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THE ELASTICITY AND VIBRATIONAL MODES OF PERCOLATING NETWORKS AND OTHER FRACTAL STRUCTURES

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A scaling theory for the macroscopic elastic properties of an elastic percolating network in the critical region is presented. A microscopic elastic Hamiltonian is used, which contains bending energy terms, leading to a rigidity threshold identical to the percolation threshold p_c. The critical exponent which describes the behavior of the elastic stiffness near p_c is considerably higher than the exponent t of the related electrical conductivity problem, suggesting that the elastic problem belongs to a different universality class. The vibrational properties of fractal structures in which the microscopic elasticity is described by this Hamiltonian are discussed.

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. It is obtained within the framework of the Born model for the microscopic elasticity of a lattice[2]. Within this model 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 this paper a new model is proposed for the elasticity of percolating lattice networks and for other tenuous fractal structures, such as diffusion limited aggregates. This model takes into account the vectorial nature of the elasticity problem, which will be shown to lead to pronounced differences between the macroscopic elastic properties and the macroscopic conductivity.

The paper contains two major parts: The model is presented in the first part and applied to the static elastic properties of percolating networks. This part is based on a recent work of Kantor and Webman[3]. In the second part, the implications of the elastic static properties to the vibrational properties of tenuous fractal structures are presented.

The lattice model described here provides a correct description of the 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 $\ell \ll L$. The rod will be relatively soft with respect to transverse bending forces and will have an effective elastic constant for bending which depends[4] 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 analogue 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 presented here leads to a correct representation of such continuous chains and can be expected to properly describe a continuous percolating system in the critical region, as well as more general fractal structures in which the elastic behavior is dominated by a stringy and tortuous backbone. For simplicity the discussion is carried out 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 the model has the following form:

$$H = \frac{G}{4} \sum_{\substack{i,j,k \\ (j,k \text{ nn of } i)}} K_{ij} K_{ik} \delta\phi_{jik}^2 + \frac{Q}{4a^2} \sum_{\substack{i,j \\ (nn)}} K_{ij} (\vec{u}_i - \vec{u}_j)_{\parallel}^2, \qquad (1)$$

where $(\vec{u}_i-\vec{u}_j)_{\parallel}$ is the relative displacement of the site j in the direction parallel to the bond (i,j), and $\delta\phi_{jik}$ is the change in the angle between the bonds (i,j) and (i,k) connected to site i. K_{ij} is a random variable assigned to the bond (i,j), which assumes values 1 and 0 with probabilities p and 1-p, respectively, G and Q are local elastic constants and a is the lattice unit length.

The macroscopic elastic moduli of a lattice network with a Hamiltonian given by Eq. (1) are evidently non-zero for $p > p_c$, and the underlying percolation behavior is that of regular bond percolation on a lattice[2].

The rigidity of the network is supported by the backbone of 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. (1), the local elastic energy depends on both the relative changes δb_i in the length of bond $\vec{b}_i$ and $\delta\phi_i$ in the angle between $\vec{b}_i$ and $\vec{b}_{i-1}$. The elastic energy of the chain is:

$$H = \frac{G}{2}\sum_{i=1}^{N}\delta\phi_i^2 + \frac{Q}{2a^2}\sum_{i=1}^{N}\delta b_i^2 \qquad (2)$$

When a force $\vec{F}$ is applied to the end of the chain, the changes $\{\delta\phi_i\}$ and $\{\delta b_i\}$ can be found by minimization of $W\equiv H-\vec{F}\cdot(\vec{R}_N-\vec{R}_N)$, where the expression in the brackets is the displacement of the end of the chain from its original position $\vec{R}_N$. Substituting $\{\delta\phi_i(F)\}$ and $\{\delta b_i(F)\}$ into Eq. (2) one obtains an expression for the strain energy H for any given configuration $\{\vec{b}_i\}$:

$$H = \frac{F^2NS_\perp^2}{2G} + \frac{F^2aL_\parallel}{2Q} \qquad (3)$$

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 $\vec{Fxz}$:

$$S_\perp^2 \equiv \frac{1}{NF^2}\sum_{i=1}^{N}((\vec{Fxz})\cdot(\vec{R}_{i-1}-\vec{R}_N))^2, \qquad (4)$$

and

$$L_\parallel \equiv \frac{1}{aF^2}\sum_{i=1}^{N}(\vec{F}\cdot\vec{b}_i)^2 \qquad (5)$$

