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Percolation in fluid mixtures containing adhesive charged hard spheres

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Percolation in a fluid mixture system (FMS) containing adhesive charged hard spheres (ACHSs) and point charges can be analytically estimated by regarding the contact of an ACHS with another ACHS as the formation of directly connected bonds between the ACHSs. A feature of the percolation in the FMS can be determined via the phase diagrams displayed for the volume fraction ϕ of the ACHSs and the reciprocal ζ_{00}^{-1} of the strength of the adhesive interaction. In the ϕ-ζ_{00}^{-1} plane, the phase diagrams indicate that the region in which percolation is induced is less dominant than that in which phase separation is induced if the ACHSs are highly charged spheres.

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I. INTRODUCTION

Percolation behavior that contributes to macroscopic phenomena induced in fluids has been determined from various phenomena such as gelation [1], the thermodynamic and dynamic properties of liquid water [2], and the conductor-insulator transition in liquid metals [3]. The contribution of percolation behavior to the properties of a water-oil microemulsion (WOM) [4] can be recognized from several macroscopic phenomena. As such phenomena, the electrical conductivity of WOMs [5,6], the dynamic viscosity of WOMs [6], and the dielectric permitivity in WOMs [7] are remarkable. The generation of the gel phase due to the aggregation of ionic colloidal particles (ICPs) [8] can be regarded as percolation behavior in a fluid that contains particles having both electrostatic repulsion and short-ranged nonelectrostatic attraction.

Percolation behavior in a fluid consisting of particles may strongly depend on the characteristics of the interactions between the particles. If an interaction between the particles yields attraction, the formation of particle clusters can be enhanced. Depending on the characteristic of the attraction, which can determine microscopic structures such as the size and number of clusters, particular features of the fluid can be formed. According to the estimation of Hagen and Frenkel [9], the liquid phase of a fluid consisting of hard particles having an attractive Yukawa interaction is unstable when the range of the attractive part of the Yukawa potential is less than approximately one-sixth of the hard-core diameter.

The present interest, generated by the fluid behavior dependent on the characteristics of the interactions between the particles, is focused on percolation in a fluid containing hard particles having both electrostatic repulsion and short-ranged nonelectrostatic attraction. The present work is concerned with continuous percolation in a fluid mixture system (FMS) composed of adhesive charged hard spheres (ACHSs) and point charges. The ACHSs are charged spheres with an adhesive interaction that contributes to attraction in the immediate vicinity of their surfaces [10].

The stability of a dispersed state in a FMS, which contains ICPs, depends on several parameters such as the densities of the ICPs and small ionic species, the charge on each ICP, the charge carried by the small ionic species, and the strength of nonelectrostatical attraction between the ICPs. As is well known, the addition of small ionic species to an ionic colloidal system can cause the ICPs to aggregate [11]. If particular conditions are satisfied, the aggregation of the ICPs may induce the gel phase [8]. In order to obtain information concerning such aggregation, a FMS composed of ACHSs and point charges can be useful as a model system since the mathematical estimation relevant to the aggregation of ICPs can be easily carried out [12]. In the present work, a FMS is employed to obtain information on the aggregation that induces percolation.

When the estimated size of the physical clusters is required to obtain information of the percolation in a fluid composed of particles with particular properties, the concept of a physical cluster as introduced by Hill [13] plays an important role. Hill demonstrated that the contribution $\exp(-\beta u_{ij})$ of the i and j particles, due to the pair potential u_{ij}, to the grand partition function for a fluid system containing these particles can be divided into two parts [13]. One part $\exp(-\beta u_{ij}^{+})$ represents the portion dependent on u_{ij}^{+} contributing to the interaction between the i and j particles having relative kinetic energy not exceeding the magnitude of $-u_{ij}$ $(u_{ij}<0)$. Here u_{ij}^{+} is the effective potential between the i and j particles that form a bound pair. The other part is given by $\exp(-\beta u_{ij}^{*})$, being dependent on u_{ij}^{*} contributing to the interaction between the i and j particles that have relative kinetic energy exceeding the magnitude of $-u_{ij}$ $(u_{ij}<0)$. In this case, u_{ij}^{*} is the effective potential between the i and j particles that form an unbound pair. If u_{ij} is positive, u_{ij}^{*} is equivalent to u_{ij}. Then, u_{ij}^{+} is infinite. The coefficient β mentioned above is defined as $\beta=1/kT$, where T is the temperature and k the Boltzmann constant.

By introducing $\exp(-\beta u_{ij}^{+})$ and $\exp(-\beta u_{ij}^{*})$, the state of a bound pair of i and j particles can be distinguished from the state of an unbound pair of i and j particles in the grand partition function [13]. This indicates that, from the products of f functions corresponding to Mayer's mathematical clusters, particular products containing f^{+} functions [defined by

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the use of $\exp(-\beta u_{ij}^{+})$] can be extracted [14]. The particular products containing f^{+} functions can then represent physical clusters. Owing to this fact, the pair-correlation function $g_{ij}(r)$ can be expressed as the sum of the two contributions, as demonstrated by Coniglio, De Angelis, and Foriani [15]. One contribution is given by the pair-connectedness function $P_{ij}(\mathbf{r}_i,\mathbf{r}_j)$. This function is defined such that $\rho_i\rho_j P_{ij}(\mathbf{r}_i,\mathbf{r}_j)d\mathbf{r}_i d\mathbf{r}_j$ represents the probability that a particle in $d\mathbf{r}_i$ at $\mathbf{r}_i$ and another particle in $d\mathbf{r}_j$ at $\mathbf{r}_j$ simultaneously belong to the same cluster. The other contribution is given by the blocking function $D_{ij}(\mathbf{r}_i,\mathbf{r}_j)$. This function is defined such that $\rho_i\rho_j D_{ij}(\mathbf{r}_i,\mathbf{r}_j)d\mathbf{r}_i d\mathbf{r}_j$ represents the probability that a particle in $d\mathbf{r}_i$ at $\mathbf{r}_i$ and one in $d\mathbf{r}_j$ at $\mathbf{r}_j$ do not simultaneously belong to the same cluster.

For estimating percolation behavior induced in a fluid, the pair-connectedness function should be known. The pair-connectedness function satisfies the Ornstein-Zernike relation established by Coniglio, De Angelis, and Foriani [15]. Using the Percus-Yevick approximation (PYA) and the Wiener-Hopf factorization technique introduced in the work of Baxter [16], Chiew and Glandt [17] analytically estimated the percolation behavior described by the Ornstein-Zernike relation in the permeable and adhesive sphere systems. The formally exact closure for solving the Ornstein-Zernike relation has been derived by Stell [18].

When the distance between particles is within at least a certain range, particular microscopic behavior, for example, electron transfer and exited energy transfer, can significantly occur between the particles. The particular macroscopic behavior induced by the microscopic behavior mentioned above, such as the electric conductor-insulator transition in a fluid, can be simply regarded as the percolation behavior in a fluid composed of hard-core permeable-shell spheres [i.e., the penetrable concentric shell model (PCSM)] or that in a fluid composed of randomly centered spheres (RCSs), although it is assumed that no attraction exists between the particles.

DeSimone, Demoulini, and Stratt [19] analytically estimated the percolation behavior in PCSM fluid systems using the PYA. From Monte Carlo simulations of PCSM fluid systems, Sevick, Monson, and Otlino [20] revealed that the success of the PYA in determining the inverse mean cluster size could be regarded as quite satisfactory in view of the simplicity with which it can be applied to complex problems. In addition, an alternative approximation scheme, beyond the Percus-Yevick closure, was applied by Chiew and Stell [21] to study the percolation behavior in a one-component RCS fluid.

