Percolation in ionic fluids and formation of a fractal structure

Tetsuo Kaneko*
Kurakenchikuzokeisha Company, Ltd., Shimo 1-27-22, Kita-ku, Tokyo 115-0042, Japan
(Received 14 May 1999)

The size of a dense region in the nonuniform distribution of particles generated in an ionic fluid can develop under certain conditions, as the charge on each particle increases. To derive this result, it is assumed that such a dense region is an ensemble of particles linked 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 $u_{ij}(r)$ the Coulomb potential. The percolation of the ensemble can be estimated analytically. The result described above has been derived from this estimation. According to the pair connectedness function derived for analytic estimation of the percolation, the dense region resulting from the contribution of the Coulomb attractive force between positive and negative particles can produce a fractal structure with a fractal dimension of 1.5. Furthermore, a configuration of charged particles, which can be approximately drawn from a characteristic of the pair connectedness function, agrees with that of the Bjerrum theory. [S1063-651X(99)11012-2]

PACS number(s): 61.43.Hv, 64.60.Ak, 61.20.Qg, 82.70.Dd

I. INTRODUCTION

The distribution of charged particles in an ionic fluid tends toward a nonuniform state, even if the densities of charged particles are low. Dense areas generated in the distribution can significantly contribute to the thermodynamics of the ionic fluid. Models describing the contribution of the dense areas have been proposed [1–3]. The present interest is focused on estimating the mean size of the dense areas.

The tendency mentioned above can be attributed to the characteristic of the Coulomb force. A force acting between positive and negative charged particles is characterized as a long-range attractive force. The attractive force can contribute to the formation of dense regions even in the fluid of low densities.

Each dense region can be an ensemble composed of particles bound to each other by the attractive force. The dominant portion of particles distributed in a dense region can be occupied by particles constituting pairs linked by the attractive force. Particles constituting each pair should then satisfy the condition $E_{ij}+u_{ij}(r)\leqslant 0$. Here, E_{ij} and $u_{ij}(r)$ for a pair of i and j particles are the relative kinetic energy and pair potential, respectively.

In the present work, a bond between the i and j particles is defined as a state satisfying the condition $E_{ij}+u_{ij}(r)\leqslant 0$ [4]. An ensemble of particles linked by such bonds is a physical cluster in the present work. The dense area is regarded as the physical cluster of particles linked by bonds described via the condition $E_{ij}+u_{ij}(r)\leqslant 0$.

For a discussion of the critical thermodynamics of an ionic fluid, the Bjerrum theory [1] can result in a satisfactory description [3]. However, it has been indicated that an ionic cluster model, beyond the ion pair model based on the Bjerrum theory, should be considered for estimating precisely the thermodynamics of ionic fluids [3]. Also, the thermodynamic necessity for including clustering has been explicity demonstrated [5].

Recently, a mathematical treatment for estimating the mean size of ionic clusters was presented for an ionic fluid composed of charged particles having the same size [6]. As a result, a numerical calculation is available for evaluating the mean cluster size.

In the present work, the mean size of the dense areas is estimated as that of the physical clusters described above. The percolation concerning the dense regions is regarded as that concerning the physical clusters. The percolation is analytically estimated, using an integral equation with a closure scheme.

To derive an analytical solution for the integral equation, a practical expression for closure is required. The expression will be obtained by estimating the behavior of the correlation functions at a great distance. The expression for a two-component mixture will be given in Sec. III D. An analytical solution for the integral equation will be presented in Sec. IV. Requirements for the percolation threshold will be derived in Sec. V B. The percolation thresholds estimated for two ionic fluids will be given in Sec. VI.

Besides the thermodynamics of ionic fluid described above, the percolation resulting from the contact of dense areas can affect other phenomena. The electrical transport phenomenon can be one of such phenomena.

In an ionic fluid, a group of charged particles which can freely migrate for the external electric field is distinguished from another group of charged particles which cannot freely migrate. If each charged particle constituting a pair satisfies the condition $E_{ij}+u_{ij}(r)\leqslant 0$, the charged particles cannot freely migrate away from each other.

If the external electric field applied to the ionic fluid is weak, charged particles of the dense area can hardly contribute to the electrical transport phenomenon induced by the external electric field. The dense area can then be polarized only by the external electric field. A free charged particle, which at least is not part of the dense areas, can significantly contribute to the electrical transport. As the densities of particles increase under the electrical neutrality condition, the number of dense areas should increase. Free charged particles contributing to the electrical transport should then de-

*Electronic address: kanekous@ppp.bekkoame.ne.jp

crease. Thus, the electrical conductivity of an ionic fluid, due to the transport of charged particles, can decrease as the densities of charged particles increase.

On the other hand, it is possible that the electrical conductivity of an ionic fluid can increase as the densities of charged particles increase, if the densities of the charged particles are high.

If the densities are high, a sufficiently developed dense region can be generated since some portions of the dense regions are in contact with each other. If a percolated dense region is generated, the percolated dense region can contribute to the electrical transport as a path for the electric current. The electrical transport via the percolated dense region is effective, since the contribution to the electric current can be generated by only a small shifft of each charged particle due to the external electric field. An increase in the densities of charged particles can increase the size of each dense region. Thus, an increase in density can enhance electrical conductivity.

Ultimately, as the densities increase from a sufficiently low level, the electrical conductivity of the ionic fluid can decrease, and reach a minimum. For additional increases in density, the electrical conductivity can increase due to the contribution of percolated dense regions to the electrical transport.

In addition, the behavior similar to that of the electrical conductivity described above has been found in a phenomenon demonstrated experimentally [7].

Hydrodynamical transport phenomena should also be influenced by percolation concerning the physical clusters described above. A viscosity anomaly was detected near the critical consolute point of an ionic ethylammonium nitrate-n-octanol mixture [8]. It is considered that such percolation can contribute to the viscosity anomaly.

The growth of a dense region can result from the contact of small dense areas. This growth process is found to be similar to the growth process known as cluster-cluster aggregation [9]. The distribution of particles resulting from cluster-cluster aggregation resulted in the fractal structure, while the fractal dimension d_f of the fractal structure was determined as $d_f \sim 1.75$ [9].

In a suspension of charged colloidal particles also, it has been demonstrated that the generated nonuniform distribution of colloidal particles can provide a fractal structure. The fractal dimension of the structure was 1.9 [10].

If the contribution of cluster-cluster aggregation to the growth process of dense areas is considered, it can be predicted that a developed dense region has at least a fractal structure. Moreover, the fractal dimension of the fractal structure should be close to 1.75. The pair connectedness estimated in the present work will demonstrate that a cluster provides a fractal structure having a fractal dimension close to 1.75. This will be revealed in Sec. VII.

II. PAIR CONNECTEDNESS

In the present work, a bound state for the i and j particles is defined as the state satisfying the condition $E_{ij}+u_{ij}(r) \leqslant 0$ having a pair potential $u_{ij}(r)$ and relative kinetic energy E_{ij}.

When the expression of the pair correlation function $g_{ij}(r)$ is given using the grand partition function, a bound state $E_{ij}+u_{ij}(r) \leqslant 0$ can be distinguished in its expression from an unbound state $E_{ij}+u_{ij}(r) > 0$. The pairwise bond probability $p_{ij}(r)$ can then play a role. The factor $\exp(-\beta u_{ij})$ in the expression can be expessed as the sum of the contributions to the bound state and the unbound state, if $p_{ij}(r)$ is used. Thus, the sum is

$$e^{-\beta u_{ij}} = p_{ij}(r) e^{-\beta u_{ij}} + [1-p_{ij}(r)] e^{-\beta u_{ij}}, \tag{2.1}$$

where β is defined as $\beta \equiv 1/kT$. Here, k is Boltzmann's constant, and T the temperature. The pairwise bond probability $p_{ij}(r)$ introduced in Eq. (2.1) is given as

$$p_{ij}(r) = 2\pi^{-1/2} \int_0^{-\beta u_{ij}} y^{1/2} e^{-y} dy, \tag{2.2}$$

where $y=[\beta E_{ij}]^{1/2}$ [4]. This function represents the probability that a pair of i and j particles satisfies the condition $E_{ij}+u_{ij}(r) \leqslant 0$. If $\beta u_{ij} > 0$, the probability should be $p_{ij}(r)=0$. In addition, pair potentials satisfying the relation $\beta u_{ij} > 0$ for an ionic fluid are the repulsive Coulomb potential and the hard core potential.

Ultimately, Eq. (2.1) 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 another factor f_{ij}^{*} not contributing to the bound state. According to Eq. (2.1), f_{ij}^{+} and f_{ij}^{*} are given as

$$f_{ij}^{+} \equiv p_{ij}(r) e^{-\beta u_{ij}}$$

and

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

The pair connectedness $P_{ij}(r)$ is useful for estimating the cluster size [11], and 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. If 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 $\rho_i \rho_j D_{ij}(r) d\mathbf{r}_i d\mathbf{r}_j$, $P_{ij}(r)$ can be related to the pair correlation function $g_{ij}(r)$ as

$$g_{ij} = P_{ij} + D_{ij}. \tag{2.3}$$

Here, the physical meanings of P_{ij} and of D_{ij} require that

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

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.

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}^{*}, since the sum $f_{ij}^{+}+f_{ij}^{*}$ is equal to the Mayer f function f_{ij}.

A physical cluster consisting of particles bound to each other under 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}^{+}.

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 consists of 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. Hence, 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}^{+}. Here, 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 determined by the convolution integral of the product of C_{ij}^{+} and P_{ij}. Thus, P_{ij} can be expressed by an integral equation [11] having the same mathematical structure as the Ornstein-Zernike equation, namely

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

where *m* is the number of species.

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}.

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

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

where N_{ij} is the sum of N_{ij}^{+} and a remainder N_{ij}^{*} (i.e., N_{ij}^{*} is all nodal diagrams which 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 D_{ij}, by considering the form $g_{ij}=P_{ij}+D_{ij}$. If the relation $P_{ij}=C_{ij}^{+}+N_{ij}^{+}$ is considered, the expressions corresponding to P_{ij} and 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

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

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

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

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 practical 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 (2.2) 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 $\lim_{r\to\infty}[(g_{ij}-1)/(-\beta u_{ij})]=\frac{1}{2}$, 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 Eq. (3.2a) for $\beta u_{il}>0$ and $1\ll r$

When the distance r_{il} between i and l is sufficiently large, Eq. (3.2a) can be approximated as

$$\beta u_{il}(P_{il}-C_{il}^{+})+C_{il}^{+}=0, \quad \text{for} \quad \beta u_{il}>0.$$

For $1 \ll r_{il}$, this relation must be satisfied, so that the dependence of $\beta u_{il} P_{il}$ on r_{il} should be the same as that of C_{il}^{+} on r_{il}. As a result, an approximate formula for $1 \ll r_{il}$ can be simplified as

$$\beta u_{il} P_{il} = -C_{il}^{+}, \quad \text{for} \quad \beta u_{il}>0. \tag{3.6}$$

Thus, C_{il}^{+} for $\beta u_{il}>0$ and $1 \ll r_{il}$ can be estimated, if P_{il} for $\beta u_{il}>0$ and $1 \ll r_{il}$ are assumed.

