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Light scattering study of microemulsions and its relation to percolation phenomena

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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 Laguès et al. [9]. In the stirred percolation model proposed by Laguès 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 \( \varphi_c \), an infinite path appears through the droplets. The electrical conductivity increases steeply (several orders of magnitude) around \( \varphi_c \).

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 \( \tau_2 \) of the second process is long (\( \sim 200 \mu s \)) : the correlation function

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decay is determined by free particle motion for 
\( \tau < \tau_1 \) and by interparticle forces for \( \tau > \tau_1 \). In our 
present problem, the mean interparticle spacing is not 
significantly different from particle radius :

\[
d \sim R(4 \varphi^{-1})^{1/3} \sim 3.5 R \quad \text{for} \quad \varphi \sim 0.1 ;
\]

\( \tau_1 \) is very small (\( \sim 10 \) ns) compared to correlation delay 
times. Consequently, the particle concentration can 
be considered as the only slowly decaying property, 
and its correlation function will be exponential as 
observed.

The analogy between the present problem and 
critical phenomena is closer. In both cases, the 
correlation function for the concentration is exponential 
(no coupling with other hydrodynamic variables).

Near a critical point, a picture of a fluid can also 
be made with transient clusters of size \( \xi \). The corre-
lation length \( \xi \) is the range over which the concentration 
fluctuations are correlated and diverges at the 
critical point. In the percolation problem, the corre-
lation length is the spatial size of the largest clusters 
and diverges also beyond the percolation threshold.
However, the analogy cannot be driven too far : 
indeed the scattering of light by a percolating system 
does not usually diverge near the threshold : the 
important fluctuations are not in the concentration 
but in the connectivity [14, 15].

An explanation of the variation of both scattered 
intensity and diffusion coefficient with scattering angle 
in our experiments will be given with the help of the 
recent theories of brownian motion of interacting 
particles [16, 17].

2. Samples and experimental set up. — The samples 
are quaternary mixtures of water, sodium dodecylsul-
fate, toluol as oil, butanol 1 (microemulsion ATB) 
or pentanol 1 (microemulsion ATP) as cosurfactant. 
The volume fraction \( \varphi \) of the droplets has been calcu-
lated according to the procedure described in refer-
cence [5]. The electrical conductivity has been mea-
sured for the two kind of samples (using a Metrohm E518 
conductimeter) as a function of concentration. The 
results are reported on figure 1. For microemulsion 
ATP the variation of electrical conductivity with 
volume fraction remains slow. But microemulsion 
ATB shows evidence of percolation phenomenon 
around \( \varphi_c \sim 0.08 \).

The light source is an argon ion laser CR3 giving an 
output power of 0.5 W at a wavelength \( \lambda = 4880 \) Å. 
Close to percolation threshold, this power has been 
considerably reduced in order to avoid heating effects 
in the samples.

Intensity measurements were performed in 1 mm 
optical path length cells (Helima) immersed in a toluol 
bath that exactly matches the indices (microemulsion, 
toluol and glass have practically the same index : 
1.485 to 1.5). The illuminated volume was kept con-
stant and entirely imaged in the photocathode of the 
photomultiplier in order to avoid angular correc-
tions. For \( \theta < 15^\circ \) or \( \theta > 165^\circ \) and microemulsions 
far from percolation threshold the amount of light 
scattered elastically becomes significant (5 % for 
microemulsion 5 ATB at \( \theta = 15^\circ \)).

The correlation function of the scattered light was 
also recorded using a full parallel correlator, with 
100 channels [5]. The detection is homodyne, excepted 
at the lowest scattering angles \( \theta (\theta < 5^\circ) \). The light 
scattered by the cell walls plays then the role of local 
oscillator, and the detection becomes heterodyne.

The scattering angles \( \theta \) were varied from 0.65° to 
140°. The scattering wave vector \( q = \frac{4 \pi n \sin \frac{\theta}{2}}{\lambda} \) (\( n \) is 
the microemulsion index) varies then from

\[
q = 2.2 \times 10^3 \text{ cm}^{-1} \quad \text{to} \quad q = 3.6 \times 10^5 \text{ cm}^{-1} .
\]

This allows to explore a wide range of length scales 
\( q^{-1} \) between 5 \( \mu \)m and 300 Å. In all cases multiple 
scattering was found negligible (\( \lesssim 10^{-2} \)).

3. Experimental results. — 3.1 Autocorrelation 
function \( g_2(\tau) \). — The autocorrelation function \( g_2(\tau) \) 
has been fitted with the simple form:

\[
g_2(\tau) = 1 + g_2^\varphi(\tau) = 1 + e^{-2Dq^2\tau} . \quad (1)
\]
The diffusion coefficient \( D \) is independent of \( q \) far 
from percolation threshold for microemulsions ATB 
and in all cases for microemulsions ATP. This is 
characteristic of Brownian motion of small particles 
and short range interactions [18]. When the percola-
tion threshold is approached in microemulsions ATB, 
\( D \) becomes dependent on \( q \).

The variation of diffusion coefficient with volume 
fraction for \( \theta = 90^\circ \) is represented on figure 2. Its 
extrapolation \( D_0 \) to \( \varphi = 0 \) allows the determination 
of the hydrodynamic radius [18] :

\[
D_0 = kT/6 \pi \eta R_0 \quad \eta \text{ viscosity of the continuous phase.}
\]

\[
R_0 = 41 \text{ Å for microemulsions ATB (toluol-butanol)} 
\]

\[
R_0 = 45 \text{ Å for microemulsions ATP (toluol-pentanol)} 
\]
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 $\theta$ is represented on figure 3 for $\phi$ values close to percolation threshold. The exponential character of $g_2(\tau)$ has been analysed with special care. For this purpose, a fit using the method of cumulants has been done:

$$\ln (g_2(\tau) - 1) = -\alpha_1 \tau + \frac{\alpha_2}{2} \tau^2 + 0(\tau^3)$$

$\alpha_1 = 2Dq^2$. The variance $\nu = \sqrt{\alpha_2/\alpha_1}$ 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

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

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 $\theta$.

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

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

$I_0$ 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 $R \approx 50$ Å. $S(q)$ is the structure factor:

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

$g(r)$ 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].

$$\frac{dg_1}{dr}(\tau) = -\frac{1}{S(q)} \int_0^{\infty} M(q, t - \tau) g_1(\tau) d\tau .$$
If the concentration is the only slowly decaying property the memory function $M$ is local in time and eq. (5) becomes

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

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 ($\phi \to 0$). For $q = 0$:

$$S(0) = \frac{kT}{\delta n/\delta \phi} \times \frac{3}{4 \pi R_0^3} H(0) = \frac{6 \pi R_0}{\lambda}.$$ 

The values of $S(q)$ as deduced from intensity data are shown on figure 5 (1). They seem unusually large, but is 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).](image)

**5. Conclusion.** A light scattering study of microemulsions in which strong attractive forces are present and in the vicinity of a percolation threshold $\phi_c$ 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 ($\sim 500 \text{ Å}$) 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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(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 $I(\theta)$ to $\theta = 0$, domain where $I$ is a very rapid function of $\phi$. [16].
References


