Analytical estimate of percolation for multicomponent fluid mixtures

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The size of a dense region of a particular constituent ($\mathcal{L}_s$) in a nonuniform distribution of particles generated in a multicomponent fluid mixture can develop under certain conditions. If both the attractive force between an $\mathcal{L}_s$ particle and a particle of the other constituents ($\mathcal{L}_s^c$) and the attractive force between $\mathcal{L}_s^c$ particles are much weaker than that between $\mathcal{L}_s$ particles, then the percolation due to the growth of the dense region of $\mathcal{L}_s$ particles can hardly be affected by the addition of $\mathcal{L}_s^c$ particles into the fluid mixture. In that case, dense regions composed of $\mathcal{L}_s^c$ particles can be formed passively. To derive these results, it is assumed that such a dense region is an ensemble of particles bound to each other as particle pairs that satisfy the condition $E_{ij}+u_{ij}(r)\leqslant 0$, where E_{ij} is the relative kinetic energy for i and j particles and $u_{ij}(r)$ is the pair potential. The percolation in the fluid mixture can be estimated analytically. According to the pair connectedness function $P_{ij}(r)$ derived for evaluating the percolation, the probability that an $\mathcal{L}_s$ particle is located near another $\mathcal{L}_s$ particle can be insensitive to the addition of $\mathcal{L}_s^c$ particles. The magnitude of $P_{ij}(r)$ can be maximized for a pair of i-j particles interacting with the most strongly attractive force having the largest value of the effective ranges in a fluid mixture system. These particles can contribute to making the phase behavior of the fluid mixture complicated.

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I. INTRODUCTION

The distribution of particles in a multicomponent fluid mixture can vary considerably depending on its composition, upon the nature of its composition, the densities of constituents, its temperature, and so on. Microscopically dense regions of particular particles formed in the fluid mixture can significantly influence its various macroscopic phenomena found for the fluid mixture. The present interest is focused on estimating the mean size of the dense regions. A criterion for the growth of dense regions into macroscopic size can be given as that for the growth of the mean size of the dense regions. Using this measure, it is possible to evaluate the percolation threshold at which the dense regions can grow without bounds due to the contact between microscopically dense regions.

For a binary fluid mixture, the viscosity anomaly can be induced near the consolute point corresponding to the critical transition point for demixing the two constituents macroscopically. Many experimental results concerning the revelation of the viscosity anomaly are known [1]. It is expected that hydrodynamical transport phenomena are influenced by the generation of a nonuniform distribution of particles in a fluid mixture. The nonuniform distribution of particular particles can be a significant factor inducing the viscosity anomaly, since this nonuniformity should develop near the consolute point.

For temperatures above the consolute point, a binary mixture composed of constituents $\mathcal{L}_1$ and $\mathcal{L}_2$ should be macroscopically homogeneous. For temperatures below the consolute point, the binary mixture separates into an $\mathcal{L}_1$-rich phase and an $\mathcal{L}_2$-rich phase with the formation of a boundary between the two phases. If the temperature is raised near the consolute point, dense regions of $\mathcal{L}_2$ particles in the $\mathcal{L}_1$-rich phase should develop microscopically near the boundary, while dense regions of $\mathcal{L}_1$ particles in the $\mathcal{L}_2$-rich phase should develop microscopically near the boundary. If colloidal particles preferring the $\mathcal{L}_2$-rich phase are distributed in this complex medium, those particles should aggregate close to the boundary in the $\mathcal{L}_2$-rich phase near the consolute point. In contrast, colloidal particles preferring the $\mathcal{L}_1$-rich phase should aggregate close to the boundary in the $\mathcal{L}_1$-rich phase near the consolute point. Such phenomena were demonstrated experimentally for the binary fluid mixtures of 2,6-lutidine plus water [2]. Thus, it is considered that the development of the nonuniform distribution of each constituent in binary fluid mixtures can induce the aggregation of colloidal particles [3] or the contraction of a flexible linear polymer [4] in the binary fluid mixtures.

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 described above. This phenomenon can be a factor complicating a phase diagram for the 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 [5].

Furthermore, complexity characterized by the extent of the density fluctuations can be found in a multicomponent fluid mixture. The diversity of dense regions for a constituent can be regarded as a measurement of the complexity. This aspect is supported by the results of Monte Carlo simulations [6].

In the present work, percolation behavior concerning dense regions of a constituent in a multicomponent fluid

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mixture provides a measure for the development of density fluctuations for a specific component.

A bond between the i and j particles in the multicomponent fluid mixture is defined as a state satisfying the condition $E_{ij}+u_{ij}(r)\leqslant 0$ [7]. An ensemble of particles linked by such bonds is considered a physical cluster in the work at hand. In the above, E_{ij} and $u_{ij}(r)$ for a pair of i and j particles are the relative kinetic energy and pair potential, respectively.

The attractive force between particles contributes to the formation of dense regions of particles in the fluid mixture. Thus, a dominant fraction in particles distributed in a dense region should be occupied by particles constituting pairs formed by the attractive force. It is possible to consider each dense region in the fluid mixture as an ensemble composed of particles bound to each other by the attractive force. Particles constituting each pair should then satisfy the condition $E_{ij}+u_{ij}(r)\leqslant 0$. Therefore, the dense region is regarded as the physical cluster of particles linked by bonds defined by the condition $E_{ij}+u_{ij}(r)\leqslant 0$.

In this paper, the mean size of the dense regions is estimated as that of the physical clusters described above. The percolation relevant to the dense regions is regarded as that which concerns the physical clusters. An analytical estimate of the percolation follows from the solution of an integral equation with a closure scheme. Requirements for the percolation threshold will be derived in Sec. V B. The percolation thresholds evaluated for specific two-component fluids will be given in Sec. VI.

In order to derive an analytical solution for the integral equation, a practical expression for closure is required. This expression will be obtained by estimating the behavior of the correlation functions at large distances. The expression for a multicomponent mixture will be given in Sec. III C. An analytical solution for the integral equation will be presented in Sec. IV.

II. PAIR CONNECTEDNESS

In the present work, a bound state for the i and j particles is defined as the state satisfying the condition $E_{ij}+u_{ij}(r)\leqslant 0$ for the sum of a pair potential $u_{ij}(r)$ plus a relative kinetic energy E_{ij}. Particle pairs that can be composed of particles constituting a fluid mixture belong to a group of pairs characterized by a bound state $E_{ij}+u_{ij}(r)\leqslant 0$ or the other group of pairs characterized by an unbound state $E_{ij}+u_{ij}(r)>0$. Complicated phase behavior of the fluid mixture should be characterized by the former.

Then, the probability $p_{ij}(r)$ that a pair of i and j particles satisfies the condition $E_{ij}+u_{ij}(r)\leqslant 0$ should be considered and is given as

$$p_{ij}(r)=2\pi^{-1/2}\int_0^{-\beta u_{ij}} y^{1/2}e^{-y}dy, \tag{2.1}$$

where y is defined as $y=(\beta E_{ij})^{1/2}$ [7] and β as $\beta\equiv 1/kT$. Here, k is Boltzmann's constant and T is is the temperature.

If u_{ij} is a repulsive potential, i.e., $\beta u_{ij}>0$, the probability should be $p_{ij}(r)=0$. In addition, the repulsive potential in the present work is only the hard-core potential.

The factor $\exp(-\beta u_{ij})$ in the grand partition function can be expressed as the sum of the contributions to the bound state and the unbound state. Then, the pairwise bond probability $p_{ij}(r)$ plays an important role as

$$e^{-\beta u_{ij}}=p_{ij}(r)e^{-\beta u_{ij}}+[1-p_{ij}(r)]e^{-\beta u_{ij}}. \tag{2.2}$$

If Eq. (2.2) is substituted into the expression of the pair correlation function $g_{ij}(r)$ described by the use of the grand partition function, the contribution of the bound state to $g_{ij}(r)$ can be separated from that of the unbound state.

Equation (2.2) signifies that the Mayer f function $f_{ij}=e^{-\beta u_{ij}}-1$ is the sum of a factor f_{ij}^{+} contributing to the bound state and the other factor f_{ij}^{*} not contributing to the bound state. Thus, Mayer's mathematical clusters (diagrams defined in terms of f bonds) constituting g_{ij} can be expressed as mathematical clusters consisting of f_{ij}^{+} and f_{ij}^{*} due to the relation $f_{ij}=f_{ij}^{+}+f_{ij}^{*}$. According to Eq. (2.2), f_{ij}^{+} and f_{ij}^{*} are given as

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

A physical cluster consisting of particles bound to each other satisfying the condition $E_{ij}+u_{ij}(r)\leqslant 0$, can be extracted from the mathematical clusters as a mathematical cluster including the product of f_{ij}^{+}. As a result, the pair correlation function $g_{ij}(r)$ can be separated into a correlation function $P_{ij}(r)$ for i-j particles belonging to the same physical cluster and a correlation function $\mathcal{D}_{ij}$ for an i particle belonging to a physical cluster and a j particle belonging to another physical cluster.

The pair connectedness $P_{ij}(r)$ is important to estimate the mean size of physical clusters [8]. According to the above, the pair connectedness $P_{ij}(r)$ can be related to the pair correlation function $g_{ij}(r)$ as

$$g_{ij}=P_{ij}+\mathcal{D}_{ij}. \tag{2.3}$$

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 for a uniform distribution, respectively. 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 $\rho_i\rho_j\mathcal{D}_{ij}(r)d\mathbf{r}_i d\mathbf{r}_j$. Hence, the physical meanings of P_{ij} and $\mathcal{D}_{ij}$ require that

$$\lim_{r\to\infty}P_{ij}=0 \quad\text{and}\quad \lim_{r\to\infty}\mathcal{D}_{ij}=1,$$

since $\lim_{r\to\infty}g_{ij}=1$. In addition, if a cluster has a fractal structure then $P_{ij}(r)$, according to the feature of $\rho_i\rho_j P_{ij}(r)d\mathbf{r}_i d\mathbf{r}_j$, provides the characteristics of the fractal structure.

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}.

The collection of diagrams contributing to P_{ij} can be separated into the sum of two parts, namely C_{ij}^+ and N_{ij}^+. The part C_{ij}^+ is the contribution of nonnodal 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 determined by the convolution integral of the product of C_{ij}^+ and P_{ij}. Thus, P_{ij} can be expressed by an integral equation [8] as

$$P_{ij}=C_{ij}^+ +\sum_{k=1}^{\mathcal{L}}\rho_k\int C_{ik}^+P_{kj}\mathrm{d}\mathbf{r}_k, \tag{2.4}$$

where $\mathcal{L}$ is the number of constituents. This equation has the same mathematical structure as the Ornstein-Zernike equation.

III. CLOSURE SCHEME FOR SIMPLIFYING THE MATHEMATICAL TREATMENT

A. Simple closure scheme for the integral equation

A closure scheme for Eq. (2.4) must be obtained to estimate P_{ij}.

The pair-correlation function g_{ij}^{PY} due to the Percus-Yevick (PY) approximation can be expressed as $g_{ij}^{\mathrm{PY}}e^{\beta u_{ij}}=1+N_{ij}$. Here, N_{ij} is the contribution of the nodal diagrams for *f* bonds. If the relation $e^{-\beta u_{ij}}=f_{ij}^+ + f_{ij}^* +1$ is considered, the above approximation is rewritten as

$$g_{ij}^{\mathrm{PY}}=f_{ij}^+(1+N_{ij}^+ +N_{ij}^*)+(f_{ij}^*+1)N_{ij}^+ +(f_{ij}^*+1)(1+N_{ij}^*).$$

To obtain this equation, the relation $N_{ij}=N_{ij}^+ +N_{ij}^*$ must be considered. The factor N_{ij}^* is due to all nodal diagrams that do not include paths of all f^+ bonds between *i* and *j*. The terms in the above equation can be separated into those constituting P_{ij} and those constituting $\mathcal{D}_{ij}$ by considering the relation $g_{ij}=P_{ij}+\mathcal{D}_{ij}$. Thus, the expressions corresponding to P_{ij} and $\mathcal{D}_{ij}$ can be determined from the separated terms as

$$P_{ij}=f_{ij}^+g_{ij}^{\mathrm{PY}}e^{\beta u_{ij}}+(f_{ij}^*+1)(P_{ij}-C_{ij}^+) \tag{3.1a}$$

and

$$\mathcal{D}_{ij}=(f_{ij}^*+1)g_{ij}^{\mathrm{PY}}e^{\beta u_{ij}}-(f_{ij}^*+1)(P_{ij}-C_{ij}^+). \tag{3.1b}$$

To obtain these equations, the relation $P_{ij}=C_{ij}^+ +N_{ij}^+$ must be considered.

By considering $f_{ij}^+=p_{ij}(r)e^{-\beta u_{ij}}$, $e^{-\beta u_{ij}}=f_{ij}^+ +f_{ij}^* +1$, and the PY approximation $g_{ij}^{\mathrm{PY}}(1-e^{\beta u_{ij}})=c_{ij}^{\mathrm{PY}}$, Eqs. (3.1a) and (3.1b) can be rewritten as

$$P_{ij}+\frac{[1-p_{ij}(r)]e^{-\beta u_{ij}}}{1-[1-p_{ij}(r)]e^{-\beta u_{ij}}}C_{ij}^+ =\frac{p_{ij}(r)c_{ij}^{\mathrm{PY}}}{(1-e^{\beta u_{ij}})\{1-[1-p_{ij}(r)]e^{-\beta u_{ij}}\}} \tag{3.2a}$$

and

$$\mathcal{D}_{ij}=-P_{ij}+\frac{c_{ij}^{\mathrm{PY}}}{1-e^{\beta u_{ij}}}. \tag{3.2b}$$

Equation (3.2a) can be used as closure for Eq. (2.4) if c_{ij}^{PY} is given. Equations (3.2a) and (3.2b) are applicable when either $\beta u_{ij}<0$ or $\beta u_{ij}>0$, respectively.

In addition, Eq. (3.2a) shows that the symmetry $C_{ij}^+ =C_{ji}^+$ is maintained due to the symmetry $P_{ij}=P_{ji}$.

B. Behavior of C_{ij}^+ for $1\ll r$

1. Behavior of C_{ij}^+ for $\beta u_{ij}<0$ and $1\ll r$

The closure scheme given by Eq. (3.2a) is not a practicable way to solve Eq. (2.4) analytically.

Fortunately, Eq. (2.4) has the same mathematical structure as the Ornstein-Zernike equation. The Ornstein-Zernike equation can be solved analytically for some fluids if the mean spherical approximation (MSA) is used. In the MSA, the direct correlation function c_{ij} is given as the sum of the short-range and long-range contributions. If C_{ij}^+ can also be given as such a sum, the procedure for solving Eq. (2.4) can be simplified, as is found in the procedures concerning the MSA.

