

ENTROPIC RIGIDITY

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INTRODUCTION

There is now, as evidenced by several papers in this conference proceedings, a significant body of work devoted to the mechanical rigidity of networks. We define rigidity as the ability of a system to resist shear. The results that have been obtained apply to diluted central force networks, glasses, and tensegrity networks, and they focus on rigidity criteria and the nature of the transition from the floppy to the rigid phase.

One important result is that the onset of mechanical rigidity in diluted central force networks does not occur at either the site or bond connectivity percolation concentration but at a higher concentration. Mechanical rigidity in such systems requires multiple connectivity. Other results are mean field predictions on the minimum coordination number of bonds required to have rigidity in glasses. Discussions of these issues have so far been in terms of arguments based on geometrical and mechanical considerations. They are intrinsically zero temperature theories and they measure the part of the rigidity whose origin can be said to be energetically derived.

Temperature can qualitatively change the picture. Temperature introduces vibrations in the network. These can modify the existing elasticity in two ways. Firstly, the force constants have to be redefined according to the new average separation between interacting components of the system. Moreover, it produces a second component that has an intrinsically different origin than the one so far discussed: one that could be called a thermodynamic rigidity. It arises from the change in entropy of the system upon deformation. It is usually small in mechanically rigid systems but can be significant in soft materials and even dominant, as in the case of rubber where the energetic part of the shear modulus is insignificant in comparison with the entropic part¹.

Entropically derived rigidity differs from energetically derived rigidity in several ways. It is strongly dependent on temperature, *i.e.*, the leading term is linear in T . It seems to be scalar in nature, rather than vectorial as will be discussed further below. It is similar in nature to springs of zero length and therefore the entropic solid behaves like a material under tension. The first and third points lead to a negative contribution to the coefficient of thermal expansion.

Random networks in the neighborhood of their mechanical rigidity point are soft materials with high entropies. We show below that an entropically derived rigidity exists in these networks and that its onset occurs at the connectivity percolation point, significantly below

the mechanical rigidity point. It dominates the elasticity up to the mechanical rigidity point, where a crossover occurs to energetically derived elasticity.

After a brief summary of findings on mechanical rigidity, we introduce entropic rigidity through a few examples and show that it is a measurable quantity that can be extracted from the temperature dependence of the elastic constants. Then we present and discuss previously published and some new results on entropic rigidity in model diluted central force networks. These results, and some models used to explain them, form the basis of a further discussion of entropic rigidity and its relevance to glasses and other materials.

A number of issues are of interest in the subject of entropic rigidity. One is an argument by de Gennes² who predicted that the elastic constants should vanish at the percolation threshold p_c as $\mu \sim (p - p_c)^f$, where f is the exponent describing the conductance of a random resistor network near percolation, and p is the concentration of bonds or sites. Although this is known not to be true for mechanical rigidity³, it seems to apply to the case of entropic rigidity.

MECHANICAL RIGIDITY

A typical rigid body at $T = 0$ will settle into a ground state configuration which minimizes its internal energy. Deformation away from this equilibrium leads, for infinitesimal or small displacements, to linear restoring forces. This is what is understood as energetically derived elasticity. The conditions that determine whether or not a network is actually rigid form a subject matter that has been studied extensively by mathematicians and physicists, in models where temperature effects are absent. These theories focus on mechanical rigidity.

For our purposes we focus on systems with no bond bending forces. These require multiple connectivity for the existence of a mechanically rigid network. For this reason, the onset of rigidity in diluted networks occurs above the percolation threshold. The nature of this onset has been discussed by a number of authors in the context of central force networks at zero temperature^{3,4,5}.

Feng and Sen⁴ were the first to point out that randomly diluted central force networks are incapable of withstanding shear or compression below a concentration of particles p_r — the rigidity percolation concentration — that is *considerably* higher than the concentration p_c at which an infinite connected cluster first appears. In the extreme case of the simple cubic lattice, $p_r = 1$, and even the perfect lattice has no resistance to shear. At the simplest level, this result can be understood in terms of the number of constraints imposed on the system of particles by the nearest neighbor forces. When this number becomes less than the remaining number of degrees of freedom, a soft mode appears. A straightforward mean field theory⁵ produces the remarkably accurate result $p_r = 2d/z$ where d is the spatial dimensionality and z the coordination number of the network. For a cubic lattice, $d = 3$, $z = 6$, and $p_r = 1$. It is important to state immediately that these results only apply to unstressed materials. The perfect cubic lattice, for instance, under hydrostatic expansion pressure, has a non-zero shear modulus which is proportional to the applied pressure.

The fact that percolation and rigidity have separate onsets in dilute systems is particular to central force networks: If there are bond-bending forces present, rigidity sets in at the percolation point⁶.

ENTROPICALLY DERIVED RIGIDITY

Entropy is a concept central to thermodynamics. In the microcanonical ensemble of statistical mechanics it is defined as $S = k_B \ln \Omega$ where Ω is the number of configurations available to a system at fixed energy. The equilibrium state is the state of maximum entropy

consistent with the constraints imposed on the system and thus the state in which the maximum number of microscopic configurations are available to the system. For systems kept at fixed temperature, the relevant thermodynamic potential is the Helmholtz free energy $A = U - TS$ where U is the internal energy (kinetic and potential) of the system. The equilibrium state in this situation is the state of minimum A . In an isothermal process, *e.g.*, one in which the system is deformed, the amount of work necessary is $\Delta W = \Delta U - T\Delta S$.

In rigid bodies with energetically derived elasticity ΔU is typically by far the dominant term in this expression, at least at moderate temperatures. There are however systems whose internal energy changes little upon deformation. These usually have a large space of available configurations of nearly identical energy, and hence high entropy. Their equilibrium state, even at fixed T , is thus the state of maximum S . If deformations which decrease the entropy are imposed on these systems, there is a restoring force, which can be far from negligible. To show that entropically derived restoring forces can be significant and to illustrate their character, we will discuss three examples: the ideal gas, a polymer chain, and a crosslinked polymer network (or vulcanized rubber).