By regarding the attraction between particles as the contribution of a square-well potential, percolation behavior due to attraction has been studied. With the use of Monte Carlo simulations, Safran, Webman, and Grest [22] estimated the percolation behavior in square-well fluid systems. Employing the PYA, Netemeyer and Glandt [23] numerically determined the percolation threshold and the pair-connectedness function for a square-well fluid system. Chiew and Wang [24] determined the percolation thresholds and the pair-connectedness function for a square-well fluid from Monte Carlo simulations. They demonstrated, furthermore, on the basis of a comparison between the Monte Carlo data and the Percus-Yevick solution, that the percolation threshold derived from the PYA yielded fairly good estimates, except at low temperatures and high densities.

The adhesive potential can be described as an infinitely narrow and infinitely deep square-well potential. Using the PYA, Chiew and Glandt [17] analytically derived the percolation threshold for a fluid system containing hard spheres interacting with the contribution of the adhesive potential in the immediate vicinity of their surfaces. This fluid system is a system where the first-order phase transition can be induced, as shown by Baxter [10]. Seaton and Glandt [25] demonstrated that the percolation threshold evaluated by means of the PYA for a fluid with adhesive hard spheres agreed rather well with that evaluated by means of Monte Carlo simulations, except at extremely low densities and sufficiently high densities. Also, simulations of a fluid system based on a recent Monte Carlo algorithm were performed by Kranendonk and Frenkel [26].

Presently, it should be noted that a size monodisperse system consisting of equally sized adhesive hard spheres, when treated in an exact manner rather than with the PYA, does not have thermodynamically stable phases that possess practically physical meaning, as was demonstrated by Stell [27]. Fortunately, when such a system is treated by an approximation in which the singularity induced by the δ function can be avoided as in the PYA, it can be regarded as a useful model having thermodynamically adequate properties [10,26,28,29]. For the approximation, it has been shown that the system can undergo a gas-liquid transition [28] or a solid-liquid transition [30]. The approximation applied in the present work corresponds to the approximation mentioned above.

The pair potential, with a hard core and Yukawa tail, is more realistic than the square-well potential having a hard core. Using the pair potential and the mean-spherical approximation (MSA), the percolation behavior in fluids consisting of Yukawa hard spheres was examined by Xu and Stell [31]. These fluids do not have a stable liquid phase if the range of the attraction part of the Yukawa potential is sufficiently short ranged [9,32]. The gas-liquid transition then disappears in the fluids. The range of the attractive part of the pair potential between particles determines the stability of the liquid phase in a system (for example, either a molecular system [33] or colloidal systems [34]).

In contrast to the gas-liquid transition, a dense system of spherical particles with a short-ranged attractive interaction, due to either the Yukawa potential or the square-well potential, can undergo a first-order transition from a dense to a more expanded solid phase having the same structure [35]. Such a solid-solid transition at finite temperatures, however, cannot occur in a system composed of noncharged adhesive hard spheres of equal diameter, as predicted in the work of Stell [27]. Frenkel and his co-workers [35] revealed that at finite temperatures, the only stable phases in this system are the close-packed solid and the infinite-dilute gas. In the system, all other phases are metastable.

When the nonelectrostatic attraction between ICPs, contributing within a sufficiently short range compared to the diameter of the ICP, can no longer be ignored, the pair potential contributing to the interaction between the ICPs may introduce a complexity to the analytical estimation of percolation. The pair potential can then be given as the sum of the

Coulomb potential, the potential contributing to the nonelectrostatic attraction, and the hard-core potential. If the potential contributing to the nonelectrostatic attraction can be regarded as an adhesive potential, the complexity should be easily avoided. This is expected from the fact that the integral equation for the pair-correlation function $g_{ij}(\mathbf{r})$ in FMSs consisting of ACHSs can be analytically solved [36,37]. In order to analytically estimate percolation behavior in a system containing ICPs, it is possible that a FMS containing ACHSs that interact with an adhesive potential, a Coulomb potential, and a hard-core potential is a rather realistic model system, when the contribution of the nonelectrostatic attraction must be considered. It has been demonstrated that a system containing adhesive hard spheres could lack adequate thermodynamics [27]. Fortunately, the FMS could be a model with thermodynamically adequate properties since the FMS is treated by an approximation in which a singularity induced by the δ function can be avoided.

Percolation behavior in the multicomponent FMS must be estimated by solving the Ornstein-Zernike relation for the pair-connectedness function. The Ornstein-Zernike relation for this FMS was established by Chiew, Stell, and Glandt [38] while deriving the formally exact closure for this relation. Employing the PYA, they also analytically obtained the pair-connectedness function, mean cluster size, and percolation thresholds for both a FMS consisting of RCSs and one consisting of permeable spheres [38]. Wu and Chiew [39] studied the percolation in binary mixtures of RCSs, based on a selective particle-connectivity criterion. When, in the criterion, particles of different species are allowed to form directly connected bonds, the percolation densities differ considerably from those found in a simple percolation problem for a binary mixture of RCSs [39].

In the present paper, percolation will be analytically estimated for the formation of directly connected bonds between the ACHSs contained in a FMS that also has point charges. The percolation threshold must be estimated for the FMS in order to find the dependence of the percolation behavior on the charge of the ACHS. The charge is a significant factor that strongly influences the aggregation of the ACHSs. Therefore, the change in the percolation threshold due to the change in the magnitude of the charge is presently of interest. For this reason, the influence of the charge on the percolation threshold will be briefly examined.

II. PAIR CONNECTEDNESS

By using the pair-correlation function g_{ij}, the probability of locating an i-species particle and a j-species particle in volume elements $d\mathbf{r}_i$ at $\mathbf{r}_i$ (point i) and $d\mathbf{r}_j$ at $\mathbf{r}_j$ (point j), respectively, is given as

$$\rho_i\rho_j g_{ij}(\mathbf{r}_i,\mathbf{r}_j)d\mathbf{r}_i\,d\mathbf{r}_j\,,$$

where ρ_i and ρ_j are the densities of the i species and j species, respectively. This probability is the sum of two contributions. The contribution is the probability $\rho_i\rho_j P_{ij}(\mathbf{r}_i,\mathbf{r}_j)d\mathbf{r}_i\,d\mathbf{r}_j$ that a particle in $d\mathbf{r}_i$ at $\mathbf{r}_i$ and another particle in $d\mathbf{r}_j$ at $\mathbf{r}_j$ belong to the same physical cluster. The other contribution is the probability $\rho_i\rho_j D_{ij}(\mathbf{r}_i,\mathbf{r}_j)d\mathbf{r}_i d\mathbf{r}_j$ that the two particles do not belong to the same cluster. Hence the pair-correlation function g_{ij} must be expressed as

$$g_{ij}=P_{ij}+D_{ij}\,. \tag{1}$$

The Mayer f function $f_{ij}=\exp(-\beta u_{ij})-1$, according to Hill's concept [13], is separated into two parts as

$$f_{ij}=f_{ij}^{+}+f_{ij}^{*}\,,$$

where f_{ij}^{+} and f_{ij}^{*} are defined as

$$f_{ij}^{+}\equiv\exp(-\beta u_{ij}^{+}),\quad f_{ij}^{*}\equiv\exp(-\beta u_{ij}^{*})-1.$$

Hence the f_{ij}^{+} and f_{ij}^{*} represent the bound and unbound pairs of particles, respectively. In Mayer's mathematical clusters (defined in terms of f_{ij} bonds), which constitute g_{ij}, each bond f_{ij} should be replaced by $f_{ij}^{+}+f_{ij}^{*}$ in order to find diagrams contributing to P_{ij}. Thus it can be proved that the diagrams that should be identified with the collection of diagrams with at least one path of all f^{+} bonds between the root points i and j are contained in the diagrams contributing to g_{ij}, as shown by Coniglio, De Angelis, and Foriani [15].

