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Development of a Laser Measurement System for the Evaluation of Dispersion State of Micro- and Nano-Emulsions for Latent Heat Storage Applications

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Abstract

We develop a new laser Doppler measurement system for the evaluation of the dispersion stability of micro- and nano-emulsions. In the future thermal managements, colloids in the form of micro- and nano-emulsions will play a major role of storing and transporting thermal energy produced by renewable energy source or waste heat. With the emulsions made of phase-change materials, a highly efficient heat exchange can be achieved through latent heat compare to the sensible one. Heat energy is stored in melting and released in solidification. An important issue of the technology is the dispersion stability of emulsions under repeated phase changes. The dispersion is achieved by the interaction of electrokinetic forces acting on the colloidal particles characterized by zeta potential. We are going to use evanescent waves for measuring the zeta potential of emulsions at thermal interfaces. The use of evanescent waves can achieve a spatial resolution in the range of nanometers, which is never feasible with a conventional optical system bounded by the diffraction limit. We present the basic concept and the prototype design of the measurement system.

Introduction

Recently we have growing concerns about global warming and climate change, which reminds us of the sustainability of our life towards the future. The apparent increase of the temperature is likely due to greenhouse effects in the atmosphere. It is largely caused by the excess emission of carbon dioxide and other relevant gasses emitted from the combustion of fossil fuel for gaining heat and electric energy. Despite the dependency of our life on the fossil fuel, natural resources are limited. Before the remaining resources become run out, solutions need to be sought. Some of the possible solutions are to increase the energy efficiency and to reduce energy waste. Another is to increase the use of renewable energy such as the sun light and wind instead of fossil fuel. However, the problem of such solutions is their time varying output, while the users demand constant energy supply. Besides, the location of the supplier of energy waste and renewable energy may be far from that of demands. Hence, one of the major problems is the gap existing between the energy suppliers and consumers.

In order to fill the gap, the excess energy can be temporary stored and used when it is needed. Thermal storage is to store the energy as heat. Beside sensible heat storage, the heat storage based on latent heat is attractive because it has a high efficiency of heat transfer at phase changes. One of the promising realizations is to use phase-change material (PCM) having flowability. Among many, we focus on the use of micro- and nano-emulsion as thermal storage medium. Emulsion is a colloid whose solute and solvent are both in liquid phase. Micro- and nano-emulsion contains micro- or nanometer scale solute in solvent. Due to the flowability of emulsion, the heat can be flexibly transferred from one place to another. The requirement for the emulsion for thermal storage and transport is their long term stability of dispersion. They must remain stably dispersed under many times of phase changes.

The dispersion of emulsion depends on the polarization of the solute and solvent. One of the key features is the zeta-potential, which is the electric potential near the surface of the solute with respect to the bulk solvent. If the solute has a sufficiently high zeta potential, the emulsion remains stably dispersed without sedimentation. The zeta potential can be evaluated by the velocities of the solutes with a laser Doppler electrophoresis [1].

In the present study, we develop a novel laser Doppler velocimetry (LDV) using evanescent waves. An LDV based on evanescent waves has once been proposed in the past [2]. However, the system has never been used in any application ever since. Details of the system are not known either. We build a new measurement system by ourselves for a new application, so that we can characterize the zeta potential in the very vicinity of the solid-liquid interface under heat exchange. The short penetration depth of the evanescent wave is attractive for evaluating the dispersion stability of opaque colloidal liquids including emulsion. In the following, we describe the basic concept of the evanescent-wave-based LDV measurement system.

Colloid and Dispersion Stability

Colloid

In colloid, suspended particles are dispersed in the suspension medium with interactions. The interaction forces include both attractive and repulsive forces. As long as the sum of the forces is dominated by the repulsive force, the suspension particles stably dispersed in the medium. Once the attractive force prevails against the repulsive one, the stability becomes hindered by aggregation and sedimentation.

One of the keys for the dispersion stability is the electric double layer formed around the particles such as depicted in Fig. 1. The electrical potential between the particle surfaces to the location apart is the zeta potential. If the particles have sufficiently large electrical charges, the resulting zeta potential becomes high and the particles remain stably dispersed.

Zeta Potential

Zeta potential is an electrical potential of the dispersion medium and the stationary layer of fluid attached to the dispersed particle. It is defined as the electric potential in the electric double layer at the location of the slipping plane relative to the bulk fluid away from the layer as depicted in Fig. 1.

