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ScienceDirect
Food Hydrocolloids 21 (2007) 831–837
FOOD HYDROCOLLOIDS
www.elsevier.com/locate/foodhyd

Fast optical sizing without dilution

A. Parker[a], C. Baravian[b,*], F. Caton[b], J. Dillet[b], J. Mougel[b]

[a]*Corporate Research, Firmenich SA, 7, rue de la Bergère, CH1217 Meyrin 2 Geneva, Switzerland*
[b]*LEMTA, 2 av. De la forêt de Haye, BP 160 54504 Vandoeuvre Cedex, France*

Received 8 June 2006; accepted 14 August 2006

Abstract

Particle size is a key characteristic of colloidal dispersions. Small-angle light scattering, the standard measurement method, requires extensive sample dilution before size measurement. This process may change the sample. It is also time-consuming and makes on-line process control difficult. We present a new method of particle sizing that does not require dilution. It is based on the static (steady) scattering of incoherent light in the multiple scattering limit. We call it steady light transport (SLT). We focus a laser onto the sample and measure the halo of backscattered light. The technique is fast, robust, inexpensive and non-invasive. Diameters between tens of nanometers and several micrometers can be measured reliably. We first describe a simple technique that does not use the polarization of light. It gives the average size when the particle volume fraction and optical contrast are known. A second, more sophisticated version measures the full light-polarizing properties of the sample. This method can give both average particle size and volume fraction. Only the optical contrast needs to be measured independently. We demonstrate the use of SLT to size emulsions and to measure emulsification in real time.

Keywords: Optical particle sizing; Multiple scattering; Polarized light; Emulsion

1. Introduction

Many foods contain colloidal dispersions. Their particle size is a key characteristic, as it contributes to their physical stability and organoleptic properties. Many methods for measuring the particle size have been suggested (Allen, 1993), but only a few are commonly used. Three of the most widespread methods are small-angle light scattering, dynamic light scattering and measurements based on the Coulter principle (Allen, 1993). They all require extensive sample dilution before size measurement; this process may change the size. It is also time-consuming and makes on-line process control difficult. Methods that can be used on undiluted samples include ultrasound (see, for example, Wang & Povey, 1999) and diffusing wave spectroscopy (Pine, Weitz, Chaikin, & Herbolzheimer, 1988; Scheffold, 2002). Note that both dynamic light scattering and diffusing wave spectroscopy require the sample viscosity for size determination, also they cannot be used if the sample is flowing.

We describe a new method of optical particle sizing that does not require dilution. It is based on static light scattering in the multiple scattering limit. Part of the work described here has already been published in a number of papers (Baravian, Caton, & Dillet, 2004; Baravian, Caton, Dillet, & Mougel, 2005; Dillet, Baravian, Caton, & Parker, 2006). Some are in optics and physics journals where they are unlikely to be read by many potential users of the technique. Here, our aim is easy understanding for non-experts, so we do not derive the equations, or justify our assumptions in detail. The original articles do this. This article is in three parts. First, we discuss the use of unpolarized light. Second, we extend this by using polarized light and finally we discuss applications of these techniques.

2. Experimental setup

Fig. 1 shows our experimental setup. It is similar to that of Hielscher et al.(1997), but with a number of improvements.

*Corresponding author. Tel.: +33 383 595 727; fax: +33 383 595 551.
E-mail address: christophe.baravian@ensem.inpl-nancy.fr (C. Baravian).

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doi:10.1016/j.foodhyd.2006.08.008

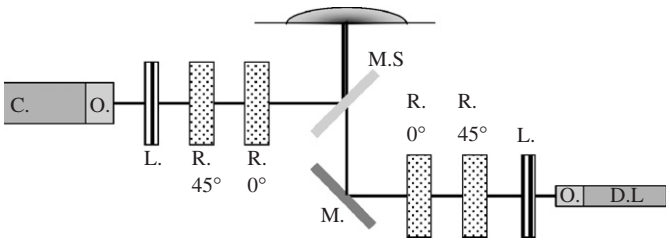

Fig. 1. Experimental set-up. DL: Diode laser, O: Focusing optics, L: Linear polarizer, R: Liquid crystal retarder, M: Polarization-maintaining mirror, MS: Polarization-maintaining semi-transparent mirror and C: CCD Camera.

