

## Entropic Elasticity of Diluted Central Force Networks

Michael Plischke

*Physics Department, Simon Fraser University, Burnaby, British Columbia, Canada V5A 1S6*

Béla Joós

*Ottawa Carleton Institute of Physics, University of Ottawa Campus, Ottawa, Ontario, Canada K1N 6N5*  
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At zero temperature, the elastic constants of diluted central force networks are known to vanish at a concentration  $p_r$  (of either sites or bonds) that is substantially higher than the corresponding geometric percolation concentration  $p_c$ . We study such diluted lattices at finite temperatures and show that there is an entropic contribution to the moduli similar to that in cross-linked polymer networks. This entropic elasticity vanishes at  $p_c$  and increases linearly with  $T$  for  $p_c < p < p_r$ . We also find that the shear modulus at fixed  $T$  vanishes as  $\mu \sim (p - p_c)^f$  with an exponent  $f$  that is, within numerical uncertainty, the same as the exponent  $t$  that describes the conductivity of randomly diluted resistor networks. [S0031-9007(98)06270-X]

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In systems with no bond bending forces, multiple connectivity is required 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 [1–3]. There are, however, classes of systems, in particular, microscopic ones, where temperature through the collisions it produces, introduces an additional component to the rigidity, entropic in nature. We show that the onset for this component in a randomly diluted central force network does occur at the percolation threshold. Near the zero temperature rigidity onset there is a crossover from the entropically to the energetically derived elastic response.

From a larger perspective, systems with no bond bending forces are the most economical structures in Nature, hence their importance in large scale engineering structures and their prevalence in living organisms [4].

Feng and Sen [1] were the first to point out that, at zero temperature, 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 theory [2] 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  $p_r = 1$ . 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 point [5].

One of the issues that has generated much work is the nature of the rigidity transition. Some years ago, de Gennes [6] argued that the elastic constants should vanish at the percolation point as  $(p - p_c)^f$  with an exponent  $f$  that is identical to the exponent  $t$  that describes the conductance of a random resistor network near the percolation point. His argument technically does not apply to either a generic central force network or to a network in which there are bond-bending forces and, indeed, although the exponent  $f$  has not been accurately determined until recently [3], it is clear that  $f \neq t$  at  $T = 0$ .

In this Letter, we consider the problem of elasticity of disordered lattices from a different point of view. In particular, we address the following questions: (i) Do diluted systems have nonzero elastic constants below  $p_r$  at finite temperatures due to entropic effects? (ii) If so, do they vanish at  $p_c$  or at some intermediate concentration? (iii) What is the exponent  $f$ ? We are motivated in this work in part by some puzzling aspects of our computer simulations of randomly cross-linked polymers [7,8]. In this work which is, because of the time consuming nature of the calculations, restricted to rather small systems we found a significant gap between the density of cross-links at which the order parameter of the amorphous phase vanishes and that at which percolation occurs. This result—which may be a finite-size effect—is counterintuitive and violates the basic assumptions of the theory of rubber elasticity. Rigidity in cross-linked macromolecules (rubber) is entropic in origin [9] and to obtain some insight into this complicated system, it is of interest to study other purely entropic systems, especially if more extensive simulations are feasible. Presumably, if the finite temperature elastic constants in our central force networks vanish at the percolation point then the same should occur in cross-linked polymers.

In this Letter, we report on molecular dynamics (MD) simulations of site-diluted triangular lattices in which nearest neighbors interact via the circularly symmetric potential  $V_{nn}(r_{ij}) = \frac{1}{2}k(r_{ij} - r_0)^2$  and where more distant neighbors are noninteracting. For this system, geometric percolation occurs at  $p_c = 0.5$  and rigidity percolation (at  $T = 0$ ) at  $p_r \approx 0.71$ . Our simulations are constant temperature, constant volume MD [10] with a time step  $\delta t = 0.0016\sqrt{k/m}$ , and have been carried out for temperatures from  $k_B T = 0.00125kr_0^2$  to  $k_B T = 0.01kr_0^2$ . The perfect system is unstressed. 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 finite range, the latter temperature is very close to the melting point [11]. We have studied lattice sizes from  $16 \times 16$  to  $128 \times 128$ , for the smaller systems over the entire concentration range  $0.5 < p \leq 1.0$  of interest 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  $2 \times 10^6$  time steps. Periodic boundary conditions were used in all cases.