For $\beta u_{il}>0$, $p_{il}(r)$ is equal to zero. It is, however, possible that $P_{il} \neq 0$ occurs, since a j particle attracting either i or l particles by the Coulomb force can exist. A cluster can grow via a particle corresponding to the j particle which satisfies the relations $\beta u_{ij}<0 (i\neq j)$ and $\beta u_{jl}<0 (j \neq l)$.

C. Behavior of C_{il}^{+} for $\beta u_{il}>0$

1. Behavior of P_{il}^{+} for $\beta u_{il}>0$ and $1\ll r$

If $L \gg 1$ is satisfied, the electroneutrality of the system can be approximately expressed as

$$2\pi \sum_k e_k \rho_k \int_0^{L+\delta L} g_{ik}(r) r^2 dr + e_i = 0, \tag{3.7}$$

where $\delta L/L \ll 1$.

If the relation given by Eq. (2.3) is considered, Eq. (3.7) results in an approximation for $P_{ik}(L)$ as

$$\begin{aligned} 2\pi \sum_k e_k \rho_k P_{ik}(L) L^2 \delta L &= -2\pi \sum_k e_k \rho_k D_{ik}(L) L^2 \delta L \\ &\quad -2\pi \sum_k e_k \rho_k \int_0^L g_{ik}(r) r^2 dr - e_i . \end{aligned} \tag{3.8}$$

A much larger value than that of the hard sphere diameter of the largest particle is then allowed for δL, since the variations in either $P_{ik}(L)$ or $D_{ik}(L)$ can be sufficiently small, even for a large change in L, if L is sufficiently large.

By considering $D_{ik}(L) \approx 1 (1 \ll L)$ and the electroneutrality condition $\Sigma_k e_k \rho_k = 0$, a feature of $P_{ik}(L)$ for $1 \ll L$ can be found from Eq. (3.8) as

$$\sum_k e_k \rho_k P_{ik}(L) = 0. \tag{3.9}$$

2. Behavior of C_{il}^{+} for $\beta u_{il}>0$ and $1\ll r$

By substituting Eq. (3.6) into Eq. (3.9), an equation for each C_{il}^{+} when $\beta u_{il}>0$ should be satisfied is given as

$$\sum_{\substack{l \\ \text{for} \;\; u_{il}>0}} \frac{e_l \rho_l}{\beta u_{il}} C_{il}^{+} = \sum_{\substack{k \\ \text{for} \;\; u_{ik}<0}} e_k \rho_k P_{ik} \quad \text{for} \quad r \gg 1. \tag{3.10}$$

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

$$\begin{aligned} P_{ij} = -\frac{c_{ij}^{\mathrm{PY}}}{-\beta u_{ij}} \Bigg[& \frac{4}{3\sqrt{\pi}}(-\beta u_{ij})^{1/2} + \frac{16}{9\pi}(-\beta u_{ij}) \\ & + \left(\frac{64}{27\pi^{3/2}} - \frac{4}{5\sqrt{\pi}} \right)(-\beta u_{ij})^{3/2} + \cdots \Bigg] + \frac{C_{ij}^{+}}{-\beta u_{ij}} \\ & \times \left[1 + \frac{4}{3\sqrt{\pi}}(-\beta u_{ij})^{1/2} + \left(\frac{1}{2} + \frac{16}{9\pi} \right)(-\beta u_{ij}) + \cdots \right]. \end{aligned} \tag{3.11}$$

If the approximation given by Eq. (3.5) and $c_{ij}^{\mathrm{PY}}/(-\beta u_{ij}) = 1$ for the MSA are considered in Eq. (3.11), the result can be expressed as

$$P_{ij} = \frac{22}{15\sqrt{\pi}}(-\beta u_{ij})^{3/2} \quad \text{for} \quad u_{ij}<0. \tag{3.12}$$

Substituting Eq. (3.12) into Eq. (3.10) results in

$$\sum_{\substack{l \\ \text{for} \;\; u_{il}>0}} \frac{e_l \rho_l}{\beta u_{il}} C_{il}^{+} = \sum_{\substack{k \\ \text{for} \;\; u_{ik}<0}} e_k \rho_k \frac{22}{15\sqrt{\pi}}(-\beta u_{ik})^{3/2}. \tag{3.13}$$

Ultimately, C_{il}^{+} for i and l particles satisfying $u_{il}>0$ can be given by Eq. (3.13) if the value of r is sufficiently large.

D. Expression of a simple closure scheme

1. A closure scheme similar to the MSA

Thus, a closure scheme similar to the MSA can be obtained using Eqs. (3.5) and (3.13) as

$$C_{ij}^{+} = C_{ij}^{0+} + \frac{4}{3\sqrt{\pi}}(-\beta u_{ij})^{3/2} \quad \text{for} \quad \beta u_{ij}<0, \tag{3.14a}$$

and

$$\sum_{\substack{l \\ \text{as} \quad u_{il}>0}} \frac{e_l\rho_l}{\beta u_{il}}(C_{il}^{+}-C_{il}^{0+})$$

$$=\sum_{\substack{k \\ \text{as} \quad u_{ik}<0}} e_k\rho_k \frac{22}{15\sqrt{\pi}}(-\beta u_{ik})^{3/2} \quad \text{for} \quad \beta u_{il}>0, \tag{3.14b}$$

where C_{ij}^{0+} is the short-range contribution. If an ionic fluid is a two-component mixture, then Eq. (3.14b) is simplified as

$$C_{ii}^{+}=C_{ii}^{0+}+\frac{22}{15\sqrt{\pi}}\frac{e_j\rho_j}{e_i\rho_i}\beta u_{ii}(-\beta u_{ij})^{3/2} \quad \text{for} \quad \beta u_{ij}<0. \tag{3.15}$$

Ultimately, Eq. (2.4) can be solved using the closure scheme given as the set of Eqs. (3.14a) and (3.15), if the ionic fluid is a two-component mixture.

2. Additional simplification of the closure scheme

Mathematical difficulty cannot be avoided when applying the above mentioned closure scheme to analytically solve Eq. (2.4), because powers of the Coulomb potential are included in the closure. To avoid this difficulty in the present work, the Coulomb potential is regarded as a Yukawa potential in which the effective range κ^{-1} is sufficiently large. Thus, u_{ij} is expressed as

$$u_{ij}(r)=-\mathcal{K}_{ij}\frac{1}{r}\exp[-\kappa r], \tag{3.16a}$$

where

$$\mathcal{K}_{ij}\equiv-\frac{\alpha_0^2}{4\pi\beta}\frac{e_i}{e}\frac{e_j}{e}, \tag{3.16b}$$

with

$$\alpha_0^2\equiv\frac{4\pi\beta e^2}{\epsilon}. \tag{3.16c}$$

Here, e is the elementary charge and ϵ the macroscopic dielectric constant of the fluid.

Since u_{ij} is expressed using Eq. (3.16a), the closure obtained above includes factors which can be described as $(\exp[-\kappa r]/r)^{\nu}$ where $\nu=3/2$ or $5/2$. In order to obtain an analytical solution for Eq. (2.4), such a factor is approximated as

$$\left(\frac{e^{-\kappa r}}{r}\right)^{\nu}\approx K\frac{e^{-zr}}{r}, \tag{3.17}$$

where $K=1/\breve{a}^{\nu-1}$ and $z=\nu\kappa$. For a particular value of $\breve{a}$, Eq. (3.17) can result in $(\exp[-\kappa\breve{a}]/\breve{a})^{\nu}=K\exp[-z\breve{a}]/\breve{a}$. In the present work, the maximum hard sphere diameter of particles distributed in the fluid is applied as $\breve{a}$.

Using this approximation, the closure scheme can be expressed as

$$C_{ij}^{+}(r)=C_{ij}^{0+}(r)+\sum_{n=1}^{2}K_{ij}^{n}\frac{e^{-z_n r}}{r}, \tag{3.18a}$$

where

$$K_{ij}^{1}\equiv\frac{4}{3\sqrt{\pi}}(\beta\mathcal{K}_{ij})^{3/2}\frac{1}{\breve{a}^{1/2}} \quad (i\neq j), \tag{3.18b}$$

$$K_{ii}^{1}\equiv0, \tag{3.18c}$$

$$K_{ij}^{2}\equiv0 \quad (i\neq j), \tag{3.18d}$$

$$K_{ii}^{2}\equiv-\frac{22}{15\sqrt{\pi}}(-\beta\mathcal{K}_{ii})(\beta\mathcal{K}_{ij})^{3/2}\frac{1}{\breve{a}^{3/2}} \quad (i\neq j), \tag{3.18e}$$

$$z_1\equiv\frac{3}{2}\kappa, \tag{3.18f}$$

and

$$z_2\equiv\frac{5}{2}\kappa. \tag{3.18g}$$

A hard core potential resulting in a completely short-range interaction between i and j 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

$$C_{ij}^{0+}(r)=0, \quad \text{for} \quad r\geqslant\sigma_{ij}, \tag{3.19}$$

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 use of Eq. (3.18a) simplifies the estimation of percolation.

The approximate form given in Eq. (3.17) somewhat overestimates the long-range contribution of $C_{ij}^{+}(r)$ if κ is zero, since the contribution of $(1/r)^{\nu}$ is approximated as $(1/\breve{a}^{\nu-1})(1/r)$. If $|\kappa|\ll1$ is satisfied while κ is not zero, the approximate form given as Eq. (3.17) can somewhat overestimate the decay of $C_{ij}^{+}(r)$, since the decay dependent on $(1/r)^{\nu}$ is approximated as $(1/\breve{a}^{\nu-1})(1/r)\exp(-\nu\kappa r)$. According to a previous study of Yukawa fluids [12], overestimation of the long-range contribution of $C_{ij}^{+}(r)$ can lead to an overestimation of $1/\mathcal{K}_{ij}$ at the percolation threshold. Fortunately, the diagrams representing the percolation threshold for the overestimation of the long-range contribution have the same pattern as those for the overestimation of the decay of $C_{ij}^{+}(r)$. Therefore, it is expected that a diagram pattern representing the percolation threshold obtained by the use of Eqs. (3.18a)–(3.18g) is valid, even for an ionic fluid.

