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SHORT COMMUNICATION

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Direct estimation of dynamic characteristics and interaction potential of latex particles interacting with a glass surface by evanescent wave light-scattering microscope method

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Abstract The dynamic and static characteristics of a polystyrene latex particle in dispersion interacting with a glass surface were studied by the evanescent wave light-scattering microscope (EVLSM) technique originally proposed by Prieve et al. for static studies. The dynamic behavior of the thermal vibration of the particle in a potential well created by electrostatic interaction between the particle and glass and gravity was clearly and quantitatively estimated, in addition to the estimation of the potential profile itself. The potential minimum became shallower with increasing added salt concentration. It was also clearly observed that the vibrational motion of the particle in the well became large in amplitude and the probability of the occurrence of the large vibration became large with increasing salt concentration. Such information on the dynamics is essential for the correct understanding of the interaction potential. The EVLSM method is shown to be a very powerful technique for the estimation of not only the potential profile but also dynamic characteristics.

Key words Evanescent wave light scattering – colloidal particle – interaction potential – thermal vibration – particle-wall interaction

Introduction

An evanescent wave is produced by total reflection of an electromagnetic wave at an interface [1]. When light coming from a medium 2 of refractive index n_2 arrives at the interface with a medium 1 of refractive index n_1 ($n_1 < n_2$), total reflection of the light occurs if the incident angle of the light beam is larger than the critical angle. Under these conditions, an evanescent wave is produced in medium 1 only in the region very close to the interface. This region is typically of the order of the wavelength of the light beam. When a He-Ne laser beam is used as the incident beam, this means that only that part of medium 1 within several thousand Å of the interface is illuminated by the evanescent wave. The depth of this region can be controlled by changing the incident angle of the laser beam, so the evanescent wave can be used as a very powerful tool for extracting information about the interfacial phenomena. Some papers on interfacial studies using a combination of evanescent wave and fluorescence techniques have been published [2].

An additional unique character of the evanescent wave is the exponential decay of its intensity as a function of the distance from the interface (z) (see Fig. 1). By taking advantage of this unique characteristic and by combining it with the light-scattering technique, the evanescent wave becomes a powerful tool for studying the behavior of colloidal particles near solid surfaces. For example, Prieve et al. [3–6] have proposed the use of the total internal reflection microscope (TIRM) technique to evaluate the interaction potential between a glass surface and

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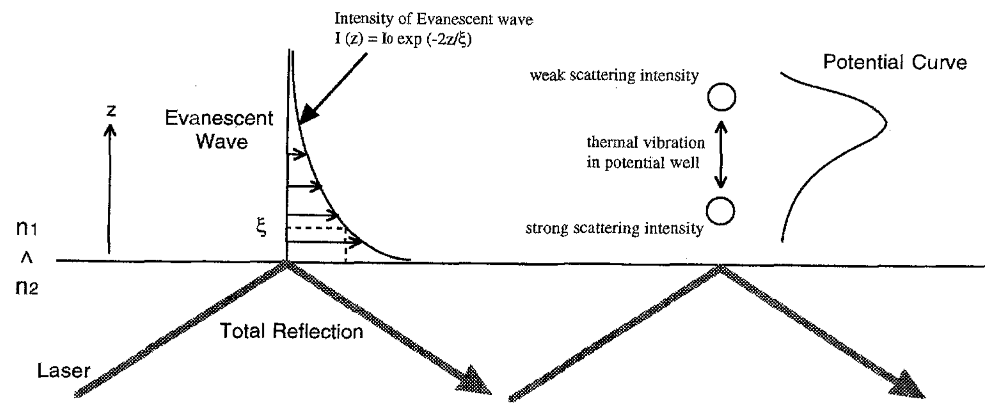

Fig. 1 Schematic illustration of the characteristics of an evanescent wave and the principle of EVLSM

a colloidal particle in a dispersion. We have constructed an evanescent wave light-scattering microscope (EVLSM) apparatus following the principle of Prieve et al., and have studied the dynamic and static behavior of a polystyrene latex particle in dispersion interacting with a glass surface. In this paper, we will show that this technique gives us very important information on the dynamic character of the particle, vibrating in a potential well near the interface, in addition to an interaction potential between the particle and the interface.

