ELASTIC PROPERTIES OF RANDOM SYSTEMS

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INTRODUCTION

Recently there has been growing interest in the elastic properties of random systems. Since various elastic model Hamiltonians produce different predictions[1-3] for the effective elastic moduli, it is important to realize that they usually apply to distinct physical systems, or treat different aspects of the same system. Our model Hamiltonian primarily aims to explain the elastic properties of macroscopically disordered systems, such as porous solids or colloidal aggregates in which the size of an elementary grain is at least several atomic radii. However, in certain cases it may also be applicable to disorder on the atomic level.

Let us consider a macroscopically inhomogeneous composite made up of very stiff regions and very compliant regions. (We will actually consider a case when the compliant regions are voids.) Effective elastic moduli of this system decrease with decreasing concentration p of the stiff component and vanish when p approaches the geometrical continuity (percolation) threshold p_c. The dependence of the effective elastic constant κ, e.g. bulk modulus or shear modulus, on p, near p_c is given by $\kappa \sim (p-p_c)^{\tau}$. This relation reminds the behavior of the effective conductivity of metal-insulator mixture: $\sigma \sim (p-p_c)^t$. The formal similarity of the differential equations governing these problems suggests some analogy in the results. Almost a decade ago de Gennes[4] noted that the rubber elasticity Hamiltonian used to describe the entropic elasticity of gels coincides with the dissipation functional of the conductivity problem and concluded that the critical exponent τ of the <u>entropic</u> elasticity coincides with t of conductivity. For a long time this conclusion has been assumed to be valid for any kind of elasticity (see, e.g. Ref. 5). We will show that in the macroscopically inhomogeneous systems τ is considerably larger than t.

Singular behavior of the elastic moduli of percolating system near p_c is caused by the divergence of the correlation length $\xi \sim (p-p_c)^{-\nu}$, and therefore, on length scales $L \gg \xi$ (homogeneous regime) we can use the relation $\kappa \sim (p-p_c)^{\tau} \sim \xi^{-\tau/\nu} \equiv \xi^{-\tilde{\tau}}$. For $L \ll \xi$ (scale invariant or fractal regime) κ does not depend on ξ, and is proportional to $L^{-\tilde{\tau}}$. Some systems, such as colloidal aggregates, do not have natural correlation length, and therefore the power law $\kappa \sim L^{-\tilde{\tau}}$ is the only way to describe their properties.

CRITICAL EXPONENT OF ELASTICITY OF A PERCOLATING SOLID

In order to investigate the critical behavior of κ we must be able to define a lattice Hamiltonian which adequately describes the elastic properties of the system even in the extremely disordered case. Feng and Sen[1] suggested to describe the elastic behavior of a two-dimensional percolating system by a random spring network on a triangular lattice. The rigidity threshold of such a system in considerably higher than the geometrical percolation threshold, since it has many geometrically connected parts which cannot transmit stress, and the geometrical properties of the "rigid clusters" near the rigidity threshold seem to differ significantly from the properties of usual percolation clusters[6]. Therefore, random spring model does not describe correctly macroscopic disorder. Various finite differences schemes of elasticity also fail in a similar fashion.

Kantor and Webman[2] suggested a lattice Hamiltonian, in which each bond accounts for stretching energy proportional to the square of its elongation, while a pair of ajacent bonds accounts for an energy ${}^1/_2\, G(\delta\phi)^2$, where $\delta\phi$ is the relative change in the orientation of the bonds: For d=2, $\delta\phi$ is simply the change in the angle between the bonds, while for $d \geqslant 3$ each bond must be treated as a d-dimensional object and $\delta\phi$ represents the d-dimensional solid rotation of one bond in the reference frame of the ajacent bond. Rigidity threshold of a percolating network described by this Hamiltonian coincides with the geometrical p_c.

For a single chain on a lattice the Hamiltonian reduces to a very simple form which is analytically solvable. It can be shown[2] that the force constant k of a long chain (related to the elastic modulus by $\kappa = kL^{2-d}$) does not depend on the bond stretching term in the Hamiltonian (except the case of comparatively straight chains which are stretched along their long dimension), and is given by

$$k = \frac{G}{NS^2} \quad , \tag{1}$$

where N is the number of bonds in the chain and S is its radius of gyration (r.m.s. size) in the direction perpendicular to the applied force.