To obtain the shear modulus we imposed a pure shear deformation, i.e., an area preserving stretch/compression of 1% on the two sides of the computational box. Within linear elasticity theory, the shear modulus  $\mu$  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. In practice, we have stretched each sample in both directions and averaged the results of the two simulations. As in the case of cross-linked polymers, the fluctuations of the shear modulus from sample to sample are substantial and it is necessary to average the results over a large number of different realizations for each concentration of sites, especially in the critical region. For lattices of dimension  $32 \times 32$  we have typically obtained well converged results from 100 to 200 samples whereas for lattices of size  $128 \times 128$  we have found 30 to 50 samples to be sufficient.

In Fig. 1 we display the shear modulus as function of concentration for diluted lattices of size  $32 \times 32$  and  $64 \times 64$  for temperatures  $T = 0.01kr_0^2/k_B$  and  $T = 0.005kr_0^2/k_B$  and as function of system size  $L$  for several values of  $p$  at these same two temperatures. Part (a) of this figure shows the well-known decrease to almost zero of the shear modulus near the rigidity concentration  $p_r \approx 0.71$ . Above this concentration,  $\mu$  is essentially independent of lattice size and not very strongly dependent on temperature—the internal energy provides the dominant contribution to  $\mu$ . In part (b) of this figure, we have replotted the data for the range  $p_c < p < p_r$  and both thermal and finite-size effects are clearly visible. In the thermodynamic limit  $L \rightarrow \infty$  one expects that the shear modulus should vanish according to a power law  $\mu(T, p) \propto (p - p_c)^f$  but this behavior is masked for systems of our size by these finite-size effects [12]. In particular, since for any