IV. SOLUTION OF THE INTEGRAL EQUATION

A. Solution including unknown coefficients

1. Using Baxter's Q function

For a single component fluid of particles interacting via the Yukawa potential, a solution of Eq. (2.4) has been obtained [12,13] using Baxter's Q function [14]. Similarly, using Baxter's Q function [14] with Eqs. (3.18a)–(3.18g) given for a two-component mixture, Eq. (2.4) can be solved analytically. Based on the mathematical procedure for the Orstein-Zernike equation [14,15], $P_{ij}(r)$ and $C_{ij}^{+}(r)$ satisfying Eq. (2.4) for a multicomponent fluid are given by

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

and

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

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 expessed in Eq. (3.19). The characteristic of the short-range contribution $C_{ij}^{0+}(r)$ can be provided by $Q_{ij}(r)$, since the relation between $C_{ij}^{+}(r)$ and $Q_{ij}(r)$ can be represented by Eq. (4.2). If this fact and a characteristic of the long-range contribution to $C_{ij}^{+}(r)$ are considered, a form of $Q_{ij}(r)$ may be expressed as

$$Q_{ij}(r)=Q_{ij}^{0}(r)+\sum_{n=1}^{2}\breve{D}_{ij}^{n}e^{-z_n r}\quad(\lambda_{ji}<r<\sigma_{ji}), \tag{4.4a}$$

$$Q_{ij}(r)=\sum_{n=1}^{2}\breve{D}_{ij}^{n}e^{-z_n r}\quad(\sigma_{ji}\leqslant r), \tag{4.4b}$$

and

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

If $\lim_{u_{ij}\to\infty}g_{ij}=0$ and $\lim_{\delta\to 0}u_{ij}(\sigma_{ij}+\delta)=\infty\ \ (\delta>0)$ are considered, the relation $P_{ij}=0$ for $\lambda_{ji}<r<\sigma_{ji}$ is derived from Eq. (3.1a). 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 as Eq. (4.4c), since the behavior of $Q_{ij}(r)$ is expressed by Eq. (4.4a), a form of $Q_{ij}^{0}(r)$ can be expressed as

$$Q_{ij}^{0}(r)=\sum_{n=1}^{2}\breve{C}_{ij}^{n}(e^{-z_n r}-e^{-z_n\sigma_{ij}})\quad(\lambda_{ji}<r<\sigma_{ji}). \tag{4.4d}$$

In addition, the unknown coefficients $\breve{C}_{ij}$ and $\breve{D}_{ij}$ given above can be determined, using Eqs. (4.1) and (4.2).

If Eqs. (4.4a)–(4.4d) and the relation $P_{ij}=0$ are considered over the range $\lambda_{ji}<r<\sigma_{ji}$, Eq. (4.1) for $r<\sigma_{ji}$ results in

$$\sum_{n=1}^{2}z_n\breve{C}_{ij}^{n}e^{-z_n r}+\sum_{n=1}^{2}z_n\breve{D}_{ij}^{n}e^{-z_n r}-2\pi\sum_{k=1}^{2}\sum_{n=1}^{2}\rho_k\breve{D}_{kj}^{n}e^{-z_n r}\int_0^{\infty}P_{ik}(t)e^{-z_n t}t\,dt=0. \tag{4.5}$$

Thus, the relation between the left- and right-hand sides of Eq. (4.5) gives the restrictions for the coefficients as

$$\breve{C}_{ij}^{n}=-\breve{D}_{ij}^{n}+2\pi\sum_{k=1}^{2}\frac{\rho_k}{z_n}\hat{P}_{ik}(z_n)\breve{D}_{kj}^{n}, \tag{4.6a}$$

where

$$\hat{P}_{ik}(z_n)\equiv\int_0^{\infty}P_{ik}(t)e^{-z_n t}t\,dt. \tag{4.6b}$$

If Eq. (4.4b) is considered, then Eq. (4.2) can result in

$$2\pi r C_{ij}^{+}(r)=\sum_{n=1}^{2}z_n\breve{D}_{ij}^{n}e^{-z_n r}-\sum_{n=1}^{2}z_n e^{-z_n r}\sum_{k=1}^{2}\rho_k\breve{D}_{ik}^{n}\hat{Q}_{jk}(z_n),\quad \text{for}\ \ \sigma_{ji}<r, \tag{4.7}$$

where

$$\hat{Q}_{jk}(s)\equiv\int_{\lambda_{kj}}^{\infty}Q_{jk}(t)e^{-st}dt=\sum_{m=1}^{2}\left[\breve{C}_{jk}^{m}e^{-s\lambda_{kj}}e^{-z_m\sigma_{kj}}\left(\frac{e^{z_m\sigma_j}-e^{-s\sigma_j}}{s+z_m}-\frac{1-e^{-s\sigma_j}}{s}\right)+\frac{1}{s+z_m}\breve{D}_{jk}^{m}e^{-z_m\lambda_{kj}}e^{-s\lambda_{kj}}\right]. \tag{4.8}$$

Here, Eq. (4.8) can be derived using Eqs. (4.4a)–(4.4d). The relation between $\hat{P}_{jk}(z_n)$ and $\hat{Q}_{jk}(z_n)$ can be obtained by substituting Eq. (4.6a) into Eq. (4.8) as

$$\hat{Q}_{jk}(z_n)=e^{-z_n\lambda_{kj}}\sum_{m=1}^{2}\left\{e^{-z_m\sigma_{kj}}\breve{D}_{jk}^{m}\left(\frac{e^{-z_n\sigma_j}}{z_n+z_m}+\frac{1-e^{-z_n\sigma_j}}{z_n}\right)+\sum_{l=1}^{2}\frac{2\pi\rho_l}{z_m}\hat{P}_{jl}(z_m)\breve{D}_{lk}^{m}\left[\frac{e^{-z_m\lambda_{kj}}}{z_n+z_m}-e^{-z_m\sigma_{kj}}\times\left(\frac{e^{-z_n\sigma_j}}{z_n+z_m}+\frac{1-e^{-z_n\sigma_j}}{z_n}\right)\right]\right\}. \tag{4.9}$$

On the other hand, Eq. (4.1) for $r<\sigma_{ji}$ can be expressed as

$$0=\sum_{n=1}^{2}z_n\breve{C}_{ij}^{n}e^{-z_nr}+\sum_{n=1}^{2}z_n\breve{D}_{ij}^{n}e^{-z_nr}+2\pi\sum_{k=1}^{2}\rho_k\int_r^{\infty}Q_{kj}(t)\times(r-t)P_{ik}(|r-t|)dt. \tag{4.10}$$

Equation (4.10) is equivalent to Eq. (4.5) which has no singularity for $0<r<\infty$, so that Eq. (4.10) is satisfied for $0<r<\infty$. If each term in Eq. (4.10) is then subtracted from each term in an equation obtained as Eq. (4.1) for $\sigma_{ji}\leqslant r$, a formula can be derived as

$$2\pi rP_{ij}(r)=-\sum_{m=1}^{2}z_m\breve{C}_{ij}^{m}e^{-z_mr}+2\pi\sum_{k=1}^{2}\rho_k\int_{\lambda_{jk}}^{r}Q_{kj}(t)\times(r-t)P_{ik}(r-t)dt. \tag{4.11}$$

The Laplace transformation of Eq. (4.11) results in

$$2\pi\hat{P}_{ij}(s)=-\sum_{m=1}^{2}\frac{z_m}{s+z_m}e^{-(s+z_m)\sigma_{ij}}\breve{C}_{ij}^{m}+2\pi\sum_{k=1}^{2}\rho_k\hat{P}_{ik}(s)\hat{Q}_{kj}(s). \tag{4.12}$$

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

By substituting Eqs. (4.6a) and (4.9) into Eq. (4.12) for $s=z_n$, a formula determining the relation between $\hat{P}_{ij}(z_n)$ and $\breve{D}_{ij}^{n}$ can be obtained as

$$2\pi\hat{P}_{ij}(z_n)=\sum_{m=1}^{2}\frac{z_m}{z_n+z_m}e^{-(z_n+z_m)\sigma_{ij}}\times\left(\breve{D}_{ij}^{m}-2\pi\sum_{k=1}^{2}\frac{\rho_k}{z_m}\hat{P}_{ik}(z_m)\breve{D}_{kj}^{m}\right)+2\pi\sum_{k=1}^{2}\rho_k\hat{P}_{ik}(z_n)e^{-z_n\lambda_{jk}}\times\sum_{m=1}^{2}\left\{e^{-z_m\sigma_{jk}}\breve{D}_{kj}^{m}\left(\frac{e^{-z_n\sigma_k}}{z_n+z_m}+\frac{1-e^{-z_n\sigma_k}}{z_n}\right)+\sum_{l=1}^{2}\frac{2\pi\rho_l}{z_m}\hat{P}_{kl}(z_m)\times\breve{D}_{lj}^{m}\left[\frac{e^{-z_m\lambda_{jk}}}{z_n+z_m}-e^{-z_m\sigma_{jk}}\left(\frac{e^{-z_n\sigma_k}}{z_n+z_m}+\frac{1-e^{-z_n\sigma_k}}{z_n}\right)\right]\right\}. \tag{4.13}$$

Since $|z_n|\ll 1$ is satisfied for $|\kappa|\ll 1$, if terms including either the first order of z_n or all higher orders of z_n are neglected, then Eq. (4.13) can be simplified as

$$2\pi\hat{P}_{ij}(z_n)=\sum_{m=1}^{2}\frac{z_m}{z_n+z_m}\breve{D}_{ij}^{m}-2\pi\sum_{m=1}^{2}\sum_{k=1}^{2}\rho_k\breve{D}_{kj}^{m}\frac{1}{z_n+z_m}[\hat{P}_{ik}(z_m)-\hat{P}_{ik}(z_n)]+2\pi\sum_{m=1}^{2}\sum_{k=1}^{2}\rho_k\sigma_k\hat{P}_{ik}(z_n)\breve{D}_{kj}^{m}+2\pi^2\sum_{m=1}^{2}\sum_{k=1}^{2}\sum_{l=1}^{2}\rho_k\rho_l\hat{P}_{ik}(z_n)\hat{P}_{kl}(z_m)\breve{D}_{lj}^{m}\sigma_k^2. \tag{4.14}$$

This approximation of Eq. (4.13) should be recognized as an approximation derived from the use of Eq. (3.18a) for both $|\kappa|\ll 1$ and $\kappa\neq 0$. In fact, Eq. (4.14) contains the coefficients z_n.