Elastic modulus of a percolation problem can be bound (in the fractal regime $L \ll \xi$) by the elastic moduli of two single chain problems[2,7]: If we assume that only the singly connected bonds[8] are flexible, while the rest of the infinite cluster is infinitely rigid, we overestimate κ and underestimate τ. If we assume that only the shortest path between two opposite boundaries, which diverges as L^z, supports the stress, while the rest of the cluster is absent, we underestimate κ and overestimate τ. Since each of these problems can be solved using Eq. 1, we can find[2,7] exact bounds on τ:

$$d\nu+1 \leqslant \tau \leqslant (d+z)\nu \quad . \tag{2}$$

The numerical values of the bounds, as well as some Monte Carlo[9] and experimental[10] estimates of τ are depicted in Fig. 1. The uncertainties in the values of the bounds (not shown) are smaller that 0.1 and are caused by uncertainties in the numerical values of ν and z, while the error bars of the Monte Carlo and experimental results (not shown) range from 0.2 to 0.5.

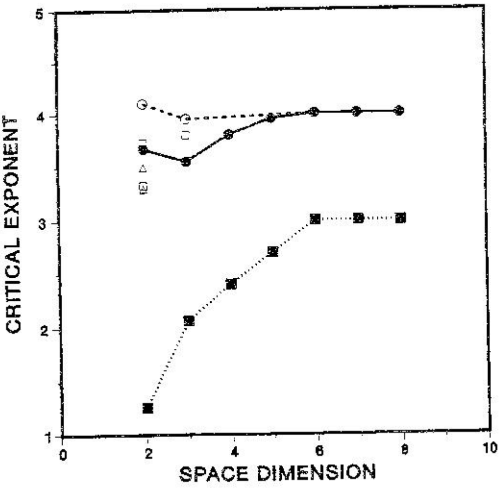

Fig. 1. Lower (full circles) and upper (open circles) bounds on the critical exponent of elasticity τ of percolation in various space dimensions. Full squares depict conductivity exponent t. Open squares show the experimental results[10] for τ, while the open triangles represent the Monte Carlo estimates[9] of τ.

All these results are consistent within the error bars. Note, that τ is close to 4 for any d, and its value is considerably larger than the conductivity exponent t. For $d = 6$, the two bounds on τ coincide and give $\tau = 4$. This value remains unchanged also for $d > 6$, while the Eq. 2 is not applicable above the critical dimension ($d = 6$) of the percolation.

MECHANICAL STABILITY OF TENUOUS STRUCTURES

Certain forms of matter, such as colloidal aggregates, have fractal nature: that is the average mass M(L) within a distance L of an arbitrary point varies as L^D, where $D < d$. As the size of the object increases, its effective elastic moduli decrease as $L^{-\tilde{\tau}}$. Thermal fluctuations and gravitational stresses tend to deform the geometry of these structures, and therefore we cannot grow them beyond some maximum size[11].

At temperature T, thermal vibrations induce an average strain ε_T given by $k_B T \approx \kappa L^d \varepsilon_T^2$. Thus in homogeneous solids ε_T fluctuates by amount proportional to $L^{-d/2}$, i.e. overall distortions are smaller in larger objects. In the tenuous structures $\kappa(L) \sim L^{-\tilde{\tau}}$ with $\tilde{\tau} > d$, and therefore the distortions increase with increasing L: $\varepsilon_T \sim L^{(\tilde{\tau}-d)/2}$. Usually aggregates are branched loopless structures, and therefore we can determine their deformation by examining the elastic properties of a single branch[11,12]. If the actual ("chemical") length of a branch N scales as L^δ, where L is the end-to-end distance, then from Eq. 1 we find $k \sim L^{-(2+\delta)}$, or $\kappa \sim L^{-(d+\delta)}$, and therefore
$\tilde{\tau} = d + \delta$. Thus, for branched structures $\varepsilon_T \sim L^{\delta/2}$. For sufficiently large L we get $\varepsilon_T \approx 1$ and the structure can no longer be regarded as a rigid body. The exact value L_{max} of this maximal thermally stable L depends on the temperature, the elastic moduli of the material from which the aggregate has been built, the diameter a of the grains from which it is built and the strength of the bonding between the grains. L_{max} strongly depends on a: larger (and thermally more stable) grains increase L_{max}. For most materials at room temperature $L_{max}/a = (Aa/b)^{d/\delta}$, where b is the atomic diameter and $1 < A < 10$. The exponent d/δ for most (three-dimensional) aggregates varies between 2.5 and 3. Typical stability curve is depicted in Fig. 2. Aggregates above the curve are thermally floppy, while the aggregates below the curve are thermally stable.