The contribution of the diagrams to P_{ij} can be divided into two parts. One part is the contribution N_{ij}^{+} of nodal diagrams with at least one path of all f^{+} bonds between i and j. The other part is the contribution C_{ij}^{+} of non-nodal diagrams with at least one path of all f^{+} bonds between i and j. Thus it should be expressed as

$$P_{ij}=C_{ij}^{+}+N_{ij}^{+}\,. \tag{2}$$

A nodal diagram is a diagram containing at least one nodal point. A nodal point is defined as a field point such that all paths between i and j pass through that point. If the nodal diagram has at least one path of all f^{+} bonds between i and j and the point k is the nodal point closest to i in the nodal diagram (so that the diagram between i and k does not have nodal points), N_{ij}^{+} is then given by a convolution integral as

$$N_{ij}^{+}=\sum_{k=0}^{m-1}\rho_k\int C_{ik}^{+}P_{kj}\,d\mathbf{r}_k\,. \tag{3}$$

Here m is the number of species that may occupy the nodal point k. Thus the Ornstein-Zernike relation similar to that derived by Coniglio, De Angelis, and Foriani [15] is obtained from Eqs. (2) and (3) as

$$P_{ij}=C_{ij}^{+}+\sum_{k=0}^{m-1}\rho_k\int C_{ik}^{+}P_{kj}\,d\mathbf{r}_k\,. \tag{4}$$

This equation is an Ornstein-Zernike relation for the pair-connectedness function in a multicomponent system and corresponds to that derived with the derivation of the formally exact closure by Chiew, Stell, and Glandt [38].

According to the PYA, the pair-correlation function g_{ij}^{PY} is given by

$$g_{ij}^{\mathrm{PY}}\exp(\beta u_{ij})=1+N_{ij}\,, \tag{5}$$

where N_{ij} is the contribution of the nodal diagrams. The contribution N_{ij} can be separated into two terms: N_{ij}^{+} and N_{ij}^{*}. The term N_{ij}^{*} is the contribution of all nodal diagrams composed of no paths of all f^{+} bonds between i and j. By considering Eqs. (1), (2), and (5) with $\exp(-\beta u_{ij})=f_{ij}^{+}+f_{ij}^{*}+1$, a closure condition imposed on P_{ij} and C_{ij}^{+} is obtained as

$$P_{ij}=\exp(-\beta u_{ij}^{+})g_{ij}^{\mathrm{PY}}\exp(\beta u_{ij})+\exp(-\beta u_{ij}^{*})(P_{ij}-C_{ij}^{+}). \tag{6}$$

This formula corresponds to that given by Coniglio, De Angelis, and Foriani [15] and is an approximate expression for the exact expression given by Chiew, Stell, and Glandt [38].

III. MEAN SIZE OF PHYSICAL CLUSTERS

A. Determination of the mean size

The mean size of physical clusters S is given by

$$S=\frac{\sum_{s} s^2 n_s}{\sum_{s} s n_s}, \tag{7}$$

where n_s is the equilibrium number of physical clusters consisting of s particles. If the number of species that may be included in the physical clusters is m, the relation between P_{ij} and n_s, according to the formula given by Coniglio, De Angelis, and Foriani [15], should be given by

$$\sum_{s\geqslant 2} s(s-1)n_s=\sum_{i=0}^{m-1}\sum_{j=0}^{m-1}\rho_i\rho_j\int P_{ij}\,d\mathbf{r}_i\,d\mathbf{r}_j. \tag{8}$$

If it can be assumed that the probability p_i of i species existing in a cluster is independent of s, ρ_i in the volume V is then given by

$$\rho_i=\frac{1}{V}\,p_i\sum_{s} s n_s. \tag{9}$$

Dividing Eq. (8) by $\Sigma_s s n_s$ and considering Eqs. (9) and (7), the mean size of the physical cluster S in an isotropic system can be determined using the pair-connectedness $P_{ij}(r)$ as

$$S=1+\frac{1}{\sum_{k=0}^{m-1}\rho_k}\sum_{i=0}^{m-1}\sum_{j=0}^{m-1}\rho_i\rho_j\int P_{ij}(r)\,d\mathbf{r}. \tag{10}$$

B. A FMS containing ACHSs

The pair potential $u_{ij}(r)$ in a FMS with ACHSs is represented as

$$\exp[-\beta u_{ij}(r)]=\frac{\zeta_{ij}}{12}\,\sigma_{ij}\delta(r-\sigma_{ij}),\quad 0<r\leqslant\sigma_{ij} \tag{11a}$$

and

$$\exp[-\beta u_{ij}(r)]=\exp[-\beta u_{ij}^{\mathrm{Coul}}(r)],\quad \sigma_{ij}<r, \tag{11b}$$

where ζ_{ij} is a parameter representing the strength of the adhesive interaction and $u_{ij}^{\mathrm{Coul}}(r)$ the Coulomb potential between the i-species ACHS and the j-species ACHS. The reciprocal ζ_{ij}^{-1} corresponds to the parameter τ introduced by Baxter [10]. In Eqs. (11a) and (11b), σ_{ij} is defined with the use of the diameter σ_i for the i species and the diameter σ_j for the j species as

$$\sigma_{ij}\equiv\tfrac{1}{2}(\sigma_i+\sigma_j). \tag{12}$$

The pair-correlation function $g_{ij}(r)$ within the core is then given by

$$g_{ij}(r)=\frac{\chi_{ij}}{12}\,\sigma_{ij}\delta(r-\sigma_{ij}),\quad 0<r\leqslant\sigma_{ij}, \tag{13}$$

where χ_{ij} is the association parameter [36,37]. The parameter χ_{ij} is expressed in terms of the mean value $\langle N_{ij}\rangle$ (an average coordination number) for the number of j ACHSs contacting an i ACHS as

$$\chi_{ij}=\frac{3\langle N_{ij}\rangle}{\pi\rho_j\sigma_{ij}^3}. \tag{14}$$

The average coordination number is expressed as

$$\langle N_{ij}\rangle=\rho_j\int_0^{\sigma_{ij}^{+}} g_{ij}(r)4\pi r^2\,dr,$$

where

$$\sigma_{ij}^{\pm}\equiv\lim_{\delta\to 0}\sigma_{ij}\pm\delta.$$

According to the definition of Chiew and Glandt [17], it is assumed that the contact of one ACHS with another results in the formation of directly connected bonds between the ACHSs. Then, Hill's concept [13] can yield the following relations owing to Eqs. (11a) and (11b):

$$\exp[-\beta u_{ij}^{+}(r)]=\frac{\zeta_{ij}}{12}\,\sigma_{ij}\delta(r-\sigma_{ij}),\quad 0<r\leqslant\sigma_{ij}, \tag{15a}$$

$$\exp[-\beta u_{ij}^{+}(r)]=0,\quad \sigma_{ij}<r, \tag{15b}$$

$$\exp[-\beta u_{ij}^{*}(r)]=0,\quad 0<r\leqslant\sigma_{ij}, \tag{15c}$$

and

$$\exp[-\beta u_{ij}^{*}(r)]=\exp[-\beta u_{ij}^{\mathrm{Coul}}(r)],\quad \sigma_{ij}<r. \tag{15d}$$

Substituting Eqs. (13), (15a), (15b), (15c), and (15d) into Eq. (6), the following relations are obtained:

$$P_{ij}(r)=\frac{\chi_{ij}}{12}\,\sigma_{ij}\delta(r-\sigma_{ij})\quad 0<r\leqslant\sigma_{ij}, \tag{16a}$$

and

$$C_{ij}^{+}(r)=P_{ij}(r)\{1-\exp[\beta u_{ij}^{\mathrm{Coul}}(r)]\},\quad \sigma_{ij}<r. \tag{16b}$$

