http://dx.doi.org/10.7566/JPSJ.82.084003

Drag Coefficient of a Rigid Spherical Particle in a Near-Critical Binary Fluid Mixture

Ryuichi OKAMOTO[1]*, Youhei FUJITANI[2]†, and Shigeyuki KOMURA[3]‡

[1]*Fukui Institute for Fundamental Chemistry, Kyoto University, Kyoto 606-8103, Japan*
[2]*School of Fundamental Science and Technology, Keio University, Yokohama 223-8522, Japan*
[3]*Department of Chemistry, Tokyo Metropolitan University, Hachioji, Tokyo 192-0397, Japan*

(Received February 1, 2013; accepted June 3, 2013; published online July 22, 2013)

We calculate the drag coefficient of a rigid spherical particle in an incompressible binary fluid mixture. A weak preferential attraction is assumed between the particle surface and one of the fluid components, and the difference in the viscosity between the two components is neglected. Using the Gaussian free-energy functional and solving the hydrodynamic equation explicitly, we can show that the preferential attraction makes the drag coefficient larger as the bulk correlation length becomes longer. The dependence of the deviation from the Stokes law on the correlation length, when it is short, turns out to be much steeper than the previous estimates.

KEYWORDS: colloid dynamics, wetting, two-component fluid, time-dependent Ginzburg–Landau equation, model H

1. Introduction

Studies on colloid particles in a fluid have contributed to progress in fundamental sciences in not only the statics but also the dynamics.[1–3] A system of particles exhibits various thermodynamic phases, while a particle exhibits Brownian motion. If it moves translationally with a sufficiently low speed in a quiescent fluid, a particle suffers a drag force, the magnitude of which is proportional to the particle speed. The constant of the proportion γ is called the drag coefficient. For a rigid spherical particle with the radius r_0 in a three-dimensional incompressible fluid with the viscosity η, the drag coefficient is given by $\gamma = 6\pi\eta r_0$, which is called the Stokes law.[4] In the theory of Brownian motion, the diffusion constant of the particle is found to be $k_B T/(6\pi\eta r_0)$, where k_B and T are the Boltzmann constant and the temperature of the fluid, respectively.[5,6]

It is probable, in a binary fluid mixture, that the surface of a colloid particle preferentially attracts one of the fluid components. This results in a concentration gradient (or adsorption layer) near the colloid particle. Several experimental groups have observed adsorption-induced an aggregation of colloid particles slightly outside the coexistence curve of water-organic solvent mixtures.[7–12] The magnitude and range of the heterogeneity in the concentration tend to become larger when the critical demixing point is approached. Furthermore, near the critical point, the concentration profile and inter-particle interaction energy exhibit universal behavior, i.e., it does not depend on the microscopic details of the surface and solvent molecules if the physical quantities are scaled appropriately.[13–16]

The adsorption layer should affect the fluid flow near the colloid particle to modify the Stokes law. Light scattering experiments have revealed that the diffusion constant of a colloid particle becomes vanishingly small when the critical point is approached.[17–21] To be more precise, in Ref. 19, the ratio γ/η diverges as $|T - T_c|^{-\nu}$, where T_c and ν are the critical temperature and the critical exponent characterizing the divergence of the bulk correlation length ξ_c, respectively. This result may be explained by the divergence of the "effective radius" of the particle, $r_0 + \xi_c$; the adsorption layer with the thickness ξ_c amplifies the drag force.[19] In Refs. 20 and 21, the authors estimated dependence of the drag coefficient on the bulk correlation length without solving the hydrodynamic equation explicitly. Recently, Nakamura et al. have developed a microscopic theory to investigate the drag coefficient of a rigid spherical particle in a binary hard-sphere solvent in which two solvent species have different radii.[22] They found that the drag coefficient grows as the molar fraction of the cosolvent (larger solvent spheres) increases, which stems from the difference between the radial distribution functions of the two solvent species near the particle surface. Camley and Brown have examined the drag coefficient of a circular inclusion in a two-dimensional fluid membrane with a nonconserved scalar order parameter surrounded by a three-dimensional fluid.[23]

In this paper, we calculate the drag coefficient of a rigid spherical particle in an incompressible near-critical binary fluid mixture, which is not extremely close to the critical point. A weak preferential attraction is assumed between the surface and one of the fluid components, and the difference in the viscosity between the two components is neglected. Still, we can show that the adsorption layer near the surface affects the drag coefficient. We formulate our problem in Sect. 2 and explicitly solve the equations in a perturbative way in Sect. 3, with some details relegated to Appendices. In Sect. 4, up to the lowest order of strength of the preferential attraction, we calculate the drag coefficient, the expression of which includes the exponential integral. Section 5 is devoted to discussion.

2. Formulation

Our system is composed of a rigid spherical particle immersed in a two-component fluid with a constant and homogeneous temperature T. Let ρ_A be the mass density of one component A and ρ_B that of the other component B. They depend on the spatial position, represented by $\boldsymbol{r}$, and vanish inside the particle. The region inside the particle is denoted by C, its surface by ∂C, and the region outside the particle by C^e. The whole region of our system is thus represented by $C \cup C^e \cup \partial C$. We define the concentration difference φ as $\rho_A - \rho_B$ and the total mass density ρ_{tot} as $\rho_A + \rho_B$.

2.1 Statics

Let us consider the equilibrium profile of φ with the particle fixed. We set the polar coordinate system (r, θ, ϕ) so that the origin coincides with the particle center. We write $\boldsymbol{e}_r$, $\boldsymbol{e}_\theta$, and $\boldsymbol{e}_\phi$ for the unit vectors along the respective coordinate curves. The unit vector along the polar axis is denoted by $\boldsymbol{e}_z$; we have $\boldsymbol{e}_r \cdot \boldsymbol{e}_z = \cos\theta$ and $\boldsymbol{e}_\theta \cdot \boldsymbol{e}_z = -\sin\theta$.

We assume the fluid to be almost incompressible for the present. Its free energy density in the bulk can be separated into the term free from the gradient, denoted by $f(\rho_{\mathrm{tot}}, \varphi)$, and the term proportional to the square gradient of φ. The free-energy functional of our system, $\mathcal{F}$, can be considered to be given by the sum of the volume integral of these terms and the surface contribution, which is assumed to be given by the surface integral of the potential f_{s} determined by φ at the surface.[24] Thus, we have

$$\mathcal{F} = \int_{C^{\mathrm{e}}} \mathrm{d}\boldsymbol{r} \left\{ f(\rho_{\mathrm{tot}}(\boldsymbol{r}), \varphi(\boldsymbol{r})) + \frac{1}{2} M |\nabla\varphi(\boldsymbol{r})|^2 \right\} + \int_{\partial C} \mathrm{d}S f_{\mathrm{s}}(\varphi(\boldsymbol{r})), \tag{2.1}$$

where M is a positive constant. Far from the particle, we can assume ρ_{A} and ρ_{B} to reach their respective plateau values, which can be realized in experiments. Thus, a constant, φ_∞, can be defined so that it satisfies

$$\varphi(\boldsymbol{r}) \to \varphi_\infty \quad \text{as } |\boldsymbol{r}| \to \infty. \tag{2.2}$$

The most probable φ is considered to be macroscopically observed in the static state, according to the mean-field approximation. In the limit of incompressibility, we can drop the constant ρ_{tot} from the variables of f. The most probable φ makes

$$\mathcal{F} - \mu \int_{C^{\mathrm{e}}} \mathrm{d}\boldsymbol{r}\, \varphi(\boldsymbol{r}) \tag{2.3}$$

stationary with respect to φ, where μ is the undetermined multiplier. Below, the prime indicates the derivative with respect to the variable, e.g., $f'(\varphi) = \mathrm{d}f(\varphi)/(\mathrm{d}\varphi)$. The stationary condition gives

$$f'(\varphi(\boldsymbol{r})) - M\Delta\varphi(\boldsymbol{r}) = \mu \quad \text{in } C^{\mathrm{e}}, \tag{2.4}$$

the left-hand side (lhs) of which is the functional derivative of $\mathcal{F}$ with respect to $\varphi(\boldsymbol{r})$, and

$$M\boldsymbol{e}_r \cdot \nabla\varphi(\boldsymbol{r}) = f_{\mathrm{s}}'(\varphi) \quad \text{at } \partial C_+, \tag{2.5}$$

where ∂C_+ implies that the derivative is evaluated just outside the particle. For simplicity, we further assume the potential function to be a linear function in φ,

$$f_{\mathrm{s}}(\varphi) = h_0 - h\varphi, \tag{2.6}$$

where h_0 and h are assumed to be constant. The right-hand side (rhs) of Eq. (2.5) thus equals $-h$. Let us write μ_{A} for the chemical potential of the component A per unit mass and μ_{B} for that of the other. The functional derivative of $\mathcal{F}$ with respect to ρ_{A} gives μ_{A}. We thus find Eq. (2.4), or μ, equal to half of the chemical potential difference, $(\mu_{\mathrm{A}} - \mu_{\mathrm{B}})/2$, considering that we have

$$\mu_{\mathrm{A}}\delta\rho_{\mathrm{A}} + \mu_{\mathrm{B}}\delta\rho_{\mathrm{B}} = \frac{(\mu_{\mathrm{A}} + \mu_{\mathrm{B}})\delta\rho_{\mathrm{tot}}}{2} + \frac{(\mu_{\mathrm{A}} - \mu_{\mathrm{B}})\delta\varphi}{2}, \tag{2.7}$$

where δ implies the infinitesimal change. Taking the limit $r \to \infty$ in Eq. (2.4), we have $\mu = f'(\varphi_\infty)$.

