

Elasticity of percolation networks

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It is generally assumed that the elasticity of percolation networks can be described correctly by drawing on an analogy with the conductance of a random network of resistances. It is shown in this letter that an interaction between the monomers of the network leads to an elasticity substantially different from that found from this analogy.

The percolation model is the basis for a quantitative description of polymers synthesized in the absence of a solvent. Since the scaling laws are of universal applicability, this model also describes networks of any type which are formed near the threshold for gelation. The elasticity of such networks is usually studied by drawing on an analogy with the conductance of a random network of resistances.¹ This analogy ignores the interactions of the monomers, which are important in real networks. Under synthesis conditions, these interactions are partially screened² by clusters of finite size. In an experiment, such clusters are washed out, and there is no screening. Because of the pronounced repulsion of monomers, the fractal dimensionality of an infinite cluster ranges from $D_0=2.5$ under synthesis conditions to $D=2.1$. In the present letter we show that incorporating this effect leads to elastic properties of a network which are quite different from those in the problem of the conductance of an infinite cluster.

We will first reproduce the results found from the analogy with the conductance in the absence of an interaction between monomers of the network. Under synthesis conditions, the network has a density $\Phi_0 \sim (p-p_c)^\beta$ and consists of V_0/R_0^d unit cells, where $R_0 \sim (p-p_c)^{-\nu}$ is the size of one cell. Here V_0 is the volume of the d -dimensional system, p is the bond formation probability, and $\beta = \nu(d - D_0)$ and ν are critical exponents. In the $d = 3$ case we have $\beta = 0.44$ and $\nu = 0.88$.

The elastic energy of a network of density Φ , stretched out by a factor $\lambda = (\Phi_0/\Phi)^{1/d}$, at a temperature T is³

$$F_{el}(\Phi) \approx T \left(\frac{V_0}{R_0^d} \right) \left(\frac{\lambda R_0}{R} \right)^2, \quad (1)$$

where R is the equilibrium size of a cell "cut out of the network." Expression (1) is simply Hooke's law, applied to each of the cells stretched out to a size $x = \lambda R_0$. The elastic energy of a cell stretched out in this manner is Tx^2/R^2 . In the problem of the electrical conductance of a network of resistances, the energy of a unit cell has a similar form: U^2/r , where U is the voltage across this cell. This voltage plays the role of the cell displacement x in the elastic problem. The quantity R^2 is thus analogous to the resistance r of a unit cell of a network of size R_0 . The behavior of the

resistance $r(x_0)$ between two points of a percolation cluster as a function of the distance between these points, x_0 , is determined by the scaling law⁴

$$r(x_0) \sim x_0^{\varphi/\nu}. \quad (2)$$

In the $d = 3$ case, the crossover exponent is $\varphi = 1.12$. With $x_0 = R_0$, we find from (2)

$$R^2 \sim r(R_0) \sim R_0^{\varphi/\nu}. \quad (3)$$

Substituting (3) into (1) in the case $\Phi = \Phi_0$, we find the expression which we have been seeking for the elastic moduli, i.e., the shear modulus μ and Young's modulus E :

$$\mu \approx E \approx F_{el} / V_0 \sim T(p - p_c)^{t_0}, \quad t_0 = (d - 2)\nu + \varphi, \quad (4)$$

where the conductance exponent in the $d = 3$ case is $t_0 = 2.0$.

We can show how the result in (4) changes when we incorporate a fractal dimensionality D of the percolation cluster at scales small in comparison with the correlation radius ξ . The radius ξ and the number (g) of monomers over a distance ξ are found from

$$g \sim \xi^D, \quad g = \Phi \xi^d. \quad (5)$$

The first of these relations is simply the definition of the fractal dimensionality D . The second relation can be understood more conveniently in the following way. We denote by $g'(x) = \Phi x^d$ the average number of monomers of the network in a given volume x^d and by $g(x) \sim x^D$ the number of monomers which are connected to the given monomer by a path which lies completely in the volume x^d . At small values $x < \xi$, we have $g(x) > g'(x)$, and there is no screening of the interaction. At large scales, $x > \xi$, the indirectly connected monomers constitute only a small fraction of the total number of monomers: $g(x) < g'(x)$. Their interaction with each other is thus effectively screened. The screening radius $x = \xi$ is therefore found from the condition $g = g'$ [see Eq. (5)].