As can be seen in Eq. (16b), the relation between $C_{ij}^{+}(r)$ and $P_{ij}(r)$ has the same form as the relation between $g_{ij}(r)$ and the direct correlation function $c_{ij}(r)$ due to the PYA. According to Eq. (16b), $C_{ij}^{+}(r)$, as well as $c_{ij}(r)$, approaches zero at least owing to the term $\{1-\exp[\beta u_{ij}^{\mathrm{Coul}}(r)]\}$ as r increases. Therefore, by considering the approximation used by Xu and Stell [31] for analytically estimating percolation in Yukawa fluids, it is assumed that $C^{+}_{ij}(r)$ has an approximate expression similar to that for $c_{ij}(r)$ due to the MSA. Thus the approximation for $C^{+}_{ij}(r)$ is represented as

$$C^{+}_{ij}(r)=C^{0+}_{ij}(r)-\lim_{\mu\to 0}\beta u^{\mathrm{Coul}}_{ij}(r)\exp(-\mu r), \tag{17a}$$

where

$$C^{0+}_{ij}(r)=0, \quad \sigma^{+}_{ij}<r. \tag{17b}$$

In Eq. (17a), $C^{+}_{ij}(r)$ is split into two parts: the short-ranged part $C^{0+}_{ij}(r)$ and the remainder, which equals the long-ranged contribution. The remainder has an exponential damping factor containing the parameter μ, introduced to avoid the divergence of the integrals. This expression for $C^{+}_{ij}(r)$ has the same form as an approximate expression for $c_{ij}(r)$, which should be given in a FMS with particles having long-ranged interactions, such as Coulomb interactions [40]. By using the approximate expression given in Eq. (17a), an analytical expression for S can be somewhat readily derived from a pair-connectedness function that satisfies Eq. (4), since a mathematical treatment used in the derivation of analytical solutions for the pair-correlation function in a FMS containing ACHSs [36,37] is applicable.

Considering Eq. (17a), the Fourier transform of Eq. (4) is given by

$$\sum_{k=0}^{m-1}[\delta_{ik}+\widetilde{P}_{ik}(k)][\delta_{kj}-\widetilde{C}^{+}_{kj}(k)]=\delta_{ij}, \tag{18}$$

where

$$\widetilde{P}_{ij}(k)=2(\rho_i\rho_j)^{1/2}\int_0^\infty \hat{J}_{ij}(r)\cos(kr)dr \tag{19}$$

and

$$\widetilde{C}^{+}_{ij}(k)=2(\rho_i\rho_j)^{1/2}\int_0^\infty S^{+}_{ij}(r)\cos(kr)dr-\lim_{\mu\to 0}\frac{\alpha_{ij}}{k^2+\mu^2}, \tag{20}$$

with

$$\hat{J}_{ij}(r)=2\pi\int_r^\infty P_{ij}(t)t\,dt, \tag{21}$$

$$S^{+}_{ij}(r)=2\pi\int_r^\infty C^{0+}_{ij}(t)t\,dt, \tag{22}$$

and

$$\alpha_{ij}=\alpha_0^2(\rho_i\rho_j)^{1/2}z_iz_j. \tag{23}$$

Here the charges of the i ACHS and j ACHS are z_ie and z_je, respectively, and α_0^2 in Eq. (23) is defined as

$$\alpha_0^2\equiv\frac{4\pi\beta e^2}{\varepsilon}, \tag{24}$$

where ε is the macroscopical dielectric constant of the FMS. Baxter's Q function, dependent on the nature of $C^{+}_{ij}(r)$, can be introduced via the equation [36,37]

$$\delta_{ij}-\widetilde{C}^{0+}_{ij}(k)+\frac{\alpha_{ij}}{k^2+\mu^2}=\sum_{k=0}^{m-1}\widetilde{Q}_{ik}(k)\widetilde{Q}_{jk}(-k), \tag{25}$$

where the left-hand side is equivalent to $\delta_{ij}-\widetilde{C}^{+}_{ij}(k)$ and $\widetilde{Q}_{ij}(k)$ is

$$\widetilde{Q}_{ij}(k)=\delta_{ij}-(\rho_i\rho_j)^{1/2}\int_{\lambda_{ji}}^{\sigma_{ji}}Q^{0}_{ij}(r)\exp(ikr)dr+(\rho_i\rho_j)^{1/2}A_{ij}\int_{\lambda_{ji}}^{\infty}\exp(-\mu r)\exp(ikr)dr, \tag{26}$$

with

$$Q^{0}_{ij}(r)\equiv Q_{ij}(r)+A_{ij}\exp(-\mu|r|) \tag{27}$$

and

$$\lambda_{ji}\equiv\tfrac{1}{2}(\sigma_j-\sigma_i). \tag{28}$$

The expression for $Q^{0}_{ij}(r)$ defined by Eq. (27) should be zero just beyond the contact distance, owing to the nature of $C^{0+}_{ij}(r)$ [36,37], i.e.,

$$Q^{0}_{ij}(r)=0 \quad (r>\sigma_{ij}). \tag{29}$$

When the formula obtained by multiplying both sides of Eq. (25) by $\exp(-ikr)$ is integrated with respect to k over the entire range from $-\infty$ to $+\infty$, the divergence of this integration [the same integration as that in the process for estimating $g_{ij}(r)$ [36]] at the limit $\mu=0$ can be avoided if the coefficients A_{ij} introduced in Eq. (26) satisfy the relation

$$\alpha_{ij}=(\rho_i\rho_j)^{1/2}\sum_{k=0}^{m-1}\rho_kA_{ik}A_{jk}.$$

As is known via the estimation of the pair-correlation function in the FMS containing ACHSs [36], the comparison of this relation with Eq. (23) results in the determination of the relation

$$A_{ij}\equiv z_ia_j, \tag{30}$$

where

$$\sum_{k=0}^{m-1}\rho_ka_k^2=\alpha_0^2. \tag{31}$$

Substitution of Eq. (25) into Eq. (18) yields

$$\delta_{ij}+\widetilde{P}_{ij}(k)=\sum_{k=0}^{m-1}\widetilde{Q}^{-1}_{ki}(-k)\widetilde{Q}^{-1}_{kj}(k). \tag{32}$$

From Eq. (32), the following formula can be derived:

$$(\rho_i\rho_j)^{1/2}\int P_{ij}(r)d\mathbf{r}=-\delta_{ij}+\sum_{k=0}^{m-1}\widetilde{Q}^{-1}_{ki}(0)\widetilde{Q}^{-1}_{kj}(0). \tag{33}$$

Substituting Eq. (33) into Eq. (10) results in the mean cluster size S being expressed with the Q function as

$$S=\sum_{i=0}^{m-1}\left[\sum_{j=0}^{m-1}\left(\frac{\rho_i}{\rho^t}\right)^{1/2}\tilde{Q}_{ij}^{-1}(0)\right]^2, \tag{34a}$$

where

$$\rho^t\equiv\sum_{i=0}^{m-1}\rho_i. \tag{34b}$$

Thus S can be evaluated when $\tilde{Q}_{ij}^{-1}(0)$ is given.

C. Estimation of $\tilde{Q}_{ij}^{-1}(0)$

The formula for the formal determination of $\tilde{Q}_{ij}^{-1}(-k)$ can be obtained by modifying Eq. (32). If both sides of this formula multiplied by $\exp(-ikr)$ are integrated with respect to k over the entire range from $-\infty$ to $+\infty$ by considering that $\tilde{Q}_{ij}^{-1}(-k)$ is nonsingular, then the following formula can be obtained [36,37]:

$$\hat{J}_{ij}(r)=Q_{ij}^0(r)-A_{ij}+\sum_{k=0}^{m-1}\rho_k\int_{\lambda_{jk}}^{\sigma_{jk}}dt\ \hat{J}_{ik}(|r-t|)Q_{kj}^0(t)$$
$$-\sum_{k=0}^{m-1}\rho_k\int_{\lambda_{jk}}^{\infty}dt\ \hat{J}_{ik}(|r-t|)A_{kj}. \tag{35}$$

