Hierarchical transport of nanoparticles in a lyotropic lamellar phase

2005 J. Phys.: Condens. Matter 17 S2937

(http://iopscience.iop.org/0953-8984/17/31/021)

INSTITUTE OF PHYSICS PUBLISHING JOURNAL OF PHYSICS: CONDENSED MATTER

J. Phys.: Condens. Matter **17** (2005) S2937–S2942 doi:10.1088/0953-8984/17/31/021

Hierarchical transport of nanoparticles in a lyotropic lamellar phase

Yasuyuki Kimura[1,2,4], **Teppei Mori**[2], **Akira Yamamoto**[2] **and Daisuke Mizuno**[2,3]

[1] Department of Physics, Graduate School of Sciences, Kyushu University, 6-10-1 Hakozaki, Higashi-ku, Fukuoka, Japan
[2] Department of Applied Physics, School of Engineering, University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo, Japan
[3] Division of Physics and Astronomy, Faculty of Sciences, Vrije Universiteit, De Boelelaan 1081, 1081 HV Amsterdam, The Netherlands

E-mail: kim8scp@mbox.nc.kyushu-u.ac.jp

Received 27 December 2004, in final form 18 February 2005
Published 22 July 2005
Online at stacks.iop.org/JPhysCM/17/S2937

Abstract

The dynamics of nanosized colloidal particles dispersed in a hyper-swollen lyotropic lamellar phase of a nonionic surfactant has been studied by ac electrophoretic light scattering and direct tracking of particles under a microscope. The frequency spectrum of electrophoretic mobility shows two relaxation processes. These are originated from the hindrance of free diffusion of particles by the interaction between membranes and particles. By direct tracking measurement, we find that particles jump from site to site where they stay for a long time. This trap-jump process greatly decreases the mobility at low frequencies.

1. 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, the lipid bilayer is one of the basic and common structures in living systems as a cell membrane and myelinated nerve cell [1]. Therefore, it is also important to study the transport property of nanosized colloidal particles such as protein molecules and charged polymers in a bilayer matrix to understand the dynamical aspect of living systems.

Recently, the local mechanical properties of soft matter such as gels and cytoplasm have been studied intensively by analysing the motion of probe particles dispersed in them. They are often called *microrheology* [2]. In most studies, the size of probe particles used is usually larger than the characteristic length of matrix, e.g. mesh size of gel networks. So, the observed

[4] Author to whom any correspondence should be addressed.

mechanical properties are identical to macroscopic continuous ones. But it is also interesting to study the case of these two sizes being comparable.

In this study, we have studied the dynamics of particles dispersed in a lyotropic lamellar phase. The size of particles is several tens of nanometres, and is a little bit smaller than the distance between membranes. In this situation, the diffraction limit and strong scattering from membranes makes it difficult to extract the information on the motion of particles alone by conventional methods of microrheology. To overcome these difficulties in using small probe 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 [3]. The change of mobility by varying the applied frequency provides the information on the dynamics of particles and the interaction between particles and membranes. We have also observed the motion of fluorescent-labelled particles directly under a microscope and obtained detailed information on their slow dynamics at a long timescale.

2. Experiment

Polystyrene latex particles with diameter of $2a = 42$ nm were dispersed in a dilute lamellar phase of n-pentaethyleneglycol monododecylether ($C_{12}E_5$)–hexanol–water mixture. The bilayer in this system has small bending elasticity $\kappa \approx 0.8k_BT$ at room temperature [4] and its lamellar structure is mainly stabilized by steric repulsion between undulating membranes. The interlayer distance d is changed from 50 to 130 nm by varying the volume fraction of the membrane ϕ. Since the number density of particles c satisfies the condition $c \ll d^{-3}$, the interaction between particles is negligible.

In this study, we measured the complex electrophoretic mobility $\mu^*(\omega)$ by a newly developed quasi-elastic light scattering (electrophoretic light scattering: ELS) under a sinusoidal electric field. Our method enables us to obtain $\mu^*(\omega)$ selectively from the scattered light by their frequency even in strongly light-scattering medium. This also makes it possible to measure $\mu^*(\omega)$ in a wider frequency range and to utilize much smaller probe particles. The details of its principle and experimental setup have been already discussed elsewhere [3].

The motion of fluorescent-labelled polystyrene latex particles ($2a = 52$ nm) in lamellar structure is directly observed under a fluorescent microscope (TE300, Nikon). The observed images are detected by a CCD camera and the centre of mass was calculated by weighting the digitized intensity from the captured digital image.

