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## ON A RELATION BETWEEN PERCOLATION THEORY AND THE ELASTICITY OF GELS

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**Résumé.** — On établit une relation entre la conductance  $\Sigma$  d'un réseau aléatoire de résistances avec une fraction  $p$  de conductances non nulles, et le module d'élasticité  $E$  d'un gel obtenu par polymérisation d'unités  $z$ -fonctionnelles ( $p$  étant ici la fraction de liaisons qui ont réagi).

**Abstract.** — We compare the macroscopic conductance  $\Sigma$  of a resistor network with a fraction  $p$  of conducting links, and the elastic modulus  $E$  of a gel obtained by polymerization of  $z$ -functional units ( $p$  being the fraction of reacted bonds).

Consider a Bravais lattice with nodes  $(i, j, \dots)$  connected by conductances  $\sigma_{ij}$ , the voltages being  $V_i, V_j \dots$ . The entropy source is

$$TS^{\circ} = \frac{1}{2} \sum_{ij} \sigma_{ij} (V_i - V_j)^2. \quad (1)$$

Minimization of  $TS^{\circ}$  with respect to  $V_i$  leads to the Kirchhoff equation. When  $\sigma_{ij}$  connects only neighbouring sites, and is a random variable with values  $\sigma$  (probability  $p$ ) and 0 (probability  $1 - p$ ) the system may show a macroscopic conductance  $\Sigma$  (such that  $TS^{\circ}/\text{cm}^3 = \Sigma E^2$ , where  $E$  is the average field).  $\Sigma$  has been investigated by Last and Thouless [1] : near the percolation threshold  $p_c$ , it is apparently of the form :

$$\Sigma = \text{const. } \delta p^{\mu} \quad (\delta p = p - p_c) \quad (2)$$

where  $\mu$  cannot be related directly to other critical exponents of the percolation problem, for which a renormalization group approach is now available [2-3]. But the analogue of  $\Sigma$  occurs in many physical problems :

a) with magnetic atoms, coupled by ferromagnetic exchange integrals  $\sigma_{ij}$ , at low temperatures,  $V_i$  being a tilt angle for the moment ( $i$ ) [4, 5] ;

b) with superconducting grains, coupled by Josephson junctions, of critical current  $\sigma_{ij}$  ( $V_i$  being the phase of the order parameter on grain  $i$ ) [6]. In the present note we add one other member to the list ;

c) polycondensation of  $z$ -functional monomers, with a fraction  $p$  of reacted bonds [7]. For the moment we assume that the monomers are point-like, and occupy all sites on a  $d$ -dimensional Bravais lattice (the number of neighbours of one site being  $z$ ). Here  $V_i$

represents one component (say  $X_i$ ) of the elastic displacement of the  $i$ th monomer from its rest position. In cases (a), (b), and (c)) the analogue of the minimization functional  $TS$  is an elastic energy (assumed to be Hookean). The analogue of  $\Sigma$  is a Landau-Lifshitz rigidity  $A$  [8] (case a)), a superfluid density  $\rho_s$  (case b)), and an elastic modulus  $E$  (case c)). All these quantities should follow eq. (2) with the same exponent  $\mu(d)$ .

The statement for case c) is rigorous only with a lattice model of gelation- or for the inverse processes of crystal degradation by mobile agents [9]. But it may plausibly be extended to more general situations where (i) the starting point is a liquid of monomers (rather than a crystal) and (ii) the connection between  $z$ -functional monomers is not through a single bond, but rather through a flexible chain of finite length (e.g. : adipic acid [10]). Of course the  $\delta p$  interval where eq. (2) holds will depend on the problem : the *zero volume* extrapolation invented by Stockmayer [11] tends to make it small [12]. We know that for  $d \geq 6$  the percolation problem on Bravais lattices is not qualitatively different from the behaviour of *tree-like structures* (mean field behaviour) [3], [13]. Conductance properties of trees have been calculated exactly : (i) the conductance  $\bar{\sigma}_{0,\infty}$  from one point to infinity behaves like  $\delta p^2$  [14]. (ii) For the gel problem a related parameter is the number  $G$  of *active network chains* per monomer and this is proportional to  $\delta p^3$  [15]. It is common belief that  $E$  is proportional to  $G$ . This is probably correct, but more accurately stated in terms of a variational calculation, as follows. Starting from one realization of the system, we first delete all *dangling ends*; we are then left with *active chains*

connecting at certain nodes  $n, m \dots$ . We can then rewrite  $T\dot{S}$  as

$$T\dot{S} = \sum_{(n,m)} \sigma_{nm} (V_n - V_m)^2 \quad (3)$$

where  $\sigma_{nm}$  is the conductance of one chain connecting  $n$  and  $m$ , and the sum  $\sum$  is over all active chains. We have  $\sigma_{nm} = \sigma/N_{(nm)}$  where  $N_{(nm)}$  is the number of bonds along the chain. As a variational voltage distribution we choose  $V_n = \mathbf{E} \cdot \mathbf{R}_n$  where  $\mathbf{R}_n$  is the position of the node  $n$ . Inserting this into (3) we are led to calculate averages :

$$\langle (R_n - R_m)^2 \rangle \sim N_{nm}. \quad (4)$$

Eq. (4) holds for large  $N_{nm}$  (i.e. near  $p = p_c$ ) even if there is more than one chain connecting  $n$  and  $m$ , and is true independently of any excluded volume effects (since we are interested in  $d \geq 6$  and these effects become trivial for  $d \geq 4$  [16]). Then each active chain contributes the same constant to  $T\dot{S}/E^2$  and

$$\Sigma \leq \text{const. } G \leq \text{const. } \delta p^3 \quad (d = 6). \quad (5)$$

Note that  $\Sigma \ll \bar{\sigma}_{0\infty}$  [17]. If the variational trial function is qualitatively correct, the inequality (5) becomes an equality, and

$$\mu(d = 6) = 3. \quad (6)$$

We end up with a conjecture concerning the values of  $\mu$  for lower dimensions. For  $p \gtrsim p_c$ , after subtraction of the dangling bonds, we have a loose network with nodes  $n, m \dots$ . The distance  $\delta$  between neighbouring nodes diverges for  $p \rightarrow p_c$ ; the spatial scaling properties associated with a simple fixed point in the renormalization group [18] then impose that  $\delta$  be proportional to the correlation length  $\xi \sim \delta p^{-\nu}$ . We postulate that the average number of bonds on one active chain between neighbouring nodes is  $\bar{N} \sim \delta p^{-1}$  [19]. Then in a field  $E$  the average current through a hypersurface of area  $\xi^{d-1}$  is of order

$$\frac{\sigma}{N} (V_n - V_m) \sim \frac{\sigma}{N} \xi E,$$

giving a macroscopic conductivity

$$\Sigma \cong \delta p \xi^{2-d} = \delta p^{1+\nu(d-2)}. \quad (7)$$

For  $d = 3$ ,  $\nu \sim \frac{5}{6}$  and we are led to  $\mu \sim \frac{11}{6}$ , not very far from the existing numerical estimates ( $\mu \sim 1.5$ ) [4]. For  $d = 2$ , eq. (7) might go to a logarithmic law  $\Sigma \sim \delta p / \ln(1/\delta p)$  which is not incompatible with the data [1], [4]. For  $d = 6$ ,  $\nu = \frac{1}{2}$  (mean field value [13]). Eq. (5) and (7) are then compatible. To have a better check it would be most interesting to carry out an expansion of  $\mu$  in powers of  $\epsilon = 6 - d$ .

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