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# Hierarchical Dynamics of Nano-Particles in Lyotropic Lamellar Phase

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*Dynamics of nano-sized colloidal particles dispersed in a dilute lyotropic lamellar phase of a nonionic surfactant has been studied experimentally by ac electrophoretic light scattering and direct tracking under a microscope. The obtained frequency spectrum of complex electrophoretic mobility shows two relaxation processes at about 1 kHz (HF relaxation) and a few Hz (LF relaxation). These relaxations are due to the hindrance of free diffusion of particles by the hierarchical local static and dynamical structures of lamellar phase. From the direct tracking of fluorescent-labeled particles under a microscope, we find that particles show jump from sites to sites where they stay for a long time. This trap-jump process extremely decreases their mobility at low frequencies.*

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**Keywords:** colloidal particles; complex electrophoretic mobility; hierarchical local structure; lyotropic lamellar phase; particle-tracking microscopy



## INTRODUCTION

One can find hierarchical structures with various shapes and sizes in biological systems. These make them difficult to understand their macroscopic properties and functions as typical *complex fluids*. Among them, a lipid bilayer is one of the basic and common structures in living systems as a cell membrane and myelinated nerve cell [1]. It is also important to study the transport property of nano-sized colloidal particles such as protein molecules and charged polymers in the structures composed of bilayers for understanding the dynamical aspects of living systems. In order to extract the information on the motion of particles in complex fluids, we have to label them by some ways or distinguish their motion from that of the matrix. One of the simple methods is to label particles by fluorescent dyes and we can directly observe their motion under a microscope. Since the upper limit of time resolution is a few ms and its spatial resolution is as large as several tens nm, it is impossible to observe much faster and smaller motion of particles by this method.

Recently, the local mechanical properties of complex fluids such as gels and cytoplasm have been intensively studied by analyzing the motion of probe particles dispersed in these complex fluids. They are often called *microrheology* [2]. In most researches of microrheology, the local mechanical properties (elasticity and viscosity) can be obtained from the measurement of Brownian motion of embedded particles by dynamic light scattering or direct tracking of their trajectory. In those studies, the probe particles used are usually larger than the characteristic length of matrix, e.g., mesh size of gel. But it is also interesting in the case of these two sizes being comparable.

In this study, we have studied the dynamics of particles between membranes and the size of probe particles is a little bit smaller than the distance between membranes. In this situation, the diffraction limit and strong scattering from matrices makes it difficult to extract information on motion of probe particles by conventional methods of microrheology. To overcome the difficulty in using small particles, we have detected their translational motion under a sinusoidal electric field by a newly developed ac electrophoretic light scattering and measured their complex mobility. The change of mobility by varying the applied frequency provides the information on the local structures of

lamellar phase and the interaction between particles and membranes. We have also studied the motion of fluorescent-labeled particles directly under a microscope and obtained detailed information on their dynamics at low frequencies.

## EXPERIMENT

The polystyrene latex particles with diameter of $2a = 42\,\mathrm{nm}$ (Dow) were dispersed in a dilute lamellar phase of *n*-pentaethyleneglycol mondodecylether ($C_{12}E_5$)-hexanol-water mixture. The surfactant bilayer in our system has small bending elasticity $\kappa \approx 0.8 k_B T$ at room temperature [3] and its lamellar structure is mainly stabilized by steric repulsion between undulating neighboring membranes. The interlayer distance $d$ follows a simple swelling law, $d = \delta/\phi$, where $\phi$ is the volume fraction of membrane and $\delta$ is the thickness of a membrane ($\approx 3\,\mathrm{nm}$) [3]. The prepared samples satisfy the relation $2a < d$ and the number density $c$ of particles satisfies the condition $c \ll d^{-3}$. In such a dilute solution, the interaction between particles is negligible.

In this study, we measured complex electrophoretic mobility $\mu^*(\omega)$ by quasi-elastic light scattering (electrophoretic light scattering: ELS) under a sinusoidal electric field. The ELS under dc field is widely used in colloid science and biotechnology to determine surface charge (namely $\zeta$-potential) of colloidal particles and to separate charged biopolymers such as polypeptide and DNA [4]. Although the frequency dependence of $\mu^*(\omega)$ offers valuable information on electrokinetics of charged colloids and polymers, large fluctuation due to their Brownian motion makes it difficult to extract information on $\mu^*(\omega)$ even at a few hundreds Hz [4].

