# Critical behavior of entropic shear rigidity

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We report on extensive molecular dynamics (MD) simulations of a model for gels in both two and three dimensions. The model consists of randomly cross-linked monomers with a concentration $p$ of cross-links above the percolation concentration so that the system is in the amorphous solid phase. As the concentration of cross-links approaches the percolation concentration, the entropic shear modulus vanishes as $G \sim (p-p_c)^t$ with $t \approx 1.9$ in three dimensions and $t \approx 1.3$ in two dimensions. These results hold whether or not the background fluid consisting of finite clusters is retained in the system. These results are also consistent with our previous calculations and with a conjecture of de Gennes but not with recent analytical results and another body of simulations.

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## I. INTRODUCTION

The nature of the critical behavior of the entropic rigidity of randomly cross-linked polymers and monomers continues to be the subject of debate and some controversy. Examples of such systems are rubber (chemically cross-linked macromolecules) and chemical gels (permanently cross-linked molecules). At nonzero temperature, these systems develop a shear modulus that is entropic in nature in the range $p_c < p \leqslant p_r$, if the cross-linking forces are central in nature. Here $p_c$ is the geometric percolation concentration and $p_r$ is the rigidity percolation concentration. Above $p_r$, energetic effects set in [1]. Some time ago, de Gennes [2] argued that the critical behavior of the shear modulus as $p \to p_c$ should be the same as that of the conductivity $\Sigma$ in a disordered mixture of conductors and insulators. The conductivity problem has been extensively studied with the result $\Sigma(p) \sim (p-p_c)^t$ with $t \approx 1.3$ in two dimensions and $t \approx 2.0$ in three dimensions. Early numerical results for disordered mechanical networks [3,4] seemed to support the de Gennes conclusion. However, the models used in these early simulations were "phantom" networks in which the particles were cross-linked through simple springs without hard cores. Moreover, only the percolating network was retained in the simulations and the calculations were performed in a constant volume ensemble. Since the values of response functions are ensemble dependent, one could argue that a different conclusion might be obtained in a constant-pressure ensemble. Subsequent work [5,6] showed that the addition of hard cores is irrelevant in both two and three dimensions. In these simulations both the percolating cluster and the finite clusters were kept. However, in at least one case [5] there is considerable variation of the pressure.

A very different conclusion was reached by a number of groups. A heuristic scaling argument [7] yielded $t = d\nu$ where $d$ is the dimensionality and $\nu$ is the correlation length exponent for geometric percolation. Since $\nu(d=2) = 4/3$ and $\nu(d=3) \approx 0.88$, this prediction produces $t(d=2) = 8/3$ and $t(d=3) \approx 2.64$ which are very different values from the de Gennes conjecture and from our results. Results consistent with the scaling argument have also been obtained from simulations of a lattice model of cross-linked monomers [8] but, in our view, these calculations are questionable for reasons that we will discuss in Sec. IV. Finally, a recent renormalization group calculation [9] that employs as a principal assumption that there is a single divergent length at $p_c$, namely, the geometric percolation correlation length $\xi(p)$, also yields $t = d\nu$. As far as the experimental situation is concerned, there is a similar division of results between values of the exponent consistent with the de Gennes conjecture [10] and with $t = d\nu$ [11].

In this paper, we report on simulations of permanently cross-linked monomers in both two and three dimensions in the amorphous solid regime. We consider the situation with the finite clusters retained as well as the case where only the percolating cluster is simulated. When the background fluid forms part of the system, the pressure is almost constant over the entire range of parameters. Our results are the same for both cases and entirely consistent with the de Gennes conjecture. We also present evidence that, as the percolation point is approached, the density-density correlation function of the background fluid becomes long ranged and diverges at $p_c$. This may explain why the renormalization group calculations of [9] do not agree with our results.

The remainder of this paper is organized as follows. In Sec. II we briefly describe our model and the computational details. Section III contains the results of the calculations and Sec. IV contains a discussion of the results and an outlook for future work.