The behavior of C_{ij}^+ at a great distance between *i* and *j* can be readily determined.

When the distance between *i* and *j* is sufficiently large, $|\beta u_{ij}|$ should be small. Equation (2.1) can then be approximated as

$$p_{ij}(r)=\frac{4}{3\sqrt{\pi}}(-\beta u_{ij})^{3/2}-\frac{4}{5\sqrt{\pi}}(-\beta u_{ij})^{5/2}+\frac{2}{7\sqrt{\pi}}(-\beta u_{ij})^{7/2}+\cdots. \tag{3.3}$$

The substitution of this approximation into Eq. (3.2a) results in

$$C_{ij}^+=\frac{c_{ij}^{\mathrm{PY}}}{-\beta u_{ij}}\left[\frac{4}{3\sqrt{\pi}}(-\beta u_{ij})^{3/2}-\frac{22}{15\sqrt{\pi}}(-\beta u_{ij})^{5/2}+\cdots\right] +P_{ij}\left[-\beta u_{ij}-\frac{4}{3\sqrt{\pi}}(-\beta u_{ij})^{3/2}-\frac{1}{2}(-\beta u_{ij})^2 +\frac{32}{15\sqrt{\pi}}(-\beta u_{ij})^{5/2}+\cdots\right]. \tag{3.4}$$

If $c_{ij}^{\mathrm{PY}}/(-\beta u_{ij})=1$ for the MSA is substituted into this result, C_{ij}^{+} for $1\ll r$ can be written as

$$C_{ij}^{+}\approx 4/(3\sqrt{\pi})(-\beta u_{ij})^{3/2}. \tag{3.5}$$

To derive Eq. (3.5) from Eq. (3.4), the condition $(-\beta u_{ij})P_{ij}\ll 4/(3\sqrt{\pi})(-\beta u_{ij})^{3/2}$ has been assumed for $1\ll r$.

The MSA results in the relation $\lim_{r\to\infty}(g_{ij}-1)/(-\beta u_{ij})=1/2$, since the PY approximation is given as $g_{ij}^{\mathrm{PY}}=c_{ij}^{\mathrm{PY}}/[1-\exp(\beta u_{ij})]$. The condition $P_{ij}/(g_{ij}-1)\leqslant 1$ is always satisfied, so that P_{ij} for $1\ll r$ should satisfy $(g_{ij}-1)/(-\beta u_{ij})\geqslant P_{ij}/(-\beta u_{ij})>P_{ij}/(-\beta u_{ij})^{1/2}$. Therefore, the relation $\lim_{r\to\infty}P_{ij}/(-\beta u_{ij})^{1/2}=0$ can be derived. Thus, the above assumption is validated.

2. Behavior of P_{ij} for $|\beta uij|\ll 1$ and $1\ll r$

Using Eq. (3.3), the expansion of Eq. (3.2a) in powers of $-\beta u_{ij}$ can be performed as

$$P_{ij}=-\frac{c_{ij}^{\mathrm{PY}}}{-\beta u_{ij}}\left[\frac{4}{3\sqrt{\pi}}(-\beta u_{ij})^{1/2}+\frac{16}{9\pi}(-\beta u_{ij})+\left(\frac{64}{27\pi^{3/2}}-\frac{4}{5\sqrt{\pi}}\right)(-\beta u_{ij})^{3/2}+\cdots\right]+\frac{C_{ij}^{+}}{-\beta u_{ij}}\times\left[1+\frac{4}{3\sqrt{\pi}}(-\beta u_{ij})^{1/2}+\left(\frac{1}{2}+\frac{16}{9\pi}\right)(-\beta u_{ij})+\cdots\right]. \tag{3.6}$$

If the approximation given by Eq. (3.5) and $c_{ij}^{\mathrm{PY}}/(-\beta u_{ij})=1$ for the MSA are considered in Eq. (3.6), the result can be expressed as

$$P_{ij}=\frac{22}{15\sqrt{\pi}}(-\beta u_{ij})^{3/2}\quad\text{for}\quad u_{ij}<0. \tag{3.7}$$

If a physical cluster in a fluid mixture has a fractal structure, then $P_{ij}(r)$ given by Eq. (3.7) should represent the characteristics of the fractal structure.

C. Expression of a simple closure scheme

1. A closure scheme similar to the MSA

According to Eqs. (3.5), a closure scheme similar to the MSA can be obtained as

$$C_{ij}^{+}=C_{ij}^{0+}+\frac{4}{3\sqrt{\pi}}(-\beta u_{ij})^{3/2}\quad\text{for}\quad \beta u_{ij}<0, \tag{3.8}$$

where C_{ij}^{0+} is the short-range contribution.

Ultimately, Eq. (2.4) can be solved using the closure scheme given as Eq. (3.8).

2. $\mathcal{N}$-term potential

Mathematical difficulty cannot be avoided when applying the above-mentioned closure scheme to analytically solve Eq. (2.4) because powers of the potential are included in the closure. To avoid this difficulty in the present work, it is assumed that the potential u_{ij} is given as the sum of $\mathcal{N}$ terms where each term has the same feature as the Yukawa potential. It is an $\mathcal{N}$-term potential given as

$$-\beta u_{ij}(r)=\sum_{n=1}^{\mathcal{N}} w_{ij}^{(n)}(r), \tag{3.9a}$$

where

$$w_{ij}^{(n)}\equiv k_0^{(n)}d_i^{(n)}d_j^{(n)}\frac{\exp(-z_n r)}{r}\quad\text{for}\quad r\geqslant\sigma_{ij}. \tag{3.9b}$$

Here, an assumption for the coefficients z_n should be provided as

$$0<z_1\leqslant z_2\leqslant\cdots\leqslant z_{\mathcal{N}}<\infty. \tag{3.9c}$$

This relation is useful, when efficient terms for $r\gg 1$ should be extracted from the power of the $\mathcal{N}$-term potential.

The effective range r_{ij}^{eff}, of the attractive force between a particle i and a particle j due to the $\mathcal{N}$-term potential can be determined for n satisfying both $d_i^{(n)}\neq 0$ and $d_j^{(n)}\neq 0$. If both $d_i^{(n)}\neq 0$ and $d_j^{(n)}\neq 0$ only for $n=n_s$ is satisfied, then the attractive force due to the $\mathcal{N}$-term potential has the effective range $r_{ij}^{\mathrm{eff}}=z_{n_s}^{-1}$.

If the effective range of the attractive force between i'-j' particles is relatively wide, the probability that the i'-j' particles fall into a bound state $E_{i'j'}+u_{i'j'}(r)\leqslant 0$ should be high enough. Thus, a pair of particles specified by $n=n_{min}$ at which z_n is the minimum value in Eq. (3.9a) should effectively contribute to the percolation due to the contact of microscopically dense regions.

The $\mathcal{N}$-term potential expressed by Eq. (3.9a) can be useful to estimate the percolation in a multicomponent mixture composed of particles interacting with attractive forces having various effective ranges.

3. Additional simplification of the closure scheme.

The substitution of Eq. (3.9a) into Eq. (3.8) results in

$$C_{ij}^{0+}(r)+\frac{4}{3\sqrt{\pi}}\{-\beta u_{ij}(r)\}^{3/2}=C_{ij}^{0+}(r)+\frac{4}{3\sqrt{\pi}}\left\{\sum_{n=1}^{\mathcal{N}}k_0^{(n)}d_i^{(n)}d_j^{(n)}\exp(-z_n r)\right\}^{3/2}\frac{1}{r^{3/2}}. \tag{3.10a}$$

In Eq. (3.8), the power $(-\beta u_{ij})^{3/2}$ should be estimated as that for $r\gg 1$. If this fact and the relation $0<z_1<z_{n'}$ $(n'=2,3,\cdots)$ assumed by Eq. (3.9c) are considered, Eq. (3.10a) should be rewritten as

$$C_{ij}^{+}(r)=C_{ij}^{0+}(r)+\frac{4}{3\sqrt{\pi}}\Bigg\{(k_0^{(1)}d_i^{(1)}d_j^{(1)})^{3/2}\exp\left(-\frac{3}{2}z_1 r\right)\frac{1}{r^{3/2}} + \frac{3}{2}(k_0^{(1)}d_i^{(1)}d_j^{(1)})^{1/2}\sum_{n'=2}^{\mathcal{N}} k_0^{(n')}d_i^{(n')}d_j^{(n')} \times\exp\left(-z_{n'}r-\frac{1}{2}z_1 r\right)\frac{1}{r^{3/2}}\Bigg\}. \tag{3.10b}$$

The second term on the right-hand side of Eq. (3.10b) decays within a longer range than the third term. Particles that interact with the attractive force contributing to the second term can efficiently contribute to inducing the percolation due to the contact of microscopically dense regions in a fluid mixture. Particles that interact with the attractive forces contributing to the third term cannot contribute efficiently to the percolation.

In Eq. (3.10b), the effect of the factor $(1/r)^{3/2}$ should be approximately treated to obtain an analytical solution for Eq. (2.4).

The decrease in $C_{ij}^{+}(r)$ due to each term of the exponential function can be much more dominant than that due to the factor $(1/r)^{3/2}$ as r increases. Considering this, the contribution from the factor $(1/r)^{3/2}$ can be approximated by $1/r$ in Eq. (3.10b).

Another approximation can be given by requiring the relation $(1/r)^{3/2}=e^{-z'r}/r$ for $0<r-a\ll 1$. An approximate expression given by the requirement can be found as

$$\frac{1}{r^{3/2}}=\frac{e^{1/2}}{\sqrt{a}}\frac{1}{r}\exp\left[-\frac{r}{2a}\right].$$

In the present work, the maximum hard sphere diameter of particles distributed in the fluid mixture is applied as a.

Thus, Eq. (3.10b) can be approximated as

$$C_{ij}^{+}(r)=C_{ij}^{0+}(r)+\sum_{n=1}^{\mathcal{N}}\breve{k}_0^{n}\breve{d}_i^{n}\breve{d}_j^{n}\frac{\exp(-\breve{z}_n r)}{r}. \tag{3.11a}$$

The comparison between Eqs. (3.10b) and (3.11a) according to Eq. (3.9c) shows that the coefficients $\breve{z}_n$ should satisfy the relation given as

$$0<\breve{z}_1\leqslant\breve{z}_2\leqslant\breve{z}_3\leqslant\cdots. \tag{3.11b}$$

Hence, pair particles interacting with the attractive force having the effective range characterized by $\breve{z}_1$ can most efficiently contribute to the percolation due to the contact of microscopically dense regions in the fluid mixture.

Besides the relation given by Eq. (3.11b), each coefficient in Eq. (3.11a) can be given as

$$\breve{z}_n=\zeta_n \quad \text{for} \quad f_c=1, \tag{3.12a}$$

$$\breve{z}_n=\zeta_n+\frac{1}{2}a^{-1} \quad \text{for} \quad f_c=e^{1/2}, \tag{3.12b}$$

$$\zeta_1\equiv\frac{3}{2}z_1, \tag{3.12c}$$

$$\zeta_{n'}\equiv z_{n'}+\frac{1}{2}z_1 \quad (n'=2,3,\ldots), \tag{3.12d}$$

$$\breve{k}_0^1\breve{d}_i^1\breve{d}_j^1=\frac{4}{3\sqrt{\pi}}\frac{f_c}{\sqrt{a}}(k_0^{(1)})^{3/2}(d_i^{(1)})^{3/2}(d_j^{(1)})^{3/2}, \tag{3.12e}$$

and

$$\breve{k}_0^{n'}\breve{d}_i^{n'}\breve{d}_j^{n'}=\frac{2}{\sqrt{\pi}}\frac{f_c}{\sqrt{a}}(k_0^{(1)})^{1/2}k_0^{(n')}(d_i^{(1)})^{1/2}d_i^{(n')} \times(d_j^{(1)})^{1/2}d_j^{(n')} \quad (n'=2,3,\ldots). \tag{3.12f}$$

Thus, the closure given by Eq. (3.11a) is characterized by the parameter f_c. The effective ranges of the attractive forces can be characterized by $\breve{z}_n$ due to Eqs. (3.12a) and (3.12b).

In the above, the product $\breve{k}_0^1\breve{d}_i^1\breve{d}_j^1$ is a factor characterizing the strength of the long-range attractive force. In contrast, a product expressed as $\breve{k}_0^{n'}\breve{d}_i^{n'}\breve{d}_j^{n'}$ can be regarded as a factor characterizing the strength of a short-range attractive force.

The approximation given by Eq. (3.11a) for $f_c=1$ somewhat overestimates the long-ranged contribution of $C_{ij}^{+}(r)$, since the contribution of $(1/r)^{3/2}$ is approximated as $(1/\sqrt{a})(1/r)$

The alternative approximation given by Eq. (3.11a) for $f_c=e^{1/2}$ somewhat overestimates the decay of $C_{ij}^{+}(r)$ dependent on r, since the contribution of $(1/r)^{3/2}$ 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-range 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. Fortunately, it is possible that the diagram representing the percolation threshold for the overestimation of the long-range contribution has the same pattern as that for the overestimation of the decay of $C_{ij}^{+}(r)$.

A hard-core potential resulting in a completely short-range interaction between ith and jth particles does not directly contribute to the interaction between them when separated beyond a particular distance σ_{ij}. By considering this for C_{ij}^{0+} it is assumed that

$$C_{ij}^{0+}(r)=0, \quad \text{for} \quad r\geqslant\sigma_{ij}, \tag{3.13}$$

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. If the short-range contribution C_{ij}^{0+} can be neglected for $r\geqslant\sigma_{ij}$, the mathematical treatment of Eq. (2.4) is considerably simplified as it was in the MSA. As a result, it is possible that the use of Eq. (3.11a) simplifies the estimation of the percolation due to the contact of microscopically dense regions.

IV. A SOLUTION OF THE INTEGRAL EQUATION

A. A solution including unknown coefficients

1. Using Baxter's Q function

Baxter's Q function [9] is useful to obtain a solution of Eq. (2.4) for either a single-component fluid of particles interacting via the Yukawa potential [10,11] or a multicomponent fluid mixture. Equation (2.4) can be solved analytically, using Baxter's Q function [9] with Eqs. (3.11a)–(3.13) given for an $\mathcal{L}$-component fluid mixture.