Zeta potential of colloid can be evaluated based on electrophoresis. A colloidal particle starts to move when an electric field is applied to the colloid. After a certain time, the translational movement reaches into terminal velocity, at which the electric force becomes balanced with the viscous drag acting on it. From the force balance, the zeta potential ζ is derived as

$$\zeta = \frac{\mu}{\varepsilon}\frac{u}{E}, \tag{1}$$

with μ [Pa·s], ε [F/m], u [m/s], and E [V/m] being the colloid viscosity, permittivity, terminal velocity and electric field strength, respectively. Hence, the zeta potential can be obtained from the terminal velocity once the applied electric field is set and the material properties are known. In order to know the terminal velocity of the particle, laser Doppler velocimetry (LDV) can be used.

Laser Doppler velocimetry (LDV)

An LDV is a well-established measurement technique in fluid mechanics. It is based on the Doppler effect of light scattering by particles distributed in fluids. The typical setup of an LDV is a differential configuration consisting of a pair of laser beams crossing at their beam waists as shown in Fig. 2. The beams create an optical interference at the crossing area, which serves as the measurement volume. The interference results in a fringe pattern parallel to the laser bisector plane. The fringe spacings *d* is described as

$$d = \lambda/(2\sin\alpha), \tag{2}$$

where λ and α being the wavelength and the half crossing angle, respectively. When a tracer particle passes through the volume, it scatters the light and generates a modulated Doppler burst signal as shown in right side of Fig. 1. The beat frequency f of the signal is proportional to the velocity u perpendicular to the fringe bisector plane

$$f = u/d. \tag{3}$$

Hence, the particle velocity is obtained by measuring the Doppler frequency. The spatial resolution is defined by the size of the measurement volume, which is determined by the beam-waist diameter of the laser beams. The minimum focusable diameter of a laser beam is bounded by the diffraction originating from the wave nature of light. Hence, the spatial resolution cannot be increased beyond the diffraction limit, typically in the range of several tens of micrometers.

Evanescent Wave

Evanescent wave is the light wave generated at the interface of a total internal reflection [3]. Consider a light wave incident at an interface of two media with different refractive indices as shown in Fig. 3. The light wave is partly refracted and partly reflected at the interface. The refraction can be described by Snell's law

$$n_1 \sin\theta_1 = n_2 \sin\theta_2, \tag{4}$$

with n_1 and n_2 being the refractive index of the incident and the refractive medium, respectively. The incident angle θ_1 is defined as the angle from the normal line at the interface, and the refractive angle θ_2 likewise. Assuming that the incident medium has a higher value of the refractive index than the other ($n_1 > n_2$), the refractive angle θ_2 is always larger than the incident one θ_1. With the increase of the incident angle, the refraction angle increases and reaches the right angle, at which the incident angle becomes

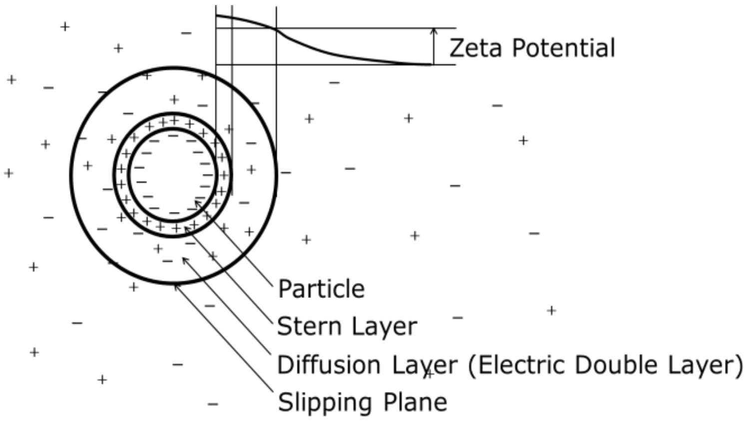

Fig. 1 Schematic of the electric double layer and the zeta potential around a suspension particle in a colloidal liquid.