In Eq. (4.14), the ratio $[1/(z_n+z_m)][\hat{P}_{ik}(z_m)-\hat{P}_{ik}(z_n)]$ for $|\kappa|\ll 1$ can be readily estimated. If the difference $2\pi[\hat{P}_{ij}(z_n)-\hat{P}_{ij}(z_{n'})]$ is calculated using Eq. (4.14), then a formula can be obtained as

$$\sum_{m=1}^{2}\frac{z_m(z_{n'}-z_n)}{(z_n+z_m)(z_{n'}+z_m)}\breve{D}_{ij}^{m}-2\pi\sum_{m=1}^{2}\sum_{k=1}^{2}\rho_k\breve{D}_{kj}^{m}\left\{\frac{1}{z_n+z_m}[\hat{P}_{ik}(z_m)-\hat{P}_{ik}(z_n)]-\frac{1}{z_{n'}+z_m}[\hat{P}_{ik}(z_m)-\hat{P}_{ik}(z_{n'})]\right\}=0\quad(n\neq n'), \tag{4.15}$$

where $|\hat{P}_{ik}(z_m)-\hat{P}_{ik}(z_n)|\ll 1$ for $|\kappa|\ll 1$ is considered. According to Eq. (4.6b), $|\hat{P}_{ik}(z_m)-\hat{P}_{ik}(z_n)|\ll 1$ for $|\kappa|\ll 1$ can be satisfied because of $z_n\ll 1$ and $z_{n'}\ll 1$ for $|\kappa|\ll 1$. If Eq. (4.15) is used, the ratio $[1/(z_n+z_m)][\hat{P}_{ik}(z_m)-\hat{P}_{ik}(z_n)]$ for $|\kappa|\ll 1$ can be estimated as

$$2\pi\frac{\hat{P}_{ij}(z_1)-\hat{P}_{ij}(z_2)}{z_1+z_2}=\frac{1}{2}\frac{z_1-z_2}{z_1+z_2}\frac{1}{\rho_i}\delta_{ij}.$$

Using this result, Eq. (4.14) can be somewhat simplified as

$$2\pi\hat{P}_{ij}(z_n)=\sum_{m=1}^{2}\frac{z_m}{z_n+z_m}\breve{D}_{ij}^{m}-\frac{1}{2}\sum_{m=1}^{2}\breve{D}_{ij}^{m}\frac{z_m-z_n}{z_m+z_n}+2\pi\sum_{m=1}^{2}\sum_{k=1}^{2}\rho_k\sigma_k\hat{P}_{ik}(z_n)\breve{D}_{kj}^{m}+2\pi^2\sum_{m=1}^{2}\sum_{k=1}^{2}\sum_{l=1}^{2}\rho_k\rho_l\hat{P}_{ik}(z_n)\hat{P}_{kl}(z_m)\breve{D}_{lj}^{m}\sigma_k^2. \tag{4.16}$$

Equation (4.16) is an approximate expression for $|\kappa|\ll 1$, while it is derived from Eq. (3.18a) for $\kappa\neq 0$. This is a remarkable fact.

In addition, the evaluations of $\hat{P}_{ij}(z_1)$ and $\hat{P}_{ij}(z_2)$ for both $\kappa\neq 0$ and $|\kappa|\ll 1$ are considerably simplified by considering the relation $\hat{P}_{ij}(z_1)=\hat{P}_{ij}(z_2)$ for $|\kappa|\ll 1$. This relation allows the use of a simple expression defined as

$$\hat{P}_{ij}\equiv\hat{P}_{ij}(z_1)=\hat{P}_{ij}(z_2)\quad\text{for}\quad|\kappa|\ll 1. \tag{4.17}$$

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

On the other hand, if Eq. (3.19) is considered, the substitution of Eq. (3.18a) into Eq. (4.7) results in

$$2\pi\hat{K}_{ij}^{n}=z_n\breve{D}_{ij}^{n}-\sum_{k=1}^{2}z_n\rho_k\breve{D}_{ik}^{n}\hat{Q}_{jk}(z_n). \tag{4.18}$$

By substituting Eq. (4.9) into Eq. (4.18), another formula to determine the relation between $\hat{P}_{ij}(z_n)$ and $\breve{D}_{ij}^{n}$ can be obtained as

$$2\pi K_{ij}^{n}=z_n\breve{D}_{ij}^{n}-\sum_{m=1}^{2}\sum_{k=1}^{2}\rho_k\breve{D}_{ik}^{n}\breve{D}_{jk}^{m}e^{-z_n\lambda_{kj}}\times e^{-z_m\sigma_{kj}}\frac{z_n+z_m-z_me^{-z_n\sigma_j}}{z_n+z_m}-\sum_{m=1}^{2}\sum_{k=1}^{2}\sum_{l=1}^{2}\rho_k\breve{D}_{ik}^{n}\breve{D}_{lk}^{m}\frac{2\pi\rho_l}{z_m}\hat{P}_{jl}(z_m)\times e^{-z_n\lambda_{kj}}e^{-z_m\sigma_{kj}}\frac{-z_n-z_m+z_me^{-z_n\sigma_j}+z_ne^{z_m\sigma_j}}{z_n+z_m}. \tag{4.19}$$

Since $|z_n|\ll 1$ is satisfied for $|\kappa|\ll 1$, if terms including either the first order of z_n or all higher orders of z_n are neglected, Eq. (4.19) can be approximated as

$$2\pi K_{ij}^{n}=-\sum_{k=1}^{2}\rho_k\breve{D}_{ik}^{n}\sum_{m=1}^{2}\breve{D}_{jk}^{m}\frac{z_n}{z_n+z_m}. \tag{4.20}$$

This approximation of Eq. (4.19) should be recognized as an approximation derived from Eq. (3.18a) for both $|\kappa|\ll 1$ and $\kappa\neq 0$. In fact, Eq. (4.20) contains the coefficients z_n. This is a remarkable fact. In addition, Eq. (4.20) can simplify the evaluation of $\breve{D}_{ij}^{n}$ for $\kappa\neq 0$, since the term including $\hat{P}_{ij}$ can be neglected for $|\kappa|\ll 1$.

B. Estimation of $\breve{D}_{ij}^{1}$ and $\breve{D}_{ij}^{2}$

1. Forms provided for $\breve{D}_{ij}^{1}$ and $\breve{D}_{ij}^{2}$

By considering Eq. (4.20) for $n=2$ and $i\neq j$, and Eq. (3.18d), the relation between $\breve{D}_{ij}^{1}$ and $\breve{D}_{ij}^{2}$ can be assumed as

$$\begin{pmatrix}\breve{D}_{11}^{2} & \breve{D}_{12}^{2}\\ \breve{D}_{21}^{2} & \breve{D}_{22}^{2}\end{pmatrix}=\begin{pmatrix}U(a_1)\breve{D}_{11}^{1} & U(a_2)\breve{D}_{12}^{1}\\ U(\tau a_1)\breve{D}_{21}^{1} & U(\tau a_2)\breve{D}_{22}^{1}\end{pmatrix}, \tag{4.21a}$$

where

$$U(x)\equiv\frac{z_2/z_1}{z_2/z_1+1}\,\frac{2x}{2-x}. \tag{4.21b}$$

In Eq. (4.21a), a_1, a_2, and τ are unknown coefficients.

If Eq. (4.21a) is used, Eq. (4.20) for $n=1$ and $i=j$, and Eq. (3.18c) can result in the expression for $\breve{D}_{ij}^{1}$ as

$$\begin{pmatrix}\breve{D}_{11}^{1} & \breve{D}_{12}^{1}\\ \breve{D}_{21}^{1} & \breve{D}_{22}^{1}\end{pmatrix}=\begin{pmatrix}I_1\sqrt{\zeta_1A_1e_1} & I_2\sqrt{\zeta_1A_2e_2}\\ I_3\sqrt{\zeta_2B_1e_1} & I_4\sqrt{\zeta_2B_2e_2}\end{pmatrix}, \tag{4.22a}$$

where

$$\frac{1}{A_1}\equiv\frac{1}{2}+\frac{1}{z_2/z_1+1}U(a_1), \tag{4.22b}$$

$$\frac{1}{A_2}\equiv\frac{1}{2}+\frac{1}{z_2/z_1+1}U(a_2), \tag{4.22c}$$

$$\frac{1}{B_1}\equiv\frac{1}{2}+\frac{1}{z_2/z_1+1}U(\tau a_1), \tag{4.22d}$$

$$\frac{1}{B_2}\equiv\frac{1}{2}+\frac{1}{z_2/z_1+1}U(\tau a_2), \tag{4.22e}$$

and

$$|I_1|=|I_2|=|I_3|=|I_4|=1. \tag{4.22f}$$

To derive Eq. (4.22a), Eq. (4.20) for $n=1$ and $i=j$ has been compared with the electroneutrality condition $\Sigma_ie_i\rho_i=0$. This comparison results in

$$\frac{1}{2}\breve{D}_{ij}^{1}+\frac{1}{\frac{z_2}{z_1}+1}\breve{D}_{ij}^{2}=\frac{\zeta_ie_j}{\breve{D}_{ij}^{1}}, \tag{4.23}$$

where ζ_i are unknown coefficients. The relation expressed by Eq. (4.23) is the reason why the coefficients ζ_i have been contained in Eq. (4.22a).

In addition, an equation similar to Eq. (4.23) can be derived from Eq. (4.20) for $n=2$ and $i\neq j$ as

$$\frac{\frac{z_2}{z_1}}{\frac{z_2}{z_1}+1}\breve{D}_{ij}^{1}+\frac{1}{2}\breve{D}_{ij}^{2}=\frac{\zeta_i'e_j}{\breve{D}_{i'j}^{1}}$$

$$(i'=1\quad\text{for}\quad i=2,\quad i'=2\quad\text{for}\quad i=1). \tag{4.24}$$

If $\breve{D}_{ij}^2$ expressed by Eq. (4.21a) are considered, the substitution of $\breve{D}_{ij}^2$ into Eq. (4.24) leads to four equations for determining the relation between ζ_i' and τ. The relation is $\zeta_1'/\zeta_2' = \tau$.

The substitution of Eq. (4.23) into Eq. (4.20) for $n=1$ and $i\neq j$ yields

$$-2\pi K_{ij}^1 = \sum_{k=1}^{2} \rho_k \breve{D}_{ik}^1 \frac{\zeta_j e_k}{\breve{D}_{jk}^1} \quad (i\neq j). \tag{4.25a}$$

By considering $K_{ij}^1 = K_{ji}^1$, the ratio of Eq. (4.25a) for $i=1$ and $j=2$ to Eq. (4.25a) for $i=2$ and $j=1$ results in

$$\frac{\breve{D}_{21}^1 \breve{D}_{22}^1}{\breve{D}_{11}^1 \breve{D}_{12}^1} = -\frac{\zeta_2}{\zeta_1}. \tag{4.25b}$$

The substitution of Eq. (4.24) into Eq. (4.20) for $n=2$ and $i=j$ results in

$$-2\pi K_{ii}^2 = \sum_{k=1}^{2} \rho_k \breve{D}_{ik}^2 \frac{\zeta_i' e_k}{\breve{D}_{i'k}^2}$$

$$(i'=1 \ \text{ for } \ i=2, i'=2 \ \text{ for } \ i=1). \tag{4.26a}$$

The ratio of Eq. (4.26a) for $i=1$ to Eq. (4.26a) for $i=2$ results in

$$\frac{\breve{D}_{11}^2 \breve{D}_{12}^2}{\breve{D}_{21}^2 \breve{D}_{22}^2} = -\frac{1}{\tau}\frac{K_{11}^2}{K_{22}^2}, \tag{4.26b}$$

where the relation $\zeta_1'/\zeta_2' = \tau$ is considered. If $\breve{D}_{ij}^2$ expressed by Eq. (4.21a) are substituted into Eq. (4.26b), then a formula is obtained by considering the ratio ζ_1/ζ_2 given by Eq. (4.25b) as

$$\zeta_1 = \left(\frac{e_1}{e_2}\right)^2 \tau \frac{(2-a_1)(2-a_2)}{(2-\tau a_1)(2-\tau a_2)} \zeta_2, \tag{4.27}$$

where the relation $K_{11}^2/K_{22}^2 = (e_1/e_2)^2$ has been considered. The ratio K_{11}^2/K_{22}^2 can be estimated using Eq. (3.18e).