## II. MODEL AND COMPUTATIONAL DETAILS

We consider systems of soft disks of functionality $f=4$ in two dimensions and soft spheres with $f=6$ in three dimensions. The particles are initially placed on the vertices of a square or simple cubic lattice and instantaneously and irreversibly connected to nearest neighbors with a probability $p$. The square and cubic topology have the advantage that rigidity percolation occurs at $p_r = 1$ and that the shear modulus is entropic over the entire range of $p$. The cross-linking process is that of simple bond percolation on the relevant lattice for which the percolation probability is $p_c(d=2) = 1/2$ and $p_c(d=3) \approx 0.2488$ [12]. The potential that connects the particles is $V_{nn}(r) = k(r-r_0)^2/2$, with $r_0$ the lattice spacing in the

 

initial configuration. In addition to the bonding potential, all particles interact through the steeply repulsive pair potential $V_{rep}=\epsilon(\sigma/r)^{36}$ which, although technically "soft," is effectively a hard core potential. Once the cross-linking process is completed, the particles are free to move anywhere in the computational box, subject to periodic boundary conditions. The areal and volume densities are $\rho\sigma^2=0.75$ and $\rho\sigma^3=0.4$ which means that the un-cross-linked systems are simple liquids. We take $\sigma$ to be our unit of length and $\epsilon$ to be the unit of energy. The temperature is set to $k_BT=\epsilon$ and the spring stiffness to $k=5\epsilon/\sigma^2$.

After cross-linking, the system is evolved through Brownian dynamics [14] with a basic time step $\delta t=0.005\sqrt{m\sigma^2/\epsilon}$ until equilibrium has been attained, typically for $1000L^2$ time steps [13], where the total number of particles $N=L^2$ in $d=2$ and $N=L^3$ in $d=3$. In two dimensions we were able to simulate systems up to size $L=128$ or 16 384 particles whereas, for $d=3$, the largest systems had $L=32$ or 32 768 particles. For each realization of the cross-linking for a given $p$, we use a virial equation to calculate the elements of the stress tensor $\sigma_{\alpha\beta}$, first for the undistorted computational box and then, after reequilibration, for a computational box that has been sheared by an amount $\gamma$ along the $z$ axis. Reequilibration is necessary because all particles are initially displaced affinely, e.g., $x_i'=x_i+\gamma z_i$. The shear modulus of a given sample is then obtained from

$$G=-\frac{\sigma_{xz}(\gamma)-\sigma_{xz}(0)}{\gamma} \tag{1}$$

and this quantity is averaged over different cross-linkings at fixed $p$. We have used a number of values of $\gamma$ ranging from 0.01 to 0.1 to check that the response is linear. The results reported in Sec. III were primarily obtained for $\gamma=0.05$, a value large enough to make the fluctuations resulting from division, in Eq. (1), by a small number manageable.

The challenge in these calculations is the sample-to-sample fluctuation of the modulus. For $p>0.75$ in the two-dimensional case, 100 samples are sufficient for convergence but in the range $0.505<p<0.55$, many thousands of samples are required for a reliable estimate of $G$. The diagonal elements of the stress tensor (pressure) converge much more rapidly and one of the checks on the calculation is that they are all the same. For every value of $p$, they are within one part in $10^4$ of each other.

As mentioned above, two types of calculations were carried out. In the majority of these, after cross-linking the finite clusters and single particles were removed from the system and only the spanning cluster retained. For selected values of $L$ the entire system was simulated. The finite clusters in this case provide an internal pressure that tends to collapse the dangling ends toward the backbone. In Figs. 1 and 2 we show the same equilibrated percolating cluster for the two situations. The compactification in the case where the fluid is present is evident.

## III. RESULTS

We separately discuss the two-dimensional and three-dimensional cases.

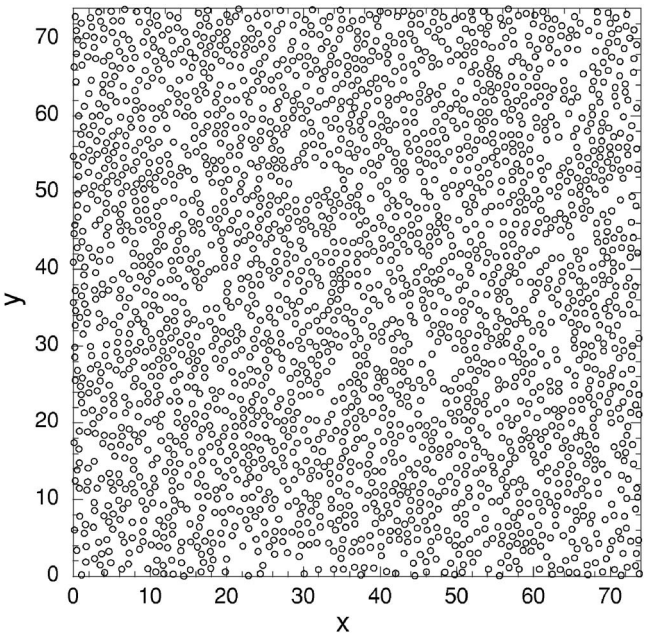


FIG. 1. Equilibrated spanning cluster for $L=64$, $p=0.502$ in two dimensions. The finite clusters were removed after cross-linking.