The first of these is obviously not a rigid material, but what makes it an interesting example is that its one nonzero modulus, the bulk modulus, is entirely entropic in origin. In an ideal gas, the molecules are non-interacting and the internal energy depends only on temperature, $U = \frac{3}{2}Nk_B T$. Upon compression at fixed T , there is an increase in pressure due to the increase in the frequency of collisions with the walls of the container. This increase in collision rate is the result of the decrease in entropy. The entropy $S = Nk_B \ln(V/N\lambda^3)$ where $\lambda(T)$ is the thermal wavelength⁷. The pressure or restoring force upon volume change is given by:

$$P = -\frac{\partial A}{\partial V} = -\frac{\partial}{\partial V}(U - TS) = \frac{\partial}{\partial V}(TNk_B \ln(V/N\lambda^3)) = \frac{Nk_B T}{V}, \quad (1)$$

the well-known ideal gas law.

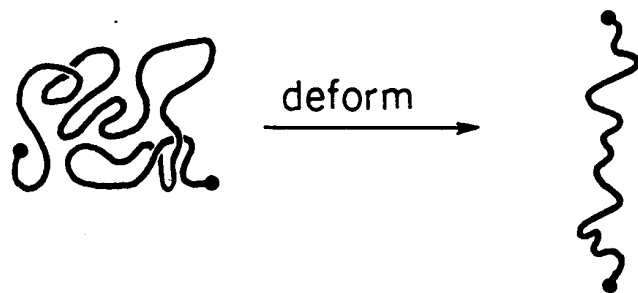


Figure 1. A polymer in two configurations: left-hand side, unstretched (high entropy), and right-hand side, stretched (low entropy). This is the archetypal example of an entropic spring. This figure, as well as Fig. 2 and 3 are inspired by similar drawings in Ref. 8.

The second is the polymer chain, which is the basic elemental component of rubber, and the simplest example of what is known as an entropic spring. A polymer may be modeled as a long flexible chain (see Fig. 1). In dilute solution it has, on a coarse-grained level, many of the properties of a self-avoiding random walk, *e.g.*, its end-to-end distance $\langle \mathbf{R}_N^2 \rangle^{1/2}$ scales as $N^\nu l_p$ where N is essentially the number of independent units, each of microscopic length l_p of the chain (l_p is the persistence length of the polymer chain, the length over which the polymer loses its orientational memory, and Nl_p , the total length of the chain)⁹. The exponent

$\nu \approx 0.6$ for a polymer in a ‘good solvent’ but in the relevant case of a dense melt, the same power-law behavior is seen but with $\nu = 0.5$, the Gaussian or ideal random walk exponent⁹. For such an ideal N -step random walk, one can calculate the probability $P(\mathbf{R}, N)$ that the separation between end points is \mathbf{R} :

$$P(\mathbf{R}, N) = \left(\frac{3}{2\pi N l_p^2} \right)^{3/2} \exp \left\{ -3\mathbf{R}^2 / 2N l_p^2 \right\} \equiv \exp \left\{ [S(\mathbf{R}, N) - S(N)] / k_B \right\}, \quad (2)$$

where we have related this probability to the entropy $S(\mathbf{R}, N)$ of this ensemble of walks. Ignoring the internal energy, we therefore obtain a Helmholtz free energy

$$A(\mathbf{R}, N) = \frac{3k_B T \mathbf{R}^2}{2N l_p^2} + \text{const.} \quad (3)$$

This leads to an elastic restoring force equivalent to that of a spring of zero equilibrium length. The ‘effective spring constant’ $3k_B T / 2N l_p^2$ is a thermodynamic quantity in this case. The fact that it is proportional to T ensures that the radius of gyration R_g of the polymer is independent of T . The radius of gyration is the most probable spatial extent of the polymer. Its probability distribution is obtained by integrating over the angular degrees of freedom of the polymer. One finds that $R_g \propto \sqrt{N}$ in both two and three dimensions.

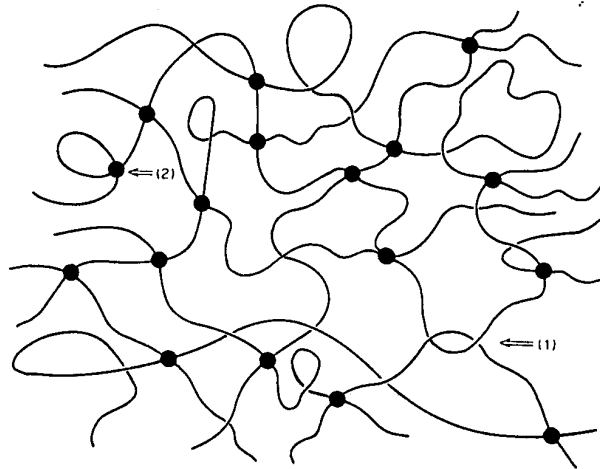


Figure 2. Sketch of a crosslinked polymer melt: The model for vulcanized rubber. (1) indicates an entanglement and (2) a permanent crosslink.

Rubber, our last example, is produced from a dense melt of polymer chains, that are substantially entangled with each other. At some instant, a number of permanent crosslinks that connect previously uncoupled monomers is imposed on the system by a chemical reaction or by radiation. These crosslinks convert the melt at least partially into a network, with chain segments of various contour lengths between the crosslinks (see Fig. 2). This is the unstressed state of the gel with the conformations of the subchains reflecting the Gaussian distribution of the melt. If this gel is distorted, *e.g.*, by stretching, the free energy of segments between two crosslinks will generically increase as the separation of the crosslinks increases and this increase is proportional to $k_B T$ (see Fig. 3). This is the qualitative explanation for the entropic elasticity of rubber.

