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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  $\phi_c$ , la conductivité semble diverger comme  $(\phi_c - \phi)^{-S'}$ , tandis qu'au-dessus de  $\phi_c$  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  $\phi_c$ ,  $G$  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  $20 \text{ }^\circ\text{C} \pm 0.1 \text{ }^\circ\text{C}$ ,

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  $\phi$  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 :

type A s/w = 0.69

type B s/w = 0.345 .

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

$G^{1/T'} \sim (\phi - \phi_c)$  is linear in  $\phi$  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  $\phi$ , 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

(\*) La version française sera publiée dans le n° 20 des C.R.A.S., série B, du 28 mai 1979.

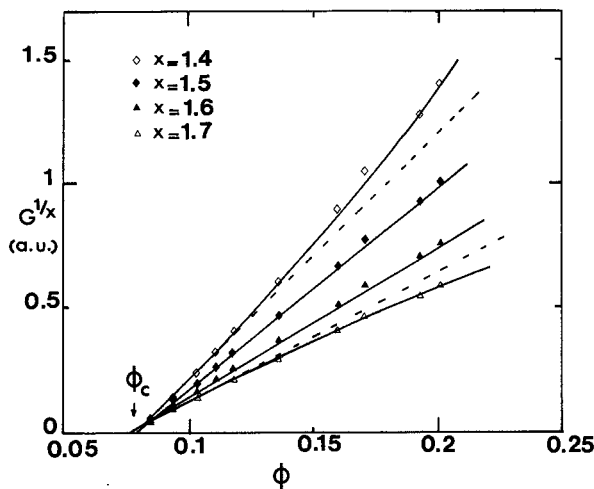


Fig. 1. — Determination of the exponent  $T'$  and of the critical water concentration  $\phi_c$ , for  $\phi > \phi_c$ :  $G^{1/x}$  is plotted for various  $x$  values as a function of  $\phi$ .

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

Microemulsion	A	B
—	—	—
Soap	0.69	0.345
Water		
$T'$	$1.6 \pm 0.1$	$1.55 \pm 0.1$
$S'$	$1.28 \pm 0.1$	$1.08 \pm 0.1$

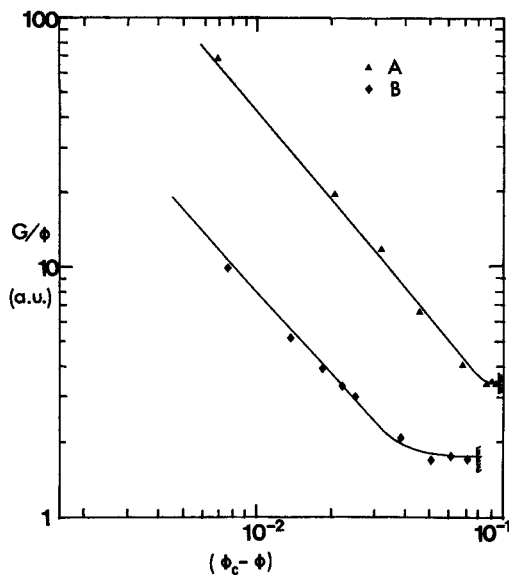


Fig. 2. — The conductivity of a microemulsion for  $\phi < \phi_c$  is plotted versus  $(\phi_c - \phi)$ . Two different ratios soap/water are presented (see text).

Log  $(G/\phi)$  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  $\phi$  is lower than a critical value  $\phi_c$  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  $\phi_c$  as [3]

$$\begin{aligned} \phi < \phi_c & \quad G = G_0(\phi_c - \phi)^{-S} \\ \phi > \phi_c & \quad G = G_1(\phi - \phi_c)^T \end{aligned}$$

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  $t$  will disappear after the time  $t + \tau_R$  and reorder in different clusters. The time  $\tau_R$  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  $\sigma_+$  (probability  $\phi$ ) and a low one  $\sigma_-$  (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  $\bar{D}_V$  of this species.

We define two times  $\theta_+$  and  $\theta_-$ , corresponding to  $\sigma_+$  and  $\sigma_-$  :

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

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

\*  $\theta_-$  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

$$G \sim \bar{D}_V \sim \left( \frac{\bar{R}_G^2}{\theta_-} \right) \quad (\text{if } \theta_+ \ll \theta_-)$$

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

$$\bar{R}_G^2 \sim (\phi_c - \phi)^{\beta - 2\nu}$$

with  $\beta$  and  $\nu$  having the common definition.

The variation of  $\theta_-$  is thus :

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

The time  $\theta_-$  thus diverges when  $\phi \rightarrow \phi_c$ , with an exponent

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

**3. Different situations.** — Depending on the values of  $\theta_+$ ,  $\theta_-$  and  $\tau_R$ , three cases appear :

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

is the frozen case :

$$G \sim \frac{\bar{R}_G^2}{\theta_-} \sim (\phi_c - \phi)^{-S}.$$

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

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  $\phi$ .

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

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

$$G \sim \frac{\bar{R}_G^2}{\tau_R} \sim (\phi_c - \phi)^{\beta - 2\nu}$$

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  $d \geq 4$  [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  $\tau_R$  of the clusters. If  $\tau_R$  is very large, the results of frozen percolation apply. If  $\tau_R$  is much shorter than the typical times  $\theta_+$  and  $\theta_-$  of charge migration in and between the clusters, the conductivity is the mean between the conductivities of both phases. When  $\tau_R$  has an intermediate value between  $\theta_+$  and  $\theta_-$ , 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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