Comparing the difference $\hat{J}_{ij}(\sigma_{ij}^-)-\hat{J}_{ij}(\sigma_{ij}^+)$ estimated by the use of Eqs. (16a) and (21) with that estimated by the use of Eqs. (35), (16a), and (29) yields

$$Q_{ij}^0(\sigma_{ij})=\frac{\pi}{6}\chi_{ij}\sigma_{ij}^2. \tag{36}$$

Substituting the derivative of Eq. (21) with respect to r into the derivative of Eq. (35) with respect to r, the following relation for the Q function can be obtained:

$$\frac{d}{dr}Q_{ij}^0(r)=\sum_{k=0}^{m-1}\rho_kJ_{ik}A_{kj}\quad(r<\sigma_{ij}), \tag{37}$$

where

$$J_{ik}\equiv\hat{J}_{ik}(0). \tag{38}$$

Integration of Eq. (37), taking into account Eqs. (29), (30), and (36), results in

$$Q_{ij}^0(r)=(r-\sigma_{ij})Q'_{ij}+Q_{ij}^\lambda\quad(r<\sigma_{ij}), \tag{39}$$

where

$$Q'_{ij}=B_ia_j \tag{40}$$

and

$$Q_{ij}^\lambda\equiv\frac{\pi}{6}\chi_{ij}\sigma_{ij}^2, \tag{41}$$

with

$$B_i\equiv\sum_{k=0}^{m-1}\rho_kJ_{ik}z_k. \tag{42}$$

If Eq. (39) is substituted into Eq. (26), the following equation can be obtained:

$$\tilde{Q}_{ij}(0)=\delta_{ij}-(\rho_i\rho_j)^{1/2}\sigma_{ii}(Q_{ij}^\lambda-\tfrac{1}{2}\sigma_{ii}Q'_{ij})$$
$$+(\rho_i\rho_j)^{1/2}a_iz_j\frac{\exp(-\mu\lambda_{ij})}{\mu}. \tag{43}$$

Assuming that C_{ij}^{0+} has a symmetry similar to that of the direct-correlation function [36,37], the following relation is determined:

$$S_{ij}^+(\lambda_{ji})=S_{ji}^+(\lambda_{ij}). \tag{44}$$

For $S_{ji}^+(r)$, which can be derived from the integration of Eq. (25) times $\exp(-ikr)$ with respect to k over the entire range $(-\infty<k<\infty)$ [36], the relation given by Eq. (44) results in

$$Q_{ij}^0(\lambda_{ji})-A_{ij}=Q_{ji}^0(\lambda_{ij})-A_{ji}. \tag{45}$$

If Eq. (39) is substituted into Eq. (45), the following relation between B_i and a_i can then be obtained:

$$-(\sigma_{ii}B_i+z_i)a_j=(\sigma_{jj}B_j+z_j)a_i+Q_{ji}^\lambda-Q_{ij}^\lambda. \tag{46}$$

Moreover, by substituting a_k given by Eq. (46) into Eq. (31), the following formula is determined:

$$a_i^2\sum_{k=0}^{m-1}\rho_kZ_k^2-2a_i\sum_{k=0}^{m-1}\rho_kZ_k(Q_{ki}^\lambda-Q_{ik}^\lambda)+\sum_{k=0}^{m-1}\rho_k(Q_{ki}^\lambda-Q_{ik}^\lambda)^2$$
$$-\alpha_0^2Z_i^2=0, \tag{47}$$

where

$$Z_j\equiv\sigma_{jj}B_j+z_j. \tag{48}$$

Next, since J_{ik} is defined by Eq. (38), substitution of Eq. (35) into Eq. (42) yields

$$B_j=-\sum_{k=0}^{m-1}\rho_k(z_k+\tfrac{1}{2}\sigma_{kk}B_k)\sigma_{kk}B_ka_j$$
$$+\sum_{k=0}^{m-1}\rho_k(z_k+\sigma_{kk}B_k)Q_{kj}^\lambda-\sum_{k=0}^{m-1}\rho_kz_k^2a_j$$
$$-2\pi\sum_{l=0}^{m-1}\sum_{k=0}^{m-1}\rho_lz_l\rho_kz_ka_j\int_0^\infty P_{lk}(t)t^2dt. \tag{49}$$

If Eq. (48) and the electroneutrality condition discussed in the Appendix are considered, Eq. (49) can be modified as

$$Z_j=-\frac{a_j\sigma_{jj}}{2}\sum_{k=0}^{m-1}\rho_kZ_k^2+\sigma_{jj}\sum_{k=0}^{m-1}\rho_kZ_kQ_{kj}^\lambda+z_j. \tag{50}$$

Thus the unknown factors a_i and Z_i can be determined by the use of Eqs. (47) and (50), so that Q'_{ij} given by Eq. (40) can also be determined since it can be estimated through Eq. (48) as

$$Q'_{ij}=\frac{Z_i-z_i}{\sigma_{ii}}\,a_j\,. \tag{51}$$

Ultimately, the unknown factors Q'_{ij} and a_i in Eq. (43) can be estimated using Eqs. (47), (50), and (51), so that $\widetilde{Q}_{ij}(0)$ given by Eq. (43) can also be determined. If the inverse of $\widetilde{Q}_{ij}(0)$ is substituted into Eq. (34a), the mean size of the physical clusters S can be obtained.

IV. PERCOLATION IN A FMS

A. A FMS composed of ACHSs and point charges

The value of $\widetilde{Q}_{ij}(0)$ is given by Eq. (43), so that $\Sigma(\rho_j)^{1/2}\widetilde{Q}_{ij}^{-1}(0)$, which is necessary for evaluating S, can be estimated. The estimation of the inverse of $\widetilde{Q}_{ij}(0)$, however, is difficult.

It is assumed that in the FMS containing ACHSs, the adhesive interaction exists only between the charged hard spheres of species 0, while species 1 and 2 are point charges. This can be expressed as

$$\lambdabar_{00}\neq 0,\quad \lambdabar_{01}=\lambdabar_{02}=\lambdabar_{10}=\lambdabar_{20}=\lambdabar_{11}=\lambdabar_{12}=\lambdabar_{21}=\lambdabar_{22}=0, \tag{52a}$$

$$\sigma_0\neq 0,\quad \sigma_1=\sigma_2=0. \tag{52b}$$

Equation (43) can then be simplified, so that $\widetilde{Q}_{ij}^{-1}(0)$ at the limit $\mu=0$ can be readily derived as

$$D_0\widetilde{Q}_{ij}^{-1}(0)=M_{ij}-\hat{A}_i\hat{B}_j+\delta_{ij}\sum_{k=0}^{2}\hat{A}_k\hat{B}_k$$

$$(i=0,1,2;\;\; j=0,1,2), \tag{53}$$

where

$$M_{ij}=(-\hat{A}_1\delta_{2j}+\hat{A}_2\delta_{1j})\begin{vmatrix}\delta_{0i} & \delta_{1i} & \delta_{2i}\\ \hat{B}_0 & \hat{B}_1 & \hat{B}_2\\ y_0 & y_1 & y_2\end{vmatrix},$$

$$\hat{A}_i\equiv(\rho_i)^{1/2}z_i\,,$$

$$\hat{B}_i\equiv(\rho_i)^{1/2}a_i\,,$$

$$y_i\equiv-(\rho_0\rho_i)^{1/2}\sigma_{00}(Q_{0i}^{\lambda}-\tfrac{1}{2}\sigma_{00}Q'_{0i}),$$

and

$$D^0\equiv\gamma(\rho_0 z_0 Z_0+\rho_1 z_1^2+\rho_2 z_2^2)$$
$$\times\left(1-\frac{\rho_1 z_1^2+\rho_2 z_2^2}{\rho_0 z_0 Z_0+\rho_1 z_1^2+\rho_2 z_2^2}\,\frac{1}{2}\,\langle N_{00}\rangle\right), \tag{54}$$

with

$$\gamma\equiv\frac{a_i}{Z_i}. \tag{55}$$

The average coordination number $\langle N_{00}\rangle$ introduced in Eq. (54) can be found by substituting Eq. (14) into Eq. (41) as

$$\langle N_{00}\rangle=2\sigma_{00}\rho_0 Q_{00}^{\lambda}. \tag{56}$$

The coefficient γ defined by Eq. (55) can be determined as a coefficient independent of species by considering Eq. (46) with Eq. (48) when $Q_{ij}^{\lambda}-Q_{ji}^{\lambda}=0$ is satisfied.