We will now present a simple quantitative model to put this notion on a slightly more formal basis. Consider a sample of dimension L_x, L_y, L_z with N_{el} elastically active chain

segments, *i.e.*, segments of a given polymer between two crosslinks. Let the vector connecting the crosslinks of segment i in the undistorted state be \mathbf{R}_i . Suppose now that a macroscopic distortion $L_\alpha \rightarrow \lambda_\alpha L_\alpha$ is imposed on the system. In the affine distortion model that is commonly used¹⁰, the individual elastically active segments follow this distortion so that $R_{i\alpha} \rightarrow \lambda_\alpha R_{i\alpha}$. The change in free energy of segment i is then given by

$$\Delta A_i(\lambda_x, \lambda_y, \lambda_z) = \frac{3k_B T}{2} \frac{\mathbf{R}_i^2(\{\lambda_\alpha\}) - \mathbf{R}_i^2(1)}{N_i l_p^2} \quad (4)$$

where N_i is the number of monomers in segment i . Using the Gaussian distribution (2) for the unperturbed separation \mathbf{R}_i and averaging, we obtain

$$\frac{\Delta A(\lambda_x, \lambda_y, \lambda_z)}{V} = \frac{3k_B T}{2} \frac{N_{el}}{V} (\lambda_x^2 + \lambda_y^2 + \lambda_z^2 - 3) = \frac{3k_B T}{\xi^3} (\lambda_x^2 + \lambda_y^2 + \lambda_z^2 - 3) \quad (5)$$

where $\xi = (V/N_{el})^{1/3}$ characterizes the mesh size of the network. ΔA is proportional to a combination of the elastic constants of the network (which combination depends on the choice of λ_α) and we see the classical form of the theory of rubber elasticity $E \propto k_B T / \xi^3$.

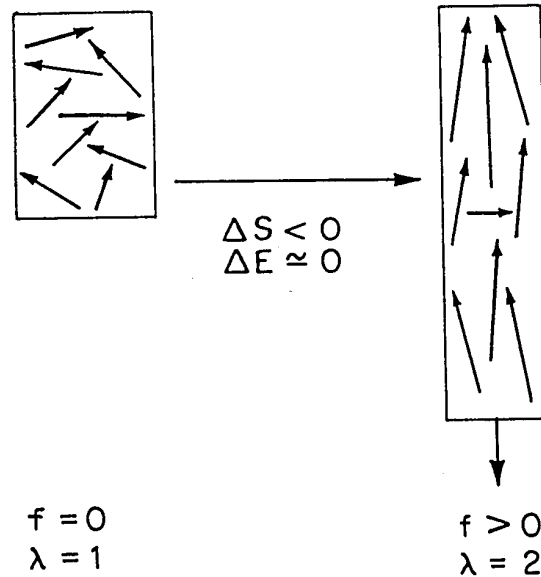


Figure 3. Schematic view of a typical crosslinked polymer melt, (a) in an isotropic state ($f=0$), and (b) extended ($f>0$). Note the increased ordering upon extension.

Experimental observation shows very little volume change under elongation. Therefore, if we assume a volume preserving ($\lambda_x \lambda_y \lambda_z = 1$) stretch along a given direction, say x ($\lambda_x = \lambda$, $\lambda_y = \lambda_z = 1/\sqrt{\lambda}$), the restoring stress, the force per unit area, is given by

$$\sigma_{xx} = \frac{\lambda}{V} \frac{\partial \Delta A}{\partial \lambda} = \frac{6k_B T}{\xi^3} \left(\lambda^2 - \frac{1}{\lambda} \right). \quad (6)$$

The above simple free energies already contain three essential features of entropic materials. First the strength of the spring constant increases linearly with temperature. Secondly, because of the zero equilibrium length of the entropic springs, the potential is separable and the restoring forces act as *scalar* forces. And thirdly, from an elasticity point of view, the