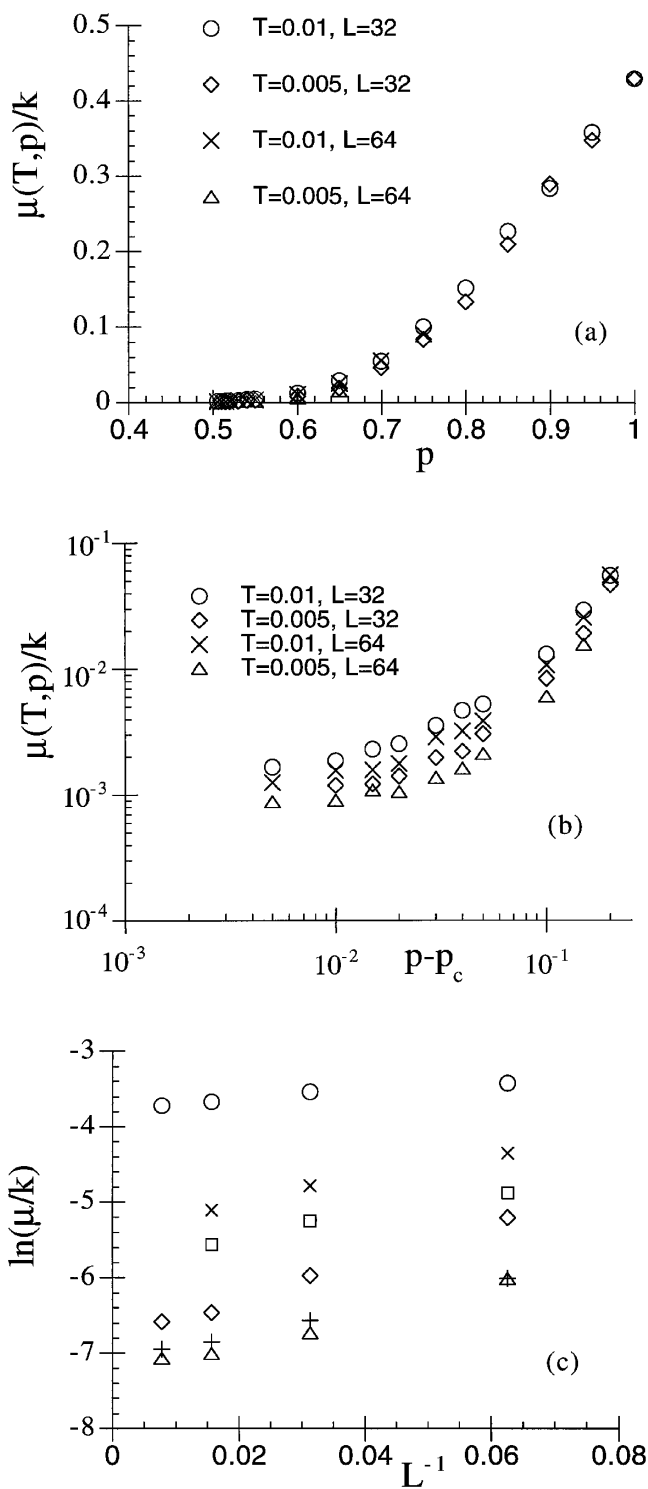


FIG. 1. The dimensionless shear modulus  $\mu/k$  plotted as function of concentration  $p$  of particles for lattices of size  $L = 32$  and  $L = 64$  for reduced temperatures  $T = 0.005kr_0^2/k_B$  and  $T = 0.01kr_0^2/k_B$ . Part (a) contains data over the entire concentration range  $p_c < p \leq 1.0$  whereas part (b) focuses on the regime  $p_c < p < p_r$ . Part (c): The logarithm of the shear modulus plotted as function of  $L^{-1}$  for  $T = 0.01kr_0^2/k_B$  for  $p = 0.65$  (circles),  $p = 0.55$  (squares),  $p = 0.515$  (diamonds), and  $T = 0.005kr_0^2/k_B$  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  $p_r$ .

sample, whether percolating or not, the shear modulus is positive semidefinite, it is not surprising that  $\mu$  seems to 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  $\mu$  whereas the nonpercolating ones serve only to reduce the mean value.

Part (c) of Fig. 1 shows the  $L$  dependence of the shear modulus for  $T = 0.01kr_0^2/k_B$  and  $T = 0.005kr_0^2/k_B$  for a selection of concentrations  $p$  in the range  $p_c < p < p_r$ . Although there is a significant size dependence, it is clear from the data that the shear modulus approaches a finite limit as  $L \rightarrow \infty$  even for the smallest concentration  $p = 0.51$  at  $T = 0.005kr_0^2/k_B$ . We therefore conclude that at finite temperature the onset of rigidity coincides with geometric percolation.

Having established the existence of entropic rigidity for  $p > p_c$ , we attempt to estimate the exponent  $f$  by carrying out a finite-size scaling analysis. The relevant length scales are reasonably assumed to be  $L$ , and the correlation length  $\xi$ , which approaches infinity at percolation as  $(p - p_c)^{-\nu}$ . These choices lead to the ansatz  $\mu(L, p) = L^{-f/\nu} \Phi(L/\xi(p))$ , where for large  $x$ , the scaling function  $\Phi(x) \sim x^{f/\nu}$ . Fortunately, the percolation concentration  $p_c$  and correlation length exponent  $\nu$  are known to be  $p_c = 0.5$  and  $\nu = 4/3$  exactly. This fact allows a finite-size scaling analysis in which only the exponent  $f$  needs to be varied. The results of such an analysis are shown in Fig. 2 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  $\mu_S$  is the entropic contribution to the shear modulus which is given by [9]

$$\mu_S(L, p) = T \left( \frac{\partial \mu}{\partial T} \right)_{p, L}. \quad (1)$$

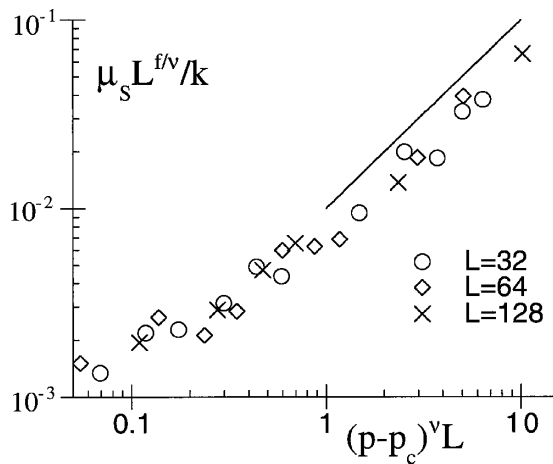


FIG. 2. Finite-size scaling analysis of the entropic piece of the shear modulus for lattices of size  $L = 32, 64,$  and  $128$ . The scaling ansatz is  $\mu_S(L, p) = L^{-f/\nu} \Phi((p - p_c)^\nu L)$ . The choice  $f = \nu = 4/3$  produces a very reasonable collapse of the data. As well, the straight line is the expected form of the scaling function  $\Phi(x) \sim x^{f/\nu}$  as  $x \rightarrow \infty$  with  $f = \nu$ .

