3.7a), (3.9), and (3.12a)–(3.12c). Open triangles represent the magnitudes of correlation functions at the percolation threshold; open circles represent limits of solutions provided by Eq. (3.7a); open squares represent limits of solutions provided by Eqs. (3.12a) and (3.12b); solid squares represent points derived from the condition $B_2^{(1)}/B_1^{(1)} \ll 1$. In addition, ϕ_1, ϕ_2, $z\sigma$, $P_{11}(\sigma)$, and kd^2/σ are dimensionless.

the ratio of their number to the total number of $i=1$ particles enhances as ϕ_1 is reduced. An increase in the ratio should lead to an increase in $[P_{11}(\sigma)]_p$. Then, the percolation state is maintained at a small value of ϕ_1, while $[g_{11}(\sigma)]_p$ increases owing to the increase in $[P_{11}(\sigma)]_p$. However, the increase in the ratio can result in decreases in local densities of unbound $i=1$ particles, so that $i=2$ particles can distribute away from each other. Thus, $[g_{12}(\sigma)]_p$ and $[g_{22}(\sigma)]_p$ can decrease. These phenomena can be realized from diagrams of Fig. 3(2). Such phenomena suggest that physical clusters confine $i=2$ particles and unbound $i=1$ particles.

Ultimately, the formation of physical clusters can be considered as a primary phenomenon resulting in density fluctuations in a multicomponent fluid mixture, and should contribute to complicating a phase diagram for the fluid mixture.

IV. CONCLUSIONS

Constituents of a multicomponent fluid mixture can be classified into two groups (group $\mathcal{A}$ and group $\mathcal{B}$). Particles belonging to the group $\mathcal{A}$ (particles of $\mathcal{A}$) have a tendency to satisfy the condition $E_{ij}+u_{ij}\leqslant 0$. Particles belonging to the other group $\mathcal{B}$ (particles of $\mathcal{B}$) have a tendency to satisfy the condition $E_{ij}+u_{ij}>0$. Thus, $i=1$ particles correspond to particles of $\mathcal{A}$, and $i=2$ particles correspond to particles of $\mathcal{B}$. A major contribution to the magnitude of $P_{ij}(r)$ can result from the distribution of particles of $\mathcal{A}$. The distribution of particles of $\mathcal{B}$ should principally contribute to the magnitude of $\mathcal{D}_{ij}(r)$.

Each physical cluster composed of particles bound to each other satisfying the condition $E_{ij}+u_{ij}\leqslant 0$ should be a dense region of particles of $\mathcal{A}$ in the fluid mixture. Branches constructing such physical clusters can confine unbound particles (i.e., particles constituting pairs characterized by an unbound state $E_{ij}+u_{ij}>0$) within regions surrounded by them. Each physical cluster can grow toward that having a larger span as densities of particles of $\mathcal{A}$ increase, since $P_{ij}(\sigma)$ hardly varies for increases in their densities. This growth of physical clusters can enhance the number of unbound particles confined by branches of the physical clusters.

Local densities of particles within regions surrounded by branches of the physical clusters should be lower than local particle densities of the physical clusters, since unbound particles are confined within the regions. Then, their branches must prohibit the boundaries of the regions from expanding freely. The confinement of unbound particles means that the physical clusters can contribute to prohibiting a transition from a macroscopically homogeneous phase of a multicomponent fluid mixture to its macroscopically inhomogeneous phase.

If particles of $\mathcal{A}$ are added into a fluid, it is possible that addition of the particles increases the stabilization of physical clusters. The phase separation of particles of $\mathcal{B}$ from a mixture fluid should, then, be prevented, since stabilized branches of physical clusters can retain the particles of $\mathcal{B}$ in regions surrounded by the branches.

Since particles of $\mathcal{B}$ should distribute with unbound particles of $\mathcal{A}$ within regions surrounded by branches of physical clusters, an increase in the number of particles of $\mathcal{B}$ should enhance local densities of particles of $\mathcal{A}$ in microscopic areas of the regions. Since the hard core potentials of particles of $\mathcal{A}$ and $\mathcal{B}$ contribute to this phenomenon, such size effects due to particles can drive into the phase separation resulting from the addition of particles of $\mathcal{B}$.