Based on the mathematical procedure for the Orstein-Zernike equation [9,12], $P_{ij}(r)$ and $C_{ij}^{+}(r)$ satisfying Eq. (2.4) for the $\mathcal{L}$-component fluid mixture are given by

$$2\pi r P_{ij}(r) = -\frac{d}{dr}Q_{ij}(r) + 2\pi\sum_{k=1}^{\mathcal{L}} \rho_k \int_{\lambda_{jk}}^{\infty} Q_{kj}(t)(r-t) \times P_{ik}(|r-t|)dt \quad \text{for } \lambda_{ji} \leqslant r < \infty \tag{4.1}$$

and

$$2\pi r C_{ij}^{+}(r) = -\frac{d}{dr}Q_{ij}(r) + \sum_{k=1}^{\mathcal{L}} \rho_k \int_{sup[\lambda_{kj},\lambda_{ki}-r]}^{\infty} Q_{jk}(t) \times \frac{d}{dr}Q_{ik}(r+t)dt \quad \text{for } \lambda_{ji} \leqslant r < \infty, \tag{4.2}$$

where λ_{ji} is defined using the hard-core diameters σ_i and σ_j as $\lambda_{ji} \equiv \frac{1}{2}(\sigma_j - \sigma_i)$.

The function $Q_{ij}(r)$ in Eqs. (4.1) and (4.2) is introduced as

$$\tilde{Q}_{ij}(k) = \delta_{ij} - (\rho_i\rho_j)^{1/2}\int_{\lambda_{ji}}^{\infty} e^{ikr}Q_{ij}(r)dr, \tag{4.3}$$

where $\delta_{ij}=0$ $(i \neq j)$ and $\delta_{ii}=1$.

The short-range contribution to $C_{ij}^{+}(r)$ is expressed in Eq. (3.13). The characteristics of the short-range contribution $C_{ij}^{0+}(r)$ should be provided by $Q_{ij}(r)$, since $Q_{ij}(r)$ should be related to $C_{ij}^{+}(r)$ owing to Eq. (4.2).

If the characteristics of the long-range contribution to $C_{ij}^{+}(r)$ are considered with the fact mentioned above, $Q_{ij}(r)$ may have a form expressed as

$$Q_{ij}(r) = Q_{ij}^{0}(r) + \sum_{n=1}^{\mathcal{N}} D_{ij}^{n} e^{-\breve{z}_n r} \quad (\lambda_{ji} < r < \sigma_{ji}), \tag{4.4a}$$

$$Q_{ij}(r) = \sum_{n=1}^{\mathcal{N}} D_{ij}^{n} e^{-\breve{z}_n r} \quad (\sigma_{ji} \leqslant r), \tag{4.4b}$$

and

$$Q_{ij}^{0}(r) = 0 \quad (\sigma_{ji} \leqslant r). \tag{4.4c}$$

In addition, the unknown coefficients D_{ij} given above must be determined using Eqs. (4.1) and (4.2).

The relation $P_{ij}=0$ for $\lambda_{ji} < r < \sigma_{ji}$ is derived from Eq. (3.1a) by considering $\lim_{u_{ij}\to\infty} g_{ij}=0$ and $\lim_{\delta\to 0} u_{ij}(\sigma_{ij}+\delta)=\infty$ $(\delta>0)$. Owing to this feature of P_{ij}, the function $Q_{ij}(r)$ derived from Eq. (4.1) for $|\rho_k| \ll 1$ cannot include powers of r in the range $\lambda_{ji} < r < \sigma_{ji}$. If this is considered with the feature of $Q_{ij}^{0}(r)$ given in Eq. (4.4c) and the behavior of $Q_{ij}(r)$ expressed by Eq. (4.4a), the function $Q_{ij}^{0}(r)$ should have a form expressed as

$$Q_{ij}^{0}(r) = \sum_{n=1}^{\mathcal{N}} \left[-D_{ij}^{n} + 2\pi\sum_{k=1}^{\mathcal{L}} \frac{\rho_k}{\breve{z}_n}\hat{P}_{ik}(\breve{z}_n)D_{kj}^{n} \right] \times (e^{-\breve{z}_n r} - e^{-\breve{z}_n \sigma_{ij}}) \quad (\lambda_{ji} < r < \sigma_{ji}), \tag{4.4d}$$

where

$$\hat{P}_{ik}(\breve{z}_n) \equiv \int_0^{\infty} P_{ik}(t) e^{-\breve{z}_n t} t dt. \tag{4.4e}$$

Owing to the relation given by Eq. (3.11b), the quantities $\hat{P}_{ik}(\breve{z}_n)$ should satisfy the relation given as

$$\hat{P}_{ik}(\breve{z}_1) \geqslant \hat{P}_{ik}(\breve{z}_2) \geqslant \cdots (0 < \breve{z}_1 \leqslant \breve{z}_2 \leqslant \cdots). \tag{4.4f}$$

This means that the quantity $\hat{P}_{ik}(\breve{z}_n)$ is small if the effective range of the attractive force between pair particles i and k is short. The coefficient $\breve{z}_n$ is given by Eqs. (3.12a) or (3.12b). The reciprocal $1/\breve{z}_n$ characterizes the effective range of the attractive force due to Eqs. (3.12c) and (3.12d).

Equation (4.4a) and the relation $P_{ij}=0$ should be satisfied over the range $\lambda_{ji} < r < \sigma_{ji}$ so that Eq. (4.1) for $r < \sigma_{ji}$ leads to a relation given due to Eqs. (4.4b), (4.4c), and (4.4d) as

$$\sum_{n=1}^{\mathcal{N}} \breve{z}_n \left[-D_{ij}^{n} + 2\pi\sum_{k=1}^{\mathcal{L}} \frac{\rho_k}{\breve{z}_n}\hat{P}_{ik}(\breve{z}_n)D_{kj}^{n} \right] e^{-\breve{z}_n r} + \sum_{n=1}^{\mathcal{N}} \breve{z}_n D_{ij}^{n} e^{-\breve{z}_n r} - 2\pi\sum_{k=1}^{\mathcal{L}}\sum_{n=1}^{\mathcal{N}} \rho_k D_{kj}^{n} e^{-\breve{z}_n r}\int_0^{\infty} P_{ik}(t)e^{-\breve{z}_n t} t dt = 0. \tag{4.5}$$

If Eq. (4.4b) is considered, then Eq. (4.2) leads to a relation expressed as

$$2\pi r C_{ij}^{+}(r) = \sum_{n=1}^{\mathcal{N}} \breve{z}_n D_{ij}^{n} e^{-\breve{z}_n r} - \sum_{n=1}^{\mathcal{N}} \breve{z}_n e^{-\breve{z}_n r}\sum_{k=1}^{\mathcal{L}} \rho_k D_{ik}^{n}\hat{Q}_{jk}(\breve{z}_n) \quad \text{for } \sigma_{ji} < r, \tag{4.6}$$

where

$$\hat{Q}_{jk}(s) \equiv \int_{\lambda_{kj}}^{\infty} Q_{jk}(t) e^{-st} dt$$
$$= \sum_{m=1}^{\mathcal{N}} \left\{ \left[-D_{jk}^{m} + 2\pi \sum_{l=1}^{\mathcal{L}} \frac{\rho_l}{\breve{z}_m} \hat{P}_{jl}(\breve{z}_m) D_{lk}^{m} \right] \times e^{-s\lambda_{kj}} e^{-\breve{z}_m \sigma_{kj}} \left(\frac{e^{\breve{z}_m \sigma_j} - e^{-s\sigma_j}}{s+\breve{z}_m} - \frac{1-e^{-s\sigma_j}}{s} \right) + \frac{1}{s+\breve{z}_m} D_{jk}^{m} e^{-\breve{z}_m \lambda_{kj}} e^{-s\lambda_{kj}} \right\}. \tag{4.7}$$

Here, Eq. (4.7) can be derived from the use of Eqs. (4.4a)–(4.4d). The relation between $\hat{P}_{jk}(\breve{z}_n)$ and $\hat{Q}_{jk}(\breve{z}_n)$ can be obtained from Eq. (4.7) as

$$\hat{Q}_{jk}(\breve{z}_n) = e^{-\breve{z}_n \lambda_{kj}} \sum_{m=1}^{\mathcal{N}} \left\{ e^{-\breve{z}_m \sigma_{kj}} D_{jk}^{m} \left(\frac{e^{-\breve{z}_n \sigma_j}}{\breve{z}_n + \breve{z}_m} + \frac{1-e^{-\breve{z}_n \sigma_j}}{\breve{z}_n} \right) + \sum_{l=1}^{\mathcal{L}} \frac{2\pi \rho_l}{\breve{z}_m} \hat{P}_{jl}(\breve{z}_m) D_{lk}^{m} \left[\frac{e^{-\breve{z}_m \lambda_{kj}}}{\breve{z}_n + \breve{z}_m} - e^{-\breve{z}_m \sigma_{kj}} \times \left(\frac{e^{-\breve{z}_n \sigma_j}}{\breve{z}_n + \breve{z}_m} + \frac{1-e^{-\breve{z}_n \sigma_j}}{\breve{z}_n} \right) \right] \right\}. \tag{4.8}$$

By considering Eqs. (4.4a) and (4.4d), Eq. (4.1) for $r < \sigma_{ji}$ can be rewritten as

$$0 = \sum_{n=1}^{\mathcal{N}} \breve{z}_n \left[-D_{ij}^{n} + 2\pi \sum_{k=1}^{\mathcal{L}} \frac{\rho_k}{\breve{z}_n} \hat{P}_{ik}(\breve{z}_n) D_{kj}^{n} \right] e^{-\breve{z}_n r} + \sum_{n=1}^{\mathcal{N}} \breve{z}_n D_{ij}^{n} e^{-\breve{z}_n r} + 2\pi \sum_{k=1}^{\mathcal{L}} \rho_k \int_{r}^{\infty} Q_{kj}(t)(r-t) \times P_{ik}(|r-t|) dt. \tag{4.9}$$

Equation (4.9) is equivalent to Eq. (4.5) that has no singularity for $0 < r < \infty$, so that Eq. (4.9) is satisfied for $0 < r < \infty$. If the terms in Eq. (4.9) are then subtracted from terms in an equation representing Eq. (4.1) for $\sigma_{ji} \leqslant r$, a formula can be derived as

$$2\pi r P_{ij}(r) = -\sum_{m=1}^{\mathcal{N}} \breve{z}_m \left[-D_{ij}^{m} + 2\pi \sum_{k=1}^{\mathcal{L}} \frac{\rho_k}{\breve{z}_m} \hat{P}_{ik}(\breve{z}_m) D_{kj}^{m} \right] e^{-\breve{z}_m r} + 2\pi \sum_{k=1}^{\mathcal{L}} \rho_k \int_{\lambda_{jk}}^{r} Q_{kj}(t)(r-t) P_{ik}(r-t) dt. \tag{4.10}$$

The Laplace transformation of Eq. (4.10) results in

$$2\pi \hat{P}_{ij}(s) = -\sum_{m=1}^{\mathcal{N}} \frac{\breve{z}_m}{s+\breve{z}_m} e^{-(s+\breve{z}_m)\sigma_{ij}} \times \left[-D_{ij}^{m} + 2\pi \sum_{k=1}^{\mathcal{L}} \frac{\rho_k}{\breve{z}_m} \hat{P}_{ik}(\breve{z}_m) D_{kj}^{m} \right] + 2\pi \sum_{k=1}^{\mathcal{L}} \rho_k \hat{P}_{ik}(s) \hat{Q}_{kj}(s). \tag{4.11}$$

2. A formula for determining $\hat{P}_{ij}(\breve{z}_n)$ and D_{ij}^{n}

By substituting Eq. (4.8) into Eq. (4.11) for $s = \breve{z}_n$, a formula determining the relation between $\hat{P}_{ij}(\breve{z}_n)$ and D_{ij}^{n} can be obtained as

$$2\pi \hat{P}_{ij}(\breve{z}_n) = \sum_{m=1}^{\mathcal{N}} \frac{\breve{z}_m}{\breve{z}_n + \breve{z}_m} e^{-(\breve{z}_n + \breve{z}_m)\sigma_{ij}} \times \left[D_{ij}^{m} - 2\pi \sum_{k=1}^{\mathcal{L}} \frac{\rho_k}{\breve{z}_m} \hat{P}_{ik}(\breve{z}_m) D_{kj}^{m} \right] + 2\pi \sum_{k=1}^{\mathcal{L}} \rho_k \hat{P}_{ik}(\breve{z}_n) e^{-\breve{z}_n \lambda_{jk}} \times \sum_{m=1}^{\mathcal{N}} \left\{ e^{-\breve{z}_m \sigma_{jk}} D_{kj}^{m} \left(\frac{e^{-\breve{z}_n \sigma_k}}{\breve{z}_n + \breve{z}_m} + \frac{1-e^{-\breve{z}_n \sigma_k}}{\breve{z}_n} \right) + \sum_{l=1}^{\mathcal{L}} \frac{2\pi \rho_l}{\breve{z}_m} \hat{P}_{kl}(\breve{z}_m) D_{lj}^{m} \left[\frac{e^{-\breve{z}_m \lambda_{jk}}}{\breve{z}_n + \breve{z}_m} - e^{-\breve{z}_m \sigma_{jk}} \left(\frac{e^{-\breve{z}_n \sigma_k}}{\breve{z}_n + \breve{z}_m} + \frac{1-e^{-\breve{z}_n \sigma_k}}{\breve{z}_n} \right) \right] \right\}. \tag{4.12}$$

3. Another formula for determining $\hat{P}_{ij}(\breve{z}_n)$ and D_{ij}^{n}

If Eq. (3.13) is considered, then the substitution of Eq. (3.11a) into Eq. (4.6) results in

$$2\pi \breve{k}_0^n \breve{d}_i^n \breve{d}_j^n = \breve{z}_n D_{ij}^{n} - \sum_{k=1}^{\mathcal{L}} \breve{z}_n \rho_k D_{ik}^{n} \hat{Q}_{jk}(\breve{z}_n). \tag{4.13}$$

By substituting Eq. (4.8) into Eq. (4.13), another formula to determine the relation between $\hat{P}_{ij}(\breve{z}_n)$ and D_{ij}^{n} can be obtained as

$$2\pi\breve{k}_0^n\breve{d}_i^n\breve{d}_j^n=\breve{z}_nD_{ij}^n-\sum_{m=1}^{\mathcal{N}}\sum_{k=1}^{\mathcal{L}}\rho_kD_{ik}^nD_{jk}^me^{-\breve{z}_n\lambda_{kj}}\times e^{-\breve{z}_m\sigma_{kj}}\frac{\breve{z}_n+\breve{z}_m-\breve{z}_me^{-\breve{z}_n\sigma_j}}{\breve{z}_n+\breve{z}_m}-\sum_{m=1}^{\mathcal{N}}\sum_{k=1}^{\mathcal{L}}\sum_{l=1}^{\mathcal{L}}\rho_kD_{ik}^nD_{lk}^m\frac{2\pi\rho_l}{\breve{z}_m}\hat{P}_{jl}(\breve{z}_m)e^{-\breve{z}_n\lambda_{kj}}\times e^{-\breve{z}_m\sigma_{kj}}\frac{-\breve{z}_n-\breve{z}_m+\breve{z}_me^{-\breve{z}_n\sigma_j}+\breve{z}_ne^{\breve{z}_m\sigma_j}}{\breve{z}_n+\breve{z}_m}. \tag{4.14}$$

B. Formulas for unknown coefficients

1. Coefficients specified for the $\mathcal{N}$-term potential

Each coefficient expressed as D_{ij}^n on the right-hand side of Eq. (4.12) has the suffix j, although it does not belong to the coefficients $\hat{P}_{ij}(\breve{z}_n)$. The suffixes i found on the right-hand side of Eq. (4.14) belong to the coefficients D_{ij}^n. The term on the left-hand side of Eq. (4.14) is a product given by $2\pi\breve{k}_0^n\breve{d}_i^n\breve{d}_j^n$. These facts indicate that a coefficient D_{ij}^n can be divided into a factor having the suffix i and the other factors having suffixes j. Thus, it is assumed that the coefficient D_{ij}^n is given as

$$D_{ij}^n=-\breve{d}_i^na_j^n\exp(\breve{z}_n\sigma_j/2), \tag{4.15a}$$

where a_j^n is an unknown coefficient.