### A. Two dimensions

In two dimensions, we carried out simulations for systems ranging in size from $N=32^2$ particles to $N=128^2$ particles before cross-linking. For the largest system, we only simulated the percolating cluster but for $L=32$ and 64 we also carried out simulations for the total number of particles. We first display results for the (dimensionless) pressure in Fig. 3. When only the spanning cluster is kept, the pressure decreases as the critical point is approached. At $p_c$, the pressure

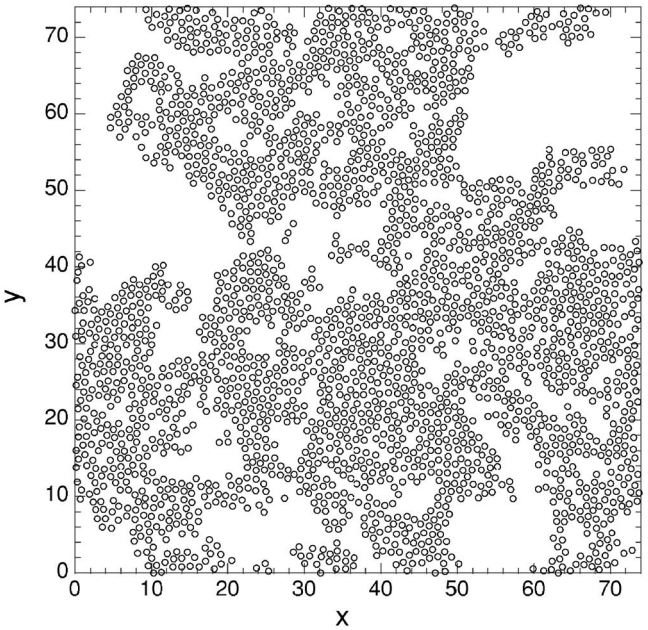


FIG. 2. The same spanning cluster as in Fig. 1, this time equilibrated with the finite clusters included. The finite clusters are not shown for clarity.

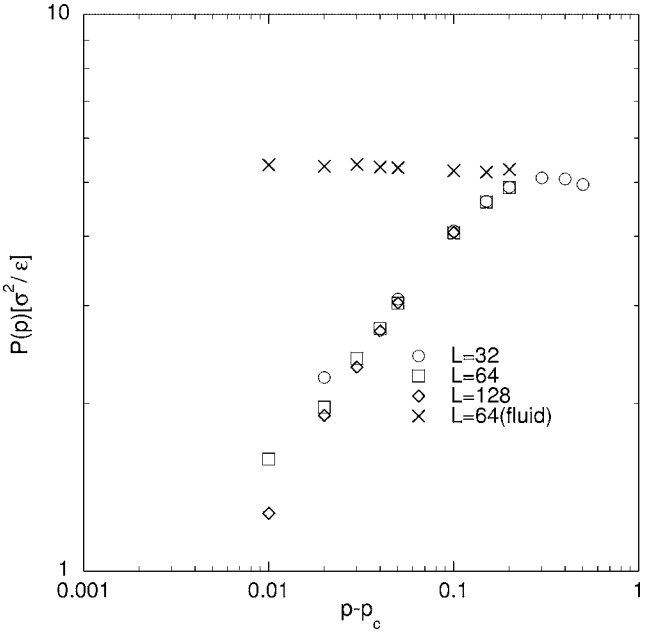


FIG. 3. The pressure $P$ as function of the probability $p$ of cross-links. In the absence of fluid, the pressure decreases as the critical point is approached. Conversely, when the fluid is retained (upper branch), the pressure increases by about 2% over the range $p=0.7-0.52$ as the negative contribution of the cross-links is progressively removed.

