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Electrical conductivity of microemulsions : a case of stirred percolation (*)

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Résumé. — La conductivité électrique G de microémulsions — eau dans l'huile — présente un comportement de percolation [1] : en-dessous d'une concentration d'eau critique ϕ_c, la conductivité semble diverger comme $(\phi_c - \phi)^{-S'}$, tandis qu'au-dessus de ϕ_c elle augmente comme $(\phi - \phi_c)^{T'}$. Dans cette situation physique que l'on peut qualifier de *percolation brassée* (par le mouvement Brownien du liquide) les exposants S' et T' n'ont *a priori* pas de raison d'être identiques aux exposants S et T de la situation classique de percolation gelée. Un modèle simplifié de percolation brassée rend compte de façon satisfaisante de l'exposant $S' = 1{,}2 \pm 0{,}1$, alors que la valeur admise pour S est 0,7. L'exposant T', dont la valeur mesurée varie de 1,4 à 1,6, est moins significatif pour la différence entre percolation gelée et brassée : Les valeurs prévues pour S' seraient environ 1,8 contre 1,6 pour S.

Abstract. — The electrical conductivity G of *water in oil* microemulsions may be described by percolation models [1] : below a critical water concentration ϕ_c, G seems to diverge as $(\phi_c - \phi)^{-S'}$, while for $\phi > \phi_c$ G increases as $(\phi - \phi_c)^{-T'}$. This physical situation may be called *stirred percolation*, referring to the Brownian motion of the medium. The exponents S' and T' are *a priori* different from the corresponding S and T in the classical situation of *frozen percolation*. A simple model of stirred percolation accounts fairly well for the measured value of $S' = 1.2 \pm 0.1$ while the accepted value for S is 0.7. The exponent T' (1.4 to 1.6 in our experimental case) is less significant of the difference between stirred and frozen percolation : the values for S' should be about 1.8 and the value accepted for S should be about 1.6.

1. **Electrical conductivity of microemulsions.** — We measured the electrical conductivity of microemulsions — water in oil — containing cyclohexan, sodium dodecyl sulphate (SDS) and 1 pentanol. The conductivity is extremely sensitive both to temperature and composition. The following procedure allowed a reproducibility of a few percent :

a) all the components, except a small quantity of alcohol, are introduced in the conductivity cell, the temperature of which is fixed at 20 °C ± 0.1 °C,

b) the alcohol is added slowly while the conductivity is measured,

c) a maximum of conductivity is reached when the mixing clears up to make a microemulsion. This value is the conductivity of the microemulsion containing the minimum of alcohol which provides stability.

A suitable dilution procedure allows ϕ to be varied while the structure of droplets remains fixed [2]. We studied two different types of microemulsions characterized by a volumic ratio, soap to water, in the droplets :

$$\text{type A} \quad s/w = 0.69$$

$$\text{type B} \quad s/w = 0.345 .$$

The conductivity increases steeply (five orders of magnitude) around a critical concentration ϕ_c. The variation above ϕ_c allows an independent determination of T and ϕ_c :

$G^{1/T'} \sim (\phi - \phi_c)$ is linear in ϕ and tends to zero at $\phi = \phi_c$.

The plot of $G^{1/x}$ for different values of x has opposite concavities when T is greater or smaller than T' (Fig. 1). The results for the three types of microemulsions are presented in table I.

When the water concentration is very low ($\phi < 0.01$) the conductivity is linear in ϕ, in agreement with a conduction mechanism involving the migration of charged droplets [1]. The percolation contribution to G is thus obtained by $G_p \sim G/\phi$. Figure 2 presents