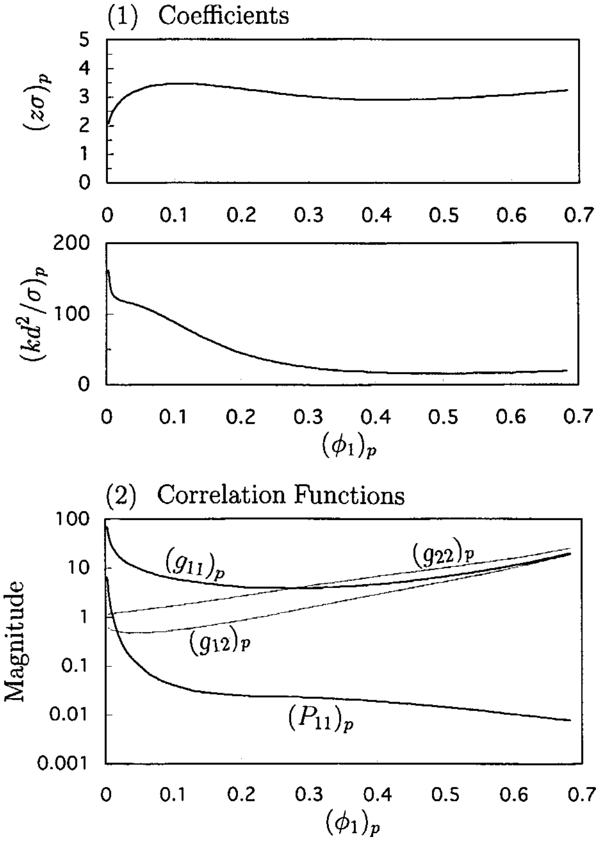

FIG. 3. Correlation functions $[P_{11}(\sigma)]_p$, $[g_{11}(\sigma)]_p$, $[g_{12}(\sigma)]_p$, and $[g_{22}(\sigma)]_p$ assessed under the condition $B_2^{(1)}/B_1^{(1)} \ll 1$ for the two component mixture fluids characterized by Eqs. (3.1)–(3.2c). The values of $[P_{11}(\sigma)]_p$ are those assessed for $f_c=1$ and ϕ_2 having an arbitrary value different from zero. The values of $[g_{11}(\sigma)]_p$, $[g_{12}(\sigma)]_p$, and $[g_{22}(\sigma)]_p$ are those assessed for $\phi_2=0.05$. The values of $[P_{11}(\sigma)]_p$ and $[g_{ij}(\sigma)]_p$ are those assessed through using Eqs. (3.6a) and (3.10) with Eqs. (3.7a), (3.9), and (3.12a)–(3.12c). Diagrams of (1) represent values of coefficients specifying particular forces that induce percolation states restricted by the condition $B_2^{(1)}/B_1^{(1)} \ll 1$. In addition, ϕ_1, ϕ_2, $z\sigma$, $P_{11}(\sigma)$, and kd^2/σ are dimensionless.

The formation of physical clusters of particles of $\mathcal{A}$ can be considered as a primary phenomenon resulting in density fluctuations. Then, the confinement of particles of $\mathcal{B}$ and $\mathcal{A}$ within regions surrounded by the branches of the physical clusters can be regarded as a secondary phenomenon. Ultimately, such phenomena can complicate phase behavior of a fluid mixture.