Experimental

Brief summary of the characteristics of evanescent waves and the principle of the evanescent wave light scattering microscope technique

The characteristics of evanescent waves and the principle of EVLSM are schematically illustrated in Fig. 1. An evanescent wave is produced by total reflection of light at the interface of media 1 and 2, whose refractive indices are n_1 and n_2 respectively, with $n_1 < n_2$. The amplitude of the evanescent wave decays exponentially with increasing distance from the interface z [1]. The intensity of the evanescent wave $I(z)$ is therefore expressed as a function of the distance from the total reflection plane, z, as

$$I(z) = I_0 \exp(-2z/\xi)\,, \tag{1}$$

where I_0 is the intensity of the evanescent wave at $z = 0$ and the penetration depth ξ is defined by

$$\xi = \lambda_0 / [2\pi n_2 (\sin^2\theta_i - \sin^2\theta_c)]^{1/2}, \tag{2}$$

where θ_i is the incident angle, θ_c the critical angle, and λ_0 the wavelength of the incident beam in vacuo.

Let us consider the situation in which medium 2 is glass, medium 1 is water, and one latex particle is dispersed in the water. The polystyrene latex particle (specific gravity 1.04) is sedimented down by the effect of gravity if it is sufficiently large. However, since the glass surface is negatively charged (say $-30 \sim -40$ mV or more in zeta potential [7]) there should be an electrostatic repulsive interaction between the latex particle and the glass surface if the latex particle is negatively charged. These two interactions may form a potential minimum near the interface, and the latex particle may show vibrational motion in this potential well. The distance from the interface z is changing with respect to time due to this vertical vibrational motion. At the same time, the particle is illuminated by the evanescent wave. The intensity of the incident evanescent wave depends on z in the exponential manner which is characterized by ξ. Since the intensity of the scattered light is proportional to that of the incident light, this situation means that the intensity of the scattered light corresponds to the distance z. (As will be described later, by EVLSM the scattered intensity for a single particle was collected by a microscope. Since the field of vision of the microscope is small enough compared with the size of the laser beam, the motion to x-y directions does not cause a change of scattering intensity.) Hence, if one measures the scattering intensity in a short period many times, the profile of the scattering intensity vs. the number of the observation of the intensity reflects the interaction potential between the particle and the glass surface. This is the principle of EVLSM which was originally proposed by Prieve et al. [3, 8]. In this paper, we will show that the raw data obtained by EVLSM clearly display the vibrational motion of the particle in the potential well, if the intensity of the scattered light can be recorded for the time intervals suitably shorter than the time scale of the thermal vibrational motion. The evaluation of the interaction potential has also been reported by other investigators [9], but the evaluation of the dynamic behavior has been never reported.

Sample

The latex particle used was polystyrene latex (N-1000, Sekisui, Osaka, Japan). Its diameter, provided by the supplier, was 1.026 μm. The sample dispersion (originally 10 vol. %) was purified by dialysis, and then diluted by a factor of about 10^6 in pure water or a salt solution for the EVLSM measurements. The cover glass (Matsunami Glass, 30 × 30 mm) used was treated with sulfonic acid and rinsed with pure water. A glass tube of outer diameter 30 mm and 10 mm height was adhered to the coverglass surface with Araldite; this unit was used as a sample container. The water used for the sample preparation was obtained from the Milli-Q system (Millipore, Bedford, MA). NaCl (analytical grade, Merck, Darmstadt) was used as the added salt. 5 mM Sodium dodecyl sulfate (SDS, Nacalai tesque, Kyoto, Japan) was also present in the sample solution to stabilize the colloidal system.

Apparatus

The evanescent wave light scattering apparatus was constructed in our laboratory using the principle of Prieve et al. [3] A schematic representation of our apparatus is shown in Fig. 2. A beam from a He-Ne laser (15 mW, Nihon Kagaku Engineering, Tokyo, Japan) enters a trapezoidal prism which was specially designed and made (material: BK-7, Sigma Koki, Saitama, Japan). The cover glass of the sample container was set on the upper face of the prism with an index-matched immersion oil, and the laser beam was totally reflected by the upper interface of the cover glass and the water. In the sample cell, a latex particle is in equilibrium in the potential well caused by the electrostatic interaction with the glass surface and gravity.

