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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 Σ 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 Σ 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 σ_{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° with respect to V_i leads to the Kirchhoff equation. When σ_{ij} connects only neighbouring sites, and is a random variable with values σ (probability p) and 0 (probability $1 - p$) the system may show a macroscopic conductance Σ (such that $TS^{\circ}/\text{cm}^3 = \Sigma E^2$, where E is the average field). Σ 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 μ 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 Σ occurs in many physical problems :

a) with magnetic atoms, coupled by ferromagnetic exchange integrals σ_{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 σ_{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 Σ is a Landau-Lifshitz rigidity A [8] (case a)), a superfluid density ρ_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 δp 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 δp^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 δp^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 σ_{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 μ 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 δ 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 δ 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 ξ^{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 μ in powers of $\epsilon = 6 - d$.

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