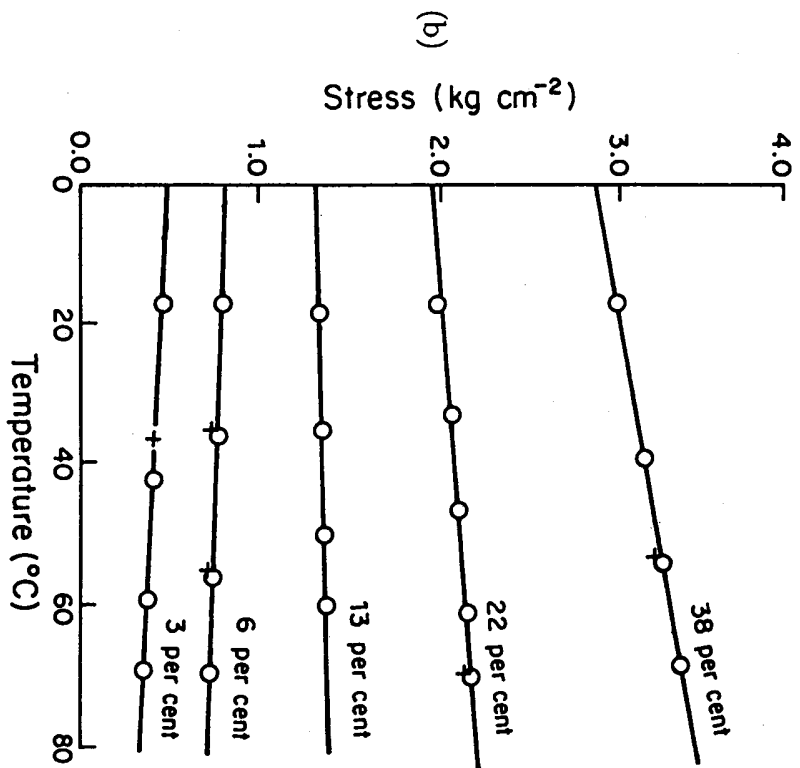
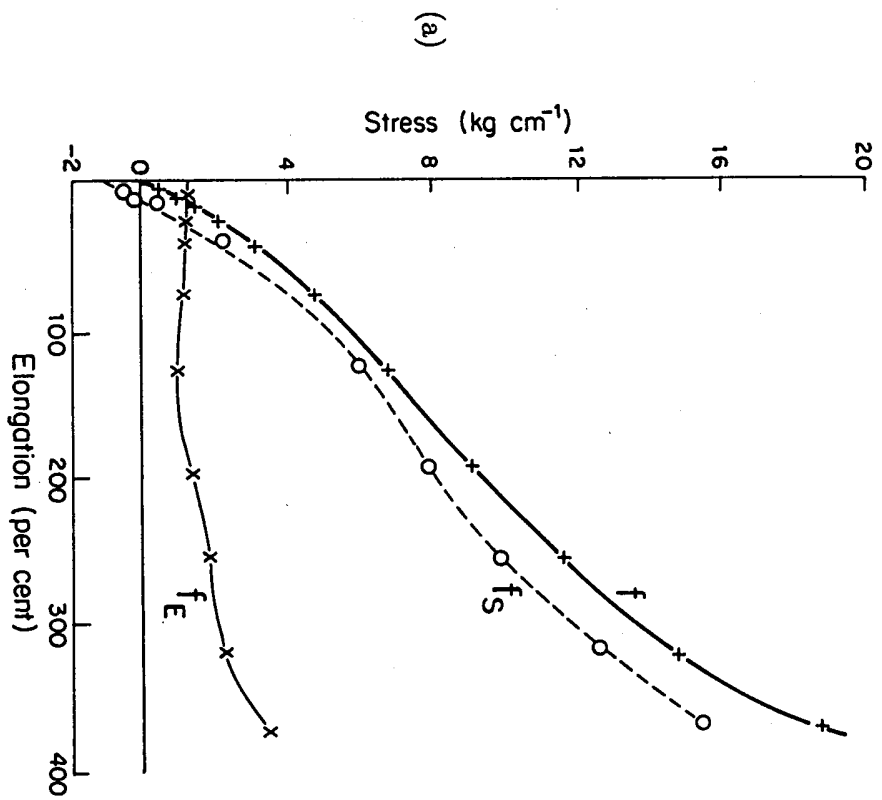


Figure 4. Typical behavior of rubber under stress: (a) Stress as function of fractional elongation separated into entropic and energetic contributions. (b) Stress as function of temperature at fixed elongation. Figure taken from Ref. 1.

materials behave as materials under tension. The third point ensures that rigidity in these networks sets in at connectivity percolation.

Lastly, vulcanized rubber shrinks upon heating for the same reason that an ideal gas will expand at constant pressure. When heat is added, the entropy is increased and it is clear from Eq. (2) that increasing the entropy implies decreasing the end-to-end distance of elastically active segments.

Experimentally, the entropic contribution can be extracted from the data if the temperature variation of the restoring force is known. Simple thermodynamic relations can be used to separate the entropic from the energetic contribution. We start from the differential form of the first law:

$$dA(L, T) = f dL - S dT \quad (7)$$

where f is the tension in the material. Therefore, at fixed T we have

$$f = f_E + f_S = \left(\frac{\partial E}{\partial L} \right)_T - T \left(\frac{\partial S}{\partial L} \right)_T, \quad (8)$$

where the first term f_E corresponds to the energetic contribution to the stress, and the second f_S to the entropic contribution. Using

$$f_S = -T \left(\frac{\partial S}{\partial L} \right)_T = T \frac{\partial}{\partial L} \left(\frac{\partial A}{\partial T} \right)_L = T \frac{\partial}{\partial T} \left(\frac{\partial A}{\partial L} \right)_T = T \left(\frac{\partial f}{\partial T} \right)_L, \quad (9)$$

we obtain

$$f_E = \left(\frac{\partial E}{\partial L} \right)_T = f - T \left(\frac{\partial f}{\partial T} \right)_L = -T f \left\{ \frac{\partial \ln(f/T)}{\partial T} \right\}_L. \quad (10)$$

These two equations are quite general. For rubber, the energetic and entropic contributions are plotted in figure 4(a) and the latter clearly dominates for all but the smallest strains. Similarly, we see from figure 4(b), for reasonably large strains, the characteristic linear increase of the stress with temperature, again an indicator of the préeminence of the entropy in the process.

ELASTICITY OF THE DILUTED CENTRAL FORCE NETWORK

As already mentioned in the introduction, diluted central force networks at $T = 0$ are soft for $p < p_r$, the rigidity percolation concentration. It is therefore of interest to investigate whether or not there is entropic rigidity at finite T in the concentration range (of bonds or sites) $p_c < p \leq p_r$. In a previous article¹¹ we reported the results of extensive molecular dynamics (MD) simulations for site-diluted triangular lattices. The conclusions of that study were that these systems are rigid for all nonzero temperatures in the entire range $p_c < p \leq p_r$ and that the shear modulus $\mu \sim (p - p_c)^f$ where the value of the exponent $f \approx t$ where t is the corresponding exponent for the conductivity of a diluted resistor network, consistent with the prediction of de Gennes². In this article, we display some of these results and include, as well, some preliminary results for bond-diluted triangular networks and site-diluted square networks.

In this section, we first present some details regarding the models that we have used and some computational techniques. This is followed by a presentation of results and a simple theory similar to the affine theory for rubber.