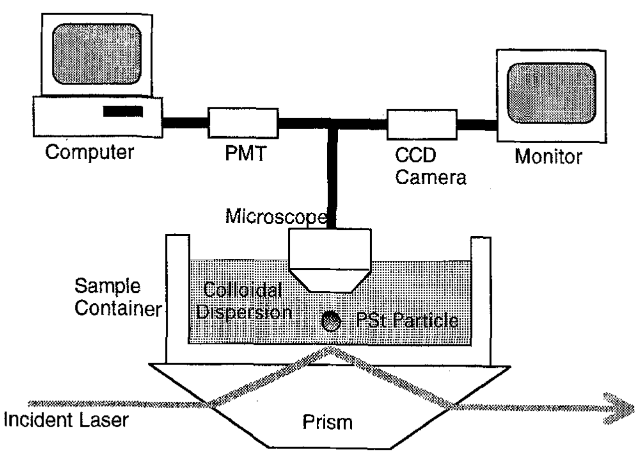

Fig. 2 Schematic representation of the EVLSM instrument. PSt means polystyrene

It took typically a half or one day to reach equilibrium. After focusing on particles near the bottom of the sample container, a single particle was centered in the observation field of measurements, which was determined in advance, using the translating stage. The scattered light from only one particle was collected by a water-immersion lens (× 40) attached to the stage-fixed microscope (Optiphot-2 UD, Nikon, Tokyo, Japan). Since the evanescent wave propagates parallel to the interface, the scattering at a scattering angle of 90 degrees was detected by this optical configuration. The scattered light was led to a photomultiplier for the light-scattering apparatus (ELS-800, Otsuka Electric, Osaka, Japan) by a multi mode glass fiber (Moritex, Tokyo, Japan). The intensity of the scattered light was collected with a time interval of 2.5 ms. The number of data points for the estimation of the interaction potential was typically 20 000. After finishing one set of measurements, which took about 30 s, the position of the latex particle in the field of vision was readjusted by x-y translating stage of the microscope, and then the next set of the measurements was started.

Results and discussion

Figure 3 shows the raw data obtained by EVLSM at various salt conditions. The abscissa is the measuring time, and the ordinate is the observed relative intensity for 2.5 ms. Figure 4 shows the interaction potential between the latex particle and the glass surface evaluated in the manner of Prieve et al. [3]. The potential minimum created by the electrostatic interaction between the particle and the glass wall and gravity is clearly seen. In Fig. 3, weak scattering intensity means that z is large, and strong scattering intensity means z is small: the time change of the scattering intensity reflects the vertical motion of the particle. Hence, it can be said that Fig. 3 reflects the dynamic character of the particle while Fig. 4 reflects the static character. From Fig. 3, it is clear that at low ionic strength (Fig. 3a) the latex particle shows a rather small-amplitude motion in the bottom of the potential well; a larger amplitude motion lasting of the order of 10^{-1} s occurred roughly 3–5 times in 1 s, but it appears to be random. With increasing salt concentration (Figs. 3b to d), the amplitude of the large motion becomes large and the probability of the large motion also increases. This means that the potential well becomes shallower due to the shielding effect of the salt on the electrostatic interaction between the latex particle and the glass surface. This tendency is clearly seen in Fig. 4, although the position of the profile is on a relative scale. [10] At the highest salt condition (1 mM, Fig. 3d), the vibrational motion is very much enhanced; there is a large amplitude and large frequency for the large

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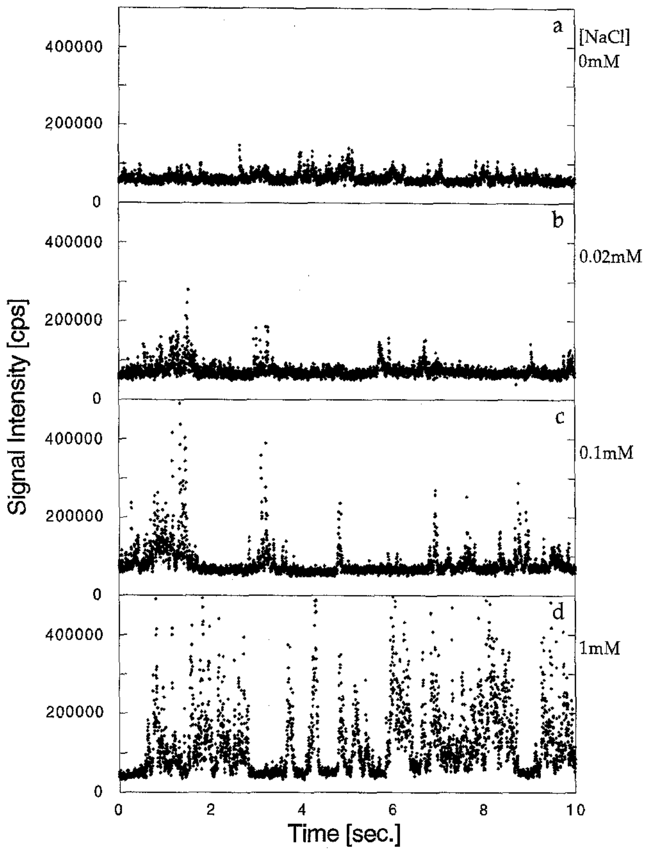

Fig. 3 The raw data obtained by EVLSM. Latex: N-1000 (diam: 1 μm), time interval 2.5 ms, salt (NaCl) concentration; (a) 0 mM, (b) 0.02 mM, (c) 0.1 mM, (d) 1 mM. 5 mM (below CMC) SDS was also added in each case, to increase the surface charge