APPENDIX: THE PAIR CORRELATION FUNCTION

For the potential given as Eq. (2.5), the Ornstein-Zernike equation can be analytically solved [15,16]. By modifying the solutions [15,16] given for the potential, the correlation function $g_{ij}(r)$ can be given as

$$
\begin{aligned}
g_{ij}(\sigma_{ij}) ={}& \Delta^{-1} + \frac{3}{2}\Delta^{-2}\sum_{l=1}^{\mathcal{L}} \phi_l \frac{\sigma_i\sigma_j}{\sigma_l\sigma_{ij}} + \frac{1}{2\pi}\sum_{n=1}^{\mathcal{N}} \Biggl\{ -\frac{12}{z_n\sigma_{ij}}\left[3\Delta^{-1}\sum_{l=1}^{\mathcal{L}} \phi_l \frac{1}{z_n\sigma_l} - \frac{1}{2} + \frac{1}{z_n\sigma_i}\right] \\
&\times \Delta^{-1}\sum_{l=1}^{\mathcal{L}} \phi_l \frac{z_n\sigma_i}{z_n\sigma_l}\left[\Psi_1(z_n\sigma_l) z_n\sigma_l e^{z_n\sigma_l} B_l^{(n)} + \frac{d_l^{(n)}}{\sigma_l}\left(\frac{1}{2}+\frac{1}{z_n\sigma_l}\right)\right] e^{-z_n\lambda_{lj}} + \frac{3}{z_n\sigma_{ij}}\Delta^{-1}\sum_{l=1}^{\mathcal{L}} \phi_l \frac{z_n\sigma_i}{z_n\sigma_l}\Biggl(\frac{d_l^{(n)}}{\sigma_l} \\
&+ \frac{\Phi_0(z_n\sigma_l)}{z_n\sigma_l} z_n\sigma_l e^{z_n\sigma_l} B_l^{(n)}\Biggr) e^{-z_n\lambda_{lj}} - \left(\frac{d_i^{(n)}}{\sigma_i} - \frac{e^{-z_n\sigma_i}}{(z_n\sigma_i)^2} z_n\sigma_i e^{z_n\sigma_i} B_i^{(n)}\right)\frac{z_n\sigma_i}{z_n\sigma_{ij}} e^{-z_n\lambda_{ij}}\Biggr\} z_n\sigma_j e^{-z_n\sigma_j/2}\frac{a_j^{(n)}}{\sigma_j},
\end{aligned}
\tag{A1}
$$

where $\Delta \equiv 1 - \Sigma_{l=1}^{\mathcal{L}}\phi_l$, $\Psi_1(z_n\sigma_l) \equiv (z_n\sigma_l)^{-3}[1 - z_n\sigma_l/2 - (1 + z_n\sigma_l/2)e^{-z_n\sigma_l}]$, and $\Phi_0(z_n\sigma_l) \equiv (z_n\sigma_l)^{-1}(1 - e^{-z_n\sigma_l})$. Moreover, a coefficient expressed as $B_i^{(n)}$ in Eq. (A1) is defined by Eq. (3.11a).

Then, values of $B_i^{(n)}$ should satisfy an equation given as

$$
\begin{aligned}
0 ={}& 2\pi z_n\sigma_i \frac{k_0^{(n)}}{z_n}\frac{d_i^{(n)}}{\sigma_i}\frac{d_j^{(n)}}{\sigma_j} e^{-z_n\sigma_j} + \sum_{l=1}^{\mathcal{L}} \frac{z_n\sigma_i}{z_n\sigma_l}\frac{d_i^{(n)}/\sigma_i}{d_l^{(n)}/\sigma_l}\left(\frac{d_l^{(n)}}{\sigma_l} z_n\sigma_l e^{-z_n\sigma_l}\frac{a_l^{(n)}}{\sigma_l}\right) e^{-z_n\lambda_{jl}}\Biggl[\frac{z_n\sigma_l}{z_n\sigma_j}\delta_{lj} + \frac{3}{\Delta}\frac{z_n\sigma_j}{z_n\sigma_l}\phi_l\Phi_0(z_n\sigma_j) \\
&- \frac{12}{\Delta}\left(\frac{z_n\sigma_j}{z_n\sigma_l}\right)^2 \phi_l\Psi_1(z_n\sigma_j)\left(1 + \frac{3}{\Delta}\sum_{h=1}^{\mathcal{L}} \phi_h\frac{z_n\sigma_l}{z_n\sigma_h} + \frac{1}{2}z_n\sigma_l\right)\Biggr] - \frac{6}{\pi}\sum_{m=1}^{N}\sum_{k=1}^{\mathcal{L}}\sum_{l=1}^{\mathcal{L}} \frac{z_n\sigma_i}{z_n\sigma_k}\frac{d_i^{(n)}/\sigma_i}{d_k^{(n)}/\sigma_k}\phi_k\left(\frac{d_k^{(n)}}{\sigma_k} z_n\sigma_k e^{-z_n\sigma_k}\frac{a_k^{(n)}}{\sigma_k}\right) \\
&\times\left(\frac{d_k^{(m)}}{\sigma_k} z_m\sigma_k e^{-z_m\sigma_k}\frac{a_k^{(m)}}{\sigma_k}\right)\mathcal{M}_{jkl}^{mn},
\end{aligned}
\tag{A2a}
$$