If $\breve{D}_{11}^1$ expressed by Eq. (4.22a) is considered, the substitution of $\breve{D}_{11}^1$ into Eq. (4.25b) leads to

$$1 = -\frac{I_3 I_4}{I_1 I_2} \frac{\frac{\zeta_1}{\zeta_2}}{\left|\frac{\zeta_1}{\zeta_2}\right|} \sqrt{\frac{B_1 B_2}{A_1 A_2}}.$$

From this equation, two relations can be extracted as

$$\frac{I_3 I_4}{I_1 I_2} \frac{\frac{\zeta_1}{\zeta_2}}{\left|\frac{\zeta_1}{\zeta_2}\right|} = -1, \tag{4.28a}$$

and

$$A_1 A_2 = B_1 B_2, \tag{4.28b}$$

where

$$A_1 A_2 < 0, \quad B_1 B_2 < 0. \tag{4.28c}$$

According to Eq. (4.22a), the following relations must be satisfied:

$$\zeta_1 A_1 e_1 > 0, \quad \zeta_1 A_2 e_2 > 0, \tag{4.28d}$$

$$\zeta_2 B_1 e_1 > 0, \quad \zeta_2 B_2 e_2 > 0, \tag{4.28e}$$

where

$$e_1 e_2 < 0. \tag{4.28f}$$

By considering Eq. (4.28f), Eqs. (4.28d) and (4.28e) lead to the relation given by Eq. (4.28c).

After Eq. (4.23) is substituted into Eq. (4.20) for $n=1$ and $i\neq j$, if Eqs. (3.18b), (4.27), and (4.28b) are considered with $\breve{D}_{ij}^1$ expressed by Eq. (4.22a), a formula for estimating ζ_2 can be obtained as

$$\zeta_2 = -\frac{1}{18\phi}\frac{I_3}{I_1}\left(\frac{\alpha_0^2}{\sigma_1}\right)^{3/2}\frac{\sigma_1^4}{e_1}\left(\frac{|e_1|}{e}\right)^3\left(\frac{|e_2|}{|e_1|}\right)^{5/2}$$
$$\times\left[\left(\tau\frac{(2-a_1)(2-a_2)}{(2-\tau a_1)(2-\tau a_2)}\frac{A_1}{B_1}\right)^{1/2} - \frac{I_2 I_3}{I_1 I_4}\left(\tau\frac{(2-a_1)(2-a_2)}{(2-\tau a_1)(2-\tau a_2)}\frac{B_1}{A_1}\right)^{1/2}\right]^{-1}, \quad \text{for } \ \breve{a}=\sigma_1, \tag{4.29a}$$

where

$$\phi \equiv \frac{\pi}{6}\sigma_1^3 \rho_1. \tag{4.29b}$$

2. A formula for estimating a_1, a_2, and τ

If $\breve{D}_{ij}^2$ expressed by Eq. (4.21a) are considered, products $\breve{D}_{ii}^1 \breve{D}_{i'i}^1$ estimated by substituting $\breve{D}_{ij}^2$ into Eq. (4.24) can obtain the ratio $\breve{D}_{11}^1 \breve{D}_{21}^1/\breve{D}_{22}^1 \breve{D}_{12}^1$ as

$$\frac{\breve{D}_{11}^1 \breve{D}_{21}^1}{\breve{D}_{22}^1 \breve{D}_{12}^1} = \frac{e_1}{e_2}\frac{(2-\tau a_1)(2-a_1)a_2}{(2-\tau a_2)(2-a_2)a_1}.$$

If $\breve{D}_{ij}^1$ expressed by Eq. (4.22a) is substituted into the above, a formula including only three coefficients (a_1, a_2, τ) can be obtained as

$$-I\frac{I_1 I_3}{I_2 I_4} = \frac{a_2(2-a_1)[2-(1-4RR')\tau a_1]}{a_1(2-\tau a_2)[2-(1-4RR')a_2]}, \tag{4.30a}$$

where

$$R \equiv \frac{\frac{z_2}{z_1}}{\frac{z_2}{z_1}+1}, \tag{4.30b}$$

$$R' \equiv \frac{1}{\frac{z_2}{z_1}+1}. \quad (4.30c)$$

By modifying Eq. (4.28b) with the substitutions of Eqs. (4.22b)–(4.22e), a formula can be obtained as

$$\frac{(2-a_1)[2-(1-4RR')\tau a_1]}{(2-\tau a_1)[2-(1-4RR')a_1]} = \frac{(2-\tau a_2)[2-(1-4RR')a_2]}{(2-a_2)[2-(1-4RR')\tau a_2]}.$$

To derive Eq. (4.30a), this relation has been used with Eqs. (4.22b)–(4.22e). Moreover, the relation $|I|=1$ is required for $|A_2/B_1| \equiv IA_2/B_1$ in order to obtain Eq. (4.30a). If the relations given by Eqs. (4.28a)–(4.28f) are considered, the relation $I(I_1I_3/I_2I_4)=1$ can be found.

Thus, the three coefficients a_1, a_2, and τ are restricted by Eq. (4.28b), so that if the restriction is considered in Eq. (4.30a), a formula for estimating the three coefficients (a_1,a_2,τ) can be obtained as

$$a_2(2-\tau a_1)[2-(1-4RR')a_1] + a_1(2-a_2)[2-(1-4RR')\tau a_2]=0. \quad (4.31)$$

Equation (4.31) does not include factors concerning temperature, density, and charge. This is a remarkable fact, since $\breve{D}^1_{ij}$ and $\breve{D}^2_{ij}$ are composed of a_1, a_2, and τ as shown by Eqs. (4.21a)–(4.22f).

V. MEAN SIZE OF PHYSICAL CLUSTERS

A. Cluster size for a finite value of κ^{-1}

The equilibrium number n_s of physical clusters consisting of s particles can be related to the pair connectedness P_{ij}, according to the formula given by Coniglio, DeAngelis, and Foriani [11], as

$$\sum_{2\leq s} s(s-1)n_s = \sum_{i=1}^{2}\sum_{j=1}^{2} \rho_i\rho_j \int_V\int_V P_{ij}(\mathbf{r}_i,\mathbf{r}_j)d\mathbf{r}_i d\mathbf{r}_j. \quad (5.1)$$

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

$$\rho_i = \frac{1}{V}p(i)\sum_s sn_s. \quad (5.2)$$

Since the mean physical cluster size S is given by $S=(\Sigma_s s^2 n_s)/(\Sigma_s s n_s)$, the substitution of Eqs. (5.1) and (5.2) into this formula results in

$$S = 1+\left(\sum_{k=1}^{2}\rho_k\right)^{-1}\sum_{i=1}^{2}\sum_{j=1}^{2}\rho_i\rho_j\int P_{ij}(r)d\mathbf{r}. \quad (5.3)$$

On the other hand, the Fourier transform of Eq. (2.4) is given as

$$\sum_{k=1}^{2}[\delta_{ik}+(\rho_i\rho_k)^{1/2}\tilde{P}_{ik}(k)][\delta_{kj}-(\rho_k\rho_j)^{1/2}\tilde{C}_{kj}(k)] = \delta_{ij}, \quad \text{for } |\mathbf{k}|=k, \quad (5.4)$$

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

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

so that Eq. (5.4) results in

$$\delta_{ij}+(\rho_i\rho_j)^{1/2}\tilde{P}_{ij}(k) = \sum_{k=1}^{2}\tilde{Q}^{-1}_{ki}(-k)\tilde{Q}^{-1}_{kj}(k). \quad (5.5)$$

Thus, Eq. (5.5) results in

$$\sum_{k=1}^{2}\tilde{Q}^{-1}_{ki}(0)\tilde{Q}^{-1}_{kj}(0) = \delta_{ij}+(\rho_i\rho_j)^{1/2}\int P_{ij}(r)d\mathbf{r}. \quad (5.6)$$

Ultimately, the substitution of Eq. (5.6) into Eq. (5.3) results in

$$S = \sum_{i=1}^{2}\left[\sum_{j=1}^{2}\left(\sum_{k=1}^{2}\frac{\rho_k}{\rho_i}\right)^{-1/2}\tilde{Q}^{-1}_{ij}(0)\right]^2. \quad (5.7a)$$

Therefore, percolation is generated if $\tilde{Q}^{-1}_{ij}(0)$ reaches infinity.

According to the comparison between Eqs. (4.3) and (4.8), the relation between $\tilde{Q}_{ij}(0)$ and $\hat{Q}_{ij}(0)$ is given as

$$\tilde{Q}_{ij}(0) = \delta_{ij}-(\rho_i\rho_j)^{1/2}\hat{Q}_{ij}(0). \quad (5.7b)$$

If Eq. (5.7b) is used, $\tilde{Q}^{-1}_{ij}(0)$ is expressed as

$$\begin{pmatrix} \tilde{Q}^{-1}_{11}(0) & \tilde{Q}^{-1}_{12}(0) \\ \tilde{Q}^{-1}_{21}(0) & \tilde{Q}^{-1}_{22}(0) \end{pmatrix} = [z_n \det|\tilde{Q}_{ij}(0)|]^{-1} z_n \times \begin{pmatrix} 1-\rho_2\hat{Q}_{22}(0) & \sqrt{\rho_1\rho_2}\hat{Q}_{12}(0) \\ \sqrt{\rho_2\rho_1}\hat{Q}_{21}(0) & 1-\rho_1\hat{Q}_{11}(0) \end{pmatrix}, \quad (5.7c)$$

where

$$\det|\tilde{Q}_{ij}(0)| \equiv 1-\rho_1\hat{Q}_{11}(0)-\rho_2\hat{Q}_{22}(0)+\rho_1\rho_2\hat{Q}_{11}(0)\hat{Q}_{22}(0) - \rho_1\rho_2\hat{Q}_{12}(0)\hat{Q}_{21}(0). \quad (5.7d)$$

If Eq. (4.8) is used, $\hat{Q}_{ij}(0)$ can be derived as

$$\hat{Q}_{ij}(0)=\sum_{m=1}^{2}\left\{e^{-z_m\sigma_{ji}}\breve{D}_{ij}^{m}\left(\frac{1}{z_m}+\sigma_i\right)+\sum_{k=1}^{2}\frac{2\pi\rho_k}{z_m}\hat{P}_{ik}(z_m)\breve{D}_{kj}^{m}\times\left[\frac{e^{-z_m\lambda_{ji}}}{z_m}-e^{-z_m\sigma_{ji}}\left(\frac{1}{z_m}+\sigma_i\right)\right]\right\}. \tag{5.8}$$