Using Eqs. (53) and (56) with Eqs. (51) and (55), the following formulas can be obtained:

$$\sum_i(\rho_i)^{1/2}\widetilde{Q}_{0i}^{-1}(0)=\frac{\gamma}{D^0}\sqrt{\rho_0}\kappa^2, \tag{56a}$$

$$\sum_i(\rho_i)^{1/2}\widetilde{Q}_{1i}^{-1}(0)=\frac{\gamma}{D^0}\sqrt{\rho_1}[\kappa^2+\rho_0(z_0-z_1)(Z_0-z_0)$$
$$+\rho_2 z_2(z_1-z_2)\tfrac{1}{2}\langle N_{00}\rangle], \tag{56b}$$

and

$$\sum_i(\rho_i)^{1/2}\widetilde{Q}_{2i}^{-1}(0)=\frac{\gamma}{D^0}\sqrt{\rho_2}[\kappa^2+\rho_0(z_0-z_2)(Z_0-z_0)$$
$$+\rho_1 z_1(z_2-z_1)\tfrac{1}{2}\langle N_{00}\rangle], \tag{56c}$$

where

$$\kappa^2\equiv\rho_0 z_0^2+\rho_1 z_1^2+\rho_2 z_2^2.$$

Substituting a_j given by Eq. (47) into Eq. (50) results in the formula

$$\frac{1}{2}\,\langle N_{00}\rangle+\frac{z_0}{Z_0}-1+\left(\frac{\alpha_0^2\sigma_0^2}{4}\,(\rho_0 Z_0^2+\rho_1 z_1^2+\rho_2 z_2^2)\right)^{1/2}=0 \tag{57}$$

since the conditions described by Eqs. (52a) and (52b) should be satisfied. Therefore, the unknown coefficient Z_0 can be determined by use of Eq. (57).

B. FMS percolation

The mean cluster size S can be evaluated by substituting Eqs. (56a), (56b), and (56c) into Eq. (34a) as

$$S=\left(\frac{\gamma}{D^0}\right)^2\frac{1}{\rho^t}\,\hat{s}, \tag{58a}$$

where, owing to Eq. (34b) and the electroneutrality condition,

$$\rho^t=\left(1-\frac{z_0}{z_1}\right)\rho_0+\left(1-\frac{z_2}{z_1}\right)\rho_2 \tag{58b}$$

and

$$\hat{s}\equiv\kappa^4\rho^t+\rho_0(Z_0-z_0)\{\kappa^2[\rho_0(Z_0-z_0)+\rho^t z_0]$$
$$+z_0\rho^t[\rho_0 z_0(Z_0-z_0)+\kappa^2]\}$$
$$+\tfrac{1}{4}\rho_2(\rho^t-\rho_0-\rho_2)(z_1-z_2)^2\langle N_{00}\rangle$$
$$\times\{(\kappa^2-\rho_0 z_0^2)\langle N_{00}\rangle-4[\rho_0 z_0(Z_0-z_0)+\kappa^2]\}. \tag{58c}$$

The mean cluster size S becomes infinite at the percolation threshold, so that the percolation transition occurs at $D^0=0$.

Hence the average coordination number at the percolation threshold should be determined by using Eq. (54) as

$$\langle N_{00}\rangle^p = 2\left(1 + \frac{\rho_0 z_0 Z_0}{\rho_1 z_1^2 + \rho_2 z_2^2}\right), \tag{59}$$

where $\langle N_{00}\rangle^p$ represents $\langle N_{00}\rangle$ at the percolation threshold. This result is the same as that obtained for a fluid of noncharged adhesive hard spheres [17] if z_0 equals zero. The value of $\langle N_{00}\rangle^p$ at $z_0 \neq 0$ is greater than 2, however, since $z_0 Z_0$ is positive, based on the relation $z_0/Z_0 > 0$, which can be derived from Eqs. (47) and (50).

Ultimately, by substituting Z_0 derived from Eq. (59) into Eq. (57), $\langle N_{00}\rangle^p$ can be obtained as

$$\langle N_{00}\rangle^p = 2\{1 + [\xi(1 - \tfrac{1}{4}\eta\phi\xi^2)]^{-1/2}\}, \tag{60}$$

where

$$\phi \equiv \pi\rho_0\sigma_0^3/6,$$

$$\eta \equiv 6\alpha_0^2 z_0^2/\pi\sigma_0,$$

and

$$\xi \equiv z_1/z_0 + (\rho_2/\rho_0)(z_1 - z_2)(z_2/z_0^2).$$

On the other hand, the relation between $\langle N_{00}\rangle$ and ζ_{00} has been given elsewhere [12]. It is assumed that Eqs. (52a) and (52b), as well as the electroneutrality condition $z_0\rho_0 + z_1\rho_1 + z_2\rho_2 = 0$, can be satisfied. The value of $\langle N_{00}\rangle$ can then be determined from the parameters ζ_{00}, η, ξ, and ϕ, by the use of the two equations

$$\langle N_{00}\rangle = 2 + 2\hat{\Gamma} + \Xi - \left(\frac{\eta\phi}{\chi(\eta,\phi,\xi;\hat{\Gamma})}\right)^{1/2} \tag{61a}$$

and

$$\langle N_{00}\rangle = 2\Xi + \frac{12}{\zeta_{00}} - 2\sqrt{2}[\chi(\eta,\phi,\xi;\hat{\Gamma}) + \Phi(\zeta_{00},\eta,\phi)]^{1/2}, \tag{61b}$$

where $\hat{\Gamma}$ is an unknown coefficient determined via these equations. The other terms are defined as

$$\chi(\eta,\phi,\xi;\hat{\Gamma}) \equiv \hat{\Gamma}^2 + \tfrac{1}{4}\eta\phi\xi,$$

$$\Phi(\zeta_{00},\eta,\phi) \equiv F(\zeta_{00},\phi) - \tfrac{1}{4}\eta\phi,$$

and

$$\Xi \equiv \frac{6\phi}{1-\phi},$$

with

$$F(\zeta_{00},\phi) \equiv \frac{1}{4}\Xi^2 + \frac{1}{2}\left(\frac{6}{\zeta_{00}}\right)^2 + \left(\frac{6}{\zeta_{00}} - 1\right)\Xi.$$

If the unknown coefficient $\hat{\Gamma}$ at $\langle N_{00}\rangle = \langle N_{00}\rangle^p$ is expressed as $\hat{\Gamma}^p$, by making use of Eq. (61b) with given values of $\eta = \eta'$ and $\xi = \xi'$, $\hat{\Gamma}^p$ can be determined as

$$[\hat{\Gamma}^p]^2 = -F(\zeta_{00}^p,\phi^p) + \frac{1}{4}\eta'\phi^p(1-\xi') + \frac{1}{8}\left(2\Xi^p + \frac{12}{\zeta_{00}^p} - \langle N_{00}\rangle^p\right)^2, \tag{62}$$

where ϕ^p, Ξ^p, and ζ_{00}^p are the values of ϕ, Ξ, and ζ_{00} at the percolation threshold, respectively. The values of ϕ^p and ζ_{00}^p at $\eta = \eta'$ and $\xi = \xi'$ can be determined by the use of Eqs. (60), (61a), and (62).

