Electrophoretic Microrheology in a Dilute Lamellar Phase of a Nonionic Surfactant

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We measured the complex electrophoretic mobility $\mu^*(\omega)$ of nanometer-sized particles dispersed in a lyotropic lamellar phase, and observed two relaxation processes corresponding to the two characteristic lengths of lamellar structure. Faster relaxation is caused by the distortion field of lamellar phase induced by the colloidal particles, and slower relaxation is presumably due to the defects in lamellar structure. Since the dynamic transport property is strongly influenced by the microscopic circumstances as shown in this paper, this method is referred to as *electrophoretic microrheology*.

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In recent years, a number of techniques referred to as *microrheology* have been developed to measure the viscoelastic properties of soft materials on a micrometer scale [1]. The experimental methods of microrheology can be generally classified into two categories. One measures the light scattered from many particles embedded in soft materials with dynamic light scattering or diffusing wave spectroscopy. The other measures the local viscoelastic property of soft materials by probing the motion of a single particle with particle tracking optical microscopy or laser interferometry. These studies are motivated to investigate the local inhomogeneity in such systems as living cells, gels, and other complex systems. In most cases, however, the minimum size of a probe particle is limited by the diffraction of light or the strong scattering from the bulk media.

In this paper, microscopic viscoelasticity of complex fluids is obtained from the complex electrophoretic mobility of nanometer-sized probe particles. This method referred to as *electrophoretic microrheology* is applied to a lyotropic lamellar phase of a nonionic surfactant. The lyotropic lamellar phase is made of periodic stacks of bilayers and solvent, and its structure is considered to be mainly stabilized by the steric interaction between the fluctuating and colliding membranes. On the other hand, lamellar phase loses orientational order in macroscopic scale, and three-dimensional packing of crumpled membranes needs topological defects which may also slowly fluctuate with time by formation and extinction. The aim of this Letter is to study the effect of structure and fluctuation of such dynamically stabilized lamellar on the dynamical transport properties of small embedded inclusions.

Complex electrophoretic mobility $\mu^*(\omega)$ is a frequency dependent response function defined as the ratio of velocity of a particle to an applied sinusoidal electric field [2]. According to the Smoluchowski equation extended to the frequency domain, the mobility $\mu^*(\omega)$ is simply proportional to the inverse of the complex viscosity of bulk solvent $\eta^*(\omega)$ as $\mu^*(\omega) = \varepsilon\zeta/\eta^*(\omega)$, where ζ is the zeta potential of colloidal surface and ε is the permittivity of the surrounding solvent. Therefore, when the intrinsic mobility of a probe particle is independent of frequency, $\mu^*(\omega)$ offers information on the local viscoelastic property of the solvent surrounding the particle.

The wide band spectrum of μ^* is measured by a recently developed method with a heterodyne technique of quasielastic light scattering under a sinusoidal electric field [3]. Since the translational motion of colloidal particles induces the phase shift φ of the scattered electric field relative to that of the reference light, the intensity of the detected signal is modulated by $\cos\varphi$. Under a sinusoidal electric field $E_0\cos\omega t$, the phase shift φ has two components. One is a randomly fluctuating part φ_B due to the Brownian motion, and the other is a sinusoidally modulated part $\varphi_E = q\mu E_0 \sin(\omega t + \delta)/\omega$ due to electrophoresis, where q is the component of the scattering wave vector parallel to the electric field and δ is the phase delay to the electric field. Therefore, the intensity of the detected light I_{out} is given as a sum of the harmonic frequency components of ω [3],

$$I_{\text{out}} \propto \cos\varphi_B \left\{ J_0(z) + 2\sum_{k=1}^{\infty} J_{2k}(z)\cos[2k(\omega t + \delta)] \right\} + 2\sin\varphi_B \sum_{k=1}^{\infty} J_{2k-1}(z)\sin[(2k-1)(\omega t + \delta)], \quad (1)$$

where $z = q\mu E_0/\omega$ and $J_k(z)$ is the Bessel function of the kth order. In Eq. (1), we consider only one particle as a scatterer for simplicity without loss of generality. It is to be noted that the amplitude of each harmonic component, $J_{2k}(z)\cos\varphi_B$ or $J_{2k-1}(z)\sin\varphi_B$, randomly fluctuates with time at about its averaged value of zero. In the measurement of μ^*, this fluctuation of the signal intensity can be removed by squaring the fundamental or second harmonic component of ω, which is extracted from the signal beforehand with a bandpass filter. The magnitude μ is obtained from the ratio of these signals $J_2^2(z)/J_1^2(z)$, and the phase delay δ is directly obtained by a two-phase lock-in amplifier.