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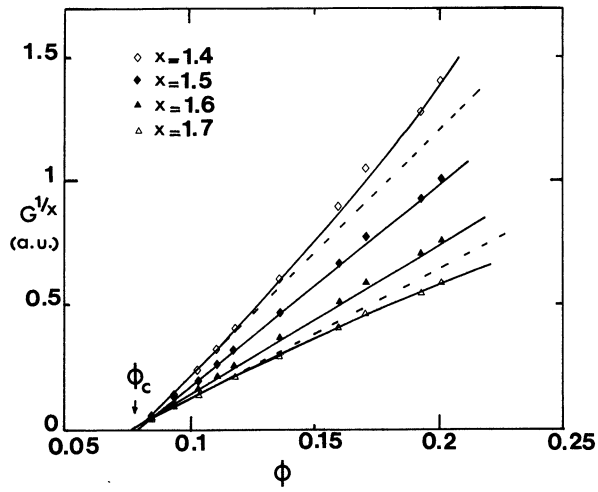

Fig. 1. — Determination of the exponent T' and of the critical water concentration ϕ_c, for $\phi > \phi_c$: $G^{1/x}$ is plotted for various x values as a function of ϕ.

Table I. — *Exponents T' and S' measured for microemulsions of different soap/water ratios.*

Microemulsion	A	B
$\frac{\text{Soap}}{\text{Water}}$	0.69	0.345
T'	1.6 $\pm$ 0.1	1.55 $\pm$ 0.1
S'	1.28 $\pm$ 0.1	1.08 $\pm$ 0.1

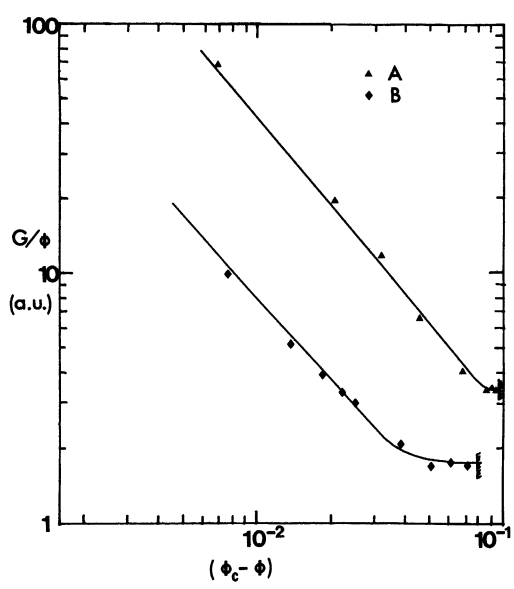

Fig. 2. — The conductivity of a microemulsion for $\phi < \phi_c$ is plotted *versus* $(\phi_c - \phi)$. Two different ratios soap/water are presented (see text).

Log (G/ϕ) *versus* Log $(\phi_c - \phi)$ for the three types of microemulsions. In each case, the slope is not much different of 1.2 (Table I).

2. **A model for stirred percolation.** —The electrical conductivity G of an insulating solid containing conductive particles is described by frozen percolation. G is very low if the concentration ϕ is lower than a critical value ϕ_c at which an infinite path through the conductive particles appears. Around and above this concentration, G increases steeply.

Essam *et al.* have suggested that G behaves in the vicinity of ϕ_c as [3]

$$\phi < \phi_c \qquad G = G_0(\phi_c - \phi)^{-S}$$

$$\phi > \phi_c \qquad G = G_1(\phi - \phi_c)^T$$

where S and T are independent of the physical details. Computer simulations [4, 5, 6] and theoretical calculation [7, 8] give the following values for a 3 D system :

$$S = 0.5 \text{ to } 0.78$$

$$T = 1.5 \text{ to } 2.0 \,.$$

Measured values of T on different physical systems are in the range 1.4 to 2, in agreement with the theory (A review of principal results is presented in reference [9]) while G. Deutscher and M. L. Rappaport measured $S = 0.7$, for the conductivity of Al-Ge films [10].

When the conductive particles are suspended in a fluid, the stirred percolation case, the conductivity may behave very differently. In the following model, conductive particles move with a diffusion coefficient D and they are assumed to interact through a *hard-sphere type* potential. A cluster which exists at time will disappear after the time $t + \tau_R$ and reorder in different clusters. The time τ_R is of the order of :

$\tau_R \sim a^2/D$ where a is the radius of particles, whatever the $(\phi - \phi_c)$.