We introduce a dimensionless correlation length in the bulk,

$$\zeta_{\mathrm{c}} \equiv \frac{\xi_{\mathrm{c}}}{r_0} = \frac{1}{r_0}\sqrt{\frac{M}{f''(\varphi_\infty)}}. \tag{2.8}$$

Here, $f''(\varphi_\infty)$ is positive for the thermodynamic stability. Linearizing Eq. (2.4) by regarding $f'(\varphi)$ as $\mu + f''(\varphi_\infty)(\varphi - \varphi_\infty)$ approximately, we can obtain

$$\varphi(\boldsymbol{r}) = \varphi_\infty + \frac{h r_0 \mathrm{e}^{(1-\rho)/\zeta_{\mathrm{c}}}}{M\rho(1 + \zeta_{\mathrm{c}}^{-1})}, \tag{2.9}$$

where $\rho \equiv r/r_0 = |\boldsymbol{r}|/r_0$ is a dimensionless radial length. The approximation would be valid when

$$|hf'''(\varphi_\infty)|\xi_{\mathrm{c}}/M \ll f''(\varphi_\infty), \tag{2.10}$$

considering that $|\varphi - \varphi_\infty|$ would not be much larger than the product of the correlation length and $|\boldsymbol{e}_r \cdot \nabla\varphi|$ at $r = r_0$, i.e., than $|h|\xi_{\mathrm{c}}/M$.

2.2 Dynamics

In the fluid dynamics out of the global equilibrium, we assume the local equilibrium to regard Eq. (2.1) as the sum of the local free energies. As in the usual thermodynamics, we can discuss an infinitesimal reversible process of a macroscopically infinitesimal comoving fluid region by assuming the environments with the temperature T, the pressure tensor $\Pi(\boldsymbol{r})$, and the chemical potentials. We need not consider a change in the temperature in this process because we will consider the isothermal dynamics. The tensor Π amounts to the reversible part of the pressure tensor in the dynamics.

We write $\mathbf{1}$ for the isotropic tensor. After the same calculations that lead to the stress tensor in the hydrodynamic model of near-critical fluids (the so-called model H),[25,26] we can find

$$\Pi = p\mathbf{1} + p_{\mathrm{osm}}\mathbf{1} + \Pi_{\mathrm{grad}}, \tag{2.11}$$

where p comes from the infinitesimal change in ρ_{tot} and can be regarded as dependent only on $\boldsymbol{r}$ in the steady state in the limit of incompressibility, and we use

$$p_{\mathrm{osm}} \equiv \varphi f'(\varphi) - f(\varphi) \tag{2.12}$$

and

$$\Pi_{\mathrm{grad}} \equiv -M\left(\frac{1}{2}|\nabla\varphi|^2 + \varphi\Delta\varphi\right)\mathbf{1} + M\nabla\varphi\nabla\varphi. \tag{2.13}$$

See Appendix A for details. The chemical potential difference is found to be

$$\hat{\mu}(\boldsymbol{r}) = f'(\varphi(\boldsymbol{r})) - M\Delta\varphi(\boldsymbol{r}), \tag{2.14}$$

which satisfies the equation,

$$\varphi\nabla\hat{\mu} = \nabla p_{\mathrm{osm}} + \nabla\cdot\Pi_{\mathrm{grad}}, \tag{2.15}$$

like the Gibbs–Duhem relation. We also find Eq. (2.5) to be valid in the infinitesimal change we now consider. We assume the local equilibrium even just outside the particle, which means that the reversible part of the force exerted on the particle by the fluid is given by

$$-\int_{\partial C^+} \mathrm{d}S(p\mathbf{1}+p_{\mathrm{osm}}\mathbf{1}+\Pi_{\mathrm{grad}})\cdot\boldsymbol{e}_r. \tag{2.16}$$

The dissipative dynamics can be formulated in terms of the irreversible thermodynamics.[27] As discussed in Appendix A, we assume that the dissipation occurs through the viscosity and the diffusive flux between the two components. Thus, Eq. (2.5) is valid in the dissipative dynamics. Let $\boldsymbol{v}$ denote the velocity field, and the dissipative stress tensor is given by $2\eta E$, where the rate-of-strain tensor E is defined as

$$E \equiv \frac{1}{2}\{\nabla\boldsymbol{v}+(\nabla\boldsymbol{v})^{\mathrm{T}}\}, \tag{2.17}$$

with the superscript "T" indicating the transposition. At the given temperature T, the viscosity far from the particle has a renormalized value, η, which depends weakly on ξ_{c}.[26] We assume for simplicity that the viscosity is given by η over the region C^{e}, irrespective of φ. Thus, we use the steady Stokes approximation to have

$$0 = \boldsymbol{v}\cdot\nabla\varphi - L\Delta\hat{\mu}, \tag{2.18}$$

$$0 = -\nabla(p+p_{\mathrm{osm}}) - \nabla\cdot\Pi_{\mathrm{grad}} + \eta\Delta\boldsymbol{v}, \tag{2.19}$$

where the Onsager coefficient L is assumed to be a positive constant, and the second term on the rhs of Eq. (2.18) represents the divergence of the diffusive flux, as is found from Eq. (A·13). We assume the fluid to be incompressible to have

$$0 = \mathrm{div}\,\boldsymbol{v}. \tag{2.20}$$

In the equilibrium state discussed in Sect. 2.1, $\hat{\mu}(\boldsymbol{r})$ equals the constant μ, and thus $p(\boldsymbol{r})$ is a constant, referred to as $p^{(0)}$ below, because of Eqs. (2.15) and (2.19).

3. Calculation

We introduce a small dimensionless parameter ϵ for the perturbation scheme formulated below. In a quiescent fluid, some external force is assumed to cause a slow translational motion of the particle. We consider the moment when the particle center coincides with the origin of the coordinate system introduced in Sect. 2.1. Let U be a nonzero constant scalar with the dimension of the speed, and we assume the particle to move with the velocity $\epsilon U\boldsymbol{e}_z$ at the moment. It is assumed that, far from the particle, the fluid tends to be static and the concentration difference is still given by φ_∞. Thus, we have

$$\boldsymbol{v}(\boldsymbol{r}) \to \boldsymbol{0} \quad \text{and} \quad \hat{\mu}(\boldsymbol{r}) \to \mu \quad \text{as } r\to\infty. \tag{3.1}$$

Far from the particle, irrespective of ϵ, we find Π_{grad} to vanish and p_{osm} to remain the same, and we can assume p to remain $p^{(0)}$. The no-slip boundary condition is imposed at the particle surface. The radial component of the diffusive flux should vanish at the moving surface, as mentioned in Eq. (A·11). Thus, we have

$$\boldsymbol{v}(\boldsymbol{r}) \to \epsilon U\boldsymbol{e}_z \quad \text{and} \quad \boldsymbol{e}_r\cdot\nabla\hat{\mu} \to 0 \quad \text{at } r\to r_0+, \tag{3.2}$$

where $r\to r_0+$ means that r approaches r_0 with $r>r_0$ being kept.

We expand the fields as

$$\begin{aligned} p(\boldsymbol{r}) &= p^{(0)} + \epsilon p^{(1)}(\boldsymbol{r}) + o(\epsilon),\\ \boldsymbol{v}(\boldsymbol{r}) &= \epsilon\boldsymbol{v}^{(1)}(\boldsymbol{r}) + o(\epsilon),\\ \hat{\mu}(\boldsymbol{r}) &= \mu + \epsilon\hat{\mu}^{(1)}(\boldsymbol{r}) + o(\epsilon). \end{aligned} \tag{3.3}$$

On each rhs of Eq. (3.3), the field with the superscript "(1)" is defined so that it becomes proportional to ϵ after being multiplied by ϵ, and $o(\epsilon)$ implies higher order terms. The rhs of Eq. (2.9) should be referred to as $\varphi^{(0)}(r)$. We define

$$\kappa(\rho) \equiv \frac{\rho+\zeta_{\mathrm{c}}}{1+\zeta_{\mathrm{c}}}\,\mathrm{e}^{(1-\rho)/\zeta_{\mathrm{c}}}, \tag{3.4}$$

so as to have $\varphi^{(0)\prime}(r) = -h\kappa(\rho)/(M\rho^2)$ with ρ being r/r_0. Using Eqs. (2.4) and (2.12)–(2.14), we have

$$\hat{\mu}^{(1)} = f''(\varphi^{(0)})\varphi^{(1)} - M\Delta\varphi^{(1)}, \tag{3.5}$$

$$p^{(1)}_{\mathrm{osm}} = f''(\varphi^{(0)})\varphi^{(0)}\varphi^{(1)}, \tag{3.6}$$

$$\begin{aligned} \Pi^{(1)}_{\mathrm{grad}} = {}& -M(\nabla\varphi^{(0)}\cdot\nabla\varphi^{(1)} + \varphi^{(1)}\Delta\varphi^{(0)} + \varphi^{(0)}\Delta\varphi^{(1)})\mathbf{1}\\ & + M(\nabla\varphi^{(0)}\nabla\varphi^{(1)} + \nabla\varphi^{(1)}\nabla\varphi^{(0)}). \end{aligned} \tag{3.7}$$

From Eqs. (2.18) and (2.19), we have

$$\boldsymbol{v}^{(1)}\cdot\nabla\varphi^{(0)} = L\Delta\hat{\mu}^{(1)}, \tag{3.8}$$

$$\nabla p^{(1)} = -\varphi^{(0)}\nabla\hat{\mu}^{(1)} + \eta\Delta\boldsymbol{v}^{(1)}. \tag{3.9}$$