Since the applied electric field does not induce the translational motion of surrounding bulk media, μ^* of

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probe particles can be extracted even under the strong scattering from background. This advantage of our method enables us to use the particles smaller than the characteristic length scale of soft materials (intermembrane distance of lyotropic lamellar in this study). Therefore, μ^* or η^* measured by electrophoretic microrheology reflects the mesoscopic structure of complex fluids or microscopic circumstances for probe particles where the assumption of continuum viscoelasticity is broken.

We measured the complex electrophoretic mobility $\mu^*(\omega)$ of polystyrene latex particles with a diameter of $2a = 42$ nm (Dow Company, Ltd.) dispersed in a dilute lamellar phase of the *n*-dodecyl pentaethyleneglycol monododecylether ($C_{12}E_5$)/1-hexanol/water system [4,5]. A sample is filled in a cylindrical cell and the distance between parallel plate electrodes in the cell is 5 mm. The volume fraction ϕ_m of bilayer membrane made up of $C_{12}E_5$ and hexanol is determined by taking into account the solubility of hexanol in water ($\approx$0.3%). It is verified in advance that the mobility μ^* of the latex particles dispersed in the aqueous phase of $C_{12}E_5$ at critical micellar concentration and 0.3% hexanol is independent of frequency in the range we studied. Its magnitude μ_0 is 5.7×10^{-8} N m/C s and is in good agreement with the dc electrophoretic mobility measured with ELS-800 (Otsuka Electric).

We used the measured value of membrane thickness $\delta_m = 3$ nm for our sample [4] to obtain the interbilayer spacing d from the simple swelling law of lyotropic lamellar phase, $d \approx \delta_m/\phi_m$. The sample is prepared in the concentration range $0.02 < \phi_m < 0.06$ ($50 < d < 130$ nm) to satisfy the relation $d > 2a$ so that the colloidal particles are homogeneously dispersed between membranes. The total amount of latex particles (about one-tenth of a percent or less) added to the lamellar sample is small enough to satisfy the condition $c \ll 1/d^3$, where c is the number density of colloidal particles. Therefore, the interaction between particles is negligible in such a dilute dispersion. Since the amplitude of the displacement of a particle due to electrophoresis is much less than d, it has little influence on the lamellar structure.

Figure 1 shows the frequency spectrum of μ^* obtained in a lamellar phase at $\phi_m = 4.7\%$. There are two relaxation modes in the spectrum and the respective relaxation frequencies are named f_L and f_H, as shown in Fig. 1. We divide the frequency spectrum into three regions by f_L and f_H as regions I, II, and III from the higher frequencies. Hereafter, the values of the mobility μ, diffusion coefficient D, and drag coefficient γ at the plateau in the respective regions are denoted by the subscripts I, II, and III. The solid lines in Fig. 1 are the best-fitted curves of the sum of two relaxation spectra with the relaxation time $\tau_L (= 1/2\pi f_L)$ and $\tau_H (= 1/2\pi f_H)$,

$$\mu^*(\omega) = (\mu_{\mathrm{I}} - \mu_{\mathrm{II}}) \frac{i\omega\tau_H}{1 + i\omega\tau_H} + \mu_{\mathrm{II}} \frac{i\omega\tau_L}{1 + i\omega\tau_L}, \tag{2}$$

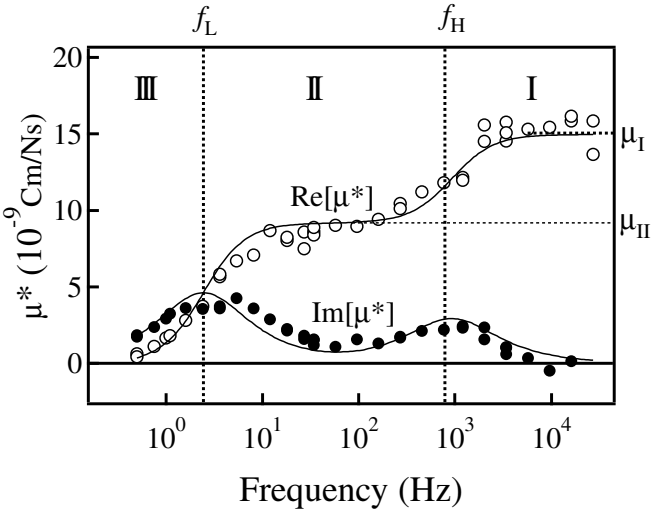

FIG. 1. Frequency dependence of complex electrophoretic mobility μ^* of latex particles dispersed in a nonionic lamellar phase of the $C_{12}E_5$/hexanol/water system ($\phi_m = 4.7\%$). The solid lines are the best-fitted curves of Eq. (2).