3. Complex electrophoretic mobility in a lamellar phase

The frequency spectrum of $\mu^*(\omega)$ for a sample of $\phi = 4.7\%$ at room temperature is shown in figure 1. There are two relaxation processes at around 1 kHz (HF relaxation) and 3 Hz (LF relaxation) [5]. Hereafter, we divide the frequency region into three from higher frequency, and denote them as I, II and III. We call the mobility at the flat part in the respective regions $\mu_{\rm I}$, $\mu_{\rm II}$ and $\mu_{\rm III}$. The mobility $\mu_{\rm III}$ is so small that we cannot measure its exact value. The mobility of the colloidal particles in aqueous solution of $C_{12}E_5$ and hexanol at critical micelle concentration is $\mu_0 = 5.7 \times 10^{-8}$ C m N^{-1} s^{-1} and it shows no frequency dependence. Therefore, these two relaxations indicate the existence of some processes which prevent free thermal motion of particles in a lamellar structure.

We can discuss the observed spectrum $\mu^*(\omega)$ by assuming that colloidal particles are trapped within the potential originating from the interaction with lamellar structures. Their characteristic sizes λ can be estimated from the relaxation time τ and mobility μ as

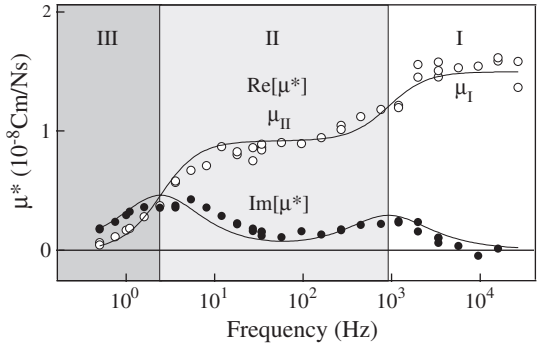

Figure 1. Frequency dependence of electrophoretic mobility $\mu^*(\omega)$ of latex particles in a lamellar phase of $\phi = 4.7\%$ ($\phi_{C_{12}E_5} = 4\%$, $\phi_{\text{hexanol}} = 1.04\%$).

$\lambda_{H(L)} = (k_B T \mu_{I(II)} \tau_{H(L)}/3\pi\eta_0 a\mu_0)^{\frac{1}{2}}$, where η_0 is the solvent viscosity. For $\phi = 4.7\%$, these lengths are $\lambda_H = 33$ nm for HF relaxation and $\lambda_L = 500$ nm for LF relaxation. These respectively correspond to the interlayer distance d and the persistence length l of orientational order of a membrane with bending elasticity $\kappa \sim k_B T$ [6] as shown in figure 2. This means the potential formed by flexible membranes traps particles within these length scales.

3.1. Effective drag coefficient in the region I

The particles between soft membranes induce a distortion field with size of d around particles [7]. Although particles are free to diffuse in this distortion field in region I, the mobility μ_I is smaller than μ_0 and decreases with decreasing d. On a macroscopic scale, it is known that the effective drag coefficient of a particle between hard walls increases due to the solvent flow near the walls [8]. The dependence of μ_I on d is found to be more remarkable than that predicted for a spherical particle between infinite parallel walls. This is due to the fact that some of the membranes also exist perpendicular to the membrane walls, and the confinement is tighter in the lamellar phase.

3.2. Mechanism of HF relaxation

In region II, the particles have to drag the distortion field around them to travel to a long distance. The excitation energy necessary to escape the distortion field is approximately given by $k_B T \ln(1 + \Delta d_0/d)$, where Δd_0 is the excess distortion field induced by osmotic pressure of a particle. The relative amplitude μ_{II}/μ_I can be estimated as $\mu_{II}/\mu_I \sim d/(\Delta d_0 + d)$. Since the static value of Δd_0 is estimated as $0.4d$ [7], μ_{II}/μ_I will be about 0.7, independent of d. But the observed ratio μ_{II}/μ_I decreases with reducing d from about 1 to 0.7 (see figure 4 in [6]). To explain this finding, we consider the dynamic process including the creation of the distortion field [9]. The time evolution of the distortion field is studied with the use of hydrodynamic equations of the lyotropic lamellar phase [10], and the characteristic time for the formation of distortion field τ_D is approximately given as $\tau_D \sim 3\eta d^3/k_B T$ (η is the 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 τ_{II}, that is the time necessary for a particle to jump out one site. Since τ_{II} can be estimated as $\tau_{II} \sim \xi^2/2D_{II}$ (D_{II} is the diffusion constant in the region II and $\xi = d/2$), τ_{II} is proportional to ϕ^{-2}. On the other hand, the time τ_D is proportional to ϕ^{-3}. Therefore, at high ϕ, where $\tau_{II} > \tau_D$, the distortion field fully grows to its equilibrium

