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Light scattering study of microemulsions and its relation to percolation phenomena

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Résumé. — Les caractéristiques de la lumière diffusée par des microémulsions au voisinage d'un seuil de percolation indiquent l'existence de forces attractives à longue portée entre micelles. Les interactions hydrodynamiques sont également présentes, mais n'ont pas de comportement à longue portée.

Abstract. — The characteristics of the light scattered by microemulsions in the vicinity of a percolation threshold indicate the existence of strong and long range attractive forces between micelles. Hydrodynamic interactions are also present but show no evidence of long range character.

1. Introduction. — Water in oil microemulsions are transparent dispersions of water droplets surrounded by amphiphilic molecules in a continuous organic medium. Light scattering techniques already allowed investigators to obtain much information about droplet sizes and interaction forces in these media [1-6]. The characteristics of the scattered light are usually typical of brownian motion of *small* particles interacting through *short* range potentials (*short* compared to optical wavelengths) : the correlation function of the scattered electric field is exponential and both the scattered intensity and the diffusion coefficient (deduced from the correlation time) are independent of the scattering angle.

In some cases however : (vicinity of a gel [7], of a flocculation point for microemulsions made with polymeric materials [4]), the correlation function of the scattered electric field becomes non exponential. The interpretation of these features is not yet clear. In the last reference, the authors remark that they are accompanied by interparticle packing : electron micrographs show the presence of compact network-like clusters made of individual droplets [8].

Our experiments deal with microemulsions made with an anionic soap, far from a gelation point. In a previous paper [6], we mentioned that when attractive forces between droplets are strong, at volume fractions close to 0.1, the diffusion coefficient depends on scattering angle. Such volume fractions correspond

to the percolation threshold already observed in electrical conductivity measurements by Lagües *et al.* [9]. In the *stirred percolation* model proposed by Lagües to interpret these measurements, it is assumed that the droplets behave as randomly distributed hard spheres. Transient clusters are statistically formed. Above a critical volume fraction ϕ_c , an infinite path appears through the droplets. The electrical conductivity increases steeply (several orders of magnitude) around ϕ_c .

In the present paper, we describe a preliminary study of the characteristics of the scattered light in the vicinity of the percolation threshold for microemulsions in which attractive forces are strong.

A careful analysis of the autocorrelation function showed no evidence of departure from exponential behaviour. However, the diffusion coefficient was found to depend on scattering angle. This is accompanied by an angular dependence of the scattered intensity which has also been measured.

Similar features were already found in other systems when the correlation length becomes of the order of the optical wavelength : fluid near a critical point [10], charged macromolecules solutions [11], latex particles dispersions [12, 13]. In the two last cases the autocorrelation function has a pronounced non exponential behaviour. Pusey [12] attributed this effect to the existence of two slow processes in the medium : diffusion of individual particles across solvent molecules and changes of the instantaneous configuration of particle neighbours. The mean interparticle spacing being large, the characteristic time τ_1 of the second process is long ($\sim 200 \mu s$) : the correlation function

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Fig. 2. — Diffusion coefficient deduced from the autocorrelation function : $g_2(\tau) = \exp(-2 D q^2 \tau) + 1$ at a scattering angle $\theta = 90^\circ$, versus volume fraction. The extrapolation to $\phi = 0$ gives D_0 .

The negative slope of $D(\phi)$ at the origin indicates that interactions are attractive, and much stronger in the case of microemulsions ATB (large negative slope) than for microemulsions ATP [6].

The variation of diffusion coefficient with θ is represented on figure 3 for ϕ values close to percolation threshold. The exponential character of $g_2(\tau)$

Fig. 3. — Correlation times $\tau = (2 D q^2)^{-1}$ multiplied by $\sin^2 \theta/2$ versus scattering angle θ ; $\tau \sin^2 \theta/2$ is a quantity inversely proportional to the diffusion coefficient D . The droplets volume fractions for the different microemulsions can be found in figures 1 and 2.

has been analysed with special care. For this purpose, a fit using the method of cumulants has been done :

$$\ln(g_2(\tau) - 1) = -\alpha_1 \tau + \frac{\alpha_2}{2} \tau^2 + O(\tau^3)$$

$\alpha_1 = 2 D q^2$. The variance $v = \sqrt{\alpha_2/\alpha_1}$ has been found equal to zero in all cases. The quality of the fit is extremely good the mean square deviation between

the experimental curve and the exponential

$$\left(\frac{1}{N} \sum_{i=1}^N [g_2^{\text{exp}}(\tau_i) - g_2^{\text{th}}(\tau_i)]^2 \right)^{1/2}$$

is typically of the order of 10^{-3} (N = number of channels).