The expression of Eq. (4.12) can be simplified by the use of a coefficient P_j^n defined as

$$P_j^n\equiv 12\sum_{l=1}^{\mathcal{L}}\phi_l\frac{\breve{d}_l^n}{\sigma_l}\frac{\hat{P}_{lj}(\breve{z}_n)}{\sigma_l^2}, \tag{4.15b}$$

where ϕ_l is the volume fraction defined as

$$\phi_l\equiv\frac{\pi}{6}\rho_l\sigma_l^3. \tag{4.15c}$$

The coefficient P_j^n defined by Eq. (4.15b) must always be positive, since $\breve{d}_j^n/\sigma_j$ should be positive for arbitary values of j and n. According to Eq. (4.4f), this coefficient should be small if the effective range characterized by $1/\breve{z}_n$ is short.

The use of the coefficient P_j^n and the volume fraction ϕ_l simplifies Eq. (4.12) as

$$-P_j^n=\sum_{m=1}^{\mathcal{N}}x_j^nx^{nm}\frac{a_j^m}{\sigma_j}, \tag{4.16a}$$

where

$$x_j^n\equiv\frac{6}{\pi}\breve{z}_n\sigma_je^{-\breve{z}_n\sigma_j/2} \tag{4.16b}$$

and

$$x^{nm}\equiv\sum_{l=1}^{\mathcal{L}}\frac{e^{\breve{z}_n\sigma_l/2}e^{-\breve{z}_m\sigma_l/2}}{\breve{z}_n\sigma_l(\breve{z}_n+\breve{z}_m)\sigma_l}\left[\breve{z}_n\sigma_le^{-\breve{z}_n\sigma_l}\frac{\breve{d}_l^n}{\sigma_l}\left(\frac{\breve{d}_l^m}{\sigma_l}-\frac{1}{\breve{z}_m\sigma_l}P_l^m\right)+P_l^n\left(\frac{\breve{d}_l^m}{\sigma_l}Y_{ll}^{mn}+P_l^mZ_{ll}^{mn}\right)\right]\phi_l, \tag{4.16c}$$

with

$$Y_{jl}^{mn}\equiv\frac{1}{\breve{z}_n\sigma_l}[(\breve{z}_n+\breve{z}_m)\sigma_l-\breve{z}_m\sigma_le^{-\breve{z}_n\sigma_j}] \tag{4.16d}$$

and

$$Z_{jl}^{mn}\equiv\frac{1}{\breve{z}_m\sigma_j\breve{z}_n\sigma_l}[\breve{z}_n\sigma_le^{\breve{z}_m\sigma_j}-(\breve{z}_n+\breve{z}_m)\sigma_l+\breve{z}_m\sigma_le^{-\breve{z}_n\sigma_j}]. \tag{4.16e}$$

Moreover, the use of the coefficient P_j^n and the volume fraction ϕ_l simplifies Eq. (4.14) as

$$2\pi\frac{\breve{k}_0}{\breve{z}_n}\frac{\breve{d}_j^n}{\sigma_j}e^{-\breve{z}_n\sigma_j/2}=-\frac{a_j^n}{\sigma_j}-\frac{6}{\pi}\sum_{m=1}^{\mathcal{N}}\sum_{l=1}^{\mathcal{L}}\phi_l\frac{a_l^n}{\sigma_l}\frac{a_l^m}{\sigma_l}\frac{e^{-\breve{z}_m\sigma_j/2}}{(\breve{z}_n+\breve{z}_m)\sigma_l}\times\left[\frac{\breve{d}_j^m}{\sigma_j}Y_{jl}^{mn}+P_j^mZ_{jl}^{mn}\right]. \tag{4.17}$$

2. Coefficients specified for the two-terms potential

The potential composed of two terms, i.e., Eq. (3.9a) for $\mathcal{N}=2$, is remarkable. If particles interacting with an attractive force contributing only within a short range constitute a fluid mixture with particles interacting with an attractive force contributing over a long range, then Eq. (3.9a) at least for $\mathcal{N}=2$ must be used to describe the features of these forces. Besides this, the coefficients a_j/σ_j for $\mathcal{N}=2$ can be readily obtained from Eq. (4.16a) as

$$\frac{a_j^n}{\sigma_j}=-\frac{1}{x}\sum_{m=1}^{2}X_j^{nm}P_j^m, \tag{4.18a}$$

where

$$\begin{pmatrix}X_j^{11} & X_j^{12}\\ X_j^{21} & X_j^{22}\end{pmatrix}\equiv\begin{pmatrix}\frac{1}{x_j^1}x^{22} & -\frac{1}{x_j^2}x^{12}\\ -\frac{1}{x_j^1}x^{21} & \frac{1}{x_j^2}x^{11}\end{pmatrix}, \tag{4.18b}$$

and

$$x\equiv x^{11}x^{22}-x^{12}x^{21}. \tag{4.18c}$$

The substitution of Eq. (4.18a) into Eq. (4.17) results in

$$2\pi e^{-\breve{z}_n\sigma_j/2}\frac{\breve{k}_0^n}{\breve{z}_n}\frac{\breve{d}_j^n}{\sigma_j}x^2-x\sum_{r=1}^{2}X_j^{nr}P_j^r$$
$$+\frac{6}{\pi}\sum_{m=1}^{2}\sum_{r=1}^{2}\sum_{s=1}^{2}\sum_{l=1}^{\mathcal{L}}\left[\phi_l X_l^{nr}X_l^{ms}P_l^rP_l^s\frac{e^{-\breve{z}_m\sigma_j/2}}{(\breve{z}_n+\breve{z}_m)\sigma_l}\right.$$
$$\left.\times\left(\frac{\breve{d}_j^m}{\sigma_j}Y_{jl}^{mn}+P_j^mZ_{jl}^{mn}\right)\right]=0 \qquad (4.19)$$

V. MEAN SIZE OF PHYSICAL CLUSTERS

A. Cluster size

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, De Angelis, and Forlani [8], as

$$\sum_{2\leq\nu}\nu(\nu-1)n_\nu=\sum_{i=1}^{\mathcal{L}}\sum_{j=1}^{\mathcal{L}}\rho_i\rho_j\int_V\int_V P_{ij}(\mathbf{r}_i,\mathbf{r}_j)d\mathbf{r}_id\mathbf{r}_j. \qquad (5.1)$$

If the probability $p(i)$ that particle i exists in a cluster is independent of ν, then the factor $\Sigma_\nu \nu n_\nu$ included in Eq. (5.1) can be related to the density ρ_i of the i particles in the volume V as

$$\rho_i=\frac{1}{V}p(i)\sum_\nu \nu n_\nu. \qquad (5.2)$$

The mean physical cluster size S is given by $S=(\Sigma_\nu\nu^2n_\nu)/(\Sigma_\nu\nu n_\nu)$, so that the substitution of Eqs. (5.1) and (5.2) into this formula results in

$$S=1+\left(\sum_{k=1}^{\mathcal{L}}\rho_k\right)^{-1}\sum_{i=1}^{\mathcal{L}}\sum_{j=1}^{\mathcal{L}}\rho_i\rho_j\int P_{ij}(r)d\mathbf{r}. \qquad (5.3)$$

According to Appendix A, the mean physical cluster size S given by Eq. (5.3) is estimated as

$$S=\sum_{i=1}^{\mathcal{L}}\left[\sum_{j=1}^{\mathcal{L}}\left\{\sum_{k=1}^{\mathcal{L}}\frac{\phi_k}{\phi_i}\left(\frac{\sigma_i}{\sigma_k}\right)^3\right\}^{-1/2}\tilde{Q}_{ij}^{-1}(0)\right]^2. \qquad (5.4a)$$

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

According to the comparison between Eqs. (4.3) and (4.7), the relation between $\tilde{Q}_{ij}(0)$ and $\hat{Q}_{ij}(0)$ is given as

$$\tilde{Q}_{ij}(0)=\delta_{ij}-\frac{6}{\pi}\left(\frac{\phi_i}{\sigma_i^3}\frac{\phi_j}{\sigma_j^3}\right)^{1/2}\hat{Q}_{ij}(0). \qquad (5.4b)$$

If Eq. (4.7) for $s=0$ is used with Eqs. (4.15a)–(4.15c), an expression for $\hat{Q}_{ij}(0)$ can be derived as

$$\frac{6}{\pi}\left(\frac{\phi_i}{\sigma_i^3}\frac{\phi_j}{\sigma_j^3}\right)^{1/2}\hat{Q}_{ij}(0)=\sum_{m=1}^{\mathcal{N}}\left(\frac{6}{\pi}\phi_i\sigma_i\right)^{1/2}Q_i^m\left(\frac{6}{\pi}\phi_j\frac{1}{\sigma_j}\right)^{1/2}\frac{a_j^m}{\sigma_j}, \qquad (5.4c)$$

where

$$Q_i^m\equiv\frac{e^{-\breve{z}_m\sigma_i/2}}{\breve{z}_m\sigma_i}\left[-\frac{e^{z_m\sigma_i}-1-\breve{z}_m\sigma_i}{\breve{z}_m\sigma_i}P_i^m-\frac{\breve{d}_i^m}{\sigma_i}(\breve{z}_m\sigma_i+1)\right]. \qquad (5.4d)$$

Thus, the coefficient $\tilde{Q}_{ij}^{-1}(0)$ in Eq. (5.4a) can be estimated.

B. Percolation at $\mathcal{L}=2$

1. A two-component mixture ($\mathcal{L}=2$, $\mathcal{N}=\mathcal{N}$)

The inverse $\tilde{Q}_{ij}^{-1}(0)$ can be readily estimated for a two-component mixture system composed of particles interacting with attractive forces that can be described by the $\mathcal{N}$-term potential. Thus, the use of Eq. (5.4b) results in $\tilde{Q}_{ij}^{-1}(0)$ expressed as

$$\begin{pmatrix}\tilde{Q}_{11}^{-1}(0) & \tilde{Q}_{12}^{-1}(0)\\ \tilde{Q}_{21}^{-1}(0) & \tilde{Q}_{22}^{-1}(0)\end{pmatrix}$$
$$=[z_n det|\tilde{Q}_{ij}(0)|]^{-1}$$
$$\times z_n\begin{pmatrix}1-\frac{6}{\pi}\frac{\phi_2}{\sigma_2^3}\hat{Q}_{22}(0) & \frac{6}{\pi}\left[\frac{\phi_1}{\sigma_1^3}\frac{\phi_2}{\sigma_2^3}\right]^{1/2}\hat{Q}_{12}(0)\\ \frac{6}{\pi}\left[\frac{\phi_2}{\sigma_2^3}\frac{\phi_1}{\sigma_1^3}\right]^{1/2}\hat{Q}_{21}(0) & 1-\frac{6}{\pi}\frac{\phi_1}{\sigma_1^3}\hat{Q}_{11}(0)\end{pmatrix}, \qquad (5.5a)$$

where

$$\det|\tilde{Q}_{ij}(0)|\equiv 1-\frac{6}{\pi}\frac{\phi_1}{\sigma_1^3}\hat{Q}_{11}(0)-\frac{6}{\pi}\frac{\phi_2}{\sigma_2^3}\hat{Q}_{22}(0)$$
$$+\left(\frac{6}{\pi}\right)^2\frac{\phi_1}{\sigma_1^3}\frac{\phi_2}{\sigma_2^3}\hat{Q}_{11}(0)\hat{Q}_{22}(0)$$
$$-\left(\frac{6}{\pi}\right)^2\frac{\phi_1}{\sigma_1^3}\frac{\phi_2}{\sigma_2^3}\hat{Q}_{12}(0)\hat{Q}_{21}(0). \qquad (5.5b)$$

If $\det|\tilde{Q}_{ij}(0)|$ reaches zero under a certain condition then $\tilde{Q}_{ij}^{-1}(0)$ diverges to infinity. Simultaneously, the mean physical cluster size S given by Eq. (5.4a) diverges to infinity. Therefore, the percolation threshold relevant to the percolation behavior of physical clusters should be estimated as a particular state satisfying the following relation:

$$\det|\tilde{Q}_{ij}(0)|=0. \qquad (5.6)$$

2. A fluid system specified by $\mathcal{L}=2$ and $\mathcal{N}=2$

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 ($\mathcal{N}=2$).

Equation (5.6) and the substitution of Eq. (5.4c) into Eq. (5.5b) lead to

$$x+\frac{6}{\pi}\sum_{l=1}^{2}\phi_l\left[Q_l^1\left(\frac{x^{22}}{x_l^1}P_l^1-\frac{x^{12}}{x_l^2}P_l^2\right)+Q_l^2\left(-\frac{x^{21}}{x_l^1}P_l^1+\frac{x^{11}}{x_l^2}P_l^2\right)\right]+\left(\frac{6}{\pi}\right)^2\phi_1\phi_2(Q_1^1Q_2^2-Q_1^2Q_2^1)\times\left(\frac{1}{x_1^1x_2^2}P_1^1P_2^2-\frac{1}{x_2^1x_1^2}P_1^2P_2^1\right)=0. \quad (5.7)$$

Here, Eqs. (4.18a)–(4.18c) must be considered to derive Eq. (5.7). Thus, the percolation threshold for the two-component mixture is given as a particular state satisfying Eq. (5.7).