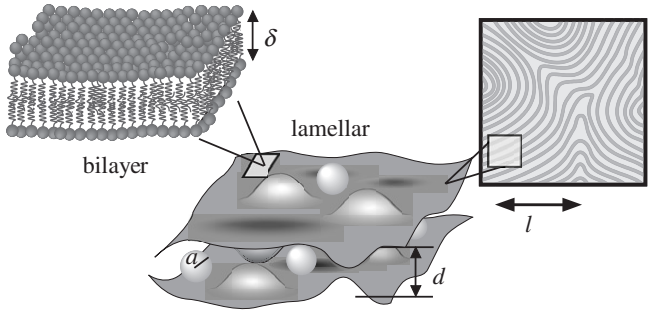

Figure 2. Schematics of hierarchical structure of a lyotropic lamellar phase. The lengths δ, d and l are respectively the layer thickness, the interlayer distance and the persistence length of orientational order of a membrane.

size before a particle will escape it. In contrast, at low ϕ, where $\tau_{\mathrm{II}} < \tau_{\mathrm{D}}$, a particle will escape before the distortion field fully grows. The dependence of $\mu_{\mathrm{II}}/\mu_{\mathrm{I}}$ on ϕ can be explained by the crossover between these two extreme situations.

3.3. Mechanism of LF relaxation

In region III, the mobility $\mu^*(\omega)$ decreases to almost zero. This indicates that most particles are trapped within a certain space. The existence of such trapping sites is also confirmed by direct observation under a fluorescent microscope, which will be discussed later. Since the lamellar structure in this study is not macroscopically oriented, there might be orientational defects of lamellae over a scale larger than d. In fact, the vesicle-like structure or folded lamellar structure composed of perforated lamellae has been frequently observed by freeze fracture electron microscopy [11]. We have recently studied the dielectric response of the lyotropic lamellar phase of $C_{12}E_5$ [12]. The observed relaxation can be interpreted quantitatively by modeling the lamellar phase as aggregates of multi-lamellar vesicles made up of perforated lamellae 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. But particles can diffuse in longer distance if the reorganization of the lamellar structure or renewal of trapping path occurs in region III.

4. Particle tracking measurement under a microscope

The motion of colloidal particles in region III can be directly tracked under a microscope due to their slow diffusion in the lamellar structure. An example of the temporal and spatial trajectory of a particle is shown in figure 3. The motion of a particle is completely different from that following a simple diffusion process. A particle stays at a certain site for a long time and suddenly jumps to another site about one micron away. As the concentration increases, the time spent at one site increases and the number of such particles increases. The trajectory in figure 3 resembles that of colloidal particles in colloidal glasses [13] and in F-actin networks [14]. 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 4 shows the time evolution of the mean square displacement (MSD) $\langle \boldsymbol{r}^2 \rangle$ in two dimensions over many particles for $\phi = 3\%$. If particles follow a pure diffusion process, $\langle \boldsymbol{r}^2 \rangle$ is proportional to the time elapsed t and its slope gives the self-diffusion constant of the particles.

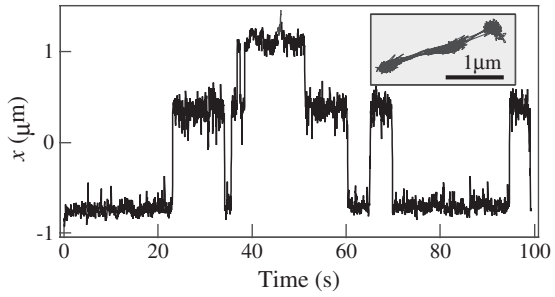

Figure 3. Typical temporal change of position of a particle in one dimension and its trajectory projected to two dimensions (inset).

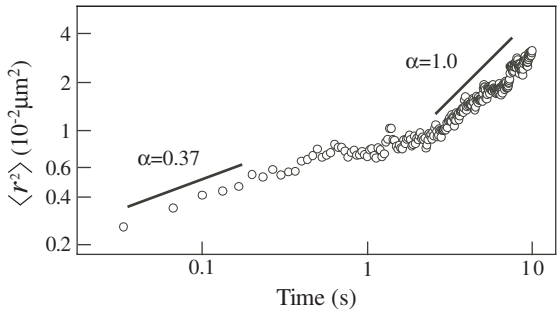

Figure 4. Time evolution of the mean square displacement $\langle \boldsymbol{r}^2 \rangle$ of particles in a lamellar phase of $\phi = 3\%$ at a long timescale.