To account for the kinetics of charge migration, we use a lattice with nodes connected by two types of conductances, a high one σ_+ (probability ϕ) and a low one σ_- (probability $1 - \phi$), each node being grounded through a capacitance C. The potential V_i at node i satisfies

$$C \frac{\partial V_i}{\partial t} = \sum_j \sigma_{ij}(t)\,(V_i - V_j)$$

which is formally identical to the diffusion equation of a species at concentration V_i with a jump frequency

$$W_{ij} = \frac{\sigma_{ij}}{C} = \frac{1}{\theta_{ij}} \,.$$

The conductivity G is thus formally identical to the diffusion coefficient $\overline{D}_V$ of this species.

We define two times θ_+ and θ_-, corresponding to σ_+ and σ_- :

* θ_+ is the (short) migration time of charges in a conducting cluster :

$$\theta_+ = \frac{C}{\sigma_+} f(\phi) \,.$$

* θ_- is the (long) migration time of charges between large clusters in the frozen case :

$$\theta_- = \frac{C}{\sigma_-} g(\phi) .$$

To calculate g, we use the variation of G in the frozen case :

$$G \sim (\phi_c - \phi)^{-S}$$

and

$$G \sim \overline{D}_V \sim \left(\frac{\overline{R_G^2}}{\theta_-}\right) \qquad (\text{if } \theta_+ \ll \theta_-)$$

where R_G, the gyration radius of the clusters, increases as [8, 11]

$$\overline{R_G^2} \sim (\phi_c - \phi)^{\beta - 2\nu}$$

with β and ν having the common definition.

The variation of θ_- is thus :

$$\theta_- \sim (\phi_c - \phi)^{S + \beta - 2\nu} .$$

The time θ_- thus diverges when $\phi \to \phi_c$, with an exponent

$$2\nu - S - \beta \sim 0.6 .$$

3. **Different situations.** — Depending on the values of θ_+, θ_- and τ_R, three cases appear :

a) $\theta_+ \ll \theta_- \ll \tau_R$

is the frozen case :

$$G \sim \frac{\overline{R_G^2}}{\theta_-} \sim (\phi_c - \phi)^{-S} .$$

b) $\tau_R \ll \theta_+ \ll \theta_-$

is the completely stirred case. G is the mean between G_+ ($\phi = 1$) and G_- ($\phi = 0$) :

$$G = \phi G_+ + (1 - \phi) G_-$$

and it increases linearly with ϕ.

c) $\theta_+ \ll \tau_R \ll \theta_-$

is the mixed case, always existing near ϕ_c, because θ_- diverges when $\phi \to \phi_c$. The migration of charges between large clusters does not depend anymore on θ_- but only on τ_R. One may then assume that

$$G \sim \frac{\overline{R_G^2}}{\tau_R} \sim (\phi_c - \phi)^{\beta - 2\nu}$$

and in three dimensions the exponent will be :

$$S' = 2\nu - \beta \sim 1.2 .$$

This value is also the value of S for a space dimension $d \geqslant 4$ [11].

For $\phi > \phi_c$, the exponent T' measured for microemulsions are not very different from the accepted value for $T \sim 1.6$.

A theoretical guess of T' could be obtained in assuming the same scaling law that for S' : one could extrapolate at $d = 3$ the law obtained by A. S. Škal and B. I. Shklovskii [12]

$$T = 1 + \nu(d - 2)$$

which should give $T' = 1.84$ in three dimensions. An experimental check would thus be difficult in view of the small difference between T and T'.

4. **Conclusion.** — We suggest here a simplified description of the intricate behaviour of stirred percolation. Three different cases appear depending on the reordering time τ_R of the clusters. If τ_R is very large, the results of frozen percolation apply. If τ_R is much shorter than the typical times θ_+ and θ_- of charge migration in and between the clusters, the conductivity is the mean between the conductivities of both phases. When τ_R has an intermediate value between θ_+ and θ_-, we assume that only the size of clusters accounts for the divergence of G for $\phi < \phi_c$.

This assumption agrees fairly with the measured conductivity of microemulsions for $\phi < \phi_c$.

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