We have recently developed a new measurement method of $\mu^*(\omega)$ by heterodyne technique of quasi-elastic light scattering under a sinusoidal electric field and succeeded in the measurement of $\mu^*(\omega)$ up to 100 kHz for the first time [5]. The component that contains information on translational motion of particles (electrophoresis) can be extracted by separating the respective harmonic components to the applied frequency from the scattered light by a band-pass filter. The fluctuation of intensity of the filtered signal due to Brownian motion can be removed by squaring them. The magnitude and the phase delay of $\mu^*(\omega)$ are respectively obtained from the ratio of harmonic components and the phase shift detected by a two-phase lock-in amplifier. The advantage of our method for the measurement of $\mu^*(\omega)$ of colloidal particles in lamellar phase is that one can selectively obtain the information on $\mu^*(\omega)$ from the scattered light by their frequency even in strongly light-scattering medium. This also makes it possible to

measure $\mu^*(\omega)$ in wider frequency range and to utilize much smaller probe particles. The details of its principle and experimental setup have been already discussed elsewhere [5].

The motion of fluorescent labeled polystyrene latex particles ($2a = 52\,\text{nm}$, Polyscience) in lamellar phase was directly observed under a fluorescent microscope (TE300, Nikon). A sample is filled in a laboratory dish with a slide glass window and sealed with a cover glass. The observed image was detected by a CCD camera and its center of mass was calculated by weighting the digitized intensity from the captured digital image. This enhances the resolution of particle's position up to 1/10 of a pixel ($\approx$10 nm).

## COMPLEX ELECTROPHORETIC MOBILITY IN LAMELLAR PHASE

The obtained frequency spectrum of $\mu^*(\omega)$ for a sample of $\phi = 3.6\%$ is shown in Figure 1. There are two relaxation processes in $\mu^*(\omega)$ at 800 Hz (HF relaxation) and 3 Hz (LF relaxation). Hereafter, we divide the frequency region into three from higher frequency as I, II and III. We call the mobility at the flat part in the respective regions $\mu_{\text{I}}$, $\mu_{\text{II}}$ and $\mu_{\text{III}}$. The mobility $\mu_{\text{III}}$ is so small that we cannot measure its exact value by ELS measurement. The solid line in Figure 1 is the best-fitted curve of the sum spectrum of two single relaxations with $\mu_{\text{III}} = 0$. The mobility of the colloidal particles in aqueous solution of $C_{12}E_5$ and hexanol at critical micelle concentration is $\mu_0 = 5.7 \times 10^{-8}\,\text{Cm/Ns}$ and shows no frequency dependence. Therefore, these two relaxations are

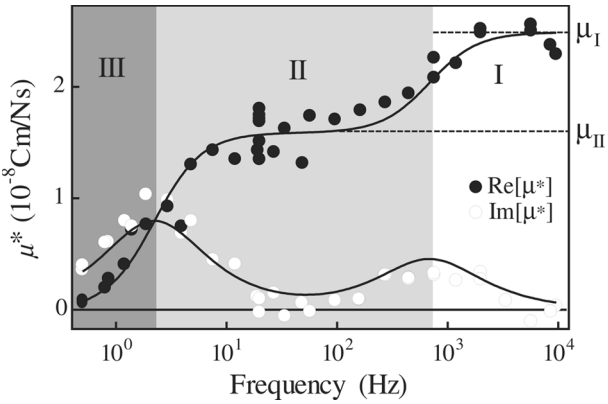


**FIGURE 1** Dependence of complex electrophoretic mobility $\mu^*(\omega)$ of colloidal particles on frequency in a lamellar phase of $\phi = 3.6\%$.

originated from the hindrance of motion of colloids in lamellar phase. It is also important to note that even $\mu_I$ is considerably smaller than $\mu_0$.

We can discuss the observed spectrum $\mu^*(\omega)$ by assuming that colloidal particles are trapped within potential originated from the interaction with lamellar structures. In this case, the characteristic sizes of the potential can be estimated from the relaxation time and mobility [6]. Their sizes estimated from Figure 1 are $\lambda_H = (k_B T \mu_I \tau_H / 3\pi\eta_0 a \mu_0)^{1/2} = 48\,\text{nm}$ for HF relaxation and $\lambda_L = (k_B T \mu_{II} \tau_L / 3\pi\eta_0 a \mu_0)^{1/2} = 700\,\text{nm}$ for LF relaxation, where $\eta_0$ is solvent viscosity. In a lamellar phase composed of soft bilayers with bending elasticity $\kappa \sim k_B T$, there are two characteristic lengths other than $d$ [7]. One is the mean distance $\Lambda$ between the points where the membranes conflict and is estimated as 4–7$d$. The other is the persistence length of orientational order of a membrane $l$ and is estimated as $l = 500\,\text{nm}$. Therefore, $\lambda_H$ and $\lambda_L$ respectively correspond to $d/2$ and $l$. This means that the potential formed by flexible membranes traps colloidal particles within these sizes.