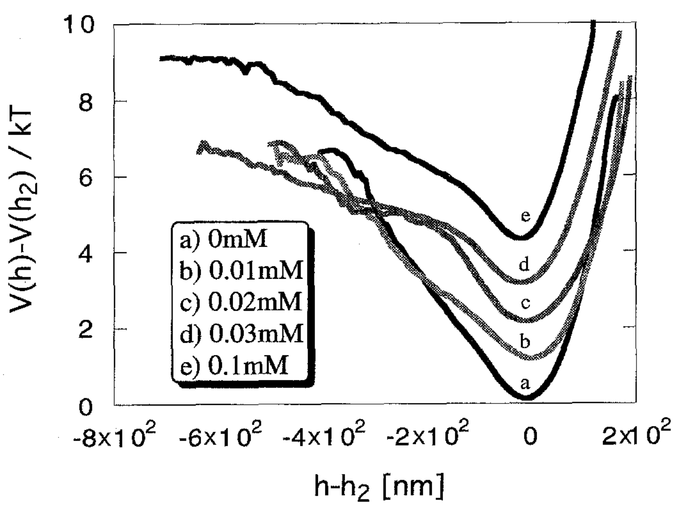

Fig. 4 The interaction potential between a latex particle and a glass surface directly determined by EVLSM at various salt conditions. The distance in the ordinate (h-h_2) is a relative distance: h normalized to the potential minimum position h_2

motion. When there is no added salt (Fig. 3a), the particle executes a small vibrational motion near the bottom of the potential well, with a probability of about 80%. By contrast, it executes the large vibrational motion with an approximately 80% probability at 1 mM NaCl (Fig. 3d). For the duration of one large amplitude motion, the difference between the no salt and higher salt conditions is also clearly observable. At 0 mM NaCl, one large vibration consists of about 10–20 points, corresponding to 25–50 ms. On the other hand, at 1 mM NaCl, it consists of about 50 points, indicating that one large vibrational motion lasts for of the order of 100–150 ms. By EVLSM, the time scale and dimension of the thermal vibration of the latex particle can be quantitatively determined.

There are some examples of analysis of Brownian motion and the vibrational motion of latex particles in their ordered state in dispersion by a combination of ordinary microscopy with a video device. [12] However, for such a case, the time interval of data collection was typically 1/30 s, which is insufficient for a detailed analysis of the motion. By EVLSM, this problem can be easily overcome.

Conclusion

The EVLSM technique is a very powerful technique for evaluating the interaction potential between a colloidal particle in dispersion and a solid surface directly. It is very interesting to compare EVLSM results with AFM (Atomic Force Microscope) results. In this study, it has been shown that EVLSM is also an extremely powerful technique for the study of the dynamic behavior of the particle if the sampling time of the measurement is suitably short; this would be difficult to be studied by the AFM technique. It is to be anticipated that much more detailed information about the motion will be obtained by significantly reducing the sampling time. If a measurement is made with time interval of the order of microseconds, a detailed trajectory of the thermal vibrational motion in the potential well may be obtained. In such circumstances, analyses in terms of time-correlation functions and Fourier series would be very interesting. Direct information about the vibrational motion of the particle in the potential well is a very important result for the correct understanding of the interaction potential. Attempts to reduce the sampling time and to study systems with various combinations of particle and surface are now in progress in our laboratory.

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References

1. Harrick NJ (1967) Internal Reflection Spectroscopy. Interscience
2. Tanimoto S, Kitano H (1995) Colloids and Surfaces B 4:259
3. Prieve DC, Frej NA (1990) Langmuir 6:396
4. Bike SG, Prieve DC (1990) Int J Multiphase Flow 16:727
5. Prieve DC, Bike SC, Frej NA (1990) Faraday Discuss Chem Soc 90:209
6. Walz JY, Prieve DC (1992) Langmuir 8:3073
7. Hunter RJ (1988) Zeta Potential in Colloid Science. Chap. 7, Academic, London
8. Although Prieve et al. call their technique "Total Internal Reflection Microscopy (TIRM)", we suggest the name EVLSM for the following reason. We do not observe "total internal reflection" by a "microscope", but the scattering from a particle illuminated by an evanescent wave (whose origin is the total reflection) detected by a photomultiplier connected to a microscope. The total reflection is just a tool for producing an evanescent wave. The principle of the technique is scattering of an evanescent wave
9. Flicker SG, Bike SG (1993) Langmuir 9:257
10. EVLSM measurement on an absolute scale is possible [11] and is now in progress
11. Flicker SG, Tipa JL, Bike SG (1993) J Coll Int Sci 158:317
12. Ito K, Nakamura H, Yoshida H, Ise N (1988) J Amer Chem Soc 110:6995