In addition, it is possible that one of the attractive forces dominantly contributes to the generation of the percolation in the two-component mixture. Then, the other attractive forces also should contribute to the percolation threshold. Equation (5.7) can be used to estimate their contribution to the percolation threshold.

VI. SPECIFIC FLUIDS

A. Formulas for evaluating the percolation threshold

1. A specific fluid

To evaluate the percolation threshold for a fluid mixture composed of particles interacting with attractive forces due to the two-term potential ($\mathcal{N}=2$), all the coefficients expressed as P_j^n in Eq. (4.19) must be evaluated. Their evaluation can be simplified for a specific two-component fluid mixture. This fluid mixture is specified as

$$\sigma_1=\sigma_2=\sigma,\quad \breve{z}_1=\breve{z},\quad 0<\breve{z}\sigma<\breve{z}_2\sigma,\quad \text{‘}\breve{z}_2\sigma\gg 1, \quad (6.1a)$$

$$\frac{\breve{d}_1^1}{\sigma_1}=\frac{\breve{d}}{\sigma},\quad 0\leqslant\frac{\breve{d}_2^1}{\sigma_2}\ll 1,\quad \frac{\breve{d}_1^2}{\sigma_1}=\frac{\breve{d}_2^2}{\sigma_2}=\frac{\delta}{\sigma},\quad 0\leqslant\frac{\delta}{\sigma}, \quad (6.1b)$$

$$\breve{k}_0^1=\breve{k},\quad \text{and}\quad 0\leqslant\breve{k}_0^2\ll 1. \quad (6.1c)$$

In the fluid mixture characterized by Eq. (6.1a), the attractive force interacting between $i=1$ and $j=1$ particles decays much more slowly than the attractive forces interacting between dissimilar particles ($i=1,j=2$) particles and between $i=2$ and $j=2$ particles. Furthermore, the attractive forces interacting between $i=1$ and $j=2$ particles and between $i=2$ and $j=2$ particles are extremely weaker than the force between $i=1$ and $j=1$ particles. The fluid mixture can be regarded as that in which hard-core spheres interacting with the attractive force are mixed with hard-core spheres in the absence of attractive forces.

2. Formulas for evaluating the coefficients P_j^n

The coefficient P_1^1 can be estimated using an equation derived from Eq. (4.19) for $j=1$ and $n=1$. According to Appendix B 1 [Eq. (B11c)], the coefficient P_1^1 satisfying the relations given by Eqs. (6.1a)–(6.1c) should be evaluated using a formula given as

$$12e^{-\breve{z}\sigma}\frac{\breve{k}}{\breve{z}}\frac{\breve{d}}{\sigma}\phi_1\left[\frac{1}{2}\left(\frac{\breve{d}}{\sigma}\right)^2e^{-\breve{z}\sigma}+\frac{1}{\breve{z}\sigma}\frac{\breve{d}}{\sigma}(1-e^{-\breve{z}\sigma})P_1^1+\frac{1}{2}(e^{\breve{z}\sigma}-2+e^{-\breve{z}\sigma})(P_1^1)^2\right]^2-\left[\frac{1}{2}\left(\frac{\breve{d}}{\sigma}\right)^2e^{-\breve{z}\sigma}+\frac{1}{\breve{z}\sigma}\frac{\breve{d}}{\sigma}\times(1-e^{-\breve{z}\sigma})P_1^1+\frac{1}{2}(e^{\breve{z}\sigma}-2+e^{-\breve{z}\sigma})(P_1^1)^2\right]\times P_1^1+\frac{(P_1^1)^2}{2(\breve{z}\sigma)^2}\left[(e^{\breve{z}\sigma}-2+e^{-\breve{z}\sigma})P_1^1+\breve{z}\sigma\frac{\breve{d}}{\sigma}(2-e^{-\breve{z}\sigma})\right]=0. \quad (6.2a)$$

Equation (6.2a) is derived for $\phi_2\neq 0$. It does not, however, include ϕ_2, since terms with P_2^1 are ignored owing to $0<P_2^1\ll 1$ for $0<\breve{d}_2^1/\sigma\ll 1$. Therefore, P_1^1 is independent of ϕ_2.

The other coefficients P_j^n, according to Appendix B 1, are given as

$$P_1^2\approx 0,\quad P_2^2\approx 0. \quad (6.2b)$$

3. The percolation threshold

The percolation threshold for the fluid mixture characterized by Eqs. (6.1a)–(6.1c) is determined by applying the relation expressed by Eq. (5.7). According to Appendix B 2 [Eq. (B14b)], the magnitude of P_1^1 at the percolation threshold can be found as

$$P_1^1=\breve{z}\sigma\frac{\breve{d}}{\sigma}[(\breve{z}\sigma)^2(e^{\breve{z}\sigma}-2+e^{-\breve{z}\sigma})-2e^{\breve{z}\sigma}+2\breve{z}\sigma+2]^{-1}\times\{\breve{z}\sigma+e^{-\breve{z}\sigma}-[\{1-(\breve{z}\sigma)^2\}(e^{-\breve{z}\sigma}-2)e^{-\breve{z}\sigma}+2]^{1/2}\}. \quad (6.3)$$

Equation (6.3) is derived for $\phi_2\neq 0$. It does not, however, include ϕ_2, since terms with P_2^1 are 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. (6.2a) and (6.3) is independent of ϕ_2.

4. The pair connectedness $P_{ij}(\sigma_{ij})$

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. According to Appendix C [Eq. (C4a)], the pair connectedness $P_{11}(\sigma)$ for $i=1$ and $j=1$ particles in the fluid mixture characterized by Eqs. (6.1a)–(6.1c) can be found as

$$P_{11}(\sigma)=\frac{\breve{z}\sigma}{12}\left(\frac{\breve{d}}{\sigma}-\frac{1}{\breve{z}\sigma}P_1^1\right)\frac{P_1^1}{\phi_1}\left[\frac{1}{2}\left(\frac{\breve{d}}{\sigma}\right)^2 e^{-\breve{z}\sigma}+\frac{1}{\breve{z}\sigma}\frac{\breve{d}}{\sigma}\times(1-e^{-\breve{z}\sigma})P_1^1+\frac{1}{2}(e^{\breve{z}\sigma}-2+e^{-\breve{z}\sigma})(P_1^1)^2\right]^{-1}. \tag{6.4a}$$

Equation (6.4a) is derived for $\phi_2\neq 0$. It does not, however, include ϕ_2, since terms with P_2^1 are ignored owing to $0<P_2^1\ll 1$ for $0<\breve{d}_2^1/\sigma\ll 1$. Therefore, $P_{11}(\sigma)$ is independent of ϕ_2.

The other pair connectedness $P_{ij}(\sigma)$ for i-j particles in the fluid characterized by Eqs. (6.1a)–(6.1c) can be found as

$$P_{12}(\sigma)=P_{21}(\sigma)=P_{22}(\sigma)=0. \tag{6.4b}$$

B. Evaluation of the percolation threshold

1. Coefficients determined from Eqs. (6.2a) and (6.3)

The percolation threshold can be evaluated using Eqs. (6.2a) and (6.3).

Coefficients, ϕ_1 and P_1^1, satisfying either Eqs. (6.2a) or (6.3) are expressed as $(\phi_1)_p$ $[(\phi_1)_p>0]$ and $(P_1^1)_p$ $[(P_1^1)_p>0]$. Then, the coefficients $(\phi_1)_p$ and $(P_1^1)_p$ represent the values of ϕ_1 and P_1^1 at the percolation threshold.

Similarly, quantities and coefficients given at the percolation threshold are expressed as those having the suffix p.

An increase in the effective range $1/z=(3/2)(\breve{z}-\ln f_c)^{-1}$ $(f_c=1,\ e^{1/2})$ of the attractive force due to a decrease in $\breve{z}\sigma$ should raise the probability that the bound state $E_{ij}+u_{ij}(r)\leqslant 0$ $(i=1,\ j=1)$ is satisfied, since the increase in the effective range can allow the strong attractive force to interact over large distances between two particles. Thus, the increase in the effective range should result in an increase in the value of $(P_{ij}(\sigma))_p$ which relates to the probability that an i particle is bound near a j particle. The value of $(P_{ij}(\sigma))_p$ should be large, if the attractive force between i and j particles is strong and its effective range is long.

On the other hand, a decrease in the magnitude of $K_0^{(1)}d^2/\sigma$ varying as the strength of the attractive force should cause a decrease in the value of $P_{11}(\sigma)$. The negative contribution of a decrease in $K_0^{(1)}d^2/\sigma$ to $P_{11}(\sigma)$ can, however, be balanced with the positive contribution of a decrease in $\breve{z}\sigma$. Figure 1 demonstrates that the former and the latter are balanced at the peak of each curve given under the condition that $(\breve{k}/\breve{z})(\breve{d}/\sigma)^2$ $[=4(3\sqrt{\pi})^{-1}f_c(K_0^{(1)}d^2/\sigma)^{3/2}(\breve{z}\sigma)^{-1}$ $(f_c=1,\ e^{1/2})]$ is constant. If $\breve{z}\sigma$ is small enough, the value of $P_{11}(\sigma)$ can sensitively depend on the magnitude of $K_0^{(1)}d^2/\sigma$.

If the probability that a 1-particle is bound near another 1-particle is high in the mixture system, then, the pair connectedness $(P_{11}(\sigma))_p$ for the mixture system should be large. Therefore, it is possible that the macroscopic homogeneity of the mixture system will become unstable, if $(P_{11}(\sigma))_p$ is extremely large. If the mixture system is characterized by a strong attractive force having a long effective range, it should be readily macroscopically separated into the 1-particle rich phase and the 2-particle rich phase. If i and j particles interact with the most strongly attractive force having the largest value of the effective ranges in a fluid mixture, the value of $(P_{ij}(r))_p$ can be large. These particles can contribute to making the phase behavior of the fluid mixture complicated.

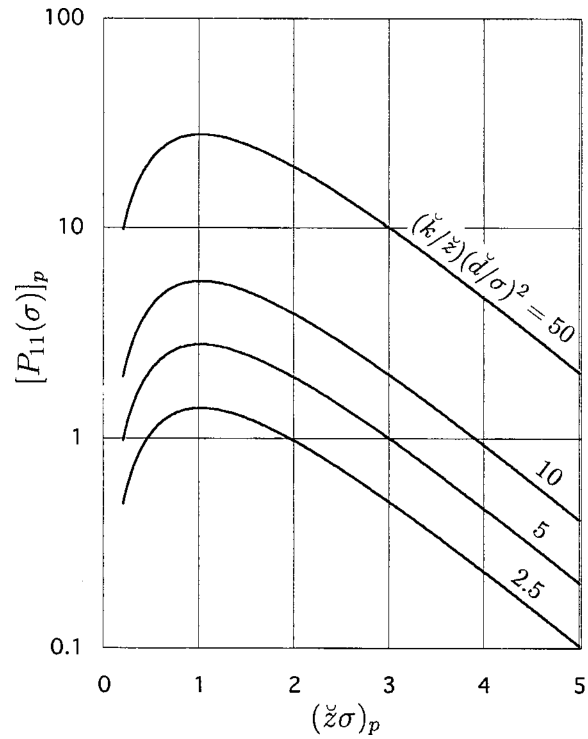

FIG. 1. The pair connectedness $(P_{11}(\sigma))_p$ for the two-component mixture fluids characterized by Eqs. (6.1a)–(6.1c) and $\breve{k}/\breve{z}=10$. To evaluate $(P_{11}(\sigma))_p$, Eq. (6.4a) is used with Eqs. (6.2a) and (6.3). The values of $(P_{11}(\sigma))_p$ should be considered as those evaluated for ϕ_2 having an arbitrary value different from zero. Here, ϕ_2 is the volume fraction of $i,j=2$ particles. Each curve represents a percolation threshold. In addition, $\breve{z}\sigma$, $P_{11}(\sigma)$, and $(\breve{k}/\breve{z})(\breve{d}/\sigma)^2$ are dimensionless. The factor $\breve{z}\sigma$ varies as the inverse of the effective range of the attractive force between $i,j=1$ particles. The factor $(\breve{k}/\breve{z})(\breve{d}/\sigma)^2$ varies as the strength of the attractive force between $i,j=1$ particles.

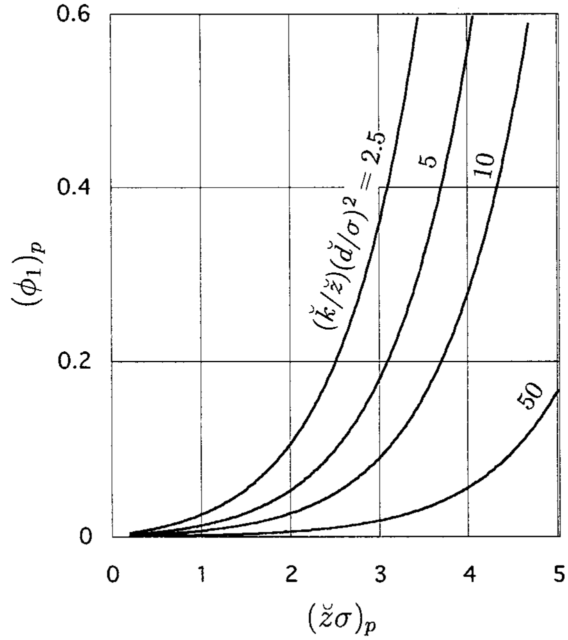

FIG. 2. Volume fraction $(\phi_1)_p$ in the two-component mixture fluids characterized by Eqs. (6.1a)–(6.1c) and $\breve{k}/\breve{z}=10$. The values of $(\phi_1)_p$ should be considered as those evaluated for ϕ_2 having an arbitrary value different from zero. Percolation takes place under the condition characterized by a point belonging to the upper region of each curve. In addition, ϕ_1 is the dimensionless volume fraction of $i,j=1$ particles.

For the weakly attractive force, percolation can be generated if $(\phi_1)_p$ takes on a large value. According to Fig. 2, the value of $(\phi_1)_p$ is larger for $[(\breve{k}/\breve{z})(\breve{d}/\sigma)^2]_p=2.5$ than that for another. Then, $(P_{11}(\sigma))_p$ is small, as known from Fig. 1. In addition, the factor $[(\breve{k}/\breve{z})(\breve{d}/\sigma)^2]_p$ is a parameter depending on the strength of the attractive force and is dimensionless.