where the coefficient $\mathcal{M}_{jkl}^{mn}$ in Eq. (A2a) are definded as

$$
\begin{aligned}
\mathcal{M}_{jkl}^{mn} \equiv{}& \frac{1}{(z_n+z_m)\sigma_j}\frac{1}{z_m\sigma_k}\frac{1}{z_m\sigma_l} e^{-z_n\lambda_{jk}} e^{-z_m\lambda_{lk}}\frac{z_n\sigma_l}{z_n\sigma_k}\Biggl\{\left[\Phi_0(z_n\sigma_j)\delta_{lj} - \frac{12}{\Delta}\phi_l\left(\frac{z_n\sigma_j}{z_n\sigma_l}\right)^3\Psi_1(z_n\sigma_j)\right]\Biggl[\frac{d_l^{(m)}/\sigma_l}{d_k^{(m)}/\sigma_k}\frac{z_m\sigma_l e^{z_m\sigma_l}B_l^{(m)}}{d_l^{(m)}/\sigma_l} \\
&- z_m\sigma_l\frac{12}{\Delta}\left(1 + \frac{1}{2}z_m\sigma_l + \frac{3}{\Delta}\sum_{h=1}^{\mathcal{L}} \phi_h\frac{z_m\sigma_l}{z_m\sigma_h}\right)\sum_{t=1}^{\mathcal{L}} \phi_t\frac{1 + z_m\sigma_t/2}{(z_m\sigma_t)^2}\frac{d_t^{(m)}/\sigma_t}{d_k^{(m)}/\sigma_k} e^{-z_m\lambda_{tl}} + \frac{3}{\Delta}\sum_{h=1}^{\mathcal{L}} \phi_h z_m\sigma_l\frac{z_m\sigma_l}{z_m\sigma_h}\frac{d_h^{(m)}/\sigma_h}{d_k^{(m)}/\sigma_k} e^{-z_m\lambda_{hl}} \\
&- \left(1 + \frac{1}{2}z_m\sigma_l + \frac{3}{\Delta}\sum_{h=1}^{\mathcal{L}} \phi_h\frac{z_m\sigma_l}{z_m\sigma_h}\right)\frac{12}{\Delta}\sum_{h=1}^{\mathcal{L}} \phi_h\Psi_1(z_m\sigma_h)\frac{d_h^{(m)}/\sigma_h}{d_k^{(m)}/\sigma_k}\frac{z_m\sigma_l}{z_m\sigma_h} z_m\sigma_h\frac{e^{z_m\sigma_h}B_h^{(m)}}{d_h^{(m)}/\sigma_h} e^{-z_m\lambda_{hl}} \\
&+ \frac{3}{\Delta}\sum_{h=1}^{\mathcal{L}} \phi_h\frac{z_m\sigma_l}{z_m\sigma_h}\Phi_0(z_m\sigma_h)\frac{d_h^{(m)}/\sigma_h}{d_k^{(m)}/\sigma_k}\frac{z_m\sigma_l}{z_m\sigma_h} z_m\sigma_h\frac{e^{z_m\sigma_h}B_h^{(m)}}{d_h^{(m)}/\sigma_h} e^{-z_m\lambda_{hl}} - (z_m\sigma_l)^2 \\