## DISCUSSIONS FOR AC ELECTROPHORETIC MOBILITY

### Effective Drag Coefficient in Lamellar Phase in the Region I

The particles between soft membranes ($\kappa \sim k_B T$) induce the distortion field whose size is as large as $d$ around particles [8]. In the region I, particles relatively free to diffuse in this distortion field, but the mobility $\mu_I$ is smaller than $\mu_0$. The ratio of the drag coefficient in regime I to that in water, $\gamma_I/\gamma_0$, increases with decreasing $d$ as shown in Figure 2. In macroscopic scale, it is well known that the confinement of a particle between hard walls increases its effective drag coefficient due to the solvent flow near walls under no-slip condition [9]. The dependence of $\gamma_I$ on $d$ is found to be more remarkable than one predicted for a spherical particle between infinite parallel walls [9] drawn as a solid line in Figure 2. This is due to the fact that a part of membranes also exist in the direction perpendicular to membranes walls and the confinement is more tightly in lamellar phase.

### Mechanism of HF Relaxation

In the region II, the particles have to drag the distortion field around them to travel to a distance. The excitation energy necessary to escape the distortion field is approximately given by $k_B T \ln(1 + \Delta d_0/d)$, where $\Delta d_0$ is the excess distortion field induced by osmotic pressure of a particle. The relative amplitude $\mu_{II}/\mu_I$ can be estimated as $\mu_{II}/$

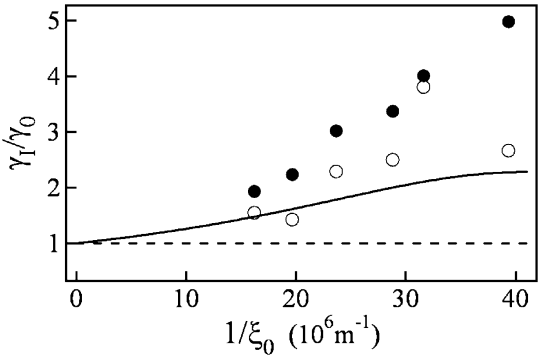


**FIGURE 2** Dependence of the ratio of drag coefficient $\gamma_I/\gamma_0$ calculated from $\mu_I$ (open circles) and from $\tau_H$ (closed circles) on half of the interlayer distance $\xi_0$ ($= d/2$). The solid curve is theoretical one calculated for a spherical particle with the same size between parallel walls separated by $2\xi_0$.

$\mu_I \sim d/(\Delta d_0 + d)$. Since the static value of $\Delta d_0$ is estimated as $0.4d$ [8], $\mu_{II}/\mu_I$ will be about 0.7 independent of the concentration $\phi$. But the observed ratio $\mu_{II}/\mu_I$ decreases with increasing concentration $\phi$ from about 1 to 0.7 as shown in Figure 3. To explain this finding, we consider the dynamic process including creation of the distortion field [10]. By calculating the step response of distortion field with use of hydrodynamic equation of lyotropic lamellar phase [11], the characteristic time for the formation of distortion field $\tau_D$ is approximately given by $\tau_D \sim 3\eta d^3/k_B T$ ($\eta$: solvent viscosity). Since the distortion only grows when a colloidal particle stays inside it, the amplitude of the distortion field becomes a function of time $\tau_{II}$ which is the time

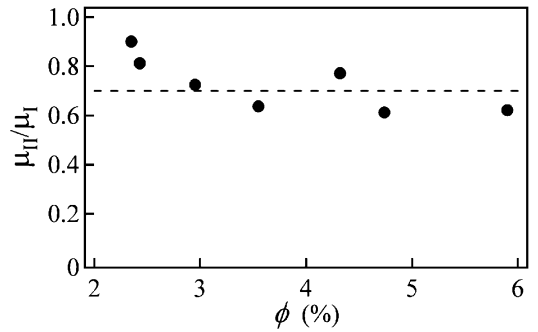


**FIGURE 3** Dependence of the ratio of electophoretic mobility in the region I and II, $\mu_{II}/\mu_I$, on the concentration of membrane $\phi$. The broken line indicates $\mu_{II}/\mu_I = 0.7$.