The models

Our models are two-dimensional networks of particles joined by unbreakable bonds, with linear central restoring forces when deformed from an equilibrium length r_0 . These bonds join nearest neighbours only and have the functional form $V_{nn}(r_{ij}) = \frac{1}{2}k(r_{ij} - r_0)^2$. Most of our results are for the site diluted triangular lattice, where we start from a perfect triangular lattice with six-fold coordination at each site and remove sites at random (for a picture see Fig. 6 in Ref. 12). This system has connectivity percolation at a probability of site occupation $p = p_c = 0.5$. Rigidity percolation (at $T = 0$) occurs at $p_r^{(ng)} \approx 0.71$ for non-generic networks. For generic networks, $p_r^{(g)} = 0.6975$ ³. Since we remove sites randomly without checking whether the resulting network is generic or not, at $T = 0$ we may have non-generic networks. At finite temperatures thermal vibrations presumably make most configurations generic. There is therefore some uncertainty as to which p_r applies. This is however not of much concern for this paper since the onset of entropic rigidity occurs at p_c .

We will also report on some simulations for bond dilution in the triangular lattice for which $p_c = 2 \sin(\pi/18) \approx 0.34729$, $p_r^{(ng)} \approx 0.641$ ¹³ and $p_r^{(g)} \approx 0.66$ ³.

Molecular dynamics simulations are done on finite size lattices with periodic boundary conditions and with the area kept constant. The starting perfect lattice is unstressed, but as sites or bonds are removed an effective tensile stress holds it at the same area. These being networks we need not worry about the generation of defects, or any topological changes. Bonds cannot break and reform.

Methods of calculation of the shear modulus

When calculating the shear modulus of soft inhomogeneous materials some care is required in the application of standard methods, in particular when, as is the case here, we are interested in the behaviour at high temperature. A direct approach is a stress-strain method (method 1) where a deformation of some kind is imposed on the computational box and the macroscopic restoring force is measured. For isotropic materials, one may impose a pure shear deformation, i.e., an area preserving stretch/compression on the two sides of the computational box of dimensions $L_x \times L_y$. Within linear elasticity theory, the shear modulus μ is then given by $\mu = (p_{yy} - p_{xx})/4\epsilon$ for a distortion in which $L_x \rightarrow (1 + \epsilon)L_x$, $L_y \rightarrow (1 - \epsilon)L_y$. Here p_{xx}, p_{yy} are the diagonal elements of the pressure tensor. If the system is not isotropic, as in the case of square networks, one may impose a *simple* shear, for example by shifting the boundaries of the computational box to $x_{\min}(y) = \epsilon y$, $x_{\max}(y) = \epsilon y + L$ where the undeformed box is an $L \times L$ square. In this situation, the shear modulus is given by $\mu = p_{xy}/\epsilon$.

A second method would be to determine the ground state configuration of the unstressed system, calculate the dynamical matrix, and then determine the elastic constants using standard harmonic theory from an appropriate sum in terms of phonon frequencies. This method is inappropriate for soft entropically rigid materials. In such systems, there are floppy regions that undoubtedly give rise to zero-frequency soft modes. The elastic constants determined in this way correspond to the zero temperature elastic constants and would vanish below p_r . Even if there are no floppy modes, only soft modes, at temperatures of interest the amplitudes of oscillations of the modes will be most likely out of the harmonic regime, and essentially act as floppy modes.

The third method, known as equilibrium fluctuation method also starts from the undeformed system. The elastic constants are obtained directly from the microscopic fluctuations, using a formal expression of the second derivative of the free energy¹⁴.

The first and third methods are suitable for molecular dynamics simulations. The first method calculates the changes in the pressure tensor upon deformation. Since these changes are only a small percentage of the total, this method is not the most accurate for energetically