&\times\sum_{h=1}^{\mathcal{L}}\left(\delta_{lh} - \frac{12}{\Delta}\phi_h\frac{1 + z_m\sigma_h/2}{(z_m\sigma_h)^2}\right)\frac{d_h^{(m)}/\sigma_h}{d_k^{(m)}/\sigma_k} e^{-z_m\lambda_{hl}} - z_m\sigma_l\sum_{h=1}^{\mathcal{L}}\Biggl(\Phi_0(z_m\sigma_l)\delta_{lh} \\
&- \frac{12}{\Delta}\phi_h\Psi_1(z_m\sigma_h)\Biggr)\frac{d_h^{(m)}/\sigma_h}{d_k^{(m)}/\sigma_k}\frac{z_m\sigma_l}{z_m\sigma_h} z_m\sigma_h\frac{e^{z_m\sigma_h}B_h^{(m)}}{d_h^{(m)}/\sigma_h} e^{-z_m\lambda_{hl}}\Biggr] - \Biggl[z_m\sigma_l\sum_{h=1}^{\mathcal{L}}\left(\delta_{lh} - \frac{12}{\Delta}\phi_h\frac{1 + z_m\sigma_h/2}{(z_m\sigma_h)^2}\right)\frac{d_h^{(m)}/\sigma_h}{d_k^{(m)}/\sigma_k} e^{-z_m\lambda_{hl}} \\
&+ \sum_{h=1}^{\mathcal{L}}\left(\Phi_0(z_m\sigma_l)\delta_{lh} - \frac{12}{\Delta}\phi_h\Psi_1(z_m\sigma_h)\right)\frac{d_h^{(m)}/\sigma_h}{d_k^{(m)}/\sigma_k}\frac{z_m\sigma_l}{z_m\sigma_h} z_m\sigma_h\frac{e^{z_m\sigma_h}B_h^{(m)}}{d_h^{(m)}/\sigma_h} e^{-z_m\lambda_{hl}}\Biggr]\Biggl[\delta_{lj} + \frac{3}{\Delta}\left(\frac{z_n\sigma_j}{z_n\sigma_l}\right)^2\phi_l\Phi_0(z_n\sigma_j) \\
&- \frac{12}{\Delta}\left(\frac{z_n\sigma_j}{z_n\sigma_l}\right)^3\phi_l\Psi_1(z_n\sigma_j)\left(1 + \frac{3}{\Delta}\sum_{h=1}^{\mathcal{L}} \phi_h\frac{z_n\sigma_l}{z_n\sigma_h} + \frac{1}{2}z_n\sigma_l\right)\Biggr]\Biggr\}.
\end{aligned}
\tag{A2b}
$$

