Elastic Properties of Random Percolating Systems

Yacov Kantor and Itzhak Webman
Corporate Research Science Laboratories, Exxon Research and Engineering Company, Annandale, New Jersey 08801
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We study the macroscopic elastic moduli of an elastic percolating network in the critical region. A microscopic elastic Hamiltonian is used, which contains a bending energy term. We find that the rigidity threshold of this system is identical to the percolation threshold p_c. By considering the elastic properties of elements of the infinite percolation cluster we calculate the critical exponent τ which describes the behavior of the elastic stiffness near p_c for $d=6$ and obtain a lower bound on τ for $d<6$. τ is considerably higher than the conductivity exponent t, suggesting that the elastic problem belongs to a different universality class.

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The problem of elasticity of random percolating networks has been mostly viewed as analogous to the problem of electrical conductivity of such systems. This analogy was first suggested by de Gennes[1] in relation to the elasticity of gels and was later applied more generally.[2] It is obtained within the framework of the Born model for the microscopic elasticity of a lattice.[3] In this model the elastic energy is given by

$$H=\tfrac{1}{2}\sum_{\substack{i,j\\(\mathrm{nn})}}K_{ij}[\alpha(\vec{u}_i-\vec{u}_j)_{\parallel}^2+\beta(\vec{u}_i-\vec{u}_j)_{\perp}^2)], \quad (1)$$

where nn denotes nearest neighbors, $(\vec{u}_i-\vec{u}_j)_{\parallel}$ is the relative displacement of the site j in the direction parallel to the bond (i,j), $(\vec{u}_i-\vec{u}_j)_{\perp}$ is the relative displacement in the perpendicular direction, and K_{ij} is a random variable which assumes values 1 and 0 with probabilities p and $1-p$, respectively. By changing the parameters of the Born Hamiltonian two extreme cases can be obtained[4]: For $\alpha=\beta$ the nature of the problem is scalar and the solution coincides with that of the conductivity problem. In particular the macroscopic elastic moduli vanish near the percolation threshold as $(p-p_c)^t$, where t is the percolation conductivity exponent. In the other case where $\alpha=1$ and $\beta=0$ the Hamiltonian represents a random network of springs. Here the analogy with the electrical problem is no longer evident, and the macroscopic rigidity vanishes at a value of p higher than the geometrical percolation threshold p_c. For simple cubic lattices in all dimensions the rigidity threshold is at $p=1$, so that a meaningful study of this problem is limited to certain particular lattices.[4] For such lattices (e.g., a triangular lattice in $d=2$) the value of the elasticity exponent found numerically is higher than that of the conductivity exponent t.[4] It is clear, however, that the percolation problem associated with this type of lattice elasticity differs from the regular bond or site percolation.

In this work we propose a new model for elasticity of a percolating lattice network. In our model the rigidity threshold is identical to the geometrical p_c and the relevance of the regular bond percolation is recovered. We invoke recent results on the structure of the infinite percolating cluster together with an analysis of an exactly solvable model of elastic chains. We obtain the critical exponent τ which describes the macroscopic elastic moduli near p_c at $d=6$, and the lower bounds for τ below six dimensions. The results show that the elastic behavior of random percolating networks belongs to a different universality class than that of the conductivity, and that the critical exponent τ is considerably larger than the conductivity exponent t.