The strongly attractive force as given by $[(\breve{k}/\breve{z})(\breve{d}/\sigma)^2]_p=50$ should allow $(\phi_1)_p$ to remain sufficiently small, i.e., should induce percolation even for the low volume fraction. As known from Fig. 2, the value of $(\phi_1)_p$ remains small for $[(\breve{k}/\breve{z})(\breve{d}/\sigma)^2]_p=50$. Figure 1, however, shows that $(P_{11}(\sigma))_p$ for the strongly attractive force is large. Thus, the strength of the attractive force plays an important role for generating a nonuniform distribution.

2. The relation between $(\phi_1)_p$ and $[1/(K_0^{(1)}d^2/\sigma)]_p$

The factor $K_0^{(1)}d^2/\sigma$ can be regarded as a dimensionless parameter representing the strength of the attractive force. Percolation thresholds can be evaluated for a particular value of $z\sigma$ as the relation between $(\phi_1)_p$ and $[1/(K_0^{(1)}d^2/\sigma)]_p$. For this purpose, the factor $K_0^{(1)}d^2/\sigma$ must be related to the factor $(\breve{k}/\breve{z})(\breve{d}/\sigma)^2$.

The curved lines shown in Fig. 3 are the percolation thresholds.

By considering Eqs. (6.1a), (6.1b), and (6.1c), it follows

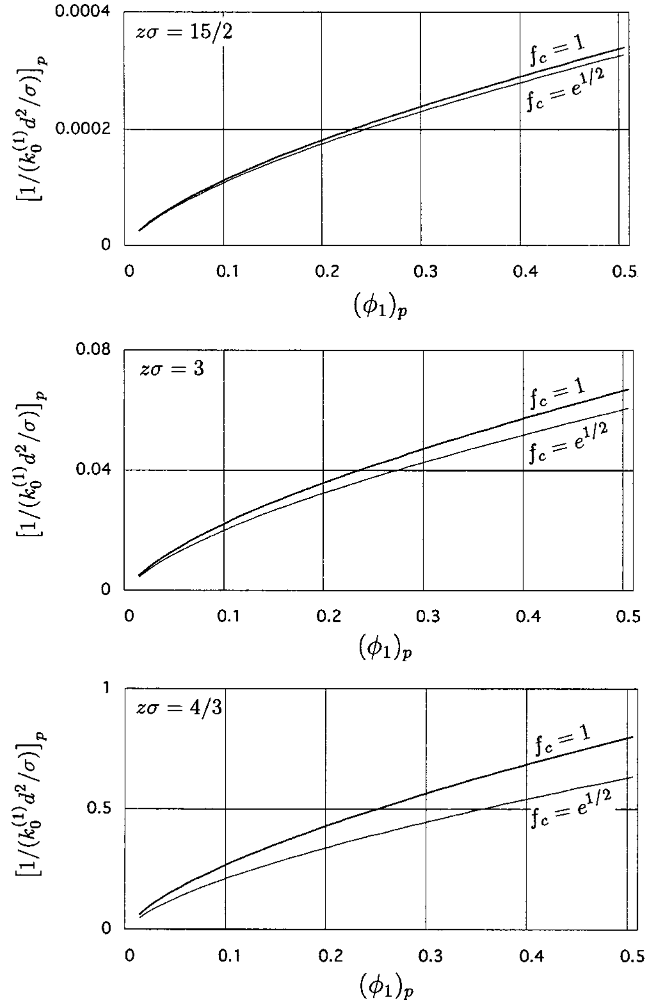

FIG. 3. Percolation thresholds for the two-component mixture fluids characterized by Eqs. (6.1a)–(6.1c) and $\breve{k}/\breve{z}=10$. The values of $[1/(k_0^{(1)}d^2/\sigma)]_p$ should be considered as those evaluated for ϕ_2 having an arbitrary value different from zero. Percolation takes place under the condition characterized by a point belonging to the lower region of each curve. In addition, $1/(k_0^{(1)}d^2/\sigma)$ is dimensionless. Here, $1/k_0^{(1)}$ takes a value proportional to the temperature because of Eqs. (3.9a) and (3.9b). The factor $k_0^{(1)}d^2/\sigma$ varies as the strength of the attractive force between $i,j=1$ particles.

that the relation between $K_0^{(1)}d^2/\sigma$ and $(\breve{k}/\breve{z})(\breve{d}/\sigma)^2$ is derived from Eqs. (3.12e) and (3.12f) as

$$d_1^{(1)}=d\neq 0, \quad k_0^{(1)}\neq 0, \quad d_i^{(n')}=0, \quad k_0^{(n')}=0$$
$$(i=1,2,\ldots, \quad n'=2,3,\ldots). \quad (6.5a)$$

The coefficient $k_0^{(1)}$ determined by Eqs. (3.12e) and (6.1c) for $\breve{\sigma}=\sigma$ is given as

$$\left(\frac{k_0^{(1)}d^2}{\sigma}\right)^{-1}=\left(\frac{3\sqrt{\pi}}{4}\frac{1}{f_c}\breve{z}\sigma\right)^{-2/3}\left[\frac{\breve{k}}{\breve{z}}\left(\frac{\breve{d}}{\sigma}\right)^2\right]^{-2/3}. \quad (6.5b)$$

Thus, the factor $[1/(K_0^{(1)}d^2/\sigma)]_p$ is evaluated, if the factors $(\breve{z}\sigma)_p$ and $[(\breve{k}/\breve{z})(\breve{d}/\sigma)^2]_p$ are determined with $(\phi_1)_p$ using Eqs. (6.2a) and (6.3).

In addition, the effective range $1/z$ of the attractive force is related to $\breve{z}\sigma$, since a relation between $z\sigma$ and $\breve{z}\sigma$ is given for $f_c=1$ by Eq. (3.12a) and the other relation for $f_c=e^{1/2}$ by Eq. (3.12b).

As illustrated in Fig. 3, percolation thresholds depend on the decay closure expressed by Eq. (3.11a). The decay of closure depends on r as

$$\frac{1}{\sqrt{\sigma}}\frac{1}{r}\exp\left(-\frac{3}{2}zr\right)\quad\text{for}\quad f_c=1$$

and

$$\frac{e^{1/2}}{\sqrt{\sigma}}\frac{1}{r}\exp\left(-\frac{1}{2\sigma}r\right)\exp\left(-\frac{3}{2}zr\right)\quad\text{for}\quad f_c=e^{1/2}.$$

The approximation given for $f_c=1$ somewhat overestimates the long-ranged contribution of $C_{ij}^{+}(r)$, since the contribution of $(1/r)^{3/2}$ is approximated as $(1/\sqrt{\sigma})(1/r)$. The alternative approximation given for $f_c=e^{1/2}$ somewhat overestimates the decay of the r-dependent $C_{ij}^{+}(r)$, since the contribution of $(1/r)^{3/2}$ is approximated as $(e^{1/2}/\sqrt{\sigma})(1/r)\exp[-r/(2\sigma)]$.

Overestimation of the long-range contribution of $C_{ij}^{+}(r)$ $(f_c=1)$ can lead to an overestimation of $[1/(k_0^{(1)}d^2/\sigma)]_p$ as follows from the thick solid lines in Fig. 3. Fortunately, the diagrams representing the percolation thresholds for the overestimation of the long-range contribution have the same pattern as those for the overestimation of the decay of $C_{ij}^{+}(r)$ $(f_c=e^{1/2})$. This behavior is similar to that found for the single-component fluid [10].

3. The addition of i,j=2 particles into the fluid mixture

Percolation can be generated through $i,j=1$ particles interacting with the attractive force characterized by Eqs. (6.1a)-(6.1c). A nonuniform distribution of $i,j=1$ particles should be formed through the attractive force in the fluid mixture. Then, $i,j=2$ particles in the absence of an attractive force should distribute in rare regions of $i,j=1$ particles. It should be considered that $i,j=2$ particles can hardly distribute in dense regions of $i,j=1$ particles, since there is no attractive force between a $i,j=1$ particle and a $i,j=2$ particle. Hence, if $i,j=2$ particles are added into the fluid mixture, they should occupy the rare regions of $i,j=1$ particles more easily than the dense regions of $i,j=1$ particles. This means that the percolation can hardly be affected by the addition of the $i,j=2$ particles. This interpretation can be demonstrated only if Eqs. (6.2a), (6.3), and (6.4a) are independent of ϕ_2. It suggests that the viscosity of the fluid will not be simply reduced by adding $i,j=1$ particles.

Furthermore, it is predicted that clusters of $i,j=1$ particles in a fluid containing $i,j=2$ particles will be less flexible than those in a fluid without $i,j=2$ particles, since $i,j=2$ particles occupy rare regions of $i,j=1$ particles. Such an effect should contribute to hydrodynamical transport phenomena found for a fluid mixture including particles such as $i,j=2$ particles. Thus, it is expected that a phenomenon similar to this can contribute to the viscosity anomaly for binary mixtures near the consolute point.

The attractive force between $i,j=2$ particles cannot be ignored, so that $i,j=2$ particles in the dense regions of $i,j=2$ particles can hardly satisfy the condition $E_{ij}+u_{ij}(r)\leqslant 0$. The addition of $i,j=2$ particles causes dense regions of $i,j=2$ particles to develop only passively. Thus, the addition can lead to a phase separation into the phase rich in $i,j=1$ particles and the phase rich in $i,j=2$ particles.

In a multicomponent fluid mixture, the attractive force between a particle of constituent $\mathcal{L}_s$ and a particle of the other constituents $\mathcal{L}_s^c$ is much weaker than the attractive force between $\mathcal{L}_s$ particles. Moreover, the attractive force between $\mathcal{L}_s^c$ particles is relatively weak. According to the above discussion, dense regions of $\mathcal{L}_s^c$ particles should form passively, if dense regions of $\mathcal{L}_s$ particles are developed in the multicomponent fluid mixture. Then, it is expected that the percolation due to constituent $\mathcal{L}_s$ can hardly be affected by the volume fractions of $\mathcal{L}_s^c$ particles.

The growth of a dense region of constituent $\mathcal{L}_s$ can result from the contact of small dense regions. This growth process can be similar to that known as cluster-cluster aggregation. The distribution of particles resulting from cluster-cluster aggregation leads to a fractal structure, while the dimension d_f of the fractal structure was determined as $d_f\sim 1.75$ [13]. If the effective range of the attractive force is sufficiently large, the dense regions can develop a structure having a fractal dimension 1.5, according to Eq. (3.7) and the previous study [10]. It follows that this structure also is little affected by the addition of $\mathcal{L}_s^c$ particles, since the added $\mathcal{L}_s^c$ particles are essentially excluded from the dense regions of $\mathcal{L}_s$ particles. Notwithstanding the quite different model from that in the present work, it has been demonstrated that the fractal dimensions found from the clusters aggregated in the binary mixtures can be insensitive to molar fraction within the range of high molar fraction [14].

VII. CONCLUSIONS

The dominant particles distributed in a dense region of a particular constituent $(\mathcal{L}_s)$ in a multicomponent fluid mixture can be defined as particles constituting pairs that should satisfy the condition $E_{ij}+u_{ij}(r)\leqslant 0$. It is assumed that the dense region corresponds to an ensemble of particles bound to each other by an attractive force. In the present work, the dense region is a cluster that can contribute to the percolation.

When both the attractive force between a particle of a constituent $\mathcal{L}_s$ and a particle of the other constituents $\mathcal{L}_s^c$, and the attractive force between $\mathcal{L}_s^c$ particles are much weaker than the attractive force between $\mathcal{L}_s$ particles in a multicomponent mixture, $\mathcal{L}_s^c$ particles should for the most part be excluded from the dense regions of $\mathcal{L}_s$ particles. As a result, $\mathcal{L}_s^c$ particles are favored to be found in rare regions of $\mathcal{L}_s$ particles. Dense regions composed of $\mathcal{L}_s^c$ particles should be formed passively in the fluid mixture. Thus, the percolation generated by $\mathcal{L}_s$ particles should hardly be affected by the volume fractions of $\mathcal{L}_s^c$ particles.

If $\mathcal{L}_s^c$ particles are added into the fluid mixture, these particles should migrate into the rare regions of $\mathcal{L}_s$ particles more easily than the dense regions of $\mathcal{L}_s$ particles. Then, the rare regions of $\mathcal{L}_s$ particles can fill up with the added $\mathcal{L}_s^c$ particles. Thus, it is possible that the clusters of $\mathcal{L}_s$ particles in the fluid including $\mathcal{L}_s^c$ particles are less flexible than those in the fluid without $\mathcal{L}_s^c$ particles. Such a phenomenon can contribute to the viscosity anomaly near the consolute point for a multicomponent mixture.

If the probability is high that an i particle is located near a j particle, then the value of $P_{ij}(\sigma_{ij})$ is large. If i-j particles interact with the most strongly attractive force having the largest value of the effective ranges in a fluid mixture system, the magnitude of $P_{ij}(\sigma_{ij})$ can be maximized. Accordingly, these particles can contribute to making phase behavior of the fluid mixture complicated.

The solution of the integral equation for the pair connectedness function requires a closure scheme. The expression for closure specified by $f_c=1$ results in the overestimation of the long-range contribution of $C_{ij}^{+}(r)$. The expression for closure specified by $f_c=e^{1/2}$ somewhat overestimates the decay of $C_{ij}^{+}(r)$, which depends on r. The overestimation of the long-range contribution of $C_{ij}^{+}(r)$ can lead to an overestimation of $(1/(k_0^{(1)}d^2/\sigma))_p$ at the percolation threshold. Fortunately, the diagrams representing the percolation thresholds for the overestimation of the long-range contribution have the same pattern as those for the overestimation of the decay of $C_{ij}^{+}(r)$.