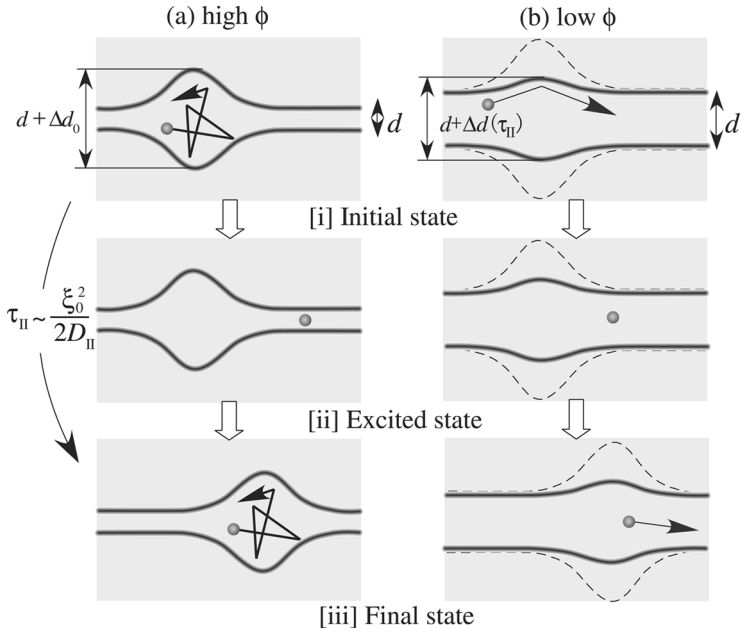


**FIGURE 4** Diffusion process of a colloidal particle between soft membranes. A colloidal particle which fluctuates in a distortion field [i] hops out [ii] and creates a new distortion field around it [iii]. At high $\phi$, distortion field fully grows to its equilibrium size (a), while at low $\phi$, the particle moves too fast to form full distortion field (b).

necessary for a particle to jump out one site. Since $\tau_{II}$ can be estimated as $\tau_{II} \sim {\xi_0}^2/2D_{II}$ ($D_{II}$ is the diffusion constant in the region II and $\xi_0 = d/2$), $\tau_{II}$ is proportional to $\phi^{-2}$. On the other hand, the time $\tau_D$ is proportional to $\phi^{-3}$. Therefore, as illustrated in Figure 4 (a), at high $\phi$ where $\tau_{II} > \tau_D$, the distortion field fully grows to its equilibrium size before a particle will escape it. On the contrary, as illustrated in Figure 4 (b), at low $\phi$ where $\tau_{II} < \tau_D$, a particle will escape before the distortion field fully grows. The dependence of $\mu_{II}/\mu_I$ on $\phi$ can be explained by the crossover between these two extreme situations.

## Mechanism of LF Relaxation

In the region III, the mobility $\mu^*(\omega)$ decreases to almost zero. This indicates that almost all particles are trapped within a space as large as several hundreds nm. The existence of trapping site is confirmed by direct observation of fluorescent particles dispersed in lamellar phase,

which is to be discussed in the following section. Since the lamellar structure in this study is not macroscopically oriented, there must be defects in a scale larger than $d$. In fact, the vesicle-like structure or folded lamellar structure surrounded by perforated lamellar has been frequently observed by freeze fracture electron microscopy [12]. We have recently studied the dielectric response of lyotropic lamellar phase of an aqueous solution of $C_{12}E_5$ [13]. The observed Maxwell–Wagner relaxation can be interpreted quantitatively by modeling the lamellar phase as aggregates of multi-lamellar vesicles made up of perforated lamellar whose size is approximately 200–400 nm. Therefore, it is plausible that the trapping sites for LF relaxation are composed of multi-lamellar vesicles which particles cannot move across. Even in the region III, particles might diffuse in longer distance if the reorganization of lamellar structure or renewal of trapping path occurs.

## PARTICLE-TRACKING MEASUREMENTS UNDER MICROSCOPE

Since the mobility in the region III is extremely small to measure, we cannot obtain detailed information on dynamics of colloidal particles in this region by ELS. On the contrary, motion of colloidal particles in the region III can be directly observed under a microscope due to their slow diffusion in lamellar structure. We can also check that the dispersed colloids do not aggregate and are homogenously dispersed in lamellar matrix. The temporal change of a particle position projected to one-dimension $x(t)$ and the spatial trajectory in two dimension are shown in Figure 5. The motion of a particle is completely different from that follows simple diffusion process. A particle stays at a certain site for a long time and suddenly jumps for the scale as long as one micron. As the concentration increases, the time spent at one site increases and the number of such particles increases. The trajectory in Figure 5 resembles that reported for the motion of colloidal particles in colloidal glasses [14] and in F-actin networks [15]. In those cases, a particle is trapped within a "cage" formed by crowding particles or entangled actin filaments, but can infrequently "jump" to different cages.