$$\theta_c = \sin^{-1}(n_2 / n_1). \tag{5}$$

This is the critical angle of incident and beyond this, the incident light is totally reflected without refraction. When an incident wave experiences a total internal reflection, an evanescent wave emerges at the interface on the other side of the incidence. Even though the incident wave is totally reflected back into the originating side with a higher refractive index, there is a penetration of wave into the other side at the interface. The penetrating wave is the evanescent wave mathematically described as

$$\mathbf{E}_{Tr} = \mathbf{E}_{In} \exp(-\beta z) \cdot \exp\{ j(kx - \omega t)\}, \tag{6}$$

where $\mathbf{E}_{Tr}$ is the transmitting wave and $\mathbf{E}_{In}$ the incident wave both in the vector form. The parameters j, t, ω denote the imaginary unit, time and the angular velocity of the wave, respectively. The coordinates x and z are defined in Fig. 3. The constants in Eq.(6) are

$$\beta = (\omega / c)\sqrt{(n_1 \sin\theta_1)^2 - n_2{}^2}, \tag{7}$$
$$k = (\omega / c) \cdot n_1 \sin\theta_1. \tag{8}$$

with c being the speed of light. These equation denote that the evanescent wave travels along the tangential direction of the interface between the two media. They also tell that the evanescent wave decays exponentially in the direction perpendicular to the interface. The inverse of β in Eq.(7) is an indication of the penetration depth

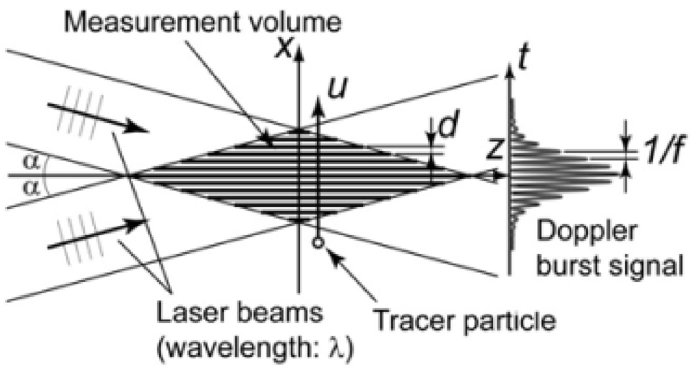

Fig. 2 Principle of a laser Doppler velocimetry (LDV) with a differential configuration of optics.

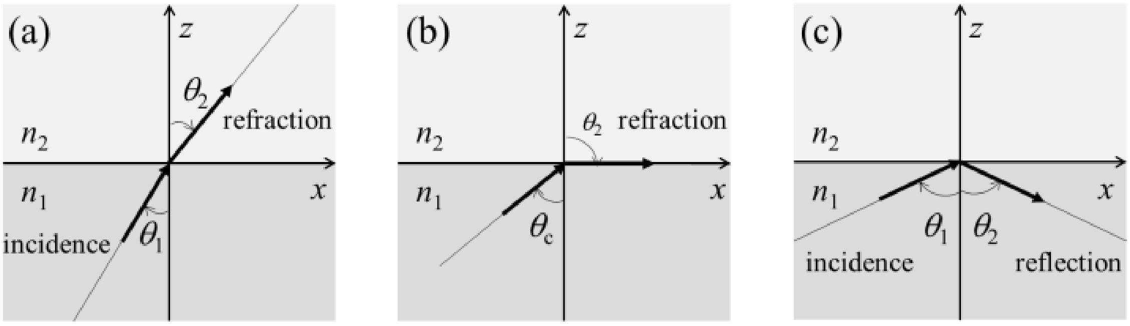

Fig. 3 Three cases of refractions of an incident light at an interface of two media with different refractive indices (n1>n2): (a) ordinary refraction, (b) refraction at the critical angle, (c) total internal reflection.

$$D = 1/\beta = (\lambda_1 / 2\pi)/\sqrt{(n_1 \sin\theta_1)^2 - n_2^{\,2}} \;. \tag{9}$$

The penetration depth becomes approximately 160 nm in the case of λ_1= 532 [nm] (frequency doubled Nd:YAG), n_1= 1.52 (for BK7), n_2=1.33 (for water) and θ_1=70°(cf. critical angle θ_χ=61°). Hence, the penetration depth is in the range of a few hundred nanometers at most.

Evanescent-Wave LDV (EV-LDV)

We use a pair of evanescent waves for creating laser Doppler measurements of the zeta potential of colloids in the vicinity of the interface. The evanescent waves are used to form an optical interference. The resulting interference field of the evanescent waves functions as the measurement volume of a laser Doppler system such as illustrated in Fig. 4. The thickness of the measurement volume would be around a few hundred of nanometers at most. This size of the measurement volume can never be achieved by a conventional laser Doppler system in which the smallest measurement volume is bounded by the diffraction limit.