As mentioned before, we still have Eqs. (2.2) and (2.5) in the dynamics. Thus, also noting Eqs. (3.1) and (3.2), we have

$$\varphi^{(1)},\ p^{(1)},\ \hat{\mu}^{(1)} \to 0 \quad \text{and} \quad \boldsymbol{v}^{(1)} \to \boldsymbol{0} \quad \text{as } r\to\infty, \tag{3.10}$$

while

$$\boldsymbol{e}_r\cdot\nabla\varphi^{(1)},\ \boldsymbol{e}_r\cdot\nabla\hat{\mu}^{(1)} \to 0 \quad \text{and} \quad \boldsymbol{v}^{(1)} \to U\boldsymbol{e}_z \quad \text{as } r\to r_0+. \tag{3.11}$$

We expand the fields of the order of ϵ with respect to the vector spherical harmonics. For the integers j and m satisfying $j\geq 0$ and $-j\leq m\leq j$, they are[28]

$$\begin{aligned} \boldsymbol{P}_{jm}(\theta,\phi) &= \boldsymbol{e}_r Y_{jm}(\theta,\phi),\\ \boldsymbol{B}_{jm}(\theta,\phi) &= N_j^{-1}(\boldsymbol{e}_\theta\partial_\theta + \boldsymbol{e}_\phi\,\mathrm{cosec}\,\theta\partial_\phi)Y_{jm}(\theta,\phi),\\ \boldsymbol{C}_{jm}(\theta,\phi) &= N_j^{-1}(\boldsymbol{e}_\theta\,\mathrm{cosec}\,\theta\partial_\phi - \boldsymbol{e}_\phi\partial_\theta)Y_{jm}(\theta,\phi), \end{aligned} \tag{3.12}$$

where $N_j \equiv \sqrt{j(j+1)}$ is used, and Y_{jm} denotes the spherical harmonics. In particular, we have $Y_{10}(\theta,\phi) = \sqrt{3/(4\pi)}\cos\theta$. Although $\boldsymbol{P}_{jm}$ is defined for $j\geq 0$, $\boldsymbol{B}_{jm}$ and $\boldsymbol{C}_{jm}$ are defined only for $j\geq 1$. Let (r,θ,ϕ) be the components of $\boldsymbol{r}$. We then define

$$\hat{\mu}^{(1)}(\boldsymbol{r}) = \sum_{jm} Q_{jm}(r)Y_{jm}(\theta,\phi), \tag{3.13}$$

$$p^{(1)}(\boldsymbol{r}) = \sum_{jm} p_{jm}(r)Y_{jm}(\theta,\phi), \tag{3.14}$$

$$\begin{aligned} \boldsymbol{v}^{(1)}(\boldsymbol{r}) = \sum_{jm}\{ & R_{jm}(r)\boldsymbol{P}_{jm}(\theta,\phi) + T_{jm}(r)\boldsymbol{B}_{jm}(\theta,\phi)\\ & + S_{jm}(r)\boldsymbol{C}_{jm}(\theta,\phi)\}, \end{aligned} \tag{3.15}$$

where $Q_{jm}, p_{jm}, \ldots, S_{jm}$ are the r-dependent expansion coefficients. We assume T_{00} and S_{00} to be equal to zero, and the sum is over all the values of j and m considered just above Eq. (3.12). Because $Y^{\mathrm{c}}_{jm} = (-1)^m Y_{j,-m}$, with the superscript "c" indicating the complex conjugate, the coefficients should share the corresponding property, such as

$$R^{\rm c}_{jm} = (-1)^m R_{j,-m}, \tag{3.16}$$

so that the fields are real.

After performing some algebra shown in Appendix B, we find S_{jm} to vanish for any (j,m), and

$$p_{jm} = R_{jm} = T_{jm} = Q_{jm} = 0 \quad \text{except for } (j,m) = (1,0). \tag{3.17}$$

Thus, we can concentrate on the mode of $(1,0)$, and Eqs. (3.13)–(3.15) are respectively reduced to

$$\hat{\mu}^{(1)} = Q_{10} Y_{10}, \quad p^{(1)} = p_{10} Y_{10}, \tag{3.18}$$

and

$$\boldsymbol{v}^{(1)} = R_{10}\boldsymbol{P}_{10} + T_{10}\boldsymbol{B}_{10}. \tag{3.19}$$

Equation (2.20) relates T_{10} with R_{10}, as shown by Eq. (B·1). We write ∂_r for the differentiation with respect to r, and ∂_r^2 for $\partial_r \partial_r$. Substituting Eqs. (3.18) and (3.19) into Eq. (3.8) gives

$$L(\partial_r^2 + 2r^{-1}\partial_r - 2r^{-2}) Q_{10} = R_{10}\partial_r \varphi^{(0)}. \tag{3.20}$$

The rhs of Eq. (3.9) is irrotational, which is combined with (3.18) and (3.19) to give

$$\eta(r^2\partial_r^4 + 8r\partial_r^3 + 8\partial_r^2 - 8r^{-1}\partial_r) R_{10} = 2Q_{10}\partial_r \varphi^{(0)}, \tag{3.21}$$

with the aid of Eq. (B·1). Equations (3.20) and (3.21) are respectively the mode of $(1,0)$ of Eq. (B·3) and that of Eq. (B·8). Equations (3.10) and (3.11) give

$$p_{10},\ R_{10},\ Q_{10} \to 0 \quad \text{as } r \to \infty, \tag{3.22}$$

$$R_{10} \to \sqrt{4\pi/3}U \quad \text{and} \quad \partial_r Q_{10},\ \partial_r R_{10} \to 0 \quad \text{as } r \to r_0+, \tag{3.23}$$

as mentioned in the third paragraph of Appendix B.

From Eqs. (3.20), (3.22), and (3.23), we find that Q_{10} vanishes if h vanishes. We introduce dimensionless functions, $\mathcal{Q}(\rho) \equiv 3ML Q_{10}(r)/(Uhr_0^2)$ and $\mathcal{R}(\rho) \equiv R_{10}(r)/U$, where we use $\rho \equiv r/r_0$ as before. We also introduce a dimensionless factor

$$\lambda \equiv \frac{hr_0^2}{3M\sqrt{5L\eta}}. \tag{3.24}$$

If h vanishes, we find $\mathcal{R}(\rho)$ to be given by

$$\mathcal{R}_{h=0}(\rho) \equiv \sqrt{\frac{4\pi}{3}}\left(-\frac{1}{2\rho^3} + \frac{3}{2\rho}\right) \tag{3.25}$$

from Eqs. (3.21)–(3.23). In general, as shown in Appendix B, applying the method of variation of parameters to Eqs. (3.20)–(3.23), we can obtain

$$\mathcal{Q}(\rho) = \int_1^\infty {\rm d}\sigma\, \kappa(\sigma)\Gamma_{\rm Q}(\rho,\sigma)\mathcal{R}(\sigma), \tag{3.26}$$

$$\mathcal{R}(\rho) = \mathcal{R}_{h=0}(\rho) + \lambda^2 \int_1^\infty {\rm d}\sigma\, \kappa(\sigma)\Gamma_{\rm R}(\rho,\sigma)\mathcal{Q}(\sigma). \tag{3.27}$$

Here,

$$\Gamma_{\rm Q}(\rho,\sigma) \equiv \begin{cases} \{(\rho\sigma)^{-2}/2\} + \sigma\rho^{-2} & \text{if } 1 \le \sigma < \rho \\ \{(\rho\sigma)^{-2}/2\} + \rho\sigma^{-2} & \text{if } \rho \le \sigma \end{cases} \tag{3.28}$$

and

$$\Gamma_{\rm R}(\rho,\sigma) \equiv \begin{cases} \Gamma_{\rm Rcom}(\rho,\sigma) + \sigma^2\rho^{-3} - 5\rho^{-1} & \text{if } 1 \le \sigma < \rho \\ \Gamma_{\rm Rcom}(\rho,\sigma) + \rho^2\sigma^{-3} - 5\sigma^{-1} & \text{if } \rho \le \sigma \end{cases}, \tag{3.29}$$

where the common term is

$$\Gamma_{\rm Rcom}(\rho,\sigma) \equiv \frac{3-5\sigma^2}{2\sigma^3\rho^3} + \frac{5(3\sigma^2-1)}{2\rho\sigma^3}. \tag{3.30}$$

The lowest-order correction due to a nonzero h value is given by replacing $\mathcal{R}$ by $\mathcal{R}_{h=0}$ on the rhs of Eq. (3.26) and substituting the resultant approximate solution of $\mathcal{Q}$ into the rhs of (3.27). Thus, up to this order, we have

$$\mathcal{Q}(\rho) = \int_1^\infty {\rm d}\sigma\, \kappa(\sigma)\Gamma_{\rm Q}(\rho,\sigma)\mathcal{R}_{h=0}(\sigma), \tag{3.31}$$

$$\mathcal{R}(\rho) = \mathcal{R}_{h=0}(\rho) + \lambda^2 \int_1^\infty {\rm d}\sigma\, \kappa(\sigma)\Gamma_{\rm R}(\rho,\sigma) \times \int_1^\infty {\rm d}\sigma'\, \kappa(\sigma')\Gamma_{\rm Q}(\sigma,\sigma')\mathcal{R}_{h=0}(\sigma'). \tag{3.32}$$