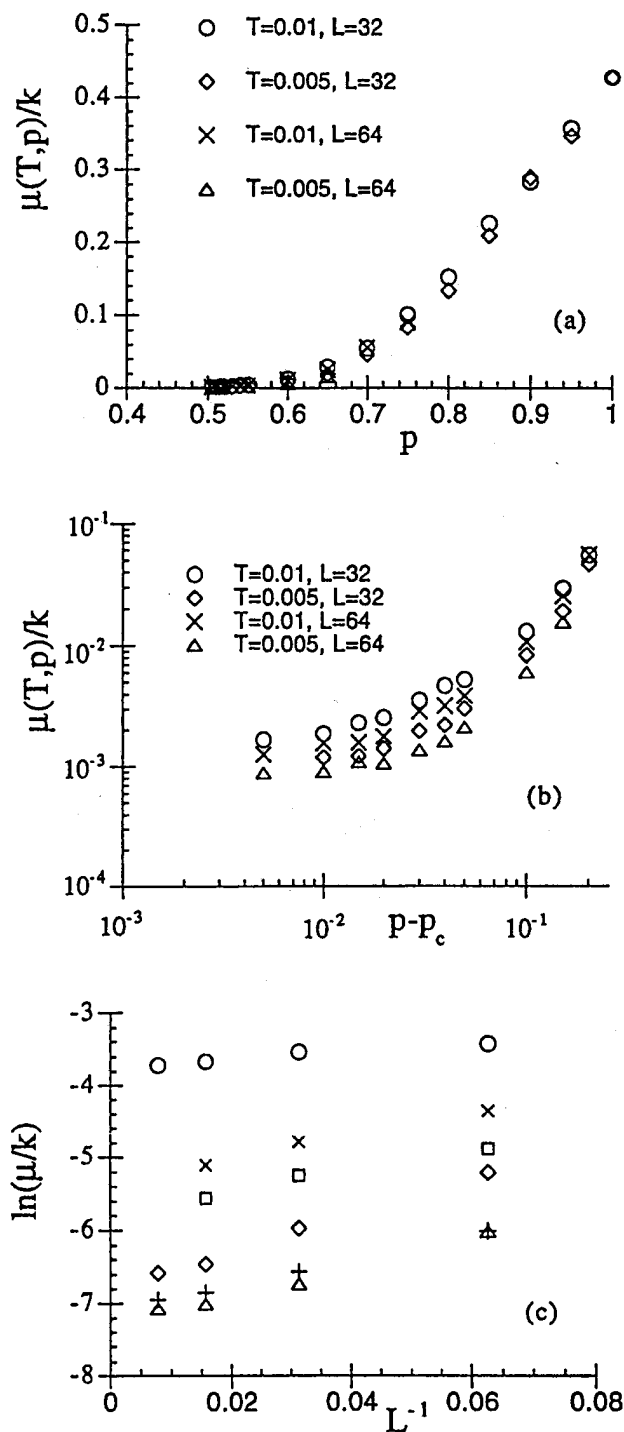


Figure 5. The dimensionless shear modulus μ / k plotted as function of concentration p of particles for site-diluted triangular lattices of size $L = 32$ and $L = 64$ for reduced temperatures $T = .005kr_0^2/k_B$ and $T = .01kr_0^2/k_B$. Part (a) contains data over the entire concentration range $p_c < p \leq 1$ whereas part (b) focuses on the regime $p_c < p < p_r$. Part (c): The logarithm of the shear modulus of the site-diluted triangular network plotted as function of L^{-1} for $T = .01kr_0^2/k_B$ for $p = 0.65$ (circles), $p = 0.55$ (squares), $p = 0.515$ (diamonds) and $T = .005kr_0^2/k_B$ for $p = 0.6$ (\times), $p = 0.52$ (crosses) and $p = 0.51$ (triangles). The values of L are 16, 32, 64, and 128. Note that all concentrations are below p_r . (From Ref. 11)

rigid materials. In addition deformations for identical regions may depend on the size of the computational cell within which they are imbedded, leading to noticeable finite size effects. But it is a very robust method since it measures a macroscopic average quantity which is a direct sum of measurables, force and velocity terms. The third method which is based on a fluctuation - dissipation theorem is the most accurate for rigid materials, because no deformations are made to the system and averaging is done at the microscopic level. This has the added advantage of reducing finite size effects. There are, however, intrinsic difficulties in applying it to soft inhomogeneous materials; if the ground state of the system is not unique, fluctuations are large and convergence is very slow¹⁵. In this paper we report the results from the first method, the stress-strain method.

The shear modulus of finite size-samples

As mentioned above, most of the calculations were done on the site diluted triangular network. With MD simulations at constant volume the changes in the stress tensor were calculated for samples of varying sizes, ranging from 16×16 to 128×128 . For the smaller systems the entire concentration range $0.5 < p \leq 1.0$ of interest was studied and for the larger systems primarily in the range of concentrations close to geometric percolation. For a given p , the largest cluster was identified and all smaller clusters discarded. The equations of motion were then integrated for either 10^6 or 2×10^6 time steps. A time step of $\delta t = 0.0016\sqrt{k/m}$ was chosen and simulations have been carried out for temperatures from $k_B T = 0.00125kr_0^2$ to $k_B T = 0.01kr_0^2$. Although our potential conserves the connectivity of the particles, it is worth noting that for a piecewise linear force function of the same strength but of range about 15% larger than r_0 , the latter temperature is very close to the melting point¹⁶.

Results for the shear modulus as a function of concentration are displayed in Fig. 5 for diluted lattices of size 32×32 and 64×64 for temperatures $T = 0.01kr_0^2/k_B$ and $T = 0.005kr_0^2/k_B$. Fig 5a shows the full range of p . Clearly at $p = p_r$ the shear modulus has not reached zero. Above p_r there is little dependence on temperature or lattice size. Fig. 5b focuses on the region close to p_c where both variables have a significant impact on μ , sufficiently so that it is still clearly visible in a logarithm plot. Since for any sample, percolating or not, the shear modulus is positive definite, μ should approach a finite limit as $p \rightarrow p_c$. Indeed, precisely at p_c the percolation probability for any finite size L is 0.5 and therefore half the samples presumably make a positive contribution to the estimate of μ whereas the non-percolating ones serve only to reduce the mean value.

The shear modulus in the thermodynamic limit

The logarithm of the shear modulus plotted as a function of L^{-1} shows a non-zero limit for $L = \infty$ for all concentrations studied, the closest to p_c being $p = 0.51$ (see Fig. 5c). This fact alone strongly suggests that at finite temperature the rigidity onset coincides with the geometric or connectivity percolation. Physical arguments can also be made to support that assertion. The network near percolation can be viewed as a system of blobs, links and nodes with the overall symmetry of the original lattice^{17,18}. Its elastic response is that of a network of entropic springs, which respond as discussed earlier as a lattice under tension. Therefore as a simple calculation using a stretched string shows, simple connectivity suffices to have a non-zero response to a simple shear, which is proportional to the tension in the string. It is therefore very natural to take p_c as the onset of entropic rigidity.

With this fact established, the behaviour of μ in the neighborhood of p_c can be more conveniently studied. One expects some power law dependence $\mu(T, p) \propto (p - p_c)^f$. This behaviour is masked in our data by finite size effects. With the availability of data for several sizes, a scaling argument can be used to obtain μ in the thermodynamic limit. The relevant

length scales are reasonably assumed to be L , and the correlation length ξ , which approaches infinity at percolation as $(p-p_c)^{-\nu}$. These choices lead to the ansatz $\mu(L, p) = L^{-\alpha}\Phi(L/\xi(p))$ where for large x , the scaling function $\Phi(x) \sim x^\beta$, with α and β constants to be determined. Requiring that at large L , $\mu(T, p) \propto (p - p_c)^f$, leads to $\mu(L, p) = L^{-f/\nu}\Phi(L/\xi(p))$ and the asymptotic behaviour for $\Phi(x) \sim x^{f/\nu}$.