where $\tau_H = 1.7 \times 10^{-4}$ s, $\tau_L = 6.6 \times 10^{-2}$ s, $\mu_{\mathrm{I}} = 1.5 \times 10^{-8}$ C m/N s, and $\mu_{\mathrm{II}} = 9.2 \times 10^{-9}$ C m/N s. The mobility μ_{I} and μ_{II} are considerably smaller than μ_0 measured in an aqueous phase without lamellar structure.

Since there is enough free space for the electric double layer around probe particles, it is assumed that electrokinetic properties of the latex particles are not influenced by the presence of membranes. Therefore, the observed frequency dependence of $\mu^*(\omega)$ is ascribable to the relaxation of microscopic viscoelasticity of surrounding media caused by the potential barriers due to some interaction between probe particles and media. In this case, the relaxation time τ is written as $\tau_{H(L)} \approx \Lambda^2_{H(L)}/2D_{\mathrm{I(II)}} = \gamma_{\mathrm{I(II)}}\Lambda^2_{H(L)}/2k_BT$, where $\Lambda_{H(L)}$ is the size of the potential barrier determined as an amplitude of fluctuation of probe particles in the potential barrier for faster (slower) relaxation. Since the drag coefficients γ_{I} and γ_{II} are given from the measured mobility by $\gamma_{\mathrm{I(II)}} = 6\pi\eta_0 a\mu_0/\mu_{\mathrm{I(II)}}$, where η_0 is the viscosity of the aqueous phase, we can estimate the size Λ of the potential barrier as $\Lambda \approx \sqrt{2k_BT\tau/\gamma}$, which is 33 nm for the high frequency relaxation and 500 nm for the low frequency relaxation.

In the lamellar phase composed of nonionic surfactant, there are two characteristic length scales, as schematically shown in Fig. 2 [6]. One is the mean distance ξ between the points, where a membrane collides with its neighboring membranes and is roughly estimated as $\xi \approx \sqrt{\kappa/k_BT}\, d$, where κ is the mean curvature elasticity of a single membrane. The other is the persistent length of the orientational order of a membrane l and is estimated as $\beta \exp(2\pi\kappa/k_BT)$, where β is a short-distance cutoff of the order of a molecular length. In the sample we studied, ξ is almost equal to d if we use the reported value $\kappa \approx 0.8k_BT$ [4] and l is about 500 nm if we regard β as δ_m. Therefore, two characteristic lengths of the potential

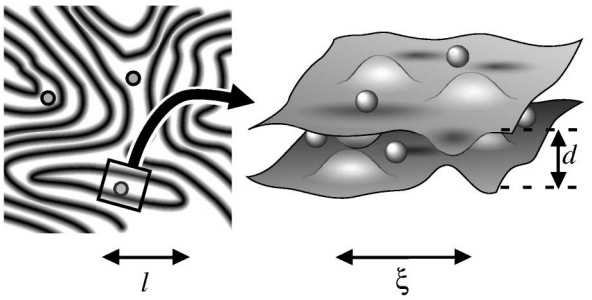

FIG. 2. Schematics of probe particles of radius a dispersed in a lyotropic lamellar phase with layer distance d. The length l is the correlation length of the orientational order of membranes and ξ is the longest wavelength of the free fluctuation of a membrane.

barrier estimated from the experiment are found to correspond to the characteristic size of the lamellar structure $\xi_0 \equiv \xi/2$ ($\approx$32 nm at $\phi_m = 4.7\%$) and l. This means that the potential barrier formed by flexible membranes traps colloidal particles within these length scales. It is to be noted that ξ_0 is a reasonable estimation for Λ_H.

Before we go into a detailed discussion of each relaxation process, we discuss the electrical property of lamellar phase. Since lamellar phase can be regarded as a series circuit of an insulating membrane and conducting aqueous phase, dielectric response of lamellar phase shows Maxwell-Wagner relaxation, and the relaxation frequency is about hundreds of kHz for our sample [7]. Therefore, at frequencies lower than this relaxation where we measured the complex electrophoretic mobility of probe particles, the electric field is parallel to membranes. That is why we guess tentatively that the trapping site for the faster relaxation is not the interbilayer spacing d but the free space between collisions of membranes ξ.