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APPENDIX A: MEAN PHYSICAL CLUSTERS SIZE S

The Fourier transform of Eq. (2.4) is given as

$$\sum_{k=1}^{\mathcal{L}} [\delta_{ik}+(\rho_i\rho_k)^{1/2}\tilde{P}_{ik}(k)][\delta_{kj}-(\rho_k\rho_j)^{1/2}\tilde{C}_{kj}(k)] = \delta_{ij} \quad \text{for} \quad |\mathbf{k}|=k, \tag{A1}$$

where

$$\tilde{P}_{ij}(k)\equiv\int P_{ij}(r)e^{i\mathbf{k}\cdot\mathbf{r}}d\mathbf{r}, \quad \tilde{C}_{ij}(k)\equiv\int C_{ij}(r)e^{i\mathbf{k}\cdot\mathbf{r}}d\mathbf{r},$$

The relation between $\tilde{C}_{ij}(k)$ and $\tilde{Q}_{ik}(k)$ is given as

$$\delta_{ij}-(\rho_i\rho_j)^{1/2}\tilde{C}_{ij}(k)=\sum_{k=1}^{\mathcal{L}} \tilde{Q}_{ik}(k)\tilde{Q}_{jk}(-k),$$

so that Eq. (A1) results in

$$\delta_{ij}+(\rho_i\rho_j)^{1/2}\tilde{P}_{ij}(k)=\sum_{k=1}^{\mathcal{L}} \tilde{Q}_{ki}^{-1}(-k)\tilde{Q}_{kj}^{-1}(k). \tag{A2}$$

From Eq. (A2), a relation is obtained as

$$\sum_{k=1}^{\mathcal{L}} \tilde{Q}_{ki}^{-1}(0)\tilde{Q}_{kj}^{-1}(0)=\delta_{ij}+(\rho_i\rho_j)^{1/2}\int P_{ij}(r)d\mathbf{r}. \tag{A3}$$

Therefore, the substitution of Eq. (A3) into Eq. (5.3) results in

$$S=\sum_{i=1}^{\mathcal{L}}\left[\sum_{j=1}^{\mathcal{L}}\left\{\sum_{k=1}^{\mathcal{L}}\frac{\phi_k}{\phi_i}\left(\frac{\sigma_i}{\sigma_k}\right)^3\right\}^{-1/2}\tilde{Q}_{ij}^{-1}(0)\right]^2. \tag{A4}$$

APPENDIX B: FORMULAS FOR SPECIFIC FLUIDS

1. Formulas for evaluating coefficients P_j^n

For the relations expressed by Eq. (6.1a), each coefficient given by Eq. (4.16b) is represented as

$$x_1^1=x_2^1=\frac{6}{\pi}\check{z}\sigma e^{-\check{z}\sigma/2}, \tag{B1a}$$

$$x_1^2=x_2^2=\frac{6}{\pi}\check{z}_2\sigma e^{-\check{z}_2\sigma/2}. \tag{B1b}$$

Each coefficient given by Eq. (4.16c) is represented for the relations expressed by Eqs. (6.1a) and (6.1b) as

$$x^{11}\approx\frac{1}{\check{z}\sigma}\left[\frac{1}{2}\left(\frac{\check{d}}{\sigma}\right)^2 e^{-\check{z}\sigma}\phi_1+\frac{1}{\check{z}\sigma}\frac{\check{d}}{\sigma}(1-e^{-\check{z}\sigma})P_1^1\phi_1 + \frac{1}{2}(e^{\check{z}\sigma}-2+e^{-\check{z}\sigma})(P_1^1P_1^1\phi_1+P_2^1P_2^1\phi_2)\right], \tag{B2a}$$

$$x^{12}\approx P_1^2 e^{\breve{z}_2\sigma/2}\frac{e^{\breve{z}\sigma/2}}{\breve{z}\sigma(1+\breve{z}/\breve{z}_2)}\Bigg\{\Bigg[\frac{1}{\breve{z}_2\sigma}\Bigg(\breve{z}\sigma e^{-\breve{z}\sigma}\frac{\breve{d}}{\sigma}\phi_1+P_1^1\phi_1+P_2^1\phi_2\Bigg)+\frac{1-e^{-\breve{z}\sigma}}{\breve{z}\sigma}(P_1^1\phi_1+P_2^1\phi_2)\Bigg]\times\frac{\delta}{\sigma}R+\Bigg(P_1^1\phi_1+P_2^1\frac{P_2^2}{P_1^2}\phi_2\Bigg)\frac{1}{(\breve{z}_2\sigma)^2}\Bigg\}, \tag{B2b}$$

$$x^{21}\approx P_1^2\frac{e^{\breve{z}_2\sigma/2}}{\breve{z}_2\sigma}\frac{e^{-\breve{z}\sigma/2}}{1+\breve{z}/\breve{z}_2}\Bigg\{\Bigg[\frac{\breve{d}}{\sigma}\phi_1-\frac{1}{\breve{z}\sigma}(P_1^1\phi_1+P_2^1\phi_2)\Bigg]\times\frac{\delta}{\sigma}R+\frac{1}{\breve{z}_2\sigma}\frac{\breve{d}}{\sigma}\phi_1+\frac{\breve{z}\sigma}{(\breve{z}_2\sigma)^2}\frac{\breve{d}}{\sigma}\phi_1+\frac{1}{\breve{z}_2\sigma}\frac{e^{\breve{z}\sigma}-1}{\breve{z}\sigma}\times\Bigg(P_1^1\phi_1+P_2^1\frac{P_2^2}{P_1^2}\phi_2\Bigg)-\frac{1}{(\breve{z}_2\sigma)^2}\Bigg(P_1^1\phi_1+P_2^1\frac{P_2^2}{P_1^2}\phi_2\Bigg)\Bigg\}, \tag{B2c}$$

$$x^{22}\approx\frac{1}{2}P_1^2P_1^2\frac{e^{\breve{z}_2\sigma}}{\breve{z}_2\sigma}\Bigg\{\frac{\delta}{\sigma}R\Bigg[\frac{\delta}{\sigma}R(\phi_1+\phi_2)+\frac{2}{\breve{z}_2\sigma}\Bigg(\phi_1+\frac{P_2^2}{P_1^2}\phi_2\Bigg)\Bigg]+\Bigg[\phi_1+\Bigg(\frac{P_2^2}{P_1^2}\Bigg)^2\phi_2\Bigg]\Bigg\}. \tag{B2d}$$

In Eqs. (B2b)–(B2d), R is defined as

$$R\equiv\frac{e^{-\breve{z}_2\sigma}}{P_1^2}. \tag{B2e}$$

The coefficient x given by Eq. (4.18c) is represented for the relations expressed by Eqs. (6.1a) and (6.1b) as

$$\begin{aligned}2\breve{z}_2\sigma e^{-\breve{z}_2\sigma}\frac{x}{P_1^2P_1^2}\breve{z}\sigma\approx&\left(\frac{\delta}{\sigma}\right)^2R^2(\phi_1+\phi_2)\breve{z}\sigma x^{11}+\left[\phi_1+\left(\frac{P_2^2}{P_1^2}\right)^2\phi_2\right]\breve{z}\sigma x^{11}-2\left(\frac{\delta}{\sigma}\right)^2R^2\frac{1-e^{-\breve{z}\sigma}}{\breve{z}\sigma}(P_1^1\phi_1+P_2^1\phi_2)\\&\times\left[\frac{\breve{d}}{\sigma}\phi_1-\frac{1}{\breve{z}\sigma}(P_1^1\phi_1+P_2^1\phi_2)\right]+\frac{2}{\breve{z}_2\sigma}\frac{\delta}{\sigma}R\left(\phi_1+\frac{P_2^2}{P_1^2}\phi_2\right)\breve{z}\sigma x^{11}+\frac{4}{\breve{z}_2\sigma}\left(\frac{\delta}{\sigma}\right)^2\\&\times R^2(1-e^{-\breve{z}\sigma})(P_1^1\phi_1+P_2^1\phi_2)\left[\frac{\breve{d}}{\sigma}\phi_1-\frac{1}{\breve{z}\sigma}(P_1^1\phi_1+P_2^1\phi_2)\right]-\frac{2}{\breve{z}_2\sigma}\frac{\delta}{\sigma}R\frac{1-e^{-\breve{z}\sigma}}{\breve{z}\sigma}(P_1^1\phi_1+P_2^1\phi_2)\\&\times\left[\frac{\breve{d}}{\sigma}\phi_1+\frac{e^{\breve{z}\sigma}-1}{\breve{z}\sigma}\left(P_1^1\phi_1+P_2^1\frac{P_2^2}{P_1^2}\phi_2\right)\right]-\frac{2}{\breve{z}_2\sigma}\left(\frac{\delta}{\sigma}\right)^2R^2\left[\frac{\breve{d}}{\sigma}\phi_1-\frac{1}{\breve{z}\sigma}(P_1^1\phi_1+P_2^1\phi_2)\right]\\&\times\left(\breve{z}\sigma e^{-\breve{z}\sigma}\frac{\breve{d}}{\sigma}\phi_1+P_1^1\phi_1+P_2^1\phi_2\right).\end{aligned} \tag{B3}$$

When the relation $\breve{z}_2\sigma\gg 1$ is satisfied, Eq. (4.15b) requires the relations given as

$$0<P_1^2\ll 1,\quad 0<P_2^2\ll 1.$$

This means that R given by Eq. (B2e) may satisfy $R\neq 0$ even at $\breve{z}_2\sigma=\infty$. By considering this fact, the formulas given above are derived.

The coefficients (P_1^1, P_2^1, P_1^2, and P_2^2) should be determined using Eq. (4.19). The coefficient R in the formulas given above can be estimated using an equation derived from Eq. (4.19) for $j=1$ and $n=2$. If the relations given by Eqs. (6.1a)–(6.1c) are considered with substituting Eqs. (B1a), (B1b), and (B2b)–(B2d) into Eq. (4.19) divided by $(P_1^2)^3$, Eq. (4.19) for $j=1$ and $n=2$ leads to

$$\begin{aligned}0\approx&-2\breve{z}_2\sigma e^{-\breve{z}_2\sigma}\frac{x}{P_1^2P_1^2}\times\left(-2e^{-\breve{z}\sigma/2}\breve{z}_2\sigma e^{-\breve{z}_2\sigma/2}\frac{x^{21}}{P_1^2}P_1^1+2\breve{z}\sigma e^{-\breve{z}\sigma}x^{11}\right)\\=&-2\breve{z}_2\sigma e^{-\breve{z}_2\sigma}\frac{x}{P_1^2P_1^2}\left\{-2e^{-\breve{z}\sigma}P_1^1\frac{\delta}{\sigma}R\times\left[\frac{\breve{d}}{\sigma}\phi_1-\frac{1}{\breve{z}\sigma}(P_1^1\phi_1+P_2^1\phi_2)\right]+2e^{-\breve{z}\sigma}\breve{z}\sigma x^{11}\right\}.\end{aligned} \tag{B4}$$

The factor x should not be zero to obtain a significant solution from Eq. (4.19). Thus, Eq. (B4) gives R as

$$\frac{\delta}{\sigma}R=\breve{z}\sigma x^{11}\frac{1}{P_1^1}\left[\frac{\breve{d}}{\sigma}\phi_1-\frac{1}{\breve{z}\sigma}(P_1^1\phi_1+P_2^1\phi_2)\right]^{-1} \quad \text{for } \breve{z}_2\sigma\gg 1. \tag{B5}$$

The ratio P_2^2/P_1^2 in the formulas given above can be estimated using an equation derived from Eq. (4.19) for $j=2$ and $n=2$. If the relations given by Eqs. (6.1a)–(6.1c) are considered with substituting Eqs. (B1a), (B1b), and (B2b)–(B2d) into Eq. (4.19) divided by $(P_1^2)^3$, Eq. (4.19) for $j=2$ and $n=2$ leads to

$$0\approx-2\breve{z}_2\sigma e^{-\breve{z}_2\sigma}\frac{x}{P_1^2P_1^2}\left(-2e^{-\breve{z}\sigma/2}\breve{z}_2\sigma e^{-\breve{z}_2\sigma/2}\frac{x^{21}}{P_1^2}P_2^1+2\breve{z}\sigma e^{-\breve{z}\sigma}x^{11}\frac{P_2^2}{P_1^2}\right). \tag{B6}$$

The comparison between Eqs. (B4) and (B6) results in

$$\frac{P_2^2}{P_2^1}=\frac{P_1^2}{P_1^1} \quad \text{for } \breve{z}_2\sigma\gg 1. \tag{B7}$$

If the relations given by Eqs. (6.1a)–(6.1c) and (B7) are considered with substituting Eqs. (B1a) and (B1b) into Eq. (4.19) divided by $(P_1^2)^4\pi/6$, Eq. (4.19) for $j=2$ and $n=1$ leads to

$$\begin{aligned}&-2\breve{z}_2\sigma e^{-\breve{z}_2\sigma}\frac{x}{P_1^2P_1^2}\left(2\frac{e^{-\breve{z}\sigma/2}}{\breve{z}\sigma}\breve{z}_2\sigma e^{-\breve{z}_2\sigma}\frac{x^{22}}{P_1^2P_1^2}-2e^{-\breve{z}_2\sigma/2}\frac{x^{12}}{P_1^2}\frac{1}{P_1^1}\right)P_2^1+P_2^1Z_{21}^{11}\frac{e^{-\breve{z}\sigma/2}}{2\breve{z}\sigma}\left\{(P_1^1P_1^1\phi_1\right.\\&+P_2^1P_2^1\phi_2)\frac{e^{\breve{z}\sigma}}{(\breve{z}\sigma)^2}\left(2\breve{z}_2\sigma e^{-\breve{z}_2\sigma}\frac{x^{22}}{P_1^2P_1^2}\right)^2-8\left(P_1^1\phi_1+P_2^1\frac{P_2^1}{P_1^1}\phi_2\right)\frac{e^{\breve{z}\sigma/2}}{\breve{z}\sigma}\breve{z}_2\sigma e^{-3\breve{z}_2\sigma/2}\frac{x^{12}}{P_1^2}\frac{x^{22}}{P_1^2P_1^2}\\&\left.+4\left[\phi_1+\left(\frac{P_2^1}{P_1^1}\right)^2\phi_2\right]e^{-\breve{z}_2\sigma}\left(\frac{x^{12}}{P_1^2}\right)^2\right\}\\&+4\frac{e^{\breve{z}\sigma}}{\breve{z}\sigma}\left[\frac{\delta}{\sigma}R\frac{Y_{21}^{21}}{(\breve{z}_2+\breve{z})\sigma}+\frac{P_2^1}{P_1^1}e^{-\breve{z}_2\sigma}\frac{Z_{21}^{21}}{(\breve{z}_2+\breve{z})\sigma}\right]\mathcal{Y}=0,\end{aligned} \tag{B8a}$$

where

$$\begin{aligned}\mathcal{Y}\equiv&-\frac{1}{\breve{z}\sigma}(P_1^1P_1^1\phi_1+P_2^1P_2^1\phi_2)(\breve{z}_2\sigma)^2e^{-3\breve{z}_2\sigma/2}\frac{x^{21}}{P_1^2}\frac{x^{22}}{P_1^2P_1^2}\\&+\left(P_1^1\phi_1+P_2^1\frac{P_2^1}{P_1^1}\phi_2\right)e^{-\breve{z}\sigma/2}\breve{z}_2\sigma e^{-\breve{z}_2\sigma}\frac{x^{12}}{P_1^2}\frac{x^{21}}{P_1^2}\\&+\left(P_1^1\phi_1+P_2^1\frac{P_2^1}{P_1^1}\phi_2\right)e^{-\breve{z}\sigma/2}\breve{z}_2\sigma e^{-\breve{z}_2\sigma}x^{11}\frac{x^{22}}{P_1^2P_1^2}\\&-\left[\phi_1+\left(\frac{P_2^1}{P_1^1}\right)^2\phi_2\right]\breve{z}\sigma e^{-\breve{z}\sigma}e^{-\breve{z}_2\sigma/2}x^{11}\frac{x^{12}}{P_1^2}.\end{aligned} \tag{B8b}$$

The coefficient $\mathcal{Y}$ can be found as $\mathcal{Y}\approx 0$ for $\breve{z}_2\gg 1$. This relation can contribute to simplifying Eq. (4.19) for $j=1$ and $n=1$. In Eq. (B8a), the ratios $Y_{21}^{21}/(\breve{z}_2\sigma+\breve{z}\sigma)$ and $e^{-\breve{z}_2\sigma}Z_{21}^{21}/(\breve{z}_2\sigma+\breve{z}\sigma)$ are finite values for $\breve{z}_2\sigma\gg 1$ because of Eqs. (4.16d) and (4.16e).