Our lattice model provides a correct description of the elastic behavior of a macroscopically inhomogeneous composite material made up of locally rigid regions and regions that are locally very soft (in the limiting case the soft regions are voids). In such a system one expects the rigidity threshold to be identical to the geometrical percolation threshold of the rigid phase. Near p_c the macroscopic rigidity of the material will be determined by the elasticity of long and tortuous thin channels of rigid material which are contained in the backbone of the percolating cluster. A suitable lattice model for a continuous inhomogeneous system at the critical region should yield a correct description of such structures. Consider for example a long thin rod made out of the rigid component of length L and width $l \ll L$. The rod will be relatively soft with respect to transverse bending forces and will have an effective elastic constant for bending which depends[5] on L as L^{-3}. The effective elastic constant for longitudinal stretching is proportional to L^{-1}. Within the framework of the scalar Born model, both longitudinal and transverse elastic constants of a linear chain of L bonds, which is the lattice analog of the

rod, are proportional to L^{-1}. A similar discrepancy appears between the elastic behavior of a contorted continuous chain and that of the corresponding lattice chain within this model. Thus the representation of a continuous system by a scalar Born lattice model would overestimate the rigidity of the system close to p_c.

The lattice model we present will lead to a correct representation of such continuous chains and can be expected to describe properly a continuous percolating system in the critical region. For simplicity we carry out our discussion for two-dimensional systems. The generalization to higher dimensions is cumbersome but straightforward and does not change our basic results. The elastic lattice Hamiltonian of our model has the following form:

$$H=\frac{G}{4}\sum_{\substack{i,j,k\\(j,k \text{ nn of } i)}} K_{ij}K_{ik}\delta\phi_{jik}^2 + \frac{Q}{4a^2}\sum_{\substack{i,j\\(\text{nn})}} K_{ij}(\vec{u}_i-\vec{u}_j)_{\parallel}^2, \tag{2}$$

where the second part is identical to the central force term in Eq. (1) and $\delta\phi_{jik}$ is the change in the angle between the bonds (i,j) and (i,k) connected to site i. The variables K_{ij} and K_{ik} have the same meaning as in Eq. (1), G and Q are local elastic constants, and a is the lattice unit length. A similar type of Hamiltonian has been used for the study of the vibrational properties of rodlike molecules,[6] while a more general related Hamiltonian has been studied by Keating for the elastic properties of covalent crystals.[7].

The macroscopic elastic moduli of a lattice network with a Hamiltonian given by Eq. (2) are evidently nonzero for $p > p_c$. The rigidity of the network is supported by the backbone of the infinite percolating cluster which is made up of rather stringy chains of bonds with more compact multiply connected regions superimposed. In order to understand the macroscopic elastic properties of such a system we first study the elastic behavior of a chain formed by a set of N vectors (or bonds) $\{\vec{b}_i\}$ of length a. In correspondence with the Hamiltonian in Eq. (2), the local elastic energy depends on both the relative change $\delta\phi_i$ in the angle between $\vec{b}_i$ and $\vec{b}_{i-1}$, and on the change δb_i in the length of bond $\vec{b}_i$. The elastic energy of the chain is thus given by

$$H=\frac{G}{2}\sum_{i=1}^{N}\delta\phi_i^2+\frac{Q}{2a^2}\sum_{i=1}^{N}\delta b_i^2. \tag{3}$$

When a force $\vec{F}$ is applied to the end of the chain, the relative changes $\delta\phi_i$ in the orientations of the bonds can be found by minimization of $W=H-\vec{F}\cdot(\vec{R}'_N-\vec{R}_N)$, where the expression in the brackets is the displacement of the end of the chain from its original position $\vec{R}_N$.[8] The component of this displacement in the direction of the force is given by:

$$\vec{F}\cdot(\vec{R}'_N-\vec{R}_N) = (\vec{F}\times\vec{z})\cdot\sum_{i=1}^{N}\delta\phi_i\sum_{j=i}^{N}\vec{b}_j+\frac{\vec{F}}{a}\cdot\sum_{i=1}^{N}\vec{b}_i\delta b_i, \tag{4}$$

where $\vec{z}$ is a unit vector perpendicular to the plane. The minimization of W leads to an explicit expression for the changes in the relative angles between the bonds:

$$\delta\phi_i=\frac{(\vec{F}\times\vec{z})}{G}\cdot\sum_{j=i}^{N}\vec{b}_j = \frac{(\vec{F}\times\vec{z})}{G}\cdot(\vec{R}_N-\vec{R}_{i-1}), \tag{5a}$$