If phase separation, the so-called spinodal decomposition, due to the aggregation of ACHSs can be induced in a FMS, the following condition [12] should be satisfied:

$$\chi(\eta,\phi,\xi;\hat{\Gamma}) + \Phi(\zeta_{00},\eta,\phi) < 0.$$

A spinodal curve found for this FMS corresponds to a curve determined with parameters that satisfy the condition [12]

$$\chi(\eta,\phi,\xi;\hat{\Gamma}) + \Phi(\zeta_{00},\eta,\phi) = 0. \tag{63}$$

Therefore, if the average coordination number evaluated for the values of the parameters on a spinodal curve is expressed as $\langle N_{00}\rangle^s$, it should satisfy the following relation owing to Eq. (61b):

$$\langle N_{00}\rangle^s = 2\Xi + \frac{12}{\zeta_{00}}. \tag{64}$$

If Eqs. (63) and (64) are substituted into Eq. (61a), the following relation, which the values of the parameters on the spinodal curve must satisfy, can be obtained:

$$\frac{1}{2}\Xi + \frac{6}{\zeta_{00}} - 1 - \frac{\sqrt{\eta\phi}}{2}\left(-\frac{4}{\eta\phi}F(\zeta_{00},\phi) + 1 - \xi\right)^{1/2} + \left(-\frac{4}{\eta\phi}F(\zeta_{00},\phi) + 1\right)^{-1/2} = 0. \tag{65}$$

Furthermore, the value of ζ_{00} for which $\langle N_{00}\rangle^p = \langle N_{00}\rangle^s$ is satisfied can readily be estimated by use of Eq. (64). If Eq. (60) is substituted into Eq. (64), the following formula can be obtained:

$$\Xi + \frac{6}{\zeta_{00}} = 1 + [\xi(1 - \tfrac{1}{4}\eta\phi\xi^2)]^{-1/2}. \tag{66}$$

Therefore, using Eqs. (65) and (66), the values of ζ_{00} and ϕ for which $\langle N_{00}\rangle^s = \langle N_{00}\rangle^p$ is satisfied can be determined if the values of η and ξ are given.

The changes in the percolation threshold, evaluated through use of Eqs. (60), (61a), and (62) for $z_0 = -4$, -6, and -7, are displayed in Fig. 1. The change in the percolation threshold evaluated for $z_0 = -7$ is remarkable. The results for $z_0 = -4$ and -6 are similar to those evaluated for $z_0 = 0$ [17,25] and are also similar to those evaluated for the square-well fluids [22–24].

It is known that a FMS containing highly charged macroparticles has a tendency to separate into dense and sparsely populated regions [41]. This results from the fact that in such a system, an ordered structure may have less energy than a disordered structure. According to the significance of this,

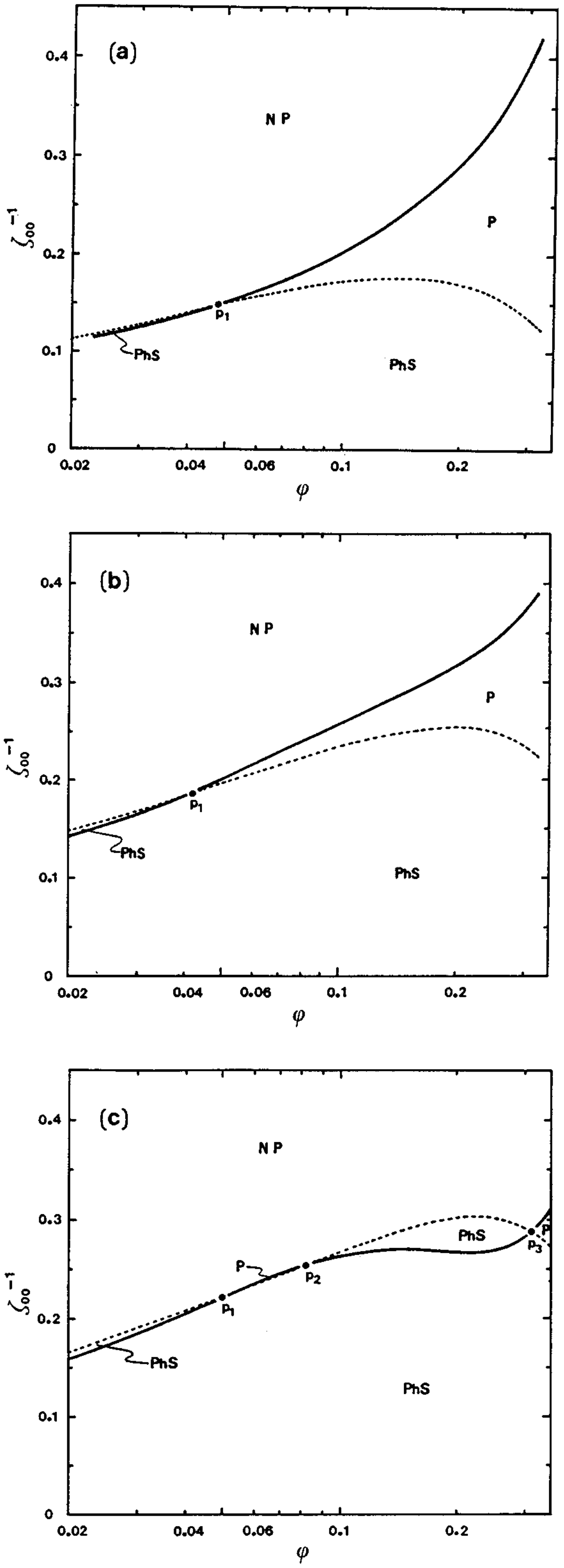

FIG. 1. Percolation loci and spinodal curves for $\alpha_0^2=8.79\times10^{-7}$ cm, $\sigma_0=5\times10^{-7}$ cm, $z_1=1$, and $z_2=-1$. (a) $z_0=-4$, (b) $z_0=-6$, and (c) $z_0=-7$. Solid curve, locus of the percolation threshold; dashed curve, spinodal curve; NP, nonpercolating region; *P*, percolating region; PhS, region in which phase separation occurs; P_1, P_2, and P_3, points where $\langle N_{00}\rangle^p=\langle N_{00}\rangle^s$ can be satisfied.

regions in which an ACHS is densely surrounded by other ACHSs can easily occur when the ACHSs are highly charged. Such a phenomenon should enhance the generation of phase separation. This suggests that phase separation should be more easily induced than percolation if the ACHSs are highly charged. With respect to the behavior of the percolation threshold depicted in Fig. 1, the derivation of the interpretation should be based on the phenomenon mentioned above. In addition, the similarity between ‘‘the disappearance of the percolation due to the increase in which $|z_0|$ induces two effects (the excitement of repulsion between ACHSs and the excitement of attraction between an ACHS and a point charge)’’ and ‘‘the nonstabilization of the liquid phase [9,32] due to the reduction of the attractive-interaction range in the Yukawa fluids’’ should be noted in view of the fact that a range, within which the behavior of the ACHSs can be effectively subjected to the potential of mean force, can depend on z_0.

Ultimately, the approximation used in the present work for $C_{ij}^{+}(r)$ is similar to that for $c_{ij}(r)$ in the MSA. The average coordination number $\langle N_{00}\rangle$ evaluated on the basis of this approximation equals 2 when z_0 is zero. This agrees with the result obtained for the PYA [17]. Therefore, it can be concluded that the accuracy when making use of the approximation is nearly equal to that when employing the PYA.

APPENDIX: ELECTRONEUTRALITY CONDITION

The electroneutrality condition in a FMS can be represented as

$$4\pi\sum_k z_k\rho_k\int_0^\infty g_{ik}(t)t^2dt+z_i=0. \tag{A1}$$

Considering Eqs. (6), (15b), (15c), and (15d) with the use of

$$\exp(\beta u_{ij})=[\exp(-\beta u_{ij}^{+})+\exp(-\beta u_{ij}^{*})]^{-1},$$

the following relations can be obtained:

$$g_{ij}^{\mathrm{PY}}(r)=P_{ij}(r)\quad(0<r\leqslant\sigma_{ij}) \tag{A2}$$

and

$$P_{ij}(r)=\frac{C_{ij}^{+}(r)}{1-\exp(\beta u_{ij}^{\mathrm{Coul}})}\quad(\sigma_{ij}<r). \tag{A3}$$

According to the PYA, the relation between $g_{ij}^{\mathrm{PY}}(r)$ and $c_{ij}^{\mathrm{PY}}(r)$ is given as

$$g_{ij}^{\mathrm{PY}}(r)=\frac{c_{ij}^{\mathrm{PY}}(r)}{1-\exp(\beta u_{ij})}. \tag{A4}$$