The setup has three main parts. The light source consists of a collimated diode laser, (635 nm, 5 mW, intensity fluctuations less than 1%), a vertical linear polarizing filter (Melles Griot; Extinction 1:10,000), two electrically controlled liquid crystal retarders (LCRs) (Meadowlark Optics) and a Pyrex mirror that maintains polarization to within 1% at 45° (Micro-Controle). The laser light is focussed to the smallest possible spot (diameter 60 μm) at the sample surface. The liquid crystal retarders select its polarization. Their polarization angle can be changed in 50 ms. The analyser is composed of a linear polarizer, two LCRs and a digital image acquisition system (Imasys; Adimec MX12P digital camera 1024^2 pixels, 12 bit, 30 frames/s) linked to a digital image acquisition card (Imasys; 100 Mo/s transfer rate). The black and white video camera must have an excellent dynamic range. The model that we use is optimized for medical imaging. It easily measures over three orders of magnitude in intensity. Each acquired image of the backscattered light is approximately $10 \times 10\,\mathrm{mm}^2$, which is 100 times larger than the laser spot. A single program, written in Delphi (Borland software), controls both the LCRs and image acquisition. The experiments were performed in a temperature-controlled room at 20 °C.

The main advantage of this system, compared to that of Hielscher et al. (1997), is that the computer automatically sets the required polarization states. In our setup, 1 s is enough to acquire images of the 16 polarization states needed for each measurement (see below). Heilscher et al. (1997) set the polarization state by manually rotating the polarizers, so that high speed operation was impossible.

We use the backscattering geometry, which we argue is preferable to transmission for several reasons: (1) there is no need for a calibration standard, as we only use the shape of the backscattered spot, not its absolute intensity. This is not the case when using transmission; (2) the same geometry can be used for a wide range of samples. This is not true for transmission, as the sample depth must often be optimized to give neither too much nor too little transmitted light; (3) it is useful for non-invasive measurements during storage, as measurements can be made through the bottom or through the wall, with no limitations on sample dimensions.

3. Theory: unpolarized light

The scattering of an electromagnetic wave by a non-absorbing spherical particle is described by Mie theory (van de Hulst, 1981). It requires only two dimensionless parameters to define the scattering: the optical contrast and the size. For a dispersion of spheres, a third parameter, the volume fraction, ϕ, is needed. For a spherical particle of radius a and refractive index n_p and an electromagnetic wave of wavelength λ in a surrounding medium of refractive index n_m, the dimensionless size is given by $x = 2\pi a n_m/\lambda$ and the optical contrast is given by $m = n_p/n_m$.

The key assumption in interpreting the incoherent multiple scattering from concentrated dispersions is the diffusion approximation. If we can assume that the path taken by photons is a random walk, the theory of diffusion can be used to model their behaviour. Dogariu and Asakura (1993) give the simplest equation for the intensity of backscattered light in a semi-infinite medium (i.e., an infinitely thick slab) as a function of the distance, ρ, from the centre of the spot:

$$I(\rho) = \frac{l_{TR}}{2\pi\left(\rho^2 + l_{TR}^2\right)^{3/2}}, \tag{1}$$

where l_{TR} is the average step length of the random walk, which is called the transport length. The equation tells us that this length is the only one parameter controlling the size of the backscattered spot. It has two limits:

(1) close to the centre, where $\rho \ll l_{TR}$, the intensity is constant
(2) far from the centre, where $\rho \gg l_{TR}$, $I \propto \frac{1}{\rho^3}$.

In fact, Eq. (1) is oversimplified, so it is only correct close to these limits. Haskell, Svaasand, Tsay, Feng, McAdams, and Tromberg (1994) developed a much more complex equation, that gives the same answers at the limits, but also the correct answer at all intermediate distances. We have adapted their equation to our conditions (Baravian et al., 2005). Fitting this equation to our data gives accurate results.

There are four possible causes of deviations from the diffusion approximation: either the measurement is being made inside the laser spot, or the photon paths are too short, or the particles absorb light, or the sample is too thin. (1) Close to the centre of the spot, we measure light directly backscattered from the glass surface, despite the anti-reflection coating. It is important to use a laser that can be focussed to the smallest possible spot, as the halo of backscattered light must be larger than the laser spot. (2) The intensity close to the centre is always above that predicted by the diffusion approximation, because some photons take short paths, being scattered only a few times. Correcting for this effect rigorously is extremely difficult. We are currently working on the problem. (3) If the sample absorbs light, then Eq. (1) is incorrect. The slope far from