For later convenience, we write $p^{(1)}$ and $\boldsymbol{v}^{(1)}$ in terms of $\mathcal{Q}$ and $\mathcal{R}$. Let $\boldsymbol{r}$ have the components $(\rho r_0, \theta, \phi)$ in the polar coordinate system. We can use Eqs. (B·1) and (B·6) to rewrite the second equation of Eq. (3.18) as

$$p^{(1)}(\boldsymbol{r}) = U\left\{\frac{\eta}{\rho r_0}\left(\frac{1}{2}\rho^3\partial_\rho^3 + 3\rho^2\partial_\rho^2 + 2\rho\partial_\rho\right)\mathcal{R}(\rho) - \frac{hr_0^2}{3ML}\varphi^{(0)}(r)\mathcal{Q}(\rho)\right\} Y_{10}(\theta,\phi), \tag{3.33}$$

and use Eq. (B·1) to rewrite Eq. (3.19) as

$$\boldsymbol{v}^{(1)}(\boldsymbol{r}) = U\left\{\boldsymbol{e}_r Y_{10}(\theta,\phi) + \boldsymbol{e}_\theta \frac{\partial Y_{10}(\theta,\phi)}{\partial\theta}\left(\frac{\rho}{2}\partial_\rho + 1\right)\right\}\mathcal{R}(\rho). \tag{3.34}$$

4. Results

For simplicity, we assume the Gaussian model

$$f(\varphi) = \frac{a}{2}(\varphi - \varphi_\infty)^2 + \mu(\varphi - \varphi_\infty), \tag{4.1}$$

where a is a positive constant. This constant, being the reciprocal susceptibility, can be assumed to be proportional to the temperature measured from the critical point. From Eqs. (3.5) and (3.18), we have

$$(a - M\Delta)\varphi^{(1)}(\boldsymbol{r}) = Q_{10} Y_{10}, \tag{4.2}$$

and $G_{10}(r)$ can be defined so as to satisfy

$$\varphi^{(1)}(\boldsymbol{r}) = G_{10}(r) Y_{10}(\theta,\phi). \tag{4.3}$$

From these two equations, we can obtain

$$\{a - M(\partial_r^2 + 2r^{-1}\partial_r - 2r^{-2})\} G_{10}(r) = Q_{10}(r). \tag{4.4}$$

Here we have $\zeta_{\rm c} = \sqrt{M/a}/r_0$ from Eq. (2.8). Introducing a dimensionless variable $\tilde{\rho} \equiv \rho/\zeta_{\rm c} = r/(r_0\zeta_{\rm c})$, we find linear independent solutions of the homogeneous equation associated with Eq. (4.4) to be given by

$$I_{3/2}(\tilde{\rho})/\sqrt{\tilde{\rho}} = \frac{1}{\tilde{\rho}}\sqrt{\frac{2}{\pi}}\left(\cosh\tilde{\rho} - \frac{1}{\tilde{\rho}}\sinh\tilde{\rho}\right), \tag{4.5}$$

$$K_{3/2}(\tilde{\rho})/\sqrt{\tilde{\rho}} = \frac{1}{\tilde{\rho}}\sqrt{\frac{\pi}{2}}\left(1 + \frac{1}{\tilde{\rho}}\right){\rm e}^{-\tilde{\rho}}, \tag{4.6}$$

where $I_{3/2}$ and $K_{3/2}$ represent modified Bessel functions. Equations (3.10) and (3.11) lead to

$$G_{10}(r) \to 0 \quad \text{as } r \to \infty, \tag{4.7}$$

$$\partial_r G_{10}(r) \to 0 \quad \text{as } r \to r_0+. \tag{4.8}$$

Applying the method of variation of parameters, we can obtain G_{10} so that it satisfies these boundary conditions. By means of $\tilde{\rho} \equiv \rho/\zeta_c$ and $\tilde{\sigma} \equiv \sigma/\zeta_c$, we first define

$$\Gamma_{\mathrm{Gcom}}(\rho,\sigma) \equiv -w(\zeta_c)K_{3/2}(\tilde{\rho})K_{3/2}(\tilde{\sigma})\tilde{\sigma}, \tag{4.9}$$

where

$$w(\zeta_c) \equiv \frac{I'_{3/2}(\zeta_c^{-1}) - \zeta_c I_{3/2}(\zeta_c^{-1})/2}{K'_{3/2}(\zeta_c^{-1}) - \zeta_c K_{3/2}(\zeta_c^{-1})/2}, \tag{4.10}$$

and then define

$$\Gamma_G(\rho,\sigma) \equiv \begin{cases} \Gamma_{\mathrm{Gcom}}(\rho,\sigma) + K_{3/2}(\tilde{\rho})I_{3/2}(\tilde{\sigma})\tilde{\sigma} & \text{if } 1 \le \sigma < \rho \\ \Gamma_{\mathrm{Gcom}}(\rho,\sigma) + I_{3/2}(\tilde{\rho})K_{3/2}(\tilde{\sigma})\tilde{\sigma} & \text{if } \rho \le \sigma \end{cases}. \tag{4.11}$$

After performing some algebra, we can obtain

$$G_{10}(r) = \frac{Uhr_0^4\zeta_c}{3M^2L\sqrt{\rho}} \int_1^\infty \mathrm{d}\sigma\, \sqrt{\sigma}\Gamma_G(\rho,\sigma)\mathcal{Q}(\sigma). \tag{4.12}$$

We can write $D_{\mathrm{rag}}\boldsymbol{e}_z$ for the drag force exerted on the particle. Noting Eq. (2.16), we obtain

$$D_{\mathrm{rag}} = -\int_{\partial C_+} \mathrm{d}S\, \boldsymbol{e}_r \cdot \{(p + p_{\mathrm{osm}})\mathbf{1} + \Pi_{\mathrm{grad}} - 2\eta E\} \cdot \boldsymbol{e}_z. \tag{4.13}$$

The unperturbed terms in Eq. (3.3) do not contribute to the drag force because they are only dependent on r. Equations (3.6) and (3.7) yield

$$p^{(1)}_{\mathrm{osm}} = a\varphi^{(0)}G_{10}Y_{10}, \tag{4.14}$$

$$\begin{aligned}\Pi^{(1)}_{\mathrm{grad}} = {} & -M\{(\varphi^{(0)\prime}\partial_r G_{10} + G_{10}\Delta\varphi^{(0)})Y_{10} + \varphi^{(0)}\Delta\varphi^{(1)}\}\mathbf{1} \\ & + M\varphi^{(0)\prime}[\boldsymbol{e}_r\nabla(G_{10}Y_{10}) + \{\nabla(G_{10}Y_{10})\}\boldsymbol{e}_r],\end{aligned} \tag{4.15}$$

where $\Delta\varphi^{(1)}$ can be rewritten as $(a\varphi^{(1)} - \hat{\mu}^{(1)})/M$ because of Eq. (3.5), and we can use

$$\nabla(G_{10}Y_{10}) = \frac{\mathrm{d}G_{10}(r)}{\mathrm{d}r}Y_{10}\boldsymbol{e}_r + \frac{G_{10}}{r}\frac{\partial Y_{10}}{\partial\theta}\boldsymbol{e}_\theta. \tag{4.16}$$

As mentioned in Eq. (2.6) of Ref. 28, we use Eq. (B·1) to obtain

$$\begin{aligned} & 2\boldsymbol{e}_r \cdot E \\ & = \epsilon(\boldsymbol{e}_r \times \mathrm{rot}\,\boldsymbol{v}^{(1)} + 2\partial_r\boldsymbol{v}^{(1)}) \qquad (4.17) \\ & = \epsilon\left\{2\partial_r R_{10}\boldsymbol{P}_{10}(\theta,\phi) + \sqrt{2}\left(\frac{1}{2}r\partial_r + 1\right)\partial_r R_{10}\boldsymbol{B}_{10}(\theta,\phi)\right\}. \qquad (4.18)\end{aligned}$$

Because of Eq. (2.5), $\varphi^{(0)\prime}$ equals $-h/M$ in the surface integral of Eq. (4.13). Thus, using Eqs. (3.23), (3.33), (4.8), and (4.14)–(4.18), we can replace the integrand of Eq. (4.13) by

$$\begin{aligned}\epsilon\Bigg\{ & -\eta r^{-1}\left(\frac{1}{2}r^3\partial_r^3 + 3r^2\partial_r^2\right)R_{10}Y_{10}\cos\theta \\ & + MG_{10}r^{-2}(r^2\partial_r^2 + 2r\partial_r)\varphi^{(0)}Y_{10}\cos\theta \\ & - r^{-1}\left(hG_{10} + \frac{\eta}{2}r^2\partial_r^2 R_{10}\right)\frac{\partial Y_{10}}{\partial\theta}\sin\theta\Bigg\}.\end{aligned} \tag{4.19}$$

Thus, we can rewrite the rhs of Eq. (4.13) as

$$-2\epsilon r_0\eta U\sqrt{\frac{\pi}{3}}\left\{\left(\frac{1}{2}\partial_\rho^3 + 2\partial_\rho^2\right)\mathcal{R}(\rho)\Big|_{\rho=1} - \frac{hW(\zeta_c)}{\eta U}G_{10}(r_0)\right\}, \tag{4.20}$$

where $|_{\rho=1}$ implies that the derivative should be evaluated at $\rho = 1$, and

$$W(\zeta_c) \equiv 2 + \frac{1}{\zeta_c^2 + \zeta_c}. \tag{4.21}$$

We define $X(\rho)$ so that $\mathcal{R}_{h=0}(\rho) = \sqrt{4\pi/3}X(\rho)$. Substituting Eqs. (3.31), (3.32), and (4.12) into Eq. (4.20), we can obtain the drag coefficient $\gamma \equiv -D_{\mathrm{rag}}/(\epsilon U)$ as

$$\gamma = 6\pi\eta r_0\left\{1 + \frac{h^2r_0^4}{27M^2L\eta}\delta(\zeta_c)\right\} \tag{4.22}$$

up to the order of $\lambda^2 \propto h^2$, where

$$\begin{aligned}\delta(\zeta_c) = {} & \int_1^\infty \mathrm{d}\rho\left(\frac{3}{\rho} - \frac{1}{\rho^3}\right)\kappa(\rho) \\ & \times \int_1^\infty \mathrm{d}\sigma\, \kappa(\sigma)\Gamma_Q(\rho,\sigma)X(\sigma) - 2\zeta_c W(\zeta_c) \\ & \times \int_1^\infty \mathrm{d}\rho\, \sqrt{\rho}\Gamma_G(1,\rho)\int_1^\infty \mathrm{d}\sigma\, \kappa(\sigma)\Gamma_Q(\rho,\sigma)X(\sigma)\end{aligned} \tag{4.23}$$

represents how the deviation from the Stokes law depends on ζ_c. Equation (4.22) shows that the drag coefficient is independent of φ_∞. The independence of Eq. (4.22) from the sign of h can be expected because neither component has a special bulk property in our formulation. Equation (4.22) would have a term proportional to h and would depend on its sign if the viscosity were assumed to depend on φ.