The piece of the shear modulus due to the internal energy  $\mu_E = \mu - \mu_S$  is much smaller than  $\mu_S$  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 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 in Fig. 2 again for  $f = \nu$ . It is clear that the data are at least consistent with this behavior.

One can construct a simple theory for the entropic elasticity of diluted networks in close analogy with the classical theory of rubber elasticity. We begin with the blobs, links, and nodes picture [13,14] of a diluted network near the percolation concentration. The nodes at which different links or filaments are joined are the analog of permanent cross-links in a system of randomly cross-linked 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  $\lambda_x, \lambda_y$  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

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

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

$$\mu = \frac{\Delta F}{2\epsilon^2 A} = -\frac{k_B T \Delta S}{2\epsilon^2 A} = \frac{k_B T}{2a^2} \frac{N_{st}}{A} \left\langle \frac{R^2(1, 1)}{N} \right\rangle, \quad (3)$$

where  $N_{st}$  is the number of strands,  $A$  the area of the system, and  $\Delta F$  the change in Helmholtz free energy obtained by ignoring any changes in internal energy.

From studies of percolation clusters [14,15], we have  $N_{st}/A \sim \xi^{-2} \sim (p - p_c)^{2\nu}$  and  $\langle R^2/N \rangle \sim \xi^2/N \sim (p - p_c)^{1-2\nu}$  [15]. 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 clusters [16] 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 [5,6] of the conductivity of random resistor networks near the percolation point also predicts  $\sigma \sim p - p_c$  [17] which is similarly inconsistent with the corresponding simulation data.

We also note that our estimate  $f \approx \nu = 4/3 \pm 0.1$  is consistent with de Gennes's argument [6] that  $f = t \approx 1.3$  [18], where  $t$  describes the critical behavior of the conductivity of the aforementioned random resistor networks near percolation. This argument, which fails for energetic elasticity at  $T = 0$  may be correct for the entropic elasticity considered here. The crucial point is the Gaussian (random walk) expression for the entropy change of the links [Eq. (2)] which puts the elasticity problem into the scalar rather than vector class [5]. We conjecture that this part of the argument will survive a more sophisticated treatment of the geometry of the fractal structure and that for  $T \neq 0$ ,  $f = t$ .

In summary, we have shown by numerical simulation that the finite-temperature behavior of the elastic constants of central-force networks is controlled by geometric percolation rather than by rigidity percolation. The elastic constants remain finite, albeit small, for all concentrations  $p_r > p > p_c$ , i.e., the rigidity percolation fixed point is accessible only at  $T = 0$ . For any finite temperature, the energetic part of the elastic constants becomes quite small for  $p \approx p_r$  but this is merely a crossover effect. It is interesting that central-force networks are nevertheless special, even at finite temperatures: If there are bond-bending forces, the energetic piece of the shear and bulk moduli presumably remains finite and at least of the same order of magnitude as the entropic piece and therefore the de Gennes argument that  $f = t$  may not apply to these systems.

Finally, we comment briefly on the relation of these results to our previous work on randomly cross-linked polymers [7,8]. Our initial work on both the order parameter and shear modulus of the amorphous phase of these systems seemed to indicate that there is a gap between the onset of geometric percolation and both order and rigidity. These early studies [7] were for systems containing a small number ( $\leq 100$ ) of chains. For these systems, neither the percolation concentration nor the critical cross-link density at which the order parameter vanishes are known exactly. It is possible to force these two to coincide but at the cost of an unrealistically large order parameter exponent  $\beta \geq 1.5$ . More recent simulations [8] have involved considerably larger systems (up to 500 chains) and the gap between the percolation cross-link density and the critical cross-link density, albeit still there, has narrowed consider-

ably. The finite-size effects in the present study are much smaller than in the polymeric systems and we now believe that in the thermodynamic limit percolation and rigidity also coincide in cross-linked polymers.

As far as future work is concerned, it would clearly be of interest to investigate three dimensional central force networks, i.e., the fcc lattice where the conductivity exponent  $t \approx 2$  with  $\nu \approx 0.88$ . This would help to rule out or support the possibility  $f = \nu$  left open by the present Letter. As well, it may be advantageous to study the bond-diluted triangular lattice since the gap between rigidity percolation and geometric percolation is almost 2 times as large as it is for site dilution, which means that crossover effects should be less important than in the present case. Such work is presently under way [19].

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