For $\mathcal{N}=2$, the factor $z_n\sigma_j e^{-z_n\sigma_j/2}a_j^{(n)}/\sigma_j$ in Eq. (A2a) in Eq. (A2a) can be given as

$$
z_n\sigma_j e^{-z_n\sigma_j/2}\frac{a_j^{(n)}}{\sigma_j} = \frac{1}{Y}\sum_{m=1}^{2} (-1)^{n+m} Y_j^{3-m,3-n}\mathcal{V}_j^m,
\tag{A3a}
$$

where

$$Y \equiv Y_j^{1,1}Y_j^{2,2}-Y_j^{1,2}Y_j^{2,1}, \tag{A3b}$$

$$\begin{aligned}
Y_j^{n,m} \equiv {} & \frac{6}{\pi}\frac{z_n\sigma_j}{z_m\sigma_j}\sum_{l=1}^{2}\phi_l\frac{z_m\sigma_j}{(z_n+z_m)\sigma_l}e^{-(z_n+z_m)\lambda_{lj}}\Bigg[\sum_{k=1}^{2}e^{-z_n\lambda_{kl}}\bigg(\delta_{lk}-\frac{12}{\Delta}\phi_k\frac{1+z_n\sigma_k/2}{(z_n\sigma_k)^2}\bigg)\frac{d_k^{(n)}}{\sigma_k} \\
& +\sum_{k=1}^{2}e^{-z_n\lambda_{kl}}\bigg(\Phi_0(z_n\sigma_l)\delta_{lk}-\frac{12}{\Delta}\phi_k\Psi_1(z_n\sigma_k)\bigg)e^{z_n\sigma_k}B_k^{(n)}\Bigg] \\
& \times\Bigg[\frac{\mathcal{V}_l^m}{(z_m\sigma_l)^2}+\sum_{h=1}^{2}e^{-z_m\lambda_{hl}}\bigg(\delta_{lh}-\frac{12}{\Delta}\phi_h\frac{1+z_m\sigma_h/2}{(z_m\sigma_h)^2}\bigg)\frac{d_h^{(m)}}{\sigma_h} \\
& +\sum_{h=1}^{2}e^{-z_m\lambda_{hl}}\bigg(\Phi_0(z_m\sigma_l)\delta_{lh}-\frac{12}{\Delta}\phi_h\Psi_1(z_m\sigma_h)\bigg)e^{z_m\sigma_h}B_h^{(m)}\Bigg] \\
& -\frac{6}{\pi}\frac{z_n\sigma_j}{z_m\sigma_j}\sum_{l=1}^{2}\phi_l\frac{z_n\sigma_j}{(z_n+z_m\sigma_l}e^{-(z_n+z_m)\lambda_{lj}}\Bigg[\sum_{k=1}^{2}e^{-z_m\lambda_{kl}}\bigg(\delta_{lk}-\frac{12}{\Delta}\phi_k\frac{1+z_m\sigma_k/2}{(z_m\sigma_k)^2}\bigg)\frac{d_k^{(m)}}{\sigma_k} \\
& +\sum_{k=1}^{2}e^{-z_m\lambda_{kl}}\bigg(\Phi_0(z_m\sigma_l)\delta_{lk}-\frac{12}{\Delta}\phi_k\Psi_1(z_m\sigma_k)\bigg)e^{z_m\sigma_k}B_k^{(m)}\Bigg]\frac{\mathcal{V}_l^n}{(z_n\sigma_l)^2},
\end{aligned} \tag{A3c}$$

$$\begin{aligned}
\mathcal{V}_j^n \equiv {} & \frac{3}{\Delta}\sum_{l=1}^{2}\Bigg[4\bigg(1+\frac{3}{\Delta}\sum_{k=1}^{2}\phi_k\frac{z_n\sigma_j}{z_n\sigma_k}+\frac{1}{2}z_n\sigma_j\bigg)\frac{1+z_n\sigma_l/2}{z_n\sigma_l}-z_n\sigma_j\Bigg]\phi_l\frac{z_n\sigma_j}{z_n\sigma_l}\frac{d_l^{(n)}}{\sigma_l}e^{-z_n\lambda_{lj}}-\frac{3}{\Delta}\sum_{l=1}^{2}\Bigg[\bigg(\frac{3}{\Delta}\frac{z_n\sigma_j}{z_n\sigma_l}e^{-z_n\lambda_{lj}}\bigg)^{-1}\delta_{lj} \\
& -4\bigg(1+\frac{3}{\Delta}\sum_{k=1}^{2}\phi_k\frac{z_n\sigma_j}{z_n\sigma_k}+\frac{1}{2}z_n\sigma_j\bigg)\phi_l\Psi_1(z_n\sigma_l)+\phi_l\frac{z_n\sigma_j}{z_n\sigma_l}\Phi_0(z_n\sigma_l)\Bigg]\frac{z_n\sigma_j}{z_n\sigma_l}e^{-z_n\lambda_{lj}}z_n\sigma_l e^{z_n\sigma_l}B_l^{(n)}.
\end{aligned} \tag{A3d}$$