By means of Mathematica version 8 (Wolfram Research),[29] we can calculate the integrals of Eq. (4.23) to obtain

$$\begin{aligned}\delta(\zeta_c) = {} & \frac{1}{1280(1+\zeta_c)^2}[A_1(\zeta_c) + 256A_2(\zeta_c)\mathrm{e}^{2/\zeta_c}\mathrm{Ei}(-2/\zeta_c) \\ & - 10A_3(\zeta_c)\mathrm{e}^{1/\zeta_c}\mathrm{Ei}(-1/\zeta_c) \\ & + 5\{A_4(\zeta_c)\mathrm{e}^{1/\zeta_c}\mathrm{Ei}(-1/\zeta_c)\}^2],\end{aligned} \tag{4.24}$$

where we use the exponential integral

$$\mathrm{Ei}(x) \equiv \int_{-\infty}^x \mathrm{d}t\, \frac{\mathrm{e}^t}{t}, \tag{4.25}$$

and introduce

$$\begin{aligned}A_1(z) \equiv {} & 3840z^3 - 6156z^2 + 168z + 568 \\ & + 32z^{-1} + 161z^{-2} - 10z^{-3} + 5z^{-4},\end{aligned} \tag{4.26}$$

$$A_2(z) \equiv 90z^2 - 45z + 2z^{-3}, \tag{4.27}$$

$$\begin{aligned}A_3(z) \equiv {} & 1152z^2 - 24 - 120z^{-1} - 18z^{-2} \\ & + 22z^{-3} + z^{-4} - z^{-5},\end{aligned} \tag{4.28}$$

$$A_4(z) \equiv -12z^{-1} + z^{-3} \tag{4.29}$$

to write Eq. (4.24) concisely. As ζ_c increases, the first term A_1 is the most relevant in the braces of Eq. (4.24), making $\delta(\zeta_c)$ almost proportional to ζ_c. Using the asymptotic expansion

$$\mathrm{e}^x\mathrm{Ei}(-x) \sim \sum_{n=1}^\infty (-1)^n\frac{(n-1)!}{x^n} \quad \text{as } x \to \infty \tag{4.30}$$

in Eq. (4.24), we obtain

$$\begin{aligned}\delta(\zeta_c) \sim {} & \frac{27\zeta_c^6}{8(1+\zeta_c)^2}(8 - 111\zeta_c + 1231\zeta_c^2) \\ & \text{as } \zeta_c \to 0+,\end{aligned} \tag{4.31}$$

which tells that δ tends to 0 as $\zeta_c \to 0+$, i.e., as ζ_c approaches 0 along the real axis from the positive side. It is to be noted that the correlation length is not assumed to be microscopic in Eq. (4.1). In Fig. 1, we show that Eq. (4.24)

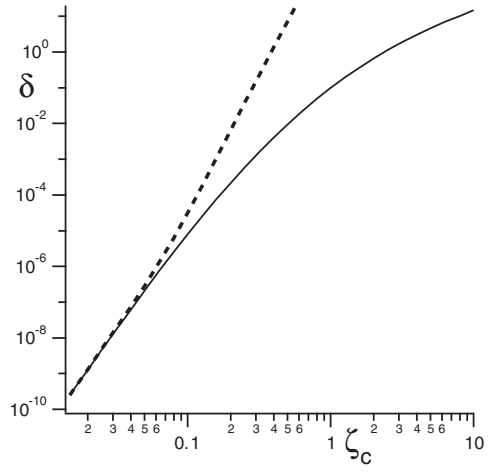

Fig. 1. Plot of δ against ζ_c. The solid and dashed curves respectively represent Eqs. (4.24) and (4.31).

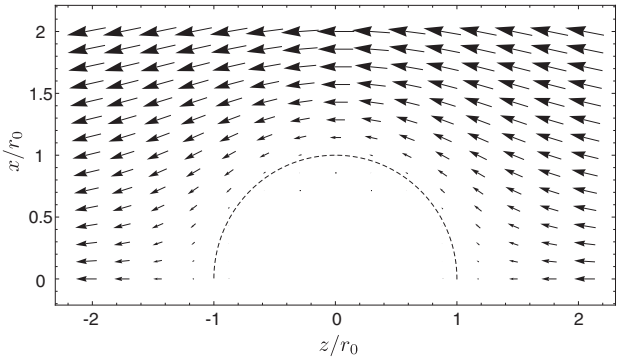

Fig. 2. The velocity field for $h = 0$ is drawn in a region with $x \geq 0$ on the xz plane when viewed from the frame comoving with the particle. The dashed curve represents the cross section of the particle surface.

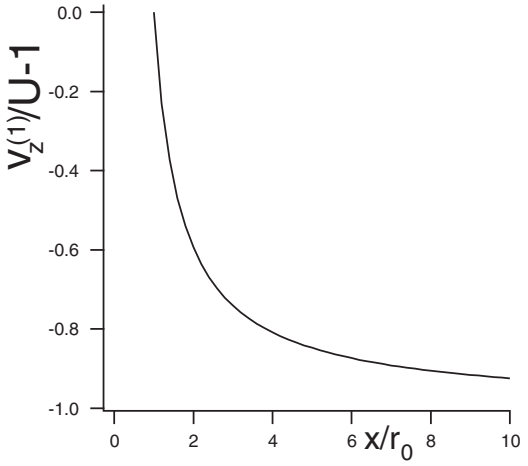

Fig. 3. Plot of $v_z^{(1)}/U - 1$ along the x-axis for $h = 0$.

is positive and increases with ζ_c. According to Eq. (4.22), this means that the drag coefficient increases from the value given by the Stokes law as the strength of the preferential attraction $|h|$ increases and/or as the bulk correlation length increases.

5. Discussion

Following the framework of the irreversible thermodynamics, we formulate the fluid dynamics to examine the drag coefficient of a rigid particle in a near-critical binary fluid mixture. We take into account the preferential attraction of one of the fluid components to the particle surface, represented by Eq. (2.6), and the dynamical coupling between the concentration heterogeneity and the hydrodynamic flow, represented by Eqs. (2.13), (2.18), and (2.19). The mean-field approximation we use holds when the correlation length, $\xi_c = r_0\zeta_c$, is so small that higher-order terms, such as the φ^4 term, are negligible in Eq. (2.1).

We use the Gaussian model by assuming Eq. (4.1), which is substituted into Eq. (2.4) to yield Eq. (2.9) without approximation. We assume a weak preferential attraction between the surface and one of the fluid components ($\lambda^2 \ll 1$), and assume the viscosity η to be independent of the composition, φ. Still, the drag coefficient deviates from the value of the Stokes law, as shown by Eq. (4.22) with Eq. (4.24). We should note the weak dependence of η on ξ_c, as mentioned above Eq. (2.18). When the correlation length is small, we find from Eq. (4.31) that the deviation of the drag coefficient from the value of the Stokes law is proportional to ξ_c^6. This dependence is much steeper than the previous estimate of the ξ_c^2 dependence due to the surface energy effect, which dependence is obtained without solving the hydrodynamic equation explicitly in Ref. 21. The slope of the plots in Fig. 1 gradually decreases from six towards the unity as ζ_c increases.

The velocity field for $h = 0$ can be calculated by means of Eqs. (3.25) and (3.34). This velocity field is well known and leads to the Stokes law. Subtracting the particle velocity from the field, we draw the resultant field on the xz plane in Fig. 2 by means of Mathematica. The figure thus shows the velocity field for $h = 0$ viewed from the frame comoving with the particle. There, an arrow represents the velocity direction with its length proportional to the magnitude. Although similar figures are given below in Figs. 4 and 6, each figure has its constant of proportion, and thus a comparison of the lengths of two arrows in different figures is meaningless. In harmony with Fig. 2, we plot $v_z^{(1)}/U - 1$ for $h = 0$ along the x-axis on the positive side in Fig. 3. It approaches -1 far from the particle and vanishes at the particle surface, because of the last equations of Eqs. (3.10) and (3.11).

As we obtained Eq. (4.24) from Eq. (4.23), we can calculate the double integral on the rhs of Eq. (3.32). The result, not shown here, contains the exponential integral. By using this result and Eq. (3.34), we can obtain the deviation of $\boldsymbol{v}^{(1)}$ caused by a nonzero h value. For $\zeta_c = 0.1$, the deviation divided by $U\lambda^2$ on the xz plane is used for Fig. 4, and its z-component on the x-axis is plotted in Fig. 5. Comparing Fig. 2 with Fig. 4, we find in the comoving frame the preferential attraction brings about a decrease in the magnitude of the fluid velocity around the particle. This tendency is also shown by Figs. 3 and 5, where $v_z^{(1)}/U - 1$ for $h = 0$ and the z-component of the deviation field do not share the same sign. Noting that the quotient of the deviation divided by $U\lambda^2 \propto h^2$ is plotted in Fig. 5, we find the decrease to be larger as h^2 is larger. This means that the particle drags the fluid more significantly then.