Figure 6 shows the time evolution of means square displacement (MSD) $\langle \boldsymbol{r}^2 \rangle$ in two dimension averaged over many particles for $\phi = 3\%$. If particles follow pure diffusion process, $\langle \boldsymbol{r}^2 \rangle$ is proportional to time elapsed $t$ and its slope gives self-diffusion constant of particles. On the other hand, if particles are completely trapped within a "cage", $\langle \boldsymbol{r}^2 \rangle$ tends to saturate at a certain value. At $\phi = 3\%$, all particles are

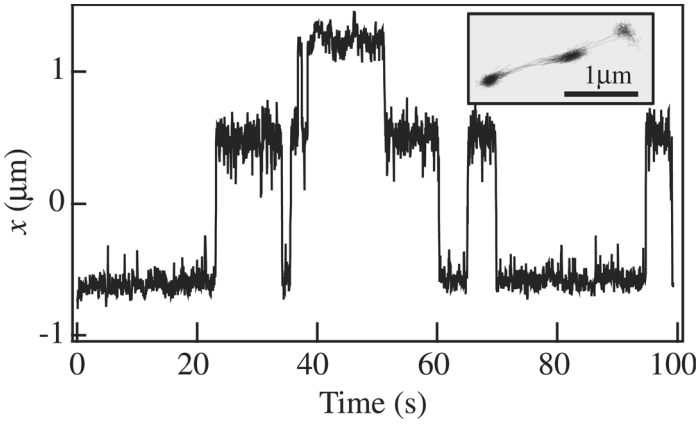


**FIGURE 5** Temporal and spatial trajectory (inset) of a fluorescent-labeled latex particle in lamellar phase of $\phi = 4.2\%$.

not in the same situation; some particles are trapped at a single site and some relative freely diffuse. In such case, the ensemble average of $\langle \boldsymbol{r}^2 \rangle$ over many particles shows so-called "sub-diffusive" behavior and $\langle \boldsymbol{r}^2 \rangle$ follows the power law, $\langle \boldsymbol{r}^2 \rangle \propto t^{\alpha}$, where $0 \leq \alpha \leq 1$ [15]. At short time in Figure 6, $\langle \boldsymbol{r}^2 \rangle$ is well ascribable by power function with $\alpha = 0.37$ drawn as a solid line. Although the statistical accuracy decreases at later stage in Figure 6, $\langle \boldsymbol{r}^2 \rangle$ at long time tends to follow normal diffusion process with $\alpha = 1$ shown as a broken line. The obtained diffusion constant is $1.3 \times 10^4$ times smaller than that in aqueous solution. This makes good agreement with that obtained by

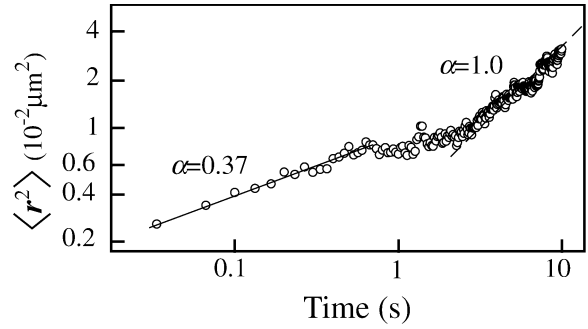


**FIGURE 6** Time dependence of means square displacement $\langle \boldsymbol{r}^2 \rangle$ of many fluorescent- labeled latex particles in lamellar phase of $\phi = 3\%$. The slope of the solid line at earlier stage is $\alpha = 0.37$ and the broken line at later stage is $\alpha = 1$.

modified ELS, which will be reported in ref. [10]. From direct observation of a particle's trajectory, it is found that a particle goes back and forth between a few sites and there seem to be a kind of connecting path between them. But at longer time scales, the connecting path will change and a particle fluctuates along another new path. Therefore, transport of a particle in region III is governed by the reorganization and renewal of a path connecting trapping sites. Such renewal process might be originated from the reorganization of lamellar structure or the dynamics of packing of vesicle-like structure. This kind of long time behavior seems to be also important to discuss the transport in biological systems those contain various size of inhomogeneity.

## CONCLUSION

We have studied dynamics of nano-sized colloidal particles between soft membranes by two complementary methods. One is ac electophoretic light scattering spectroscopy and the other is particle-tracking microscopy. These methods offer valuable information on dynamics of particles in lamellar phase from several $\mu$s to several tens seconds. The hierarchical structure is found in the dynamics of particles from diffusion of a particle under static confinement of membranes, one under dynamic interaction with membranes and that under the heterogeneity of lamellar structure with micron scales. This kind of hierarchical dynamic structure is ubiquitous in complex fluids and living systems. These experimental methods utilized in this work will a powerful tool to investigate these systems.

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