Note that for very long chains the second term in Eq. (3) 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. This term will be disregarded 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:

$$k = \frac{G}{NS_\perp^2} \qquad (6)$$

It is important to note that the results given in Eqs. (3)-(6) can be easily generalized to the case in which only a fraction of the angles $\{\delta\phi_i\}$ contribute to the energy in Eq. (2), and the rest of the angles are completely rigid. In this case the summations in Eq. (4) and Eq. (5) are only over the flexible angles.

Note that in contrast to elastic force constant, the analogous electrical characteristics, 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[5].

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 used is related to the nodes and links picture of the backbone of the infinite cluster above p_c used by Skal and Shklovskii[6] and de Gennes[1] to estimate the conductivity exponent t. Pike and Stanley[7] and Coniglio[8] 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 $L_1(\xi)\sim\xi^{-1/\nu}\sim(p-p_c)^{-1}$ [7]. The macroscopic elastic stiffness of the backbone is now given by:

$$K_e = K_0(p-p_c)^\tau = \xi^{2-d}k_\xi \qquad (7)$$

where K_0 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: $k_\xi\propto\xi^{-\zeta_E}$ leading to $\tau = (d-2)\nu + \zeta_E\nu$.

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. (6) 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:

$$\tilde{\zeta}_E = 2 + 1/\nu \tag{8}$$

resulting in the following expression for τ:

$$\tau = d\nu + 1. \tag{9}$$

Using the values of ν for percolation[9] one obtains $\tau = 3.6$ in $d = 2$ and $\tau = 3.55$ in $d = 3$.

Above and at $d = 6$ the elements of the network consist almost totally of singly connected bonds. There $\nu = 1/2$ and therefore $L_1(\xi) \sim \xi^2$. Since the fractal dimensionality of the backbone in this case[10] 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. (6) with $N \sim \xi^2$ and $S_\perp^2 \sim \xi^2$ together with Eq. (7) one obtains $\tilde{\zeta}_E = 4$ and $\tau = 4$. We thus propose that $\tau = 4$ is exact for $d \geq 6$. Note that the corresponding conductivity exponent has the value $t = 3$ for $d \geq 6$ [1].

The arguments given here 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. The lattice elastic 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. The results of this work should be relevant to experiments on such systems.

Whether this theory can be applied to the problem of the elasticity of gels has not yet been fully clarified. It has been suggested recently[11] that the appropriate microscopic elasticity for gels and rubber networks may be described by the scalar Born Hamiltonian. The experimental values of the elasticity exponent for gels are in the range: $\tau \sim 2.0$-3.6[12] where the value of τ depends on the type of gels. For polycondensed gels $\tau = 3.0$-3.6. The values are even higher than the value of the conductivity exponent for perfect branching networks ($t=3$), and much higher than the value of t for percolative networks in three dimensions. The possibility that the present model explains these high τ values at least for certain type of gel is intriguing.