Applying (3) to scales x which are large in comparison with ξ , at which the interaction is screened, we find

$$R^2 \sim \xi^2 (L/g)^{\varphi'/D_0\nu}, \quad L \sim R_0^{D_0}, \quad (6)$$

where L is the number of monomers of a unit cell of the network. In contrast with case (3), the crossover exponent φ' in (6) does not contain fluctuation corrections. The physical reason for such corrections lies in fluctuations of the density of an infinite cluster.⁴ When there is an interaction, these fluctuations are suppressed at scales large in comparison with ξ , and the exponent φ' is equal to the mean-field value $\varphi' = 1$. Since the fluctuations are small at scales $x > \xi$, the elastic energy of the network is determined by mean-field expression (1) with an elasticity coefficient R^{-2} [see (6)], renormalized to account for fluctuations of the density with scales $x < \xi$. Substituting (6) into (1), and using (5), we find the shear modulus (or torsional modulus) of a stretched network of volume $V = V_0 \Phi_0 / \Phi$:

$$\mu \approx F_{el} / V \sim T(p - p_c)^{t_{\Phi^s/q}}, \quad t = (d - 2)\nu D_0/d + \varphi',$$

$$s = d_v D_0 / D - t, \quad q = D_0 v (d - D) / D. \quad (7)$$

In contrast with (4), which holds only in the case $\Phi = \Phi_0$, we have also incorporated in (7) a dependence of the elastic modulus on the density of the network.

The total free energy of the network,

$$F(\Phi) = F_{el}(\Phi) + F_{int}(\Phi), \quad F_{int}(\Phi) \approx VT/\xi^d, \quad (8)$$

is equal to the sum of elastic contribution (7) and the contribution F_{int} , which incorporates the interaction of the monomers of the network: Each fluctuation cell of volume ξ^d makes a contribution $\approx T$. We wish to stress that the interactions of the monomers lead to effects of two types: a) At scales $x < \xi$, they alter the fractal dimensionality D of the percolation cluster. b) At scales $x > \xi$ they suppress density fluctuations, leading to the mean-field expression for the exponent φ' [see (6)] and to the possibility of a mean-field representation of free energy (8) as a sum of elastic and energy components. Since the interaction energy F_{int} in (8) depends on only the total density Φ , it does not contribute the shear modulus (7), which is determined by deforming the network in which its volume V is retained. Differentiating $F(\Phi)$ [see (8)] with respect to Φ , we find the modulus of isotropic compression of a network:

$$E \approx F_{int} / V = T \Phi^{d/(d-D)}. \quad (9)$$

This modulus does not depend on the proximity of p to the percolation threshold p_c ; it is much larger than the shear modulus in (7).

Of considerable interest for experimentalists is the equilibrium value of the density, $\Phi = \Phi_{eq}$, of a gel "floating" in an excess of solvent. This value can be found by minimizing the free energy of the network, (8), with respect to Φ . The minimization condition has a simple physical meaning: Fragments of the network tend to move apart as far as possible until their mutual repulsion becomes balanced by the elastic force of the stretched chains:

$$\Phi_{eq} \sim (p - p_c)^q. \quad (10)$$

The exponent q in (10) is given by (7). Expression (10) was proposed previously⁵ without derivation. It is analogous to the Flory theorem:¹ The density of monomers established at equilibrium, Φ_{eq} , corresponds to the overlap threshold $g = L$ between dilute and semidilute solutions of percolation clusters. This theorem thus applies to only percolation networks (see also Ref. 3).

In summary, the interaction of the monomers of a network leads to scaling laws for the elastic moduli of the network as functions of p and Φ , (7) and (9), which are fundamentally different from the classical results, (4). These laws are of universal applicability and must also hold for networks generated by vulcanizing linear chains sufficiently close to the gelatination threshold. In the $d=3$ case we find $t=1.7$, $s=1.3$, and $q=0.9$ from (7); there is an experimental value⁶ $t \approx 1.7$. The difference between the exponent q and the result $q \approx 1.1$ of Ref. 5 is due to our use of a refined value of the fractal dimensionality D .

¹ P.-G. De Gennes, *Scaling Concepts in Polymer Physics* (Cornell U. Press, Ithaca, New York, 1979).

- ²M. Doi and S. F. Edwards, *Theory of Polymer Dynamics* (Oxford University Press, Oxford, 1986).
- ³S. V. Panyukov, *Zh. Eksp. Teor. Fiz.* **98**, 668 (1990) [*Sov. Phys. JETP* **71**, 372 (1990)].
- ⁴A. B. Harris and T. C. Lubensky, *Phys. Rev. B* **13**, 6964 (1987).
- ⁵M. Daoud, E. Bouchaud, and G. Jannink, *Macromolecules* **19**, 1955 (1986).
- ⁶C. Peniche-Covacs, S. Dev, M. Gordon *et al.*, *Faraday Disc. (Chem. Soc.)* **57**, 165 (1974).

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