Design of the EV-LDV

We are designing the prototype setup of the measurement system based on the evanescent wave. Fig. 4 shows the design of an EV-LDV. There are several concerns on the realization of an EV-LDV. There are different optics for its realization. Another concern is on the signal analysis of the scattering lights from the colloidal particles under electrophoresis. Signals

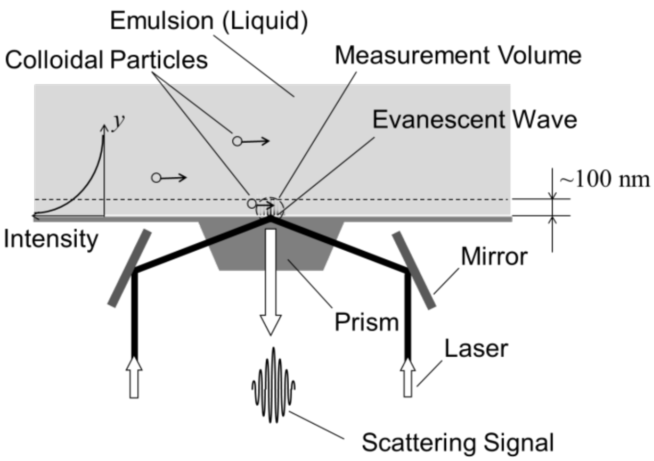

Fig. 4 Concept of the evanescent-wave laser Doppler velocimetry (EV-LDV) for the measurement of zeta potential of the suspension particles in colloids.

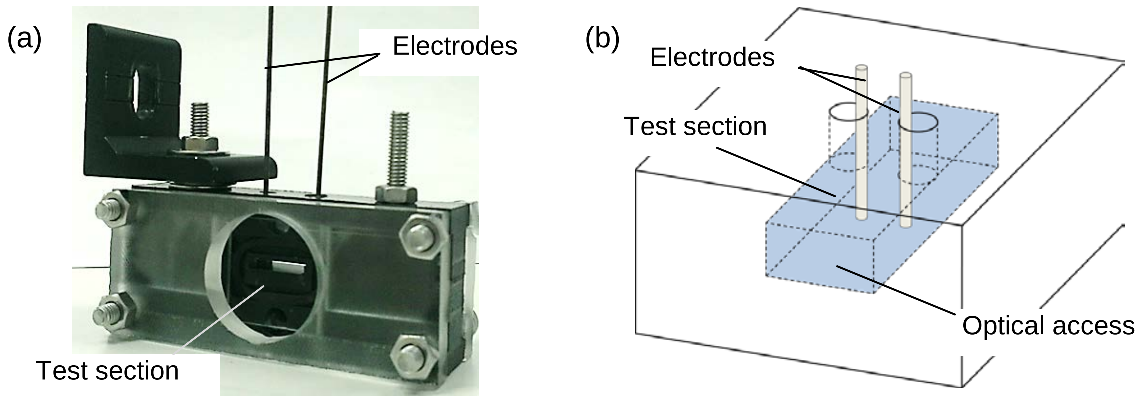

Fig. 5 The test cell built for the electrophoresis experiment: (a) picture of the electrolysis cell, (b) schematic overview of the test section.

with low Doppler frequencies need to be analyzed. Multi-particle scattering expected in EV-LDV measurements generates frequency spectra different from those encountered in conventional LDV measurements where single-particle scattering dominates.

Preliminary Experiment

We perform a preliminary experiment using a conventional LDV. A test cell was built for the electrophoresis experiment as shown in Fig. 5. The cell was made of glass and plastic. The test section is surrounded by the plastic walls and two sides of the walls were made of glass plates for allowing an optical access. The two vertical holes are equipped for the evacuation of the gas bubbles created by the electrolysis at the electrodes made of platinum titanium. We used a conventional LDV with a differential configuration for the experiment. The experiment will be done using standard electrolyte with known characteristics of the zeta potential.

Summary and Perspectives

We develop a laser measurement system for the measurement of zeta potential of colloidal liquids for latent heat storage applications. The concept of the EV-LDV is proposed and the theoretical design is provided based on the theoretical consideration of evanescent waves. We carried out preliminary measurements of zeta potential under electrophoresis using conventional LDV before using evanescent waves. Measurement feasibility of the system is under examination using standard electrolyte with a known zeta potential. The details of the experiments and the results will be presented at the conference.

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