At the highest frequencies (region I), colloidal particles can freely diffuse within the extent of ξ, and drag coefficient γ_{I} is directly given by the observed mobility by $\gamma_{\mathrm{I}} = 6\pi\eta_0 a\mu_0/\mu_{\mathrm{I}}$. The open circles in Fig. 3 show the $1/\xi_0$ dependence of the ratio of $\gamma_0 (= 6\pi\eta_0 a)$ to γ_{I}. The obtained value of γ_{I} is always larger than γ_0 and increases with ϕ_m due to the confinement of particles between membrane walls. The drag coefficient for a spherical particle near a hard boundary wall under no-slip conditions was calculated for infinite parallel plates separated by a distance $2\xi_0$ (solid curve in Fig. 3) or an infinite cylinder with radius ξ_0 (dotted curve in Fig. 3) [8]. These are calculated only for a particle restricted to move on the center line of each wall, but it is experimentally known that the position dependence of $\gamma_0/\gamma_{\mathrm{I}}$ is not so large, except for the particles attached to the wall [9]. The excess stress experienced by a moving particle can be roughly discussed by the geometry of the surrounding wall. There is two-dimensional free space for a probe particle in a slit between parallel flat plates, but there is only one dimension in a cylinder. If it is considered that the bilayer membrane is not a flat wall and a colliding point of membranes also disturbs the flow field as shown in Fig. 2, it is reasonable

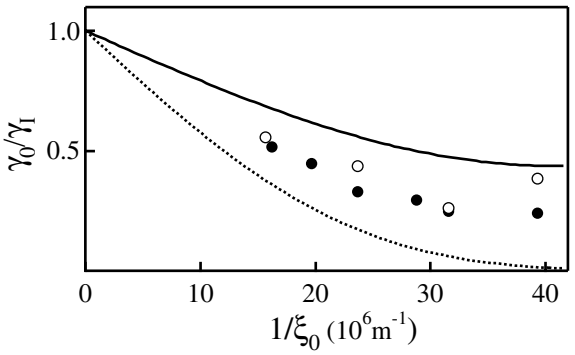

FIG. 3. Half of the interlamellar space $\xi_0 (= d/2)$ dependence of the ratio of drag coefficient $\gamma_0/\gamma_{\mathrm{I}}$ calculated from μ_{I} (open circles) and from relaxation time τ_H (closed circles). ξ_0 is calculated from the volume fraction ϕ_m by the simple swelling law. The solid curve and dotted curve are theoretical values calculated for the spherical particles in between parallel walls and in a cylindrical wall, respectively.

that experimental data situate between the two theoretical curves. Therefore, it can be said that the drag coefficient in a nanometer-sized structure is still roughly estimated from continuum hydrodynamics, and there is no relaxation process at frequencies higher than the measured frequency region.

At the lower end of frequency region I, a faster relaxation process arises due to the trapping potential of size Λ_H. Since the relaxation time of the faster relaxation process is written as $\tau_H \approx \Lambda_H^2/2D_{\mathrm{I}} = \gamma_{\mathrm{I}}\Lambda_H^2/2k_BT$, γ_{I} can be also estimated from τ_H as $\gamma_{\mathrm{I}} = 2k_BT\tau_H/\xi_0^2$ by assuming Λ_H being equal to ξ_0. The values of $\gamma_0/\gamma_{\mathrm{I}}$ calculated by this method are plotted as closed circles in Fig. 3 and approximately agree with the open circles obtained without any assumption. It is to be noted that we have implicitly made another assumption that the trapping site for faster relaxation is stable for a time longer than τ_H.

At the middle frequencies (region II), colloidal particles weakly confined within the length between the colliding points of membranes need to hop from trapping site-to-site to diffuse longer distance. However, colloidal particles may diffuse without hopping if the membrane collision disappears with time by itself. Such a process is called dynamic disorder transport [10]. When this transport process is taken into account, the theoretical spectrum of mobility $\mu^*(\omega)$ is rewritten as

$$\mu^*(\omega) = \mu_0 + \Delta\mu\,\frac{\tau_f(1 + i\omega\tau_m)}{\tau_f + \tau_m + i\omega\tau_f\tau_m}, \qquad (3)$$