B. Percolation threshold for $|\kappa|\ll 1$

1. Restriction for values of a_1, a_2, and τ

Furthermore, if $|z_n|\ll 1$ for $|\kappa|\ll 1$ is considered, $\hat{Q}_{ij}(0)$ given by Eq. (5.8) can be approximated as

$$\hat{Q}_{ij}(0)=\sigma_i\sum_{m=1}^{2}\hat{q}_{ij}^{m}+\sum_{m=1}^{2}\frac{1}{z_m}\breve{D}_{ij}^{m}, \tag{5.9a}$$

where

$$\hat{q}_{ij}^{m}\equiv\breve{D}_{ij}^{m}+\pi\sigma_i\sum_{k=1}^{2}\rho_k\hat{P}_{ik}(z_m)\breve{D}_{kj}^{m}. \tag{5.9b}$$

Although the behavior of $\hat{Q}_{ij}(0)$ for $|\kappa|\ll 1$ is represented by Eq. (5.9a), the divergence of $\det|\tilde{Q}_{ij}(0)|$ for $|\kappa|\ll 1$ can be avoided. The restriction required for avoiding this divergence can be found using Eqs. (5.7d) and (5.9a) as

$$\begin{vmatrix}\sum_{m=1}^{2}\frac{1}{z_m}\breve{D}_{11}^{m} & \sum_{m=1}^{2}\frac{1}{z_m}\breve{D}_{12}^{m}\\ \sum_{m=1}^{2}\frac{1}{z_m}\breve{D}_{21}^{m} & \sum_{m=1}^{2}\frac{1}{z_m}\breve{D}_{22}^{m}\end{vmatrix}=0. \tag{5.10}$$

If Eq. (4.21a) and Eqs. (4.22a)–(4.22e) are substituted into Eq. (5.10), the formula for estimating the three coefficients (a_1,a_2,τ) can be obtained as

$$(2-a_2)[2-(1-2R')\tau a_2][2-(1-4RR')\tau a_1]\times[2-(1-2R')a_1]+(2-\tau a_2)[2-(1-2R')a_2]\times[2-(1-4RR')a_1][2-(1-2R')\tau a_1]=0. \tag{5.11}$$

To obtain Eq. (5.11), the relation $I'(I_1I_3/I_2I_4)=-1$ is required. Here, I' is defined as $|A_1/B_1|\equiv I'A_1/B_1$. If the relation given by Eqs. (4.28a)–(4.28f) is considered, the relation $I'(I_1I_3/I_2I_4)=-1$ can be found. Equation (5.11) is used with Eq. (4.31) for estimating a_1, a_2, and τ.

Equation (5.11) does not include factors concerning temperature, density, and charge. This is similar to Eq. (4.31) and is a remarkable fact. In addition, $\breve{D}_{ij}^{1}$ and $\breve{D}_{ij}^{2}$ are composed of a_1, a_2, and τ as given by Eqs. (4.21) and (4.22).

2. Percolation threshold

If the relations given by Eq. (5.7d) and Eq. (5.10) are considered, the factor $z_n\det|\tilde{Q}_{ij}(0)|$ found in Eq. (5.7c) can be approximated for $|\kappa|\ll 1$ as

$$z_n\det|\tilde{Q}_{ij}(0)|=-\sum_{m=1}^{2}\left(\rho_1\breve{D}_{11}^{m}\frac{z_n}{z_m}+\rho_2\breve{D}_{22}^{m}\frac{z_n}{z_m}\right)+\rho_1\rho_2\sum_{m=1}^{2}\sum_{m'=1}^{2}\left(\sigma_1\hat{q}_{11}^{m}\frac{z_n}{z_{m'}}\breve{D}_{22}^{m'}+\frac{z_n}{z_m}\breve{D}_{11}^{m}\sigma_2\hat{q}_{22}^{m'}-\sigma_1\hat{q}_{12}^{m}\frac{z_n}{z_{m'}}\breve{D}_{21}^{m'}-\frac{z_n}{z_m}\breve{D}_{12}^{m}\sigma_2\hat{q}_{21}^{m'}\right). \tag{5.12}$$

If $z_n\det|\tilde{Q}_{ij}(0)|$ reaches zero under a certain condition, then, $\tilde{Q}_{ij}^{-1}(0)$ diverges to infinity. This means that the mean physical cluster size S given by Eq. (5.7a) diverges to infinity. Therefore, the percolation threshold should be estimated as particular states at which $z_n\det|\tilde{Q}_{ij}(0)|=0$ is satisfied. Thus, a requirement for the percolation threshold can be obtained from Eq. (5.12) as

$$\begin{aligned}&\rho_1\breve{D}_{11}^{1}+\rho_2\breve{D}_{22}^{1}+\frac{z_1}{z_2}(\rho_1\breve{D}_{11}^{2}+\rho_2\breve{D}_{22}^{2})\\&-\rho_1\rho_2\sum_{m=1}^{2}\sum_{k=1}^{2}[\sigma_1\delta_{1k}+\pi\sigma_1^2\rho_k\hat{P}_{1k}(z_m)]\\&\times\left(\breve{D}_{k1}^{m}\breve{D}_{22}^{1}+\frac{z_1}{z_2}\breve{D}_{k1}^{m}\breve{D}_{22}^{2}-\breve{D}_{k2}^{m}\breve{D}_{21}^{1}-\frac{z_1}{z_2}\breve{D}_{k2}^{m}\breve{D}_{21}^{2}\right)\\&-\rho_1\rho_2\sum_{m=1}^{2}\sum_{k=1}^{2}[\sigma_2\delta_{2k}+\pi\sigma_2^2\rho_k\hat{P}_{2k}(z_m)]\\&\times\left(\breve{D}_{k2}^{m}\breve{D}_{11}^{1}+\frac{z_1}{z_2}\breve{D}_{k2}^{m}\breve{D}_{11}^{2}-\breve{D}_{k1}^{m}\breve{D}_{12}^{1}-\frac{z_1}{z_2}\breve{D}_{k1}^{m}\breve{D}_{12}^{2}\right)=0.\end{aligned} \tag{5.13}$$

Here, Eq. (5.9b) defìnding $\hat{q}_{ij}^{m}$ is considered to derived Eq. (5.13).

VI. SPECIFIC IONIC FLUIDS

A. Fluid composed of point charges and sized particles

1. Formulas for evaluating the percolation threshold

Percolation in an ionic fluid composed of point charges and sized particles can be estimated somewhat simply. To evaluate the percolation threshold, the coefficients expressed as $\hat{P}_{11}(z_1)$, $\hat{P}_{12}(z_1)$, and $\hat{P}_{21}(z_1)$ in Eq. (4.16) must be evaluated. In an ionic fluid, the evaluation of these coefficients can be somewhat simplified.

By considering $\sigma_1\neq 0$ and $\sigma_2=0$ for the ionic fluid, Eq. (4.16) for $i=1$ and $j=1$ results in a formula including $\hat{P}_{11}$ and $\hat{P}_{12}$ as

$$\frac{1}{\breve{T}}\frac{1}{\sqrt{\phi}}=-\left(\frac{\phi}{\sigma_1^2}\hat{P}_{12}\right)+\breve{S}\left(\frac{\phi}{\sigma_1^2}\hat{P}_{11}\right)+\frac{\breve{S}}{144}\left(\frac{\phi}{\sigma_1^2}\hat{P}_{11}\right)^{-1}+\frac{\breve{S}}{6}, \tag{6.1a}$$

where

$$\check{S}\equiv \frac{e_2}{e_1}\frac{1+U(a_1)}{1+U(\tau a_1)}\frac{\check{D}_{11}^1}{\check{D}_{21}^1}, \tag{6.1b}$$

and

$$\check{T}\equiv \frac{36}{\pi}\frac{e_1}{e_2}[1+U(\tau a_1)]I_3\sqrt{\frac{\zeta_2}{\sigma_1^4}B_1 e_1\phi}. \tag{6.1c}$$

In the above, the expression given by Eq. (4.17) is considered. To obtain the expression in Eq. (6.1a), $\check{D}_{ij}^2$ expressed by Eq. (4.21a) and $\check{D}_{ij}^1$ expressed by Eq. (4.22a) have been used with the electroneutrality condition $e_1\rho_1+e_2\rho_2=0$ and the volume fraction ϕ defined by Eq. (4.29b). In addition, ϕ should be of a positive value, so that I_3 in Eq. (6.1c) can be determined.

For an ionic fluid, the difference between Eq. (4.16) for $i=1$ and $j=2$, and Eq. (4.16) for $i=2$ and $j=1$ can be simplified by considering $\sigma_1\neq 0$, $\sigma_2=0$, and $\hat{P}_{12}-\hat{P}_{21}=0$ for $|\kappa|\ll 1$. As a result, the difference is written as

$$\frac{1}{2}(\check{D}_{12}^1-\check{D}_{21}^1)+\frac{1}{2}[U(a_2)\check{D}_{12}^1-U(\tau a_1)\check{D}_{21}^1]-2\pi\rho_1\sigma_1\check{D}_{11}^1 \times[1+U(a_1)]\hat{P}_{12}-2\pi^2\rho_1\rho_2\sigma_1^2\check{D}_{21}^1[1+U(\tau a_1)] \times\hat{P}_{12}\hat{P}_{12}+\{2\pi\rho_1\sigma_1\check{D}_{12}^1[1+U(a_2)]+2\pi^2\rho_1\sigma_1^2 \times\{\rho_2\check{D}_{22}^1[1+U(\tau a_2)]-\rho_1\check{D}_{11}^1 \times[1+U(a_1)]\}\hat{P}_{12}\}\hat{P}_{11}+2\pi^2\rho_1^2\sigma_1^2\check{D}_{12}^1 \times[1+U(a_2)]\hat{P}_{11}\hat{P}_{11}=0. \tag{6.2}$$

To obtain the expression in Eq. (6.2), $\check{D}_{ij}^2$ expressed by Eq. (4.21a) has been used. If the volume fraction ϕ and the electroneutrality condition $e_1\rho_1+e_2\rho_2=0$ are considered, Eq. (6.2) results in

$$-\frac{1}{144}\left(1-\frac{1+U(\tau a_1)}{1+U(a_2)}\frac{\check{D}_{21}^1}{\check{D}_{12}^1}\right)-\left(\frac{\phi}{\sigma_1^2}\hat{P}_{11}\right)^2-\frac{1}{6}\left(\frac{\phi}{\sigma_1^2}\hat{P}_{11}\right) +\check{U}\left(\frac{\phi}{\sigma_1^2}\hat{P}_{11}\right)\left(\frac{\phi}{\sigma_1^2}\hat{P}_{12}\right)+\frac{1}{6}\check{V}\left(\frac{\phi}{\sigma_1^2}\hat{P}_{12}\right) -\frac{e_1}{e_2}\frac{1+U(\tau a_1)}{1+U(a_2)}\frac{\check{D}_{21}^1}{\check{D}_{12}^1}\left(\frac{\phi}{\sigma_1^2}\hat{P}_{12}\right)^2=0, \tag{6.3a}$$

where

$$\check{U}\equiv \frac{e_1}{e_2}\frac{1+U(\tau a_2)}{1+U(a_2)}\frac{\check{D}_{22}^1}{\check{D}_{12}^1}+\frac{1+U(a_1)}{1+U(a_2)}\frac{\check{D}_{11}^1}{\check{D}_{12}^1}, \tag{6.3b}$$

and

$$\check{V}\equiv \frac{1+U(a_1)}{1+U(a_2)}\frac{\check{D}_{11}^1}{\check{D}_{12}^1}. \tag{6.3c}$$

Equations (6.1a) and (6.3a) are used to evaluate the values of $\hat{P}_{11}$ and $\hat{P}_{12}$. In Eqs. (6.1a) and (6.3a), the coefficients $\check{S}$, $\check{T}$, $\check{U}$, and $\check{V}$ are independent of temperature, density, and charge, if $|e_1|$ equals $|e_2|$.