When considering the MSA, Eq. (A4) can be modified as

$$g_{ij}^{\mathrm{PY}}(r)=\frac{-\beta u_{ij}^{\mathrm{Coul}}}{1-\exp(\beta u_{ij}^{\mathrm{Coul}})}\quad(\sigma_{ij}<r). \tag{A5}$$

On the other hand, considering Eqs. (17a) and (17b), Eq. (A3) can be modified as

$$P_{ij}(r)=\frac{-\beta u_{ij}^{\mathrm{Coul}}}{1-\exp(\beta u_{ij}^{\mathrm{Coul}})} \quad (\sigma_{ij}<r). \tag{A6}$$

Comparing Eq. (A5) with Eq. (A6) yields

$$g_{ij}^{\mathrm{PY}}(r)\approx P_{ij}(r) \quad (\sigma_{ij}<r). \tag{A7}$$

Therefore, by considering Eqs. (A1), (A2), and (A7), an approximation for the electroneutrality condition can be obtained as

$$4\pi\sum_{k} z_k\rho_k\int_0^{\infty}P_{ik}(t)t^2dt+z_i=0. \tag{A8}$$

[1] A. Coniglio, H. E. Stanley, and W. Klein, Phys. Rev. Lett. **42**, 518 (1979); Phys. Rev. B **25**, 6805 (1982).
[2] H. E. Stanley and J. Texeira, J. Chem. Phys. **73**, 3404 (1980).
[3] L. A. Turkevich and M. H. Cohen, J. Phys. Chem. **88**, 3751 (1984).
[4] M. S. Skaf and G. Stell, Phys. Rev. A **46**, R3020 (1992); J. Chem. Phys. **97**, 7699 (1992).
[5] M. Lagues, J. Phys. (Paris) Lett. **40**, L331 (1979); M. W. Kim and J. S. Huang, Phys. Rev. A **34**, 719 (1986); G. S. Grest, I. Webman, S. A. Safran, and A. L. R. Bug, *ibid.* **33**, 2842 (1986); S. Bhattacharya, J. P. Stokes, M. W. Kim, and J. S. Huang, Phys. Rev. Lett. **55**, 1884 (1985); C. Cametti, P. Codastefano, P. Tartaglia, S. H. Chen, and J. Rouch, Phys. Rev. A **45**, R5358 (1992).
[6] C. Boned, Z. Saidi, P. Xans, and J. Peyrelasse, Phys. Rev. E **49**, 5295 (1994).
[7] M. A. V. Dijk, Phys. Rev. Lett. **55**, 1003 (1985).
[8] J. Bibette, T. G. Mason, Hu Gang, and D. A. Weitz, Phys. Rev. Lett. **69**, 981 (1992).
[9] M. H. J. Hagen and D. Frenkel, J. Chem. Phys. **101**, 4093 (1994).
[10] R. J. Baxter, J. Chem. Phys. **49**, 2770 (1968).
[11] M. Y. Lin, H. M. Lindsay, D. A. Weitz, R. C. Ball, R. Klein, and P. Meakin, Phys. Rev. A **41**, 2005 (1990); M. Y. Lin, H. M. Lindsay, D. A. Weitz, R. Klein, R. C. Ball, and P. Meakin, J. Phys. Condens. Matter, **2**, 3093 (1990); D. Asnaghi, M. Carpineti, M. Giglio, and M. Sozzi, Phys. Rev. A **45**, 1018 (1992); M. Carpineti and M. Giglio, Phys. Rev. Lett. **68**, 3327 (1992).
[12] T. Kaneko, J. Phys. Soc. Jpn. **64**, 1810 (1995).
[13] T. L. Hill, J. Chem. Phys. **23**, 617 (1955).
[14] A. Coniglio, U. De Angelis, A. Forlani, and G. Lauro, J. Phys. A **10**, 219 (1977).
[15] A. Coniglio, U. De Angelis, and A. Forlani, J. Phys. A **10**, 1123 (1977).
[16] R. J. Baxter, Austral. J. Phys. **21**, 563 (1968); R. J. Baxter, J. Chem. Phys. **52**, 4559 (1970).
[17] Y. C. Chiew and E. D. Glandt, J. Phys. A **16**, 2599 (1983).
[18] G. Stell, J. Phys. A **17**, L855 (1984).
[19] T. DeSimone, S. Demoulini, and R. M. Stratt, J. Chem. Phys. **85**, 391 (1986).
[20] E. M. Sevick, P. A. Monson, and J. M. Otlino, J. Chem. Phys. **88**, 1198 (1988).
[21] Y. C. Chiew and G. Stell, J. Chem. Phys. **90**, 4956 (1989).
[22] S. A. Safran, I. Webman, and G. S. Grest, Phys. Rev. A **32**, 506 (1985).
[23] S. C. Netemeyer and E. D. Glandt, J. Chem. Phys. **85**, 6054 (1986).
[24] Y. C. Chiew and Y. H. Wang, J. Chem. Phys. **89**, 6385 (1988).
[25] N. A. Seaton and E. D. Glandt, J. Chem. Phys. **86**, 4668 (1987).
[26] W. G. T. Kranendonk and D. Frenkel, Mol. Phys. **64**, 403 (1988).
[27] G. Stell, J. Stat. Phys. **63**, 1203 (1991).
[28] B. Barboy, J. Chem. Phys. **61**, 3194 (1974).
[29] B. Barboy, Chem. Phys. **11**, 357 (1975); B. Barboy and R. Tenne, *ibid.* **38**, 369 (1979); N. A. Seaton and D. Glandt, J. Chem. Phys. **87**, 1785 (1987).
[30] S. C. J. Smithline and A. D. J. Haymet, J. Chem. Phys. **83**, 4103 (1985); C. Cerjan and B. Bagchi, Phys. Rev. A **31**, 1647 (1985).
[31] J. Xu and G. Stell, J. Chem. Phys. **89**, 1101 (1988).
[32] L. Mederos and G. Navascues, J. Chem. Phys. **101**, 9841 (1994); E. Lomba and N. G. Almarza, *ibid.* **100**, 8367 (1994).
[33] M. H. J. Hagen, E. J. Meijer, G. C. A. M. Mooij, D. Frenkel, and H. M. W. Lekkerkerker, Nature **365**, 425 (1993).
[34] H. N. W. Lekkerkerker, W. C. K. Poon, P. N. Pusey, A. Stroobants, and P. B. Warren, Europhys. Lett. **20**, 559 (1992); F. Leal Calderon, J. Bibette, and J. Biais, *ibid.* **23**, 653 (1993); E. J. Meijer and D. Frenkel, Phys. Rev. Lett. **67**, 1110 (1991); J. Chem. Phys. **100**, 6873 (1994).
[35] P. Bolhuis, M. Hagen, and D. Frenkel, Phys. Rev. E **50**, 4880 (1994); P. Bolhuis, and D. Frenkel, Phys. Rev. Lett. **72**, 2211 (1994).
[36] J. Zhu and J. C. Rasaiah, J. Chem. Phys. **94**, 3141 (1991).
[37] J. N. Herrera and L. Blum, J. Chem. Phys. **94**, 5077 (1991).
[38] Y. C. Chiew, G. Stell, and E. D. Glandt, J. Chem. Phys. **83**, 761 (1985).
[39] G. Wu and Y. C. Chiew, J. Chem. Phys. **90**, 5024 (1989).
[40] L. Blum, Mol. Phys. **30**, 1529 (1975).
[41] S. Hachisu, Y. Kobayashi, and A. Kose, J. Colloid Interface Sci. **42**, 342 (1973); A. K. Arora, B. V. R. Tata, A. K. Sood, and R. Kesavamoorthy, Phys. Rev. Lett. **60**, 2438 (1988); R. Williams and R. S. Crandall, Phys. Lett. **48A**, 225 (1974); L. Belloni, Phys. Rev. Lett. **57**, 2026 (1986); B. V. R. Tata, A. K. Arora, and M. C. Valsakumar, Phys. Rev. E **47**, 3404 (1993).