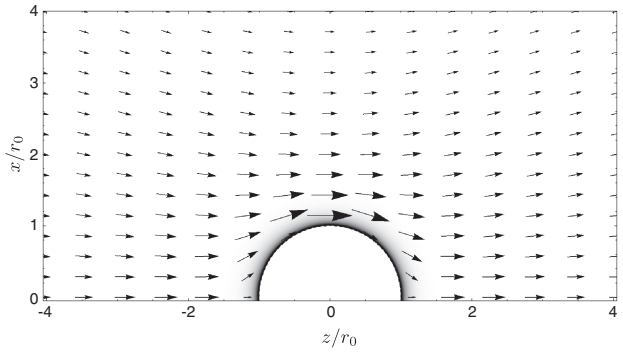

Fig. 4. For $\zeta_c = 0.1$, the deviation of $\boldsymbol{v}^{(1)}$ from $\boldsymbol{v}^{(1)}$ for $h = 0$ is represented by the arrows in a region with $x \geq 0$ on the xz plane. We calculate the deviation by using the second term on the rhs of Eq. (3.32), and use the result divided by $U\lambda^2$ for the arrows. In a darker-gray region, the dimensionless difference $(\varphi^{(0)} - \varphi_\infty)M/(hr_0)$ is larger. The white semicircular region surrounded by the dark adsorption layer represents the cross section of the particle.

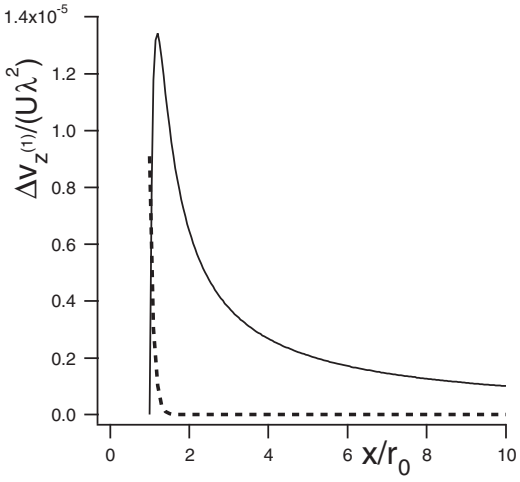

Fig. 5. For $\zeta_c = 0.1$, the deviation of $v_z^{(1)}$ from its value for $h = 0$ is divided by $U\lambda^2$, and the quotient is plotted along the x-axis by means of the solid curve. The symbol Δ in the axis label means the deviation. The dashed curve is drawn for reference to represent $(\varphi^{(0)} - \varphi_\infty)M/(10^4 hr_0)$ for $\zeta_c = 0.1$.

The second term on the rhs of Eq. (2.9) is proportional to h, and the function $\epsilon\varphi^{(1)}(\boldsymbol{r})$, induced by the imposed flow, also has a term proportional to h. This term can be calculated from Eqs. (3.31), (4.3), and (4.12). The calculation can be performed by Mathematica, like that of the integral in Eq. (3.32), although the result is not shown here. The gray level in Fig. 4 simply represents $(\varphi^{(0)} - \varphi_\infty)M/hr_0$; its value, divided by 10^4 for convenience, is plotted along the x-axis by means of the dashed curve in Fig. 5.

Similar figures for $\zeta_c = 1$ are shown in Figs. 6 and 7. The solid curve of the latter figure takes larger values than that of Fig. 5. This implies that the particle should drag the fluid more significantly not only as the preferential attraction becomes stronger but also as the correlation length increases. Then, in other words, the particle becomes apparently sticky and effectively larger. This is also deduced from Eq. (4.22) and Fig. 1. The ζ_c^6 dependence in Eq. (4.31) tempts us to associate the factor h with ξ_c^3, representing the volume of

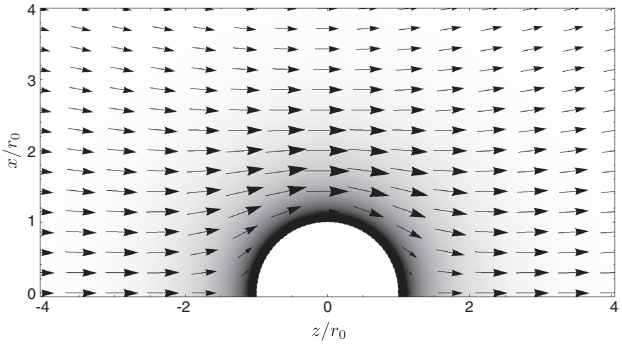

Fig. 6. Same as in Fig. 4, except for $\zeta_c = 1$.

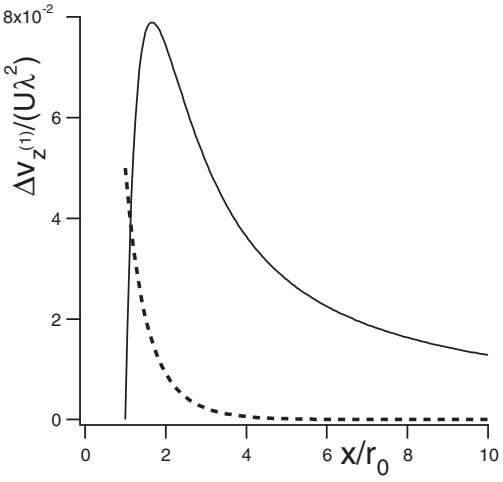

Fig. 7. For $\zeta_c = 1$, the quotient of the deviation of $v_z^{(1)}$ divided by $U\lambda^2$ is plotted by means of the solid curve, as in Fig. 5. The dashed curve represents $(\varphi^{(0)} - \varphi_\infty)M/(10hr_0)$ for $\zeta_c = 1$. Here, the divisor 10 is introduced for convenience of the graphical presentation.

the spherical region with the effective radius. This steep dependence cannot be explained simply by replacing r_0 with $r_0 + \xi_c$ in the Stokes law.

Finally, we make some remarks. (i) Near the critical point, a mixture solvent is very sensitive to selective impurities such as ions which interact with each solvent species asymmetrically.[30–32] Theoretical works have shown that even a small amount of salt can play a significant role in the static behavior of the adsorption layer.[33–35] The ion effect on the drag coefficient would be significant in experiments. (ii) Several groups have devised numerical schemes for simulating the dynamics of colloid particles in a binary fluid mixture in a two-phase state ($T < T_c$).[36–39] Araki and Tanaka have examined the dynamic effect on the adsorption-induced force between colloid particles.[38,39] In Refs. 40 and 41, Cates and coworkers have utilized the scheme of Refs. 36 and 37 to investigate bicontinuous interfacially jammed emulsion gels ("bijels"), in which colloid particles are trapped at the liquid–liquid interface of the phase-separated mixture solvent. In the present paper, we have assumed that the fluid is in a one-phase state. However, our formulation can also be applied to these problems if the free-energy density $f(\varphi)$ is chosen so that it describes the phase-separated fluids (e.g., φ^4 model). (iii) When the mixture is very close to the critical point, the effect of critical

fluctuations would be important. Because of the critical fluctuations, the concentration profile near the surface becomes universal, as mentioned in Sect. 1. The fluctuation effect (or the renormalization effect) on the drag coefficient can be taken into account by replacing the free-energy functional Eq. (2.1) by the "renormalized local functional" in Ref. 16.

Acknowledgement

The authors thank Professor A. Onuki for helpful comments on the critical dynamics.

Appendix A: Colloid Dynamics in the Model H

The irreversible thermodynamics, based on the local equilibrium and the conservation laws, provides us with a framework of phenomenological dynamics.[27] The model H dynamics for a *bulk* fluid mixture with a constant and homogeneous temperature is also formulated in terms of this framework.[26] Below we show that the formulation still works well even if colloid particles are immersed in the mixture. We assume a single particle in the following discussion for simplicity, but the extension to a system containing many particles is straightforward.