On the other hand, if the particles are completely trapped within a 'cage', $\langle \boldsymbol{r}^2 \rangle$ saturates at a certain value. At $\phi = 3\%$, all particles do not behave in the same manner; some are trapped at a single site and some diffuse relatively freely. In such a case, the ensemble averaged value of $\langle \boldsymbol{r}^2 \rangle$ over many particles shows so-called 'sub-diffusive' behaviour and $\langle \boldsymbol{r}^2 \rangle$ follows the power law, $\langle \boldsymbol{r}^2 \rangle \propto t^{\alpha}$, where $0 < \alpha < 1$ [14]. At the short time in figure 4, $\langle \boldsymbol{r}^2 \rangle$ is well ascribable by a power function with $\alpha = 0.37$, drawn as a solid line. Although the statistical accuracy decreases at a later stage in figure 4, $\langle \boldsymbol{r}^2 \rangle$ at a long time tends to follow normal diffusion process with $\alpha = 1$. The obtained diffusion constant is 1.3×10^4 times smaller than that in aqueous solution. This makes good agreement with that obtained by ELS reported in [9]. From direct observation of particle trajectories, it is found that a particle goes back and forth between a few sites and there is a kind of connecting path between them. But at longer timescales, such a path will vanish and a particle fluctuates along another new one. Therefore, the transport of a particle in region III is governed by the reorganization and renewal of a path connecting trapping sites. Such a process might be originated from the reorganization of lamellar structure or the change in packing of vesicle-like structure. This kind of long time behaviour is important in discussing the transport in biological systems with dynamical inhomogeneity.

5. Conclusions

We have experimentally studied the dynamics of nanosized colloidal particles between soft membranes. We utilized both ac electrophoretic light scattering spectroscopy and particle tracking microscopy. These methods offer valuable information on the dynamics of particles

in the lamellar phase from several μs to several tens of seconds. A hierarchical structure is found in the dynamics of particles. This kind of hierarchical dynamics is ubiquitous in soft complex fluids and living systems, and the experimental methods used in this work are powerful tools to investigate these systems.

Acknowledgments

This work is supported by Grants-in-Aid for Scientific Research from Japan Society for the Promotion of Science and from the Ministry of Education, Culture, Sports, Science and Technology of Japan. DM is supported with a post-doctoral fellowship from the Japan Society for the Promotion of Science.

References

[1] Brown G H and Wolken J J 1979 *Liquid Crystals and Biological Structures* (New York: Academic)
[2] MacKintosh F C and Schmidt C F 1999 *Curr. Opin. Colloid Interface Sci.* **4** 300
[3] Mizuno D, Kimura Y and Hayakawa R 2000 *Langmuir* **16** 9547
[4] Freyssingeas E, Nallet F and Roux D 1996 *Langmuir* **12** 6028
[5] Mizuno D, Kimura Y and Hayakawa R 2001 *Phys. Rev. Lett.* **87** 88104
[6] Sornette D and Ostrowsky N 1994 *Micells, Membranes, Microemulsions and Monolayers* ed W M Gelbart, A Ben-Shaul and D Roux (Berlin: Springer)
[7] Sens P, Turner M S and Pincus P 1997 *Phys. Rev.* E **55** 4394
[8] Happel J and Brenner H 1991 *Low Reynolds Number Hydrodynamics* (Dordrecht: Kluwer)
[9] Mizuno D, Kimura Y and Hayakawa R 2004 *Phys. Rev.* E **70** 11509
[10] Brochard F and de Gennes P G 1975 *Pramana* **1** (Suppl.) 1
[11] Hoffmann H, Munkert U, Thunig C and Valiente M 1994 *J. Colloid Interface Sci.* **163** 217
[12] Mizuno D, Nishino T, Kimura Y and Hayakawa R 2003 *Phys. Rev.* E **67** 61505
[13] Weeks E R, Crocker J C, Levitt A C, Schofield A and Weitz D A 2000 *Science* **287** 627
[14] Wong I Y, Gardel M L, Reichman D R, Weeks E R, Valentine M T, Bausch A R and Weitz D A 2004 *Phys. Rev. Lett.* **92** 178101