In addition, the relation expressed by Eq. (6.3a) should be satisfied, even when the value of ϕ is sufficiently small. This requires that the first term on the left-hand side of Eq. (6.3a) is zero. This fact leads to the restriction for the coefficients (a_1,a_2,τ) as

$$2-(1-2R)a_2-[2-(1-2R)\tau a_1]\frac{I_3}{I_1} \times\left[\frac{e_2}{e_1}\frac{(2-\tau a_2)[2-(1-4RR')a_2]}{\tau(2-a_1)[2-(1-4RR')\tau a_1]}\right]^{1/2}=0, \tag{6.4}$$

where $\check{D}_{ij}^1$ expressed by Eq. (4.22a) has been used in the derivation. Equation (6.4) is used with Eqs. (4.31) and (5.11) for estimating a_1, a_2, and τ.

Equation (6.4) does not include factors concerning temperature and density. Basically, such a feature of Eq. (6.4) is similar to that of Eq. (4.31) and (5.11), except for the charge. Equation (6.4) with Eqs. (4.31) and (5.11) indicates that a_1, a_2, and τ are independent of temperature, density, and charge, if $|e_1|$ equals $|e_2|$. The ratios $\check{D}_{ij}^1/\check{D}_{kl}^1$ can also be independent of temperature, density, and charge, if $|e_1|$ equals $|e_2|$. According to Eq. (4.22a), the ratios are composed of coefficients a_1, a_2, and τ.

2. The relation between $\hat{P}_{11}$ and $\hat{P}_{12}$ at the percolation threshold

The relation between $\hat{P}_{11}$ and $\hat{P}_{12}$ at the percolation threshold can be derived from the substitution of $\check{D}_{ij}^2$ expressed by Eq. (4.21a) and $\check{D}_{ij}^1$ expressed by Eq. (4.22a) into Eq. (5.13). Thus, the obtained relation is

$$\check{W}\frac{1}{\sqrt{\phi}}=-\check{X}-6\check{X}\left(\frac{\phi}{\sigma_1^2}\hat{P}_{11}\right)-6\check{Y}\left(\frac{\phi}{\sigma_1^2}\hat{P}_{12}\right), \tag{6.5a}$$

where

$$\check{W}\equiv \frac{\pi}{6}\frac{e_2}{e_1}\frac{1}{I_4}\left(\frac{\zeta_2}{\sigma_1^4}B_2e_2\phi\right)^{-1/2}\left[1+\frac{z_1}{z_2}U(a_1)\right] \times\left[1-\frac{e_1}{e_2}\frac{1+\frac{z_1}{z_2}U(\tau a_2)}{1+\frac{z_1}{z_2}U(a_1)}\frac{I_4}{I_1}\sqrt{\frac{\zeta_2B_2e_2}{\zeta_1A_1e_1}}\right], \tag{6.5b}$$

$$\check{X}\equiv[1+U(a_1)]\left[1+\frac{z_1}{z_2}U(\tau a_2)\right]+[1+U(a_2)] \times\left[1+\frac{z_1}{z_2}U(\tau a_1)\right]\frac{B_1}{A_1}, \tag{6.5c}$$

and

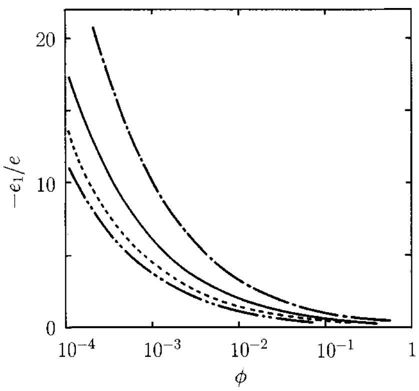

FIG. 1. Percolation thresholds for ionic fluids satisfying the conditions $\sigma_2=0$ and $4\pi\beta e^2/\epsilon=8.79\times10^{-7}$ cm. Each curve represents a percolation threshold. Percolation takes place under the condition specified by the point belonging to the upper region of each curve. The dot-dash line represents $\sigma_1=1\times10^{-6}$ cm and $e_2/e=1$, the solid line $\sigma_1=5\times10^{-7}$ cm and $e_2/e=1$, the dashed line $\sigma_1=5\times10^{-7}$ cm and $e_2/e=2$, and the dot-dot-dash line $\sigma_1=5\times10^{-7}$ cm and $e_2/e=3$. For the evaluations, ratios concerning I_1, I_2, I_3, and I_4 are determined as $I_2I_3/I_1I_4=1$, $I_2/I_1=-1$, $I_3/I_1=-1$, and $I_4/I_1=1$. In addition, ϕ is dimensionless.

$$\check{Y}\equiv-\frac{e_1}{e_2}\left(1-\frac{z_1}{z_2}\right)[U(\tau a_1)-U(\tau a_2)]\frac{I_2}{I_1}\sqrt{\frac{A_2e_2}{A_1e_1}}. \tag{6.5d}$$

To obtain the expression in Eq. (6.5a), $e_1\rho_1+e_2\rho_2=0$, $\sigma_1\neq0$, and $\sigma_2=0$ have been considered, with ϕ defined by Eq. (4.29b). The coefficients $\check{X}$ and $\check{Y}$ in Eq. (6.5a) are independent of temperature, density, and charge, if $|e_1|$ equals $|e_2|$. In addition, ϕ should be of a positive value, so that I_4 in Eq. (6.5b) can be determined.

The values of $(\phi/\sigma_1^2)\hat{P}_{11}$ and $(\phi/\sigma_1^2)\hat{P}_{12}$ at the percolation threshold are evaluated using Eqs. (6.1a), (6.3a), and (6.5a). These equations indicate that the factors $(\phi/\sigma_1^2)\hat{P}_{11}$ and $(\phi/\sigma_1^2)\hat{P}_{12}$ at the percolation threshold are independent of σ_1 and ϕ.

3. Evaluation of the percolation threshold

Using Eq. (6.5a) with Eqs. (6.1a) and (6.3a), the values of ϕ, $\hat{P}_{11}$, and $\hat{P}_{12}$ at the percolation threshold are determined. The percolation thresholds shown in Fig. 1 are evaluated using these equations. The coefficients a_1, a_2, and τ are evaluated using Eq. (6.4) with Eqs. (4.31) and (5.11).

The curves shown in Fig. 1 demonstrate that percolation is generated at a smaller value of ϕ if the value of $|e_2|$ is larger. On the contrary, percolation is generated at a larger value of ϕ if the electric field on the surface of the particle corresponding to $i=1$ is weaker. Such phenomena mean that developed dense regions can be formed in an ionic fluid containing more highly charged particles, even if the density of the particles is lower. If the ionic fluid is composed of smaller particles, percolation can be generated at a smaller value of ϕ, since the electric field on the surface of each particle is strong.

The evaluation of the percolation threshold includes the contribution of the expression for closure. The relation between the closure expression and the percolation threshold should be considered, although it has already been briefly discussed in Sec. III D 2.

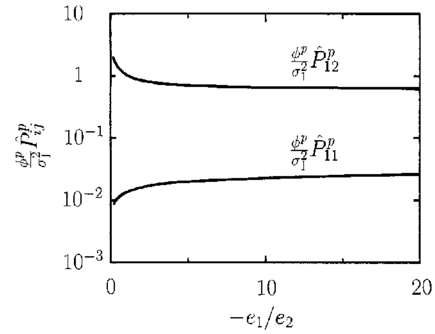

FIG. 2. Correlations between 1-1 particles and between 1-2 particles in an ionic fluid satisfying the conditions $\sigma_1\neq0$, $\sigma_2=0$, and $4\pi\beta e^2/\epsilon=8.79\times10^{-7}$ cm. For the evaluations, ratios concerning I_1, I_2, I_3, and I_4 are determined as $I_2I_3/I_1I_4=1$, $I_2/I_1=-1$, $I_3/I_1=-1$, and $I_4/I_1=1$. In addition, $(\phi^p/\sigma_1^2)\hat{P}^p_{ij}$ is dimensionless.

The decay of closure expressed by Eq. (3.14a) depends on $r^{-3/2}$. If the closure is expressed by the form of Eq. (3.18a), then the decay of closure depends on $r^{-1}\sigma_1^{-1/2}\exp(-\frac{3}{2}\kappa r)$, which can be determined using the maximum diameter σ_1 of the distributed particles. The decay of closure expressed by Eq. (3.15) depends on $r^{-5/2}$. If the closure is expressed by the form of Eq. (3.18a), the decay of closure then depends on $r^{-1}\sigma_1^{-3/2}\exp(-\frac{5}{2}\kappa r)$. Equation (3.18a) is a simplified closure scheme for solving the integral equation analytically.

Equation (3.18a) provides an overestimation of the long-range contribution of the closure, if κ is regarded as zero. If κ is not zero, it is possible that Eq. (3.18a) for $|\kappa|\ll1$ provides an overestimation of the decay of closure. The effect of the former can result in an overestimation of e_1 and ϕ at the percolation threshold. Evaluation under the condition related to the latter can underestimate e_1 and ϕ at the percolation threshold. These are considered on the basis of a previous study of Yukawa fluids [12].

Equation (4.16) containing the coefficients z_n is an approximation derived by use of Eq. (3.18a) for both $|\kappa|\ll1$ and $\kappa\neq0$. Equation (4.20) also is an approximation derived from Eq. (3.18a) for both $|\kappa|\ll1$ and $\kappa\neq0$. Therefore, Eq. (4.20) contains the coefficients z_n. All the formulas derived from Eqs. (4.16) and (4.20) do not depend on the magnitude of κ, although Eqs. (4.16) and (4.20) contain the coefficients z_n. For the estimate of percolation, the magnitude of κ is not required, if the condition $|\kappa|\ll1$ is satisfied. This is an advantage for simplifying the estimation.

In contrast, the degree of overestimation for the decay of closure cannot be determined, when the magnitude of κ is unknown. It is not clear whether the percolation thresholds expressed in Fig. 1 can provide a quantitative estimation. Fortunately, it is expected that the pattern of the curves represented in Fig. 1 can provide a fair estimate. This is supported by a previous study [12].