To consider an infinitesimal reversible change of a local region, we define $\delta\boldsymbol{r}$ as a small change in the positional vector. The displacement is represented by $\boldsymbol{r} \mapsto \boldsymbol{r}' \equiv \boldsymbol{r} + \delta\boldsymbol{r}$, where $\delta\boldsymbol{r}$ should be homogeneous in C. We can assume the no-slip condition at ∂C because it is assumed in the dynamics we consider. The volume element $\mathrm{d}\boldsymbol{r}$ is changed into $\mathrm{d}\boldsymbol{r}'$ by the accompanying deformation, and their relationship is given by

$$\mathrm{d}\boldsymbol{r} = (1 - \nabla \cdot \delta\boldsymbol{r})\,\mathrm{d}\boldsymbol{r}'. \tag{A·1}$$

We can regard the local region as an open system so that the concentration difference φ is changed not only by the deformation above but also by the flux into or from the particle bath although the flux is assumed not to change ρ_{tot}. The total change in φ is thus represented by

$$\varphi(\boldsymbol{r}) \mapsto \varphi'(\boldsymbol{r}') \equiv \varphi(\boldsymbol{r}) + \delta\varphi_{\mathrm{d}}(\boldsymbol{r}') + \delta\varphi_{\mathrm{p}}(\boldsymbol{r}'), \tag{A·2}$$

where $\delta\varphi_{\mathrm{d}}$ represents the change due to the deformation and $\delta\varphi_{\mathrm{p}}$ due to the flux. With the aid of Eq. (A·1), we have

$$\delta\varphi_{\mathrm{d}}(\boldsymbol{r}') = -\varphi(\boldsymbol{r})\nabla \cdot \delta\boldsymbol{r}. \tag{A·3}$$

After some calculations similar to those in Appendix 6A of Ref. 26, we can derive

$$\begin{aligned}\delta\mathcal{F} = &\int_{C^{\mathrm{e}}} \mathrm{d}\boldsymbol{r}[\{f'(\varphi(\boldsymbol{r})) - M\Delta\varphi(\boldsymbol{r})\}\delta\varphi_{\mathrm{p}}(\boldsymbol{r}) - \Pi_{\mathrm{osm}}(\boldsymbol{r}) : \nabla\delta\boldsymbol{r}] \\ &+ \int_{\partial C} \mathrm{d}S\{f_{\mathrm{s}}'(\varphi(\boldsymbol{r})) - M\boldsymbol{e}_r \cdot \nabla\varphi(\boldsymbol{r})\}\{\delta\varphi_{\mathrm{d}}(\boldsymbol{r}) + \delta\varphi_{\mathrm{p}}(\boldsymbol{r})\},\end{aligned} \tag{A·4}$$

where Π_{osm} is defined as the sum of $p_{\mathrm{osm}}\mathbf{1}$ and Π_{grad} given by Eqs. (2.12) and (2.13), respectively. According to the thermodynamics, Eq. (A·4) should be equal to the sum of

$$\int_{C^{\mathrm{e}}} \mathrm{d}\boldsymbol{r}\{\hat{\mu}(\boldsymbol{r})\delta\varphi_{\mathrm{p}}(\boldsymbol{r}) - \Pi(\boldsymbol{r}) : \nabla\delta\boldsymbol{r}\} \tag{A·5}$$

and similar contributions from the colloid surface and interior. These contributions are neglected in this paper; neither A nor B is assumed to chemically bond to the surface. We thus find Eqs. (2.5) and (2.14) to hold under the local equilibrium. Also, considering the contribution due to the infinitesimal change of ρ_{tot}, we can obtain Eq. (2.11).

We have derived Eq. (A·4) to discuss the dynamics, but we can also use it to discuss the statics. Requiring Eq. (A·4) to vanish for arbitrary $\delta\varphi_{\mathrm{p}}$, we can derive Eqs. (2.4) and (2.5). When φ satisfies them, requiring Eq. (A·4) to vanish for an arbitrary displacement with the particle fixed, we find $\nabla \cdot \Pi_{\mathrm{osm}}$ to vanish in the equilibrium fluid containing the particle fixed externally, which is consistent with Eqs. (2.4) and (2.15). This result is obtained by applying the integration by parts to the second term in the volume integral of Eq. (A·4). We can obtain Eq. (2.16) by considering the infinitesimal translational displacement of the particle in the equilibrium fluid after taking into account the contribution involving ρ_{tot}.

The local equilibrium is assumed in the irreversible thermodynamics.[27,42] Thus, we have

$$\rho_{\mathrm{tot}}\frac{D}{Dt}\left(\frac{\tilde{f}}{\rho_{\mathrm{tot}}}\right) = -\Pi : \nabla\boldsymbol{v} + \hat{\mu}\rho_{\mathrm{tot}}\frac{D}{Dt}\left(\frac{\varphi}{\rho_{\mathrm{tot}}}\right), \tag{A·6}$$

where $\tilde{f}$ is the free-energy density and D/Dt indicates the Lagrangian time derivative. Here we consider the dynamics in more general than considered in the text, allowing the unsteady dynamics. If we regard $\delta\boldsymbol{r}/\delta t$ as the velocity, with δt denoting the infinitesimal change in time t, we can also find the rhs of Eq. (A·4) to be equal to Eq. (A·5) by integrating Eq. (A·6) over the whole region of our system. A similar procedure is mentioned in Sect. 3 of Ref. 43 and below Eq. (2.9) of Ref. 44. Introducing the dissipative stress tensor τ and the diffusive flux $\boldsymbol{j}_{\mathrm{irr}}$, we can assume the conservation laws,

$$\rho_{\mathrm{tot}}\frac{D}{Dt}\left(\frac{\varphi}{\rho_{\mathrm{tot}}}\right) = -\nabla \cdot \boldsymbol{j}_{\mathrm{irr}}, \tag{A·7}$$

$$\rho_{\mathrm{tot}}\frac{D\boldsymbol{v}}{Dt} = \nabla \cdot (-\Pi + \tau), \tag{A·8}$$

and

$$m\frac{\mathrm{d}\boldsymbol{V}}{\mathrm{d}t} = \int_{\partial C_t} \mathrm{d}S\,\boldsymbol{n} \cdot (-\Pi + \tau), \tag{A·9}$$

where m and $\boldsymbol{V}$ respectively denote the mass and the velocity of the particle, the subscript t of C_t means the time dependence of the comoving region, and $\boldsymbol{n}$ is the unit normal vector of ∂C_t directed outside the particle. Here, for simplicity, we assume no rotation of the particle, no external conservative force exerted on the particle, and no dissipation at the surface. The total free energy is given by

$$\mathcal{F}_{\mathrm{tot}} = \mathcal{F} + \int_{C_t^{\mathrm{e}}} \frac{\rho_{\mathrm{tot}}}{2}|\boldsymbol{v}|^2\mathrm{d}\boldsymbol{r} + \frac{m}{2}|\boldsymbol{V}|^2. \tag{A·10}$$

The normal component of the diffusive flux should vanish at the surface, i.e.,

$$\boldsymbol{n} \cdot \boldsymbol{j}_{\mathrm{irr}} = 0 \quad \text{at } \partial C_t^+. \tag{A·11}$$

Substituting Eqs. (A·7)–(A·9) into Eq. (A·6), we integrate the result over the whole region of our system to obtain

$$\frac{\mathrm{d}}{\mathrm{d}t}\mathcal{F}_{\mathrm{tot}} = \int_{C_t^{\mathrm{e}}} \mathrm{d}\boldsymbol{r}(\boldsymbol{j}_{\mathrm{irr}} \cdot \nabla\hat{\mu} - \tau : \nabla\boldsymbol{v}) \tag{A·12}$$

with the aid of Eq. (2.5).

Noting Eq. (2.20), we can derive the linear phenomenological laws,

$$\boldsymbol{j}_{\rm irr} = -L\nabla\hat{\mu} \quad \text{and} \quad \tau = 2\eta E, \tag{A·13}$$

from Eq. (A·12) in terms of the irreversible thermodynamics. Positive L and η ensure that the time derivative of $\mathcal{F}_{\rm tot}$ is not positive. Substituting Eq. (A·13) into Eqs. (A·7) and (A·8) yields Eqs. (2.18) and (2.19), respectively. The second equation of Eq. (3.2) follows Eq. (A·11).

Appendix B: Details in the Perturbative Calculation

Substituting Eq. (3.15) into Eq. (2.20) gives

$$T_{jm} = N_j^{-1} r^{-1} \partial_r r^2 R_{jm} \quad \text{for } j \geq 1, \tag{B·1}$$

and $R_{00} \propto r^{-2}$, which leads to

$$R_{00} = 0 \tag{B·2}$$

because of the boundary condition for $\boldsymbol{v}^{(1)}$ in Eq. (3.11). Substituting Eqs. (3.13) and (3.15) into Eq. (3.8) gives

$$Lr^{-2}(r^2\partial_r^2 + 2r\partial_r - N_j^2)Q_{jm} = R_{jm}\partial_r\varphi^{(0)} \tag{B·3}$$

for $j \geq 0$. From Eqs. (B·2) and (B·3), we find $Q_{00} = 0$ with the aid of the boundary condition for $\hat{\mu}$ in Eqs. (3.10) and (3.11).

Substituting Eqs. (3.13)–(3.15) into Eq. (3.9) gives

$$0 = \sum_{jm}\{O_{1jm}(r)\boldsymbol{P}_{jm} + O_{2jm}(r)\boldsymbol{B}_{jm} + O_{3jm}(r)\boldsymbol{C}_{jm}\}, \tag{B·4}$$

where O_{ijm}'s are defined below. They vanish because of the orthogonality of the vector spherical harmonics, and we have

$$\begin{aligned} 0 = O_{1jm}(r) \equiv & -\partial_r p_{jm} \\ & + \eta r^{-2}\{(\partial_r r^2\partial_r - (N_j^2+2))R_{jm} + 2N_j T_{jm}\} - \varphi^{(0)}\partial_r Q_{jm} \end{aligned} \tag{B·5}$$

for $j \geq 0$,

$$\begin{aligned} 0 = O_{2jm}(r) \equiv & -N_j r^{-1} p_{jm} \\ & + \eta r^{-2}\{2N_j R_{jm} + (\partial_r r^2\partial_r - N_j^2)T_{jm}\} - N_j r^{-1}\varphi^{(0)} Q_{jm} \end{aligned} \tag{B·6}$$

for $j \geq 1$, and

$$0 = O_{3jm}(r) \equiv \eta r^{-2}(\partial_r r^2\partial_r - N_j^2)S_{jm} \quad \text{for } j \geq 1. \tag{B·7}$$

From Eqs. (B·2) and (B·5), we find $p_{00} = 0$ because of the boundary condition for p in Eq. (3.10). Deleting p_{jm} from Eqs. (B·5) and (B·6) for $j \geq 1$, we can substitute Eq. (B·1) into the resultant equation to obtain

$$\begin{aligned} & \eta r^{-2}\{r^4\partial_r^4 + 8r^3\partial_r^3 + 2(6 - N_j^2)r^2\partial_r^2 \\ & \quad - 4N_j^2 r\partial_r + N_j^2\tilde{N}_j^2\}R_{jm} = N_j^2 Q_{jm}\partial_r\varphi^{(0)} \end{aligned} \tag{B·8}$$

for $j \geq 1$, where $\tilde{N}_j \equiv \sqrt{(j-1)(j+2)}$.