On the other hand, Eqs. (4.4e) and (4.15b) for $0\leqslant\breve{d}_2^1/\sigma\ll 1$ show that the coefficient P_2^1 should be given as

$$0<P_2^1\ll 1 \quad \text{for} \quad 0<\breve{d}_2^1/\sigma\ll 1, \tag{B9}$$

since the pair connectedness should satisfy $P_{12}(r)\approx 0$ for $p_{12}(r)\approx 0$ derived from Eq. (2.1). As a result, Eq. (B2a) should be rewritten as

$$\breve{z}\sigma x^{11}\approx\mathcal{P}_p\phi_1\equiv\frac{1}{2}\left(\frac{\breve{d}}{\sigma}\right)^2e^{-\breve{z}\sigma}\phi_1+\frac{1}{\breve{z}\sigma}\frac{\breve{d}}{\sigma}(1-e^{-\breve{z}\sigma})P_1^1\phi_1+\frac{1}{2}(e^{\breve{z}\sigma}-2+e^{-\breve{z}\sigma})(P_1^1)^2\phi_1. \tag{B10}$$

In addition, the coefficient P_1^2 defined by Eq. (4.15b) includes $\hat{P}_{12}(\breve{z})$ and $\hat{P}_{22}(\breve{z})$. The coefficients $\hat{P}_{ij}(\breve{z})$ are given as the integration of $P_{ij}(r)$ expressed by Eq. (4.4e). Hence, the coeficients $\hat{P}_{12}(\breve{z})$ and $\hat{P}_{22}(\breve{z})$ should be zero, if attractive forces do not exist between $i=1$ and $j=2$ particles and between $i=2$ and $j=2$ particles. Thus, the features of $P_{12}(r)$ and $P_{22}(r)$ in the absence of attractive forces can be demonstrated by Eq. (B9).

The coefficient P_1^1 can be estimated using an equation derived from Eq. (4.19) for $j=1$ and $n=1$. If the relations given by Eqs. (6.1a)–(6.1c) are considered with Eqs. (B5), (B7), and (B9) after substituting Eqs. (B1a), (B1b), (B2b)–(B2d), and (B3) into Eq. (4.19) divided by $(P_1^2)^4$, Eq. (4.19) for $j=1$ and $n=1$ leads to a factorized equation composed of two factors as

$$[\mathcal{P}\phi_1+(\mathcal{P}_p)^2\phi_2]^2\left\{12e^{-\breve{z}\sigma}\frac{\breve{k}}{\breve{z}}\frac{\breve{d}}{\sigma}(\mathcal{P}_p)^2\phi_1-\mathcal{P}_pP_1^1+\frac{(P_1^1)^2}{2(\breve{z}\sigma)^2}\left[(e^{\breve{z}\sigma}-2+e^{-\breve{z}\sigma})P_1^1+\breve{z}\sigma\frac{\breve{d}}{\sigma}(2-e^{-\breve{z}\sigma})\right]\right\}=0, \tag{B11a}$$

where

$$\mathcal{P}\equiv(\mathcal{P}_p)^2+(P_1^1)^2\left(\frac{\breve{d}}{\sigma}-\frac{1}{\breve{z}\sigma}P_1^1\right)^2 -\frac{2}{\breve{z}\sigma}(1-e^{-\breve{z}\sigma})P_1^1\mathcal{P}_p\left(\frac{\breve{d}}{\sigma}-\frac{1}{\breve{z}\sigma}P_1^1\right). \quad \text{(B11b)}$$

An equation that includes at least $\breve{k}/\breve{z}$ should be meaningful, so that Eq. (B11a) leads to

$$12e^{-\breve{z}\sigma}\frac{\breve{k}}{\breve{z}}\frac{\breve{d}}{\sigma}(\mathcal{P}_p)^2\phi_1-\mathcal{P}_pP_1^1+\frac{(P_1^1)^2}{2(\breve{z}\sigma)^2} \times\left[(e^{\breve{z}\sigma}-2+e^{-\breve{z}\sigma})P_1^1+\breve{z}\sigma\frac{\breve{d}}{\sigma}(2-e^{-\breve{z}\sigma})\right]=0, \quad \text{(B11c)}$$

In Eq. (B11c), terms with P_2^1 are ignored owing to $0<P_2^1 \ll 1$ for $0<\breve{d}_2^1/\sigma\ll 1$. As a result, Eq. (B11c) does not include ϕ_2.

2. A formula for evaluating the percolation threshold

The percolation threshold for the fluid mixture characterized by Eqs. (6.1a)–(6.1c) is determined using Eq. (5.7). If the relations given by Eqs. (6.1a)–(6.1c) are considered with the coefficient R given by Eq. (B2e) and the ratios given by Eq. (B7) after substituting Eqs. (B1a) and (B1b) into Eq. (5.7) multiplied by $\breve{z}_2\sigma e^{-\breve{z}_2\sigma}(P_1^2)^{-2}$, a specific form of Eq. (5.7) can be found for the fluid mixture as

$$\breve{z}_2\sigma e^{-\breve{z}_2\sigma}\frac{x}{P_1^2P_1^2}+\frac{1}{2}\frac{e^{\breve{z}\sigma/2}}{\breve{z}\sigma}\breve{z}_2\sigma e^{-\breve{z}_2\sigma}\frac{x^{22}}{P_1^2P_1^2}(Q_1^1P_1^1\phi_1 +Q_2^1P_2^1\phi_2)-e^{-\breve{z}_2\sigma/2}\frac{x^{12}}{P_1^2}\left(Q_1^1\phi_1+Q_2^1\frac{P_2^1}{P_1^1}\phi_2\right) +\frac{\delta}{\sigma}R\frac{e^{\breve{z}\sigma/2}}{\breve{z}\sigma}\breve{z}_2\sigma e^{-\breve{z}_2\sigma/2}\frac{x^{21}}{P_1^2}(P_1^1\phi_1+P_2^1\phi_2) -\frac{\delta}{\sigma}Rx^{11}\left(\phi_1+\frac{P_2^1}{P_1^1}\phi_2\right)\approx 0 \quad \text{for } \breve{z}_2\sigma\gg 1. \quad \text{(B12)}$$

For the relations given by Eqs. (6.1a)–(6.1c), the coefficients Q_i^m defined by Eq. (5.4d) results in

$$Q_1^1=\frac{e^{-\breve{z}\sigma/2}}{\breve{z}\sigma}\left[-\frac{e^{-\breve{z}\sigma}-1-\breve{z}\sigma}{\breve{z}\sigma}P_1^1-\frac{\breve{d}}{\sigma}(\breve{z}\sigma+1)\right], \quad \text{(B13a)}$$

$$Q_2^1=\frac{e^{-\breve{z}\sigma/2}}{\breve{z}\sigma}\left[-\frac{e^{-\breve{z}\sigma}-1-\breve{z}\sigma}{\breve{z}\sigma}P_2^1\right], \quad \text{(B13b)}$$

$$\frac{Q_1^2}{P_1^2}\approx -e^{\breve{z}_2\sigma/2}\frac{\delta}{\sigma}R, \quad \text{(B13c)}$$

and

$$\frac{Q_2^2}{P_1^2}\approx -e^{\breve{z}_2\sigma/2}\frac{\delta}{\sigma}R. \quad \text{(B13d)}$$

In Eqs. (B13c) and (B13d), the expression given by Eq. (B2e) is used.

If the coefficient R given by Eq. (B5), the ratios given by Eq. (B7), and the coefficient given by Eq. (B9) are considered after the substitution of Eqs. (B13a)–(B13d), Eqs. (B2a)–(B2d), and (B3) into Eq. (B12), the percolation threshold should be found from a formula given as

$$[\mathcal{P}\phi_1+(\mathcal{P}_p)^2\phi_2]\left[\mathcal{P}_p-\left\{\frac{e^{\breve{z}\sigma}-1-\breve{z}\sigma}{(\breve{z}\sigma)^2}P_1^1+\frac{\breve{d}}{\sigma}+\frac{1}{\breve{z}\sigma}\frac{\breve{d}}{\sigma}\right\}P_1^1\right] =0. \quad \text{(B14a)}$$

Equation (B11c) is independent of ϕ_2. The percolation threshold also should be independent of ϕ_2. Therefore, the relation between the coefficients at the percolation threshold should, according to Eq. (B14a), be given by the formula

$$\mathcal{P}_p-\left[\frac{e^{\breve{z}\sigma}-1-\breve{z}\sigma}{(\breve{z}\sigma)^2}P_1^1+\frac{\breve{d}}{\sigma}+\frac{1}{\breve{z}\sigma}\frac{\breve{d}}{\sigma}\right]P_1^1=0. \quad \text{(B14b)}$$

In Eq. (B14b), terms with P_2^1 are ignored owing to $0<P_2^1 \ll 1$ for $0<\breve{d}_2^1/\sigma\ll 1$. As a result it does not include ϕ_2.

APPENDIX C: THE PAIR CONNECTEDNESS

The behavior of the pair connectedness $P_{ij}(r)$ can be readily estimated at the particular distance $r=\sigma_{ij}$.

The second term on the right-hand side of Eq. (4.1) is a continuous function of r at $r=\sigma_{ij}$. Accordingly, the pair connectedness $P_{ij}(r)$ given by Eq. (4.1) must satisfy

$$\lim_{\epsilon\to 0}2\pi\sigma_{ij}[P_{ij}(\sigma_{ij}+\epsilon)-P_{ij}(\sigma_{ij}-\epsilon)] =-\lim_{\epsilon\to 0}\left\{\left[\frac{d}{dr}Q_{ij}(r)\right]_{r=\sigma_{ij}+\epsilon}-\left[\frac{d}{dr}Q_{ij}(r)\right]_{r=\sigma_{ij}-\epsilon}\right\}. \quad \text{(C1)}$$

If Eqs. (4.4c) and (4.4d) are considered with the relation $P_{ij}(r)=0$ $(r<\sigma_{ij})$ after substituting Eq. (4.4a) into Eq. (C1), the pair connectedness $P_{ij}(r)$ at $r=\sigma_{ij}$ can be found as

$$P_{ij}(\sigma_{ij})=-\frac{1}{2\pi}\frac{\sigma_j}{\sigma_{ij}}\sum_{n=1}^{\mathcal{N}}\left(\breve{z}_n\sigma_i\frac{\breve{d}_i^n}{\sigma_i}-P_i^n\right)e^{-\breve{z}_n\sigma_i/2}\frac{a_j^n}{\sigma_j}. \quad \text{(C2)}$$

To derive Eq. (C2), Eqs. (4.15a) and (4.15b) must be considered.

By considering Eq. (6.1a), the coefficients a_j^n/σ_j given by Eq. (4.18a) can be rewritten as

$$e^{-\breve{z}\sigma/2}\frac{a_j^1}{\sigma}=\frac{\pi}{3}\left(2\breve{z}_2\sigma e^{-\breve{z}_2\sigma}\frac{x}{P_1^2P_1^2}\right)^{-1}\times\left[-\frac{1}{\breve{z}\sigma}\breve{z}_2\sigma e^{-\breve{z}_2\sigma}\frac{x^{22}}{P_1^2P_1^2}P_j^1+e^{-\breve{z}\sigma/2}e^{-\breve{z}_2\sigma/2}\frac{x^{12}}{P_1^2}\frac{P_j^2}{P_1^2}\right], \tag{C3a}$$

$$e^{-\breve{z}_2\sigma/2}\frac{a_j^2}{\sigma}=\frac{\pi}{3}R\left(2\breve{z}_2\sigma e^{-\breve{z}_2\sigma}\frac{x}{P_1^2P_1^2}\right)^{-1}\times\left[\frac{e^{\breve{z}\sigma/2}}{\breve{z}\sigma}\breve{z}_2\sigma e^{-\breve{z}_2\sigma/2}\frac{x^{21}}{P_1^2}P_j^1-x^{11}\frac{P_j^2}{P_1^2}\right], \tag{C3b}$$

where R given by Eq. (B2e) is used.

If the use of Eqs. (B2a)–(B2d) and (B3) is considered with the relations given by Eqs. (6.1a) and (6.1b) after substituting the coefficients a_j^n/σ_j given by Eqs. (C3a) and (C3b) into Eq. (C2), the pair connectedness $P_{11}(\sigma)$ for $i=1$ and $j=1$ particles can be found at $\delta/\sigma=0$ as

$$P_{11}(\sigma)=\frac{\breve{z}\sigma}{12}\left(\frac{\breve{d}}{\sigma}-\frac{1}{\breve{z}\sigma}P_1^1\right)P_1^1(\mathcal{P}_p\phi_1)^{-1}. \tag{C4a}$$

In Eq. (C4a), terms with P_2^1 are ignored owing to $0<P_2^1\ll 1$ for $0<\breve{d}_2^1/\sigma\ll 1$. As a result, Eq. (C4a) does not include ϕ_2.

Similarly, the other pair connectedness $P_{ij}(\sigma)$ for i-j particles can be found as

$$P_{12}(\sigma)=P_{21}(\sigma)=P_{22}(\sigma)=0. \tag{C4b}$$

In addition, Eqs. (B5), (B7), and (B9) are used to derive Eqs. (C4a) and (C4b).

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