The behavior of $(\phi^p/\sigma_1^2)\hat{P}^p_{11}$ and $(\phi^p/\sigma_1^2)\hat{P}^p_{12}$ in Fig. 2 is evaluated from Eqs. (6.1a), (6.3a), and (6.5a). Here, the values of $\hat{P}_{11}$ and $\hat{P}_{12}$ at the percolation threshold are expressed as $\hat{P}^p_{11}$ and $\hat{P}^p_{12}$, respectively. The expression ϕ^p is the value of ϕ at the percolation threshold. According to Fig. 2, $(\phi^p/\sigma_1^2)\hat{P}_{12}^p$ is much larger than $(\phi^p/\sigma_1^2)\hat{P}_{11}^p$.

The coefficients $\hat{P}_{11}$ and $\hat{P}_{12}$ found in Eqs. (6.1a), (6.3a), and (6.5a) are quantities corresponding to the integral given in Eq. (4.6b). Hence, the magnitude of $\hat{P}_{11}$ depends on the probability that particles correspoding to $i=1$ belong to a cluster. The magnitude of $\hat{P}_{12}$ depends on the probability that a particle correspoding to $i=1$ and a particle correspoding to $i=2$ belong to a cluster.

Thus, it is possible that the magnitude of $\hat{P}_{11}$ is large, if the probability is high that a particle corresponding to $i=1$ is located near another particle corresponding to $i=1$. Similarly, it is possible that the magnitude of $\hat{P}_{12}$ is large, if the probability is high that a particle corresponding to $i=2$ is located near a particle corresponding to $i=1$.

These interpretations for $\hat{P}_{11}$ and $\hat{P}_{12}$ can result in an additional interpretation based on the relation $(\phi^p/\sigma_1^2)\hat{P}_{11}^p \ll (\phi^p/\sigma_1^2)\hat{P}_{12}^p$ expressed by Fig. 2. Namely, a pair of 1-2 particles (a positive-negative particle pair) can be regarded as a unit, which constitutes a dense area in the ionic fluid. According to this interpretation, it is inferred that the thermodynamics based on the Bjerrum theory can provide a satisfactory description.

As found in Fig. 1, an increase in $|e_1|$ results in a decrease in ϕ^p. Either $(\phi^p/\sigma_1^2)\hat{P}_{11}^p$ or $(\phi^p/\sigma_1^2)\hat{P}_{12}^p$ continue to be sufficiently constant for an increase in $|e_1|$. Hence, Fig. 2 indicates that the increase in $|e_1|$ results in increases in both $\hat{P}_{11}^p$ and $\hat{P}_{12}^p$. An increase in $|e_2|$ also results in a decrease in ϕ^p as shown in Fig. 1, even when $|e_1|$ has a constant value. For an increase in $|e_2|$, both $\hat{P}_{11}^p$ and $\hat{P}_{12}^p$ increase also. The behavior of $\hat{P}_{11}^p$ and $\hat{P}_{12}^p$ reveals that the generation of a nonuniform distribution of particles can be enhanced by an increase in the charge on each particle.

B. The percolation in a fluid consisting of point charges

When an ionic fluid system is composed of only point charges, $\sigma_1=0$ and $\sigma_2=0$, so that Eq. (5.13) for estimating the percolation threshold results in an equation expressed as

$$0=\rho_1\left[1+\frac{z_1}{z_2}U(a_1)\right]I_1\sqrt{\zeta_1 A_1 e_1}\times\left[1-\frac{e_1}{e_2}\frac{1+\frac{z_1}{z_2}U(\tau a_2)}{1+\frac{z_1}{z_2}U(a_1)}\frac{I_4}{I_1}\sqrt{\frac{\zeta_2 B_2 e_2}{\zeta_1 A_1 e_1}}\right]. \quad (6.6)$$

To obtain Eq. (6.6), Eqs. (4.21a) and (4.22a) are considered with the condition $e_1\rho_1+e_2\rho_2=0$. The percolation threshold in the fluid can be evaluated using Eq. (6.6) with Eqs. (6.1a) and (6.3a).

Equation (6.6) does not have the factors concerning temperature, density, and charge if $|e_1|$ equals $|e_2|$, since ρ_1 and $\sqrt{\zeta_1 A_1 e_1}$ can be eliminated from Eq. (6.6). The percolation threshold for $|e_1|=|e_2|$ is then independent of temperature, density, and charge.

This result is reasonable. It is considered that the pair potential $u_{12}(r)$ can diverge toward $-\infty$ for $T=0$, since point charges in a classical fluid can be extremely close to each other. On the other hand, the relative kinetic energy E_{12} cannot exceed $|u_{12}(r)|$ for a finite temperature. Thus, it is inferred that the condition $E_{12}<|u_{12}(r)|$ is always satisfied.

For $|e_1|\neq|e_2|$, the percolation threshold depends on e_1/e_2. This fact is unreasonable, since the percolation threshold is independent of temperature and density. It is considered that a defective result can be avoided if an improved expression for closure can be obtained and the integral equation can be solved with the use of it.

VII. FRACTAL STRUCTURE

In an ionic fluid, dense regions are generated, while the distribution of particles becomes nonuniform. Each dense region can be regarded as an ensemble of particles bound to each other by an attractive force. The dominant portion of particles distributed in a dense region can be particles constituting pairs linked by the attractive force. Particles constituting each pair should then satisfy the condition $E_{ij}+u_{ij}(r)\leqslant 0$.

A cluster of i particles characterized by $P_{ii}(r)$ is an ensemble of i particles bound to each other via j particles satisfying the condition $u_{ij}(r)<0$. Each pair in the ensemble then satisfies the condition $E_{ij}+u_{ij}(r)\leqslant 0$. It is expected that the structure of the cluster described by $P_{ii}(r)$ can provide a feature of the dense region structure. The pair connectedness $P_{ii}(r)$ can be estimated using Eqs. (3.6) and (3.15).

For a two component mixture, Eq. (3.6) is rewritten as

$$\beta u_{ii}(r)P_{ii}(r)=-C_{ii}^{+}(r). \quad (7.1)$$

If Eq. (3.15) for $r\gg 1$ is substituted into Eq. (7.1), then $P_{ii}(r)$ for $r\gg 1$ is estimated as

$$P_{ii}(r)=-\frac{22}{15\sqrt{\pi}}\frac{e_j\rho_j}{e_i\rho_i}(-\beta u_{ij}(r))^{3/2} \quad (i\neq j). \quad (7.2)$$

According to Eq. (7.2), the average distribution of i particles in a cluster decays as

$$P_{ii}(r)\sim r^{-\alpha}, \quad \alpha=1.5. \quad (7.3)$$

This means that the cluster has a fractal structure with the fractal dimension 1.5 $(=3-\alpha)$.

Thus, it is expected that the dense region formed in an ionic fluid has a fractal structure. In fact, a fractal structure with the fractal dimension 1.9 was found for a nonuniform colloidal suspension [10]. It is considered that the fractal dimension found in the present work is close to that for the nonuniform colloidal suspension.

According to Eq. (7.2), the dependence of $P_{ii}(r)$ on r can be independent of the sign of the charge. Therefore, the decay of the positive charge distribution in a cluster depends on $r^{-3/2}$, and the decay of the negative charge distribution in the cluster also depends on $r^{-3/2}$. Thus, each decay in the cluster has the same dependence on r. As a result, a large cluster having a fractal structure can be generated in the ionic fluid.

VIII. CONCLUSIONS

The nonuniform distribution of particles in an ionic fluid can be developed by increasing the charge on each particle. A bound state ''$E_{ij}+u_{ij}(r)\leqslant 0$'' between positive-negative particles can significantly contribute to the formation of dense regions in the ionic fluid.

This is supported by the relation $(\phi^p/\sigma_1^2)\hat{P}_{11}^p \ll (\phi^p/\sigma_1^2)\hat{P}_{12}^p$ given at the percolation threshold.

From this relation, it can be interpreted that the probability that 1-2 particles approach each other is much higher than the probability that 1-1 particles approach each other, even at the percolation threshold. According to this fact, a configuration of charged particles can agree with that of the Bjerrum theory.

Each dense region formed in the ionic fluid has a fractal structure with the fractal dimension 1.5. This fractal dimension is close to the known fractal dimension ($\sim$1.75) for the fractal structure resulting from cluster-cluster aggregation.

To solve the integral equation for the pair connectedness function, a closure scheme is required. The expression for closure given in the present work results in the overestimation of the long-range contribution of closure, if κ is regarded as zero. If $\kappa\neq 0$ is satisfied even for $|\kappa|\ll 1$, it is possible that the expression results in an overestimation of the decay of closure. The effect of the former can result in an overestimation of e_1 and ϕ at the percolation threshold. Evaluation under the condition related to the latter can underestimate e_1 and ϕ at the percolation threshold.

For percolation estimates in the present work, the magnitude of κ is not required, if $|\kappa|\ll 1$ is satisfied. This is an advantage for simplifying the estimate.

In contrast, the degree of overestimation for the decay of closure cannot be estimated, when the magnitude of κ is unknown. For this reason, it is not clear whether the percolation threshold given in the present work can be quantitatively estimated. It is expected, however, that the pattern of the curves representing the percolation threshold can provide a valid estimate.

ACKNOWLEDGMENT

The author would like to thank Professor Y. Hayashi for a careful reading of the manuscript.

[1] N. Bjerrum, K. Dan. Vidensk. Selsk. Mat. Fys. Medd. **7**, 1 (1926).
[2] A. Tani and D. Henderson, J. Chem. Phys. **79**, 2390 (1983); M. J. Gillan, Mol. Phys. **49**, 421 (1983); G. Stell, J. Stat. Phys. **78**, 197 (1995).
[3] M. E. Fisher, J. Stat. Phys. **75**, 1 (1994); Y. Levin and M. E. Fisher, Physica A **225**, 164 (1996); B. P. Lee and M. E. Fisher, Phys. Rev. Lett. **76**, 2906 (1996).
[4] T. L. Hill, *Statistical Mechanics* (Dover, New York, 1987).
[5] D. M. Zuckerman, M. E. Fisher, and B. P. Lee, Phys. Rev. E **56**, 6569 (1997).
[6] J. A. Given and G. Stell, J. Chem. Phys. **106**, 1195 (1997).
[7] D. R. Schreiber, M. C. P. de Lima, and K. S. Pitzer, J. Phys. Chem. **91**, 4087 (1987).
[8] A. Oleinikova and M. Bonetti, J. Chem. Phys. **104**, 3111 (1996).
[9] T. Vicsek, *Fractal Growth Phenomena* (World Scientific, New Jersey, 1992).
[10] M. Carpineti and M. Giglio, Phys. Rev. Lett. **68**, 3327 (1992).
[11] A. Coniglio, U. De Angelis, and A. Forlani, J. Phys. A **10**, 1123 (1977).
[12] T. Kaneko, Phys. Rev. E **58**, 5808 (1998).
[13] J. Xu and G. Stell, J. Chem. Phys. **89**, 1101 (1988).
[14] R. J. Baxter, J. Chem. Phys. **52**, 4559 (1970).
[15] M. Ginoza, J. Phys.: Condens. Matter **6**, 1439 (1994); L. Blum and J. S. Høye, J. Stat. Phys. **19**, 317 (1978).