The boundary condition at the surface is given by Eq. (3.11). As $r \to r_0+$, we thus have $S_{jm} \to 0$ for any (j,m), while $R_{jm} \to 0$ and $T_{jm} \to 0$ except for $(j,m) = (1,0)$. We also have Eq. (3.23), and

$$T_{10} \to 2\sqrt{2\pi/3}U \quad \text{as } r \to r_0+. \tag{B·9}$$

Substituting these two equations into Eq. (B·1) gives

$$\partial_r R_{jm} \to 0 \quad \text{as } r \to r_0+. \tag{B·10}$$

The condition for $\hat{\mu}^{(1)}$ in Eq. (3.11) gives

$$\partial_r Q_{jm} \to 0 \quad \text{as } r \to r_0+. \tag{B·11}$$

Equation (3.10) gives

$$p_{jm},\ Q_{jm},\ R_{jm},\ S_{jm} \to 0 \quad \text{as } r \to \infty. \tag{B·12}$$

We find S_{jm} to vanish for any (j,m) because of Eq. (B·7) together with the boundary conditions shown above. We also find Eq. (3.17) to satisfy Eqs. (B·1)–(B·4) and all the boundary conditions shown above.

We can regard Eqs. (3.20) and (3.21) as inhomogeneous differential equations with respect to $\mathcal{Q}$ and $\mathcal{R}$, respectively. The homogeneous equations associated with them are both equidimensional in r.[45] A set of linear independent solutions for the former equation is $\{r^{-2}, r\}$, while a set for the latter is $\{r^{-3}, r^{-1}, 1, r^2\}$. Applying the method of variation of parameters to the inhomogeneous equations, we obtain

$$\begin{aligned} \mathcal{Q}(\rho) = & \rho^{-2}\left\{c_1 + \int_1^\rho \mathrm{d}\sigma\,\sigma\kappa(\sigma)\mathcal{R}(\sigma)\right\} \\ & + \rho\left\{c_2 - \int_1^\rho \mathrm{d}\sigma\,\sigma^{-2}\kappa(\sigma)\mathcal{R}(\sigma)\right\}, \end{aligned} \tag{B·13}$$

where c_1 and c_2 are constants, and

$$\begin{aligned} \mathcal{R}(\rho) = & \rho^{-3}\left\{d_1 + \lambda^2\int_1^\rho \mathrm{d}\sigma\,\sigma^2\kappa(\sigma)\mathcal{Q}(\sigma)\right\} \\ & + \rho^{-1}\left\{d_2 - 5\lambda^2\int_1^\rho \mathrm{d}\sigma\,\kappa(\sigma)\mathcal{Q}(\sigma)\right\} \\ & + d_3 + 5\lambda^2\int_1^\rho \mathrm{d}\sigma\,\sigma^{-1}\kappa(\sigma)\mathcal{Q}(\sigma) \\ & + \rho^2\left\{d_4 - \lambda^2\int_1^\rho \mathrm{d}\sigma\,\sigma^{-3}\kappa(\sigma)\mathcal{Q}(\sigma)\right\}, \end{aligned} \tag{B·14}$$

where $d_1, \ldots, d_4$ are constants. After determining the constants by means of the boundary conditions given by Eqs. (3.22) and (3.23), we obtain Eqs. (3.26) and (3.27).

*okamoto_r@fukui.kyoto-u.ac.jp
†youhei@appi.keio.ac.jp
‡komura@tmu.ac.jp

1) B. V. Derjaguin and L. D. Landau: Acta Physicochim. (USSR) **14** (1941) 633.
2) E. J. W. Verwey and J. Th. G. Overbeek: *Theory of the Stability of Lyophobic Colloids* (Elsevier, Amsterdam, 1948) Chaps. 8–12.
3) W. B. Russel, D. A. Saville, and W. R. Schowalter: *Colloidal Dispersions* (Cambridge University Press, Cambridge, U.K., 1989) Chaps. 1–5.
4) G. G. Stokes: Trans. Cambridge Philos. Soc. **9** (1851) 8.
5) W. Sutherland: Philos. Mag. **9** (1905) 781.
6) A. Einstein: Ann. Phys. (Leipzig) **322** (1905) 549.
7) D. Beysens and D. Estève: Phys. Rev. Lett. **54** (1985) 2123.
8) B. M. Law, J.-M. Petit, and D. Beysens: Phys. Rev. E **57** (1998) 5782.
9) J.-M. Petit, B. M. Law, and D. Beysens: J. Colloid Interface Sci. **202** (1998) 441.
10) D. Beysens and T. Narayanan: J. Stat. Phys. **95** (1999) 997.
11) H. Guo, T. Narayanan, M. Sztuchi, P. Schall, and G. H. Wegdam: Phys. Rev. Lett. **100** (2008) 188303.
12) D. Bonn, J. Otwinowski, S. Sacanna, H. Guo, G. Wegdam, and P. Schall: Phys. Rev. Lett. **103** (2009) 156101.
13) M. E. Fisher and P. G. de Gennes: C. R. Seances Acad. Sci., Ser. B **287** (1978) 207.
14) C. Hertlein, L. Helden, A. Gambassi, S. Dietrich, and C. Bechinger: Nature **451** (2008) 172.
15) A. Gambassi, A. Maciołek, C. Hertlein, U. Nellen, L. Helden, C. Bechinger, and S. Dietrich: Phys. Rev. E **80** (2009) 061143.

16) R. Okamoto and A. Onuki: J. Chem. Phys. **136** (2012) 114704.
17) Ya. A. Bal'tsevich, V. G. Martynets, and E. V. Matizen: Zh. Eksp. Teor. Fiz. **51** (1966) 983 [Sov. Phys. JETP **24** (1967) 654].
18) V. G. Martynets and E. V. Matizen: Zh. Eksp. Teor. Fiz. **58** (1970) 430 [Sov. Phys. JETP **31** (1970) 228].
19) S. P. Lee: Phys. Rev. Lett. **36** (1976) 1319.
20) K. B. Lyons, R. C. Mockler, and W. J. O'Sullivan: Phys. Rev. Lett. **30** (1973) 42.
21) K. B. Lyons, R. C. Mockler, and W. J. O'Sullivan: Phys. Rev. A **10** (1974) 393.
22) Y. Nakamura, A. Yoshimori, and R. Akiyama: J. Phys. Soc. Jpn. **81** (2012) SA026.
23) B. A. Camley and F. L. H. Brown: Phys. Rev. E **85** (2012) 061921.
24) J. W. Cahn: J. Chem. Phys. **66** (1977) 3667.
25) P. C. Hohenberg and B. I. Halperin: Rev. Mod. Phys. **49** (1977) 435.
26) A. Onuki: *Phase Transition Dynamics* (Cambridge University Press, Cambridge, U.K., 2002) Chap. 6.
27) S. R. de Groot and P. Mazur: *Non-Equilibrium Thermodynamics* (Dover, New York, 1984) Chap. 4.
28) Y. Fujitani: J. Phys. Soc. Jpn. **76** (2007) 064401.
29) To calculate the integral with respect to σ, we replaced $1/\zeta_c$ with a variable α in the integrand, took $e^{\alpha}/(1+\alpha^{-1})$, which lies in Eq. (3.4), out of the integral sign, and added the option "Assumptions $\rightarrow \rho \geq 1$ && $\alpha > 0$".
30) A. Onuki, R. Okamoto, and T. Araki: Bull. Chem. Soc. Jpn. **84** (2011) 569.
31) A. Onuki and R. Okamoto: Curr. Opin. Colloid Interface Sci. **16** (2011) 525.
32) R. Okamoto and A. Onuki: Phys. Rev. E **82** (2010) 051501.
33) R. Okamoto and A. Onuki: Phys. Rev. E **84** (2011) 051401.
34) S. Samin and Y. Tsori: Europhys. Lett. **95** (2011) 36002.
35) U. Nellen, J. Dietrich, L. Helden, S. Chodankar, K. Nygård, J. F. van der Veen, and C. Bechinger: Soft Matter **7** (2011) 5360.
36) J.-C. Desplat, I. Pagonabarraga, and P. Bladon: Comput. Phys. Commun. **134** (2001) 273.
37) K. Stratford, R. Adhikari, I. Pagonabarraga, and J.-C. Desplat: J. Stat. Phys. **121** (2005) 163.
38) T. Araki and H. Tanaka: Phys. Rev. E **73** (2006) 061506.
39) T. Araki and H. Tanaka: J. Phys.: Condens. Matter **20** (2008) 072101.
40) M. E. Cates and P. S. Clegg: Soft Matter **4** (2008) 2132.
41) E. Kim, K. Stratford, R. Adhikari, and M. E. Cates: Langmuir **24** (2008) 6549.
42) H. Fukagawa and Y. Fujitani: Prog. Theor. Phys. **127** (2012) 921.
43) Y. Fujitani: J. Phys. Soc. Jpn. **70** (2001) 1556.
44) Y. Fujitani: J. Phys. Soc. Jpn. **79** (2010) 074002.
45) C. Bender and S. A. Orszag: *Advanced Mathematical Methods for Scientists and Engineers* (Springer, New York, 1999) Chap. 1.