$$\delta b_i=\frac{a}{Q}\vec{F}\cdot\vec{b}_i, \tag{5b}$$

where $\vec{R}_i$ denotes the original position of the end point of the vector $\vec{b}_i$. Substituting Eq. (5) into Eq. (3) we obtain the expression for H for any given configuration $\{\vec{b}_i\}$:

$$H=F^2NS_{\perp}^2/2G+F^2aL_{\parallel}/2Q, \tag{6}$$

where $S_{\perp}^2$ is the squared radius of gyration of the projection of the locations of sites $\vec{R}_i$ on the direction of $\vec{F}\times\vec{z}$:

$$S_{\perp}^2=\frac{1}{NF^2}\sum_{i=1}^{N}[(\vec{F}\times\vec{z})\cdot(\vec{R}_{i-1}-\vec{R}_N)]^2, \tag{7}$$

and

$$L_{\parallel}=\frac{1}{aF^2}\sum_{i=1}^{N}(\vec{F}\cdot\vec{b}_i)^2. \tag{8}$$

Note that for very long chains the second term in Eq. (6) is negligible in comparison with the first one. This term will be important only for comparatively straight chains which are stretched along their long dimension. We shall disregard this term in the following calculations. The force constant of the chain relating the elastic energy to the displacement squared of the end of the chain is given by

$$k=G/NS_{\perp}^2. \tag{9}$$

It is important to note that the results given in Eqs. (6)–(9) can easily generalized to the case in which only a fraction of the angles $\{\delta\phi_i\}$ contribute to the energy in Eq. (3), and the rest of the angles

are completely rigid.[9] In this case the summations in Eqs. (7) and (8) are only over the flexible angles. Thus N and $S_\perp^2$ in Eqs. (6) and (9) should be replaced by the total number of flexible angles and by the squared radius of gyration of the corresponding set of points, respectively.

If the chain has a form of random walk then $S_\perp^2 \sim N$ and the force constant would be

$$k_{\mathrm{RW}} \sim (G/a^2N^2). \tag{10}$$

Note that in contrast to the elastic force constant, the analogous electrical characteristic, namely the conductance of the chain, is proportional to $1/N$. Moreover, the conductance does not depend on the shape of the chain, while the force constant strongly depends on both the geometry and the direction of the force.

The above two-dimensional treatment can be generalized to higher dimensions. The deformation of the chain is represented by a sequence of transformations, where the ith transformation includes stretching of the bond $\vec{b}_i$ and the rotation of the bonds $\vec{b}_i, \ldots, \vec{b}_N$ around the point $\vec{R}_{i-1}$. A d-dimensional infinitesimal rotation can be defined by a set of $(d+1)(d-2)/2$ parameters which define the orientation of a two-dimensional plane in d-dimensional space and an angle $\delta\phi_i$ which determines the magnitude of rotation in this plane. Replacing the angles in Eq. (3) by the set of rotation angles ϕ_i leads to results which are analogous to Eqs. (6)–(10).[10]

The results obtained above will now be applied to estimate the critical exponent τ which describes the behavior of the macroscopic elastic constants above the percolation threshold of the network. The argument we use is related to the nodes and links picture of the backbone of the infinite cluster above p_c used by Skal and Shklovskii[11] and de Gennes[1] to estimate the conductivity exponent t. Pike and Stanley[12] and Coniglio[13] have recently shown that the backbone of the infinite cluster can be described as a network of elements of mean size of the percolation correlation length $\xi \sim (p-p_c)^{-\nu}$. Each element is made of a sequence of multiply connected regions of bonds linked by chains of singly connected bonds. (The entire element can be disconnected by cutting any pair of singly connected bonds.) The number of bonds $L_1(\xi)$ which belong to those singly connected chains diverges near p_c as $L_1(\xi) \sim \xi^{-1/\nu}(p-p_c)^{-1}$.[13] The macroscopic elastic stiffness of the backbone is now given by