The ideas discussed above will now be applied to discuss the low frequency vibrational properties of percolation clusters and tenuous fractal objects such as DLA clusters[13] and other non-compact growth aggregates. Consider a region of size L of a tenuous fractal structure of Hausdorff dimensionality D. A dilation of the length by a factor λ will lead to the following transformation for the L dependent force constant:

$$k(\lambda L) = \lambda^{-\tilde{\zeta}_E} k(L) \tag{10}$$

For percolation clusters $\tilde{\zeta}_E$ is given by Eq. (8). As in the above discussion of the static elasticity, $\tilde{\zeta}_E$ depends on certain geometrical features of the backbone of the specific fractal structure. The mass in a region of size L scales in the following manner with L: $M(\lambda L) = \lambda^D M(L)$. From this relation together with Eq. (10) one can obtain the following scaling property for the frequencies of the vibrational modes:

$$\omega(\lambda L) = \lambda^{-(\tilde{\zeta}_E + D)/2} \omega(L) \tag{11}$$

The density of vibrational states is approximately given by: $\rho(\omega, L) \sim 1/L^D \Delta\omega$, where $\Delta\omega$ is the spacing between the frequencies of the low vibrational eigenmodes of a piece of structure of size L. The spacing $\Delta\omega$ is of the order of the frequency of the lowest eigenstate, and it scales with L in the same manner as ω in Eq. (11). The above scaling relations can be combined to yield the exponent $\tilde{d}_E$ which describes the low frequency behavior of the density of states:[14]

$$N(\omega) \sim \omega^{\tilde{d}_E - 1}$$

$$\tilde{d}_E = \frac{2D}{\tilde{\zeta}_E + D} \tag{12}$$

For percolating clusters the discussion of the static properties led to $\tilde{\zeta}_E = 2 + 1/\nu$ (see Eq. (8)) and the Hausdorff dimensionality is: $D = d - \beta/\nu$. Thus:

$$\tilde{d}_E = \frac{2(d\nu - \beta)}{(d+2)\nu + 1 - \beta} \tag{13}$$

The mean field value of $\tilde{d}_E$ is $\tilde{d}_E = 1$. For $d = 2$ and $d = 3$ the static results lead to $\tilde{d}_E \sim 0.8$ and $\tilde{d}_E = 0.9$ respectively. These results lead to the interesting prediction that the density of states of a large percolating cluster at $p = p_c$ may have a slightly divergent density of states as $\omega \to 0$. This behavior should be contrasted with that of a percolation network in which the elasticity is determined by the Born model.[14] There $\tilde{d} = 4/3$ and the density of states vanishes as $\omega^{\tilde{d}-1}$ a $\omega \to 0$. For $p > p_c$ the density of states will be

characterized by two regimes:

$$N(\omega)=\begin{cases} \omega^{\tilde{d}_E-1} & \omega < \omega_c \\ \dfrac{\omega^{d-1}}{c(p-p_c)^d} & \omega > \omega_c \end{cases} \qquad (14)$$

Here ω_c is a crossover frequency given by: $\omega_c = \xi^{-(\tilde{\zeta}_E + D)/2} = (p-p_c)^{(\tilde{\zeta}_E + D)\nu/2}$, and $c(p-p_c)$ is a sound velocity given by $c(p-p_c) \sim (p-p_c)^{(\tau-\beta)/2}$. If ω_c is sufficiently small, a peak should appear in the density of states in the crossover region.

In order to apply this model to DLA structures one needs an estimate of $\tilde{\zeta}_E$ for this system. The elastic backbone of the DLA has a fractal dimensionality very close to unity. Since for a one dimensional object of size L, $k(L) \sim L^{-3}$, we can use the approximation $\tilde{\zeta}_E = 3$ which leads to:

$$\tilde{d}_{E\ (DLA)} = \frac{2D}{3 + D} \qquad (15)$$

Using the values of D for DLA in d = 2 and d = 3 one obtains $\tilde{d}_E = 0.7$ in d = 2 and $\tilde{d}_E = 0.9$ in d = 3. In this case, as in the case of percolation clusters, a divergence of the density of states at low frequencies can be expected. Preliminary results of numerical calculation of the density of states of both systems[16] confirm this divergent behavior. It would be very interesting to test these predictions by dynamic neutron scattering experiments on mesoscopic fractal growth structures.

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