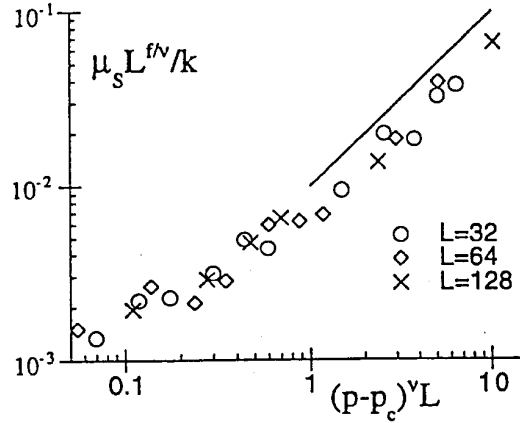


Figure 6. Finite-size scaling analysis of the entropic piece of the shear modulus for lattices of size $L = 32, 64,$ and 128 . The scaling ansatz is $\mu_S(L, p) = L^{-f/\nu}\Phi((p-p_c)L^{1/\nu})$. The choice $f = \nu = 4/3$ produces a very reasonable collapse of the data. As well, the straight line is the expected form of the scaling function $\Phi(x) \sim x^{f/\nu}$ as $x \rightarrow \infty$ with $f = \nu$. (From Ref. 11)

Since $p_c = 0.5$ and $\nu = 4/3$ exactly, the finite size scaling analysis requires only the exponent f to be varied. The results of such an analysis are shown in Fig. 6 where $L^{f/\nu}\mu_S(L, p)/k$ is plotted as function of $L(p - p_c)^\nu$ for $f = \nu = 4/3$. The quantity μ_S is the *entropic* contribution to the shear modulus which is given by ¹

$$\mu_S(L, p) = T \left(\frac{\partial \mu}{\partial T} \right)_{p, L} \quad (11)$$

The piece of the shear modulus due to the internal energy $\mu_E = \mu - \mu_S$ is much smaller than μ_S for $p < p_r$ and should be at least second order in the temperature T . In any case, subtracting off this piece of the shear modulus has a smoothing effect on the data and improves the scaling analysis. Although the data are rather noisy, the collapse of the data in Fig. 6 becomes noticeably worse if the exponent f is increased or decreased by more than 0.1. We therefore conclude that $f = 1.33 \pm 0.10$. The expected power law for the asymptotic form of $\Phi(x) \sim x^{f/\nu}$ is also shown in the form of the solid line again for $f = \nu$. It is clear that the data are at least consistent with this behavior. We note, however, that the currently accepted value of the exponent t for the conductivity of two-dimensional random resistor networks is $t \approx 1.3$ and our data clearly cannot distinguish between the alternatives $f = \nu$ or the de Gennes prediction $f = t$.

As further evidence for the conclusion that entropic rigidity persists to $p = p_c$, we display the shear modulus of triangular bond-diluted networks. These data come from work in progress¹⁹ and are not yet extensive or well converged enough to permit the finite size scaling analysis discussed above. However, it is clear from Fig. 7 that there is entropic elasticity for $p > p_c$.

Theoretical models

One can construct a simple theory for the entropic elasticity of diluted networks in close analogy with the classical theory of rubber elasticity. One ingredient is the blobs, links and nodes picture^{17,18} of a diluted network near the percolation concentration. The nodes are connected by strands made of blobs separated by links of single bonds. The network of nodes has on average the symmetry of the original lattice. A second ingredient is that the entropic springs behave as springs of zero length, and hence the forces are separable. This turns it into a one-dimensional problem, or a scalar problem. These two aspects link the entropic elasticity problem to the random resistor problem. Here we will discuss the elasticity of the diluted network within the affine approximation of the classical theory of rubber elasticity.

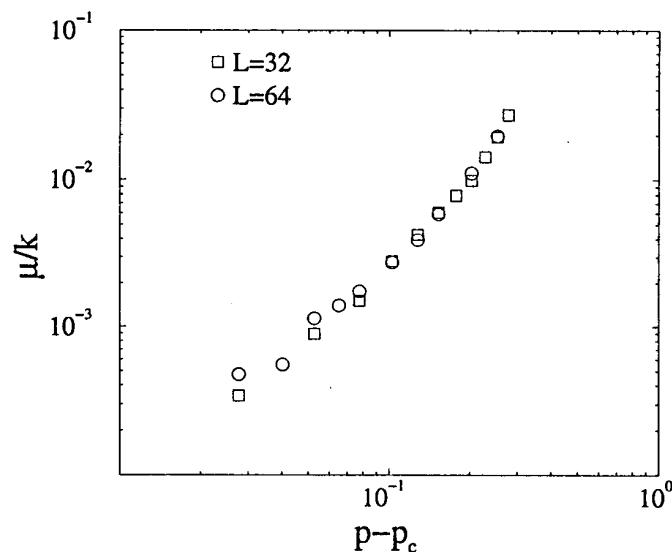


Figure 7. Shear modulus for the bond diluted triangular lattice as a function of bond concentration p for two lattice sizes, 32×32 and 64×64 at the temperature $T = .005kr_0^2/k_B$.

The nodes at which different links or filaments are joined are the analog of permanent crosslinks in a system of randomly crosslinked macromolecules. The links themselves consist in part of single strands and in part of more rigid blobs. If such a tenuous system is deformed, one expects that the principal effect will be to lengthen (shorten) the distance between nodes and thus to modify the entropy of the filaments. Consider two nodes i, j with relative position X_{ij}, Y_{ij} . If a distortion characterized by stretching factors (λ_x, λ_y) is applied to the system and if the nodes follow this distortion in an affine manner, we expect that the entropy change of the filament connecting these nodes due to this distortion will be

$$\Delta S_{ij} = -\frac{k_B}{a^2} \frac{R_{ij}^2(\lambda_x, \lambda_y) - R_{ij}^2(1, 1)}{N} \quad (12)$$

where a is the nearest neighbor distance, N the number of links (single bonds) between the nodes and $R^2 = X_{ij}^2 + Y_{ij}^2$. This expression is obtained by treating the filament as a Gaussian random walk as is usually done in the classical theories of rubber elasticity. Averaging over all pairs of nodes for $\lambda_x = 1 + \epsilon$, $\lambda_y = 1 - \epsilon$, we obtain the estimate

$$\mu = \frac{\Delta F}{2\epsilon^2 A} = \frac{k_B T \Delta S}{2\epsilon^2 A} = \frac{k_B T N_{st}}{2a^2 A} \left\langle \frac{R^2(1, 1)}{N} \right\rangle \quad (13)$$

where N_{st} is the number of links, A the area of the system and ΔF the change in Helmholtz free energy obtained by ignoring any changes in internal energy.