For a two-component fluid mixture specified by Eqs. (3.1)–(3.2c), Eq. (A3a) can be simplified as

$$\begin{aligned}
e^{-z\sigma/2}\frac{a_j^{(1)}}{\sigma} \approx {} & -\frac{\pi}{3}\Bigg\{e^{z\sigma}B_j^{(1)}-\frac{12}{\Delta}\bigg(1+\frac{1}{2}z\sigma+\frac{3}{\Delta}(\phi_1+\phi_2)\bigg)\frac{1+z\sigma/2}{(z\sigma)^2}\phi_1\frac{d}{\sigma}+\frac{3}{\Delta}\phi_1\frac{d}{\sigma}-\frac{3}{\Delta}\Bigg[4\bigg(1+\frac{1}{2}z\sigma+\frac{3}{\Delta}(\phi_1+\phi_2)\bigg)\Psi_1(z\sigma) \\
& +\Phi_0(z\sigma)\Bigg]\sum_{h=1}^{2}\phi_h e^{z\sigma}B_h^{(1)}\Bigg\}\Bigg\{\sum_{h=1}^{2}\phi_h\Bigg[\frac{d_h^{(1)}}{\sigma}-\frac{12(1+z\sigma/2)}{\Delta(z\sigma)^2}\phi_1\frac{d}{\sigma}+\Phi_0(z\sigma)e^{z\sigma}B_h^{(1)} \\
& -\frac{12}{\Delta}\Psi_1(z\sigma)\sum_{k=1}^{2}\phi_k e^{z\sigma}B_k^{(1)}\Bigg]^2\Bigg\}^{-1},
\end{aligned} \tag{A4a}$$

$$e^{-z_2\sigma/2}\frac{a_j^{(2)}}{\sigma}\approx 0. \tag{A4b}$$

---

[1] I.R. Tsang and I.J. Tsang, Phys. Rev. E **60**, 2684 (1999).

[2] N.B. Wilding, F. Schmid, and P. Nielaba, Phys. Rev. E **58**, 2201 (1998).

[3] T.L. Hill, *Statistical Mechanics* (Dover, New York, 1987).

[4] M. Yao and H. Endo, J. Phys. Soc. Jpn. **51**, 974 (1982).

[5] J.C. Nieuwoudt and J.V. Sengers, J. Chem. Phys. **90**, 457 (1988).

[6] N.G. Almarza and E. Enciso, Phys. Rev. E **59**, 4426 (1999).

[7] P.D. Gallagher, M.L. Kurnaz, and J.V. Maher, Phys. Rev. A **46**, 7750 (1992); P.D. Gallagher and J.V. Maher, *ibid.* **46**, 2012 (1992); D. Beysens and D. Estève, Phys. Rev. Lett. **54**, 2123 (1985).

[8] M.E. Fisher and P.G. de Gennes, C. R. Acad. Sci. Hebd. Seances Acad. Sci. B **287**, 207 (1978); P. Attard, C.P. Ursenbach, and G.N. Partey, Phys. Rev. A **45**, 7621 (1992); T.W. Burkhardt and E. Eisenriegler, Phys. Rev. Lett. **74**, 3189 (1995); R.R. Netz, *ibid.* **76**, 3646 (1996); M. Krech, Phys. Rev. E **56**, 1642 (1997); A. Hanke, F. Schlesener, E. Eisenriegler, and S. Dietrich, Phys. Rev. Lett. **81**, 1885 (1998).

[9] A. Coniglio, U. De Angelis, and A. Forlani, J. Phys. A **10**, 1123 (1977).

[10] T. Kaneko, Phys. Rev. E **58**, 5808 (1998).

[11] T. Vicsek, *Fractal Growth Phenomena* (World Scientific, New Jersey, 1992).
[12] J. Xu and G. Stell, J. Chem. Phys. **89**, 1101 (1988).
[13] T. Kaneko, Phys. Rev. E **64**, 31201 (2001).
[14] C. Tutschka, G. Kahl, and G. Pastore, Phys. Rev. E **63**, 61110 (2001).
[15] L. Blum and J.S. Høye, J. Stat. Phys. **19**, 317 (1978).
[16] M. Ginoza and M. Yasutomi, Phys. Rev. E **59**, 2060 (1999).
[17] R.J. Baxter, J. Chem. Phys. **52**, 4559 (1970).
[18] M. Ginoza, J. Phys.: Condens. Matter **6**, 1439 (1994).