Another limit on the rigidity of an aggregate comes from gravitational effects. For an aggregate sedimenting under gravity, the weight force is compensated by hydrodynamic friction. For aggregate of weight Mg and size L, the gravitational stress $\sigma_g \approx Mg/L^{d-1} \sim L^{D-d+1}$. This stress induces strain $\varepsilon_g = \sigma_g/\kappa(L) \sim \sigma_g L^{\tilde{\tau}} \sim L^{D+\delta+1}$, and for sufficiently large L, $\varepsilon_g \approx 1$.

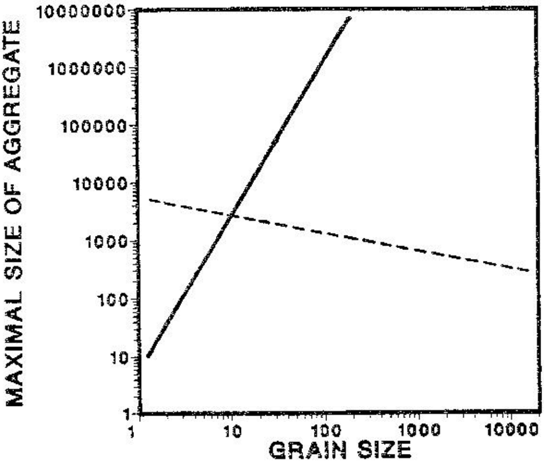

Fig. 2. Double logarithmic plot showing the dependence the maximal stable size of an aggregate L_{max}, measured in grain diameters, on the grain diameter, measured in atomic diameters. Typical lines for thermal stability (solid line) and gravitational stability (dashed line) are shown. For any particular aggregate the location and slope of the curves may slightly vary. An aggregate is stable if it is located below both lines.

As in the thermal case L_{max} mainly depends on a, but now smaller (and lighter) grains are needed to increase L_{max}. For most materials $L_{max}/a = (Bb/a))^{1/(D+\delta+1)}$, where $B \approx 10^{15}$. The exponent $1/(D+\delta+1)$ for most structures is approximately 1/4. Typical gravitational stability line is depicted in Fig. 2. Aggregates above the line are gravitationally saggy, while the aggregates below the line are stable.

Note that the largest stable aggregates can be obtained for $a/b \approx 10 \div 100$. For such grain sizes the size of the aggregate may reach $10^3 \div 10^4$ grain diameters. It appears that aggregates approaching these limits are actually produced in practice, and thus, the prospects for extending the range are distinctly limited.

DISCUSSION

We described a particular model of elasticity of random systems, which primarily intended to explain the properties of macroscopically disordered systems. Critical exponents predicted by this model are considerably larger than the values which could be expected from elasticity-conductivity analogy, i.e. the tenuous structures are considerably softer than the analogy could suggest. This softness leads to such effects as lack of thermal stability.

The applicability of these results to gels depends on the details of the systems. Since the critical exponent of entropic elasticity is smaller than τ predicted by our model, we can expect that sufficiently close to the gel point we will see mainly the entropic contribution to the critical behavior[13]. The crossover point between the two behaviors will be determined by G/k_BT (G is the microscopic bending/twisting force constant), which usually is not a very large number. However, for systems with $G/k_BT \approx 10$ we can expect that mainly the contribution predicted by our elasticity model will be seen experimentally. While some measurements of τ of gels are consistent with the predictions of our model, it is not clear whether this indicates the negligible contribution of the entropy or an inadequate description of the gel geometry by percolation model.

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Scaling Phenomena in Disordered Systems

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