From studies of percolation clusters^{18,20}, we have $N_{st}/A \sim \xi^{-2} \sim (p - p_c)^{2\nu}$ and $\langle R^2/N \rangle \sim \xi^2/N \sim (p - p_c)^{1-2\nu}$ ²⁰. Therefore, on the basis of this very simple picture, we obtain $\mu \sim (p - p_c)$, *i.e.* $f = 1$ which is *not* consistent with the results of our simulations. Of course, there are at least two aspects of the above argument that are suspect. First, the assumption that the deformation of the system is affine clearly ignores fluctuations in density and therefore of local rigidity. Second and probably more important is the fact that we have ignored the self-similarity of percolation clusters²¹ and modeled the known fractal structure by a network of nodes that effectively has fractal dimension $D = 2$. It is perhaps worth noting that an analogous calculation^{2,6} of the conductivity of random resistor networks near the percolation point also predicts $\sigma \sim (p - p_c)$ which is similarly inconsistent with the corresponding simulation data.

DISCUSSION AND CONCLUSION

In this paper we introduced a new dimension to the problem of the rigidity of random networks, that brought about by the effects of temperature. These will be important in the region between the connectivity percolation and the rigidity percolation, where the network is soft, and its entropy is large.

The onset of entropic rigidity has to occur at the geometric percolation point. It is a thermodynamic rigidity tied to the change in entropy upon deformation. The closest that one can come to think in terms of mechanical rigidity is to note that entropic springs are equivalent to stretched springs, and therefore a single spring under shear will have a lateral linear restoring force. This is indeed quite contrary to the situation of an unstretched spring — the whole issue of mechanical rigidity changes if the system is stressed²².

The displacement of the critical point from p_r to p_c at finite temperature, raises a number of interesting issue about the critical behaviour of this system. At finite temperature, there will be a crossover from entropic to mechanical rigidity in the neighborhood of p_r .

The models that we have studied to date are two-dimensional. Exploring three dimensional equivalents would obviously help to distinguish between the possibilities $f = \nu$ and $f = t$: for the 3D *f.c.c* lattice, the conductivity exponent $t \approx 2$ and $\nu \approx 0.88$.

Glasses are random networks, usually with bond-bending forces. Near percolation with strands longer than the persistence length of connecting bonds, we will have a situation similar to the one we studied, albeit three dimensional. The onset of entropic rigidity is therefore expected to occur at the percolation threshold. If data was available on the temperature variation of the elastic constants, the entropic contribution to the elastic constants could be extracted, as discussed in the section titled Entropic Rigidity. The entropic contribution should rise linearly with temperature, and will have an effect on the coefficient of thermal expansivity which is expected to decrease with temperature. Temperature increases the force constant and therefore for equal tension the elongation will be smaller: entropic solids like rubber shrink with increasing temperature.

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REFERENCES

1. L.R.G. Treloar, *The Physics of Rubber Elasticity*, Clarendon, Oxford (1975).
2. P.G. de Gennes, *J. Phys. (Paris) Lett.* 37:L1 (1976).
3. C. Moukarzel and P.M. Duxbury, *Phys. Rev. Lett.* 75:4055 (1995); D.J. Jacobs and M.F. Thorpe, *Phys. Rev. E* 53:3682 (1996).
4. S. Feng and P.N. Sen, *Phys. Rev. Lett.* 52:1891 (1984).
5. S. Feng, M.F. Thorpe and E. Garboczi *Phys. Rev. B* 31:276 (1985).
6. Y. Kantor and I. Webman, *Phys. Rev. Lett.* 52:1891 (1984).
7. F. Reif, *Fundamentals of Statistical and Thermal Physics*, McGraw-Hill, New York, N.Y. (1965).
8. J.E. Mark and B. Erman, *Rubberlike Elasticity: a Molecular Primer*, John Wiley and Sons, New York (1988).
9. P.G. de Gennes, *Scaling Concepts in Polymer Physics*, Cornell University Press, Ithaca, N.Y. (1979).
10. P.J. Flory, *Principles of Polymer Chemistry*, Cornell University Press, Ithaca, N.Y. (1953).
11. M. Plischke and B. Joós, *Phys. Rev. Lett.* 80:4907 (1998).
12. C. Moukarzel and P.M. Duxbury, *Comparison of Connectivity and Rigidity Percolation*, an article in this volume.
13. S. Arbabi and M. Sahini, *Phys. Rev. B* 47:695 (1993).
14. Z. Zhou and B. Joós, *Phys. Rev. B* 54:3841 (1996).
15. Z. Zhou and B. Joós, unpublished.
16. J.A. Combs, *Phys. Rev. Lett.* 61:714 (1988); *Phys. Rev. B* 38:6751 (1988).
17. H.E. Stanley, *J. Phys. A* 10:L211 (1977).
18. A. Coniglio, *Phys. Rev. Lett.* 46:250 (1981).
19. D.C. Vernon, M. Plischke and B. Joós, to be published.
20. A. Coniglio, *J. Phys. A* 15:3829 (1982).
21. H.J. Herrmann and H.E. Stanley, *Phys. Rev. Lett.* 53:1121 (1984).
22. S. Alexander, *Phys. Rep.* 296:65 (1998).