$$\kappa_e = \kappa(p-p_c)^\tau = \xi^{2-d}k_\xi, \tag{11}$$

where κ is the local stiffness constant of the rigid component and k_ξ is the force constant of a typical element of linear size ξ of the network forming the backbone of the infinite cluster. This force constant can be related to ξ by

$$k_\xi = \kappa(p-p_c)^{\zeta_E} = \kappa\xi^{-\zeta_E/\nu}, \tag{12}$$

where ζ_E is the elastic analog of ζ_R in the case of conductivity.[11] From Eqs. (11) and (12) we obtain

$$\tau = (d-2)\nu + \zeta_E. \tag{13}$$

The force constant k_ξ would be mostly determined by the softness of the singly connected channels which contain $L_1(\xi)$ bonds. By assuming that the multiply connected regions are totally rigid we obtain stiffness of the network which is larger than the actual one, for all values of $p-p_c$. Therefore the following expression which is based on this assumption is a lower bound on τ. We use Eq. (9) with $N = L_1(\xi)$, while $S_\perp$ is replaced by the radius of gyration of the set of singly connected bonds S_ξ, so that $k_\xi \sim S_\xi^{-2}L_1^{-1}(\xi)$. Since the singly connected bonds are distributed randomly over the entire region of size ξ, $S_\xi \sim \xi$. Thus, we obtain $\zeta_E = 2\nu + 1$, and from Eqs. (12) and (13)[14]:

$$\tau = d\nu + 1. \tag{14}$$

Using the values of ν for percolation[15] one obtains $\tau = 3.6$ in $d = 2$ and $\tau = 3.55$ in $d = 3$. A more conservative lower bound for τ can be obtained by invoking the extreme assumption that all the singly connected bonds are concentrated in one region and that they possess a geometry of a random walk. In this case $S_\xi^2 \sim L_1(\xi)$ and $\zeta_E = 2$, so that $\tau > (d-2)\nu + 2$. This lower bound has the values of 2 in $d = 2$ and 2.85 in $d = 3$. Even these values are considerably higher than the corresponding values of the conductivity exponent: $t = 1.2$–1.3 in $d = 2$, and $t = 1.9$–2.0 in $d = 3$.

Above and at $d = 6$ the elements of the network consist almost totally of singly connected bonds. There $\nu = \frac{1}{2}$ and therefore $L_1(\xi) \sim \xi^2$. Since the fractal dimensionality of the backbone in this case[16] is $D = 2$, the total number of bonds on the backbone in a region of size ξ is also of the order of ξ^2. Thus, in this case the number of bonds in the multiply connected regions is negligible, and the assumption about the rigidity of these regions is not needed. From Eq. (9) with $N \sim \xi^2$ and $S_\perp^2 \sim \xi^2$ together with Eq. (12) one obtains $\zeta_E = 2$ and $\tau = 4$. We thus propose that $\tau = 4$ is exact for $d \geq 6$. Note that the corresponding conductivity exponent has the value of $t = 3$ for $d \geq 6$.[1]

The arguments we have given lead to the conclusion that the problem of the elastic behavior of a

percolating network with local bending elasticity belongs to a different universality class than that of the related conductivity problem, and that it is characterized by a different critical exponent. Our lattice Hamiltonian was chosen to represent correctly the elastic behavior of continuous random composites made up of rigid regions and very soft regions, near the percolation threshold. We suggest that our results would be relevant to experiments on such systems. It would also be interesting to study further the relation between our results and the numerical results of Ref. 4 which were obtained for a different elastic Hamiltonian, and to a recent calculation of the elasticity of an ordered fractal,[17] both of which indicate a value for the elastic critical exponent higher than that of the corresponding electrical conductivity exponent.

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