3.2 SCATTERED INTENSITY I . — As one approaches the percolation threshold, microemulsions ATB show large intensity angular variations represented on figure 4. The scattered intensity is much smaller for microemulsions ATP, but is independent of θ .

Fig. 4. — Normalized scattered intensity versus scattering angle for different microemulsions ATB. The corresponding volume fraction values can be found figures 1 and 2.

4. Interpretation. — Light scattering arises mainly from concentration fluctuations of the particles in the solution. Then the scattered intensity is given by [19]':

$$I(q) = A \phi I_0 P(q) S(q) \quad (3)$$

I_0 is the intensity of the incident beam, A a constant. $P(q)$ is the particle form factor : $P(q) \approx 1$ for particles of radius $R \sim 50 \text{ \AA}$. $S(q)$ is the structure factor :

$$S(q) = 1 + \frac{3 \phi}{R^3} \int_0^\infty r^2 (g(r) - 1) \frac{\sin qr}{qr} dr \quad (4)$$

$g(r)$ being the radial distribution function.

The correlation function of the scattered electric field is proportional to the correlation function of the concentration and follows the memory equation [11, 17].

$$\frac{dg_1}{dt}(\tau) = -\frac{1}{S(q)} \int_0^\infty M(\mathbf{q}, t - \tau) g_1(\tau) d\tau \quad (5)$$

If the concentration is the only slowlydecaying property the memory function M is local in time and eq. (5) becomes

$$\frac{dg_1}{dt}(\tau) = -D(q) q^2 g_1(\tau)$$

(6)

with

$$D(q) = D_0 \frac{H(q)}{S(q)}$$

$H(q)$ contains the hydrodynamic interactions [17].

$S(q)$ and $H(q)$ become 1 in the low density limit ($\varphi \rightarrow 0$). For $q = 0$:

$$S(0) = \frac{kT}{\partial\pi/\partial\varphi} \times \frac{3}{4\pi R_0^3} \quad H(0) = \frac{6\pi\eta R_0}{f}$$

The values of $S(q)$ as deduced from intensity data are shown on figure 5 (¹). They seem unusually large, but it must be kept in mind that the particle concentration is large and that the effect of interaction forces is important. The values of $H(q)$ have also been derived using eq. (6) and the measured values of $D(q)$ (Fig. 3) and $S(q)$ (Fig. 5). $H(q)$ differs slightly from the low density limit value of 1 due to hydrodynamic interactions (¹). But its variation with q falls beyond experimental accuracy.

Fig. 5. — q dependence of the structure factor S for different volume fractions in microemulsions ATB (smoothed curves).

5. Conclusion. — A light scattering study of microemulsions in which strong attractive forces are present

(¹) The variations with q of $S(q)$ and $H(q)$ are known with a good precision since they are deduced directly from $I(\theta)$ and $D(\theta)$ (Figs. 3 and 4). But the absolute values of $S(q)$ and $H(q)$ are much less accurate since they involve the extrapolation of I/φ to $\varphi = 0$, domain where I is a very rapid function of φ [⁶].

Fig. 6. — q dependence of the hydrodynamic contribution H for different volume fractions in microemulsions ATB.

and in the vicinity of a percolation threshold φ_c allowed us to obtain information about interaction ranges.

A structure factor variation was found : $S(q)$ decreases when q increases. Similar observations have been made for other kinds of small interacting particles [11-13]. For instance in electrolyte solutions, $S(q)$ decreases when q decreases. This has been interpreted in terms of long range repulsive interactions [11]. In microemulsions the variation of $S(q)$ indicates the existence of long range ($\sim 500 \text{ \AA}$) attractive interactions. Unfortunately, the nature of the interaction potential is not sufficiently well known to permit a comparison with experimental data. Far from the percolation threshold, it was pointed out that the nature of attractive interactions may arise from preferential soap chains solvation effects [1, 6]. However, such interactions are of much shorter range ($\sim R_0$). It is clear that another interaction mechanism exists at least as one approaches the percolation threshold.

The increase of interaction range can probably be related to the divergence of the correlation length near the percolation threshold. However the interpretation of the data with percolation theory is not straightforward. A stirred percolation model should be developed for interacting spheres.

The problem of hydrodynamic interactions is even more complicated. But the experiments indicate that long range contributions are not important. The mechanism of hydrodynamic interactions can therefore be expected not to be affected by percolation.

The study of the influence of interaction strength on droplet interaction range is currently under way to try to elucidate these problems.

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