where $\tau_m \approx \eta\xi^3/\kappa$ is the reorganization time of the trapping site, which is the relaxation time of fluctuation for a free membrane of size ξ [11], $\tau_f \approx \eta a\xi^2/k_BT$ is the time required for probe particles to diffuse ξ, and $\Delta\mu$ is the increment without dynamic disorder process. From Eq. (3), $\mu_{\mathrm{II}}/\mu_{\mathrm{I}}$ is roughly written as

$$\frac{\mu_{\mathrm{II}}}{\mu_{\mathrm{I}}} = \frac{\mu_0 + \Delta\mu[\tau_f/(\tau_f + \tau_m)]}{\mu_0 + \Delta\mu}, \qquad (4)$$

which is a monotonous increasing function of membrane concentration ϕ_m. However, experimental values of $\mu_{\rm II}/\mu_{\rm I}$ are rather a decreasing function of ϕ_m, as shown in Fig. 4. This discrepancy indicates that the dynamic disorder process has a little influence on the diffusion of particles.

Recently, Sens *et al.* theoretically derived a static distortion field caused by particulate inclusions in lyotropic lamellar phase [12]. According to their theory, the in-plane size of the distortion for the membrane neighboring an inclusion is almost the same as the interbilayer spacing. Therefore, at a concentrated solution where $\tau_m < \tau_f$, lamellar phase has enough time to form this distortion field. Even in this case, probe particles can freely fluctuate in the length of the mean distance of a membrane collision, but they have to drag the distortion field to diffuse the longer length. It is easily shown that excitation energy ΔE is of order k_BT and has little concentration dependence if there is no specific interaction between membrane and probe particles other than steric interaction. Experimentally, a reasonable value of $0.4k_BT$ for ΔE is obtained from $\mu_{\rm II}/\mu_{\rm I} \approx \exp(-\Delta E/k_BT)$. At lower concentrations, on the other hand, probe particles diffuse out rapidly by finding a free path in the colliding membrane before the membrane distorts; that is why $\mu_{\rm II}/\mu_{\rm I}$ increases in dilute solution.

At the lowest frequencies (region III), μ^* decreases to zero and almost all the particles are trapped within the domain of size l. The sizes of the potential barrier estimated from τ_L and $\mu_{\rm II}$ as $\Lambda_L \approx \sqrt{2k_BT\tau_L/\gamma_{\rm II}}$ agree well with the persistent length of orientation at the concentrated solution ($\phi_m = 4.7\%$ and 5.9%), but it becomes longer as ϕ_m decreases. Although this slower relaxation mode is presumably related to microscopic defects joining one bilayer to the other, it is also necessary to measure $\gamma_{\rm III}$ for various conditions to clarify the detailed mechanism of the slower relaxation process. However, $\gamma_{\rm III}$ is not obtained from the frequency spectrum of μ^* since $\mu_{\rm III}$ is almost zero. Therefore, it must be determined by some other method. Probably, $\gamma_{\rm III}$ can be determined from the self-diffusion coefficient of probe particles in this region, $D_{\rm III}$, which is possible to measure by a slight modification of our experimental system [3].

In conclusion, we studied the spectrum of the complex electrophoretic mobility μ^* of nanometer-sized colloidal particles dispersed in a nonionic dilute lamellar phase and observed two relaxations corresponding to the two characteristic lengths of lamellar structure. The developed technique, called electrophoretic microrheology, enables us to measure the spectrum of μ^* of probe particles which reflects the local structure and viscoelasticity of surrounding media. The advantage of this technique is its availability of a probe particle smaller than the characteristic size of structure in complex fluids. It is expected that the transport properties obtained in this study might throw new light on the transport phenomena in much more complex systems such as biological cells and so on.

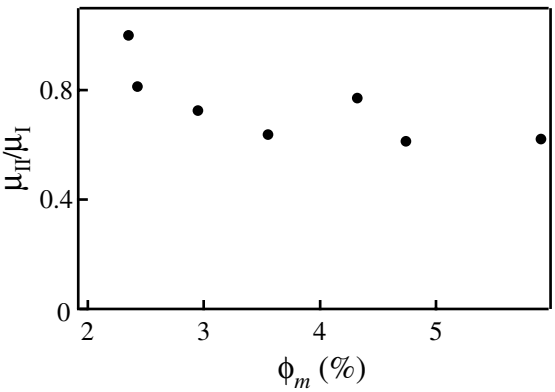

FIG. 4. Concentration dependence of the ratio of the complex electrophoretic mobility in the frequency regions I and II, $\mu_{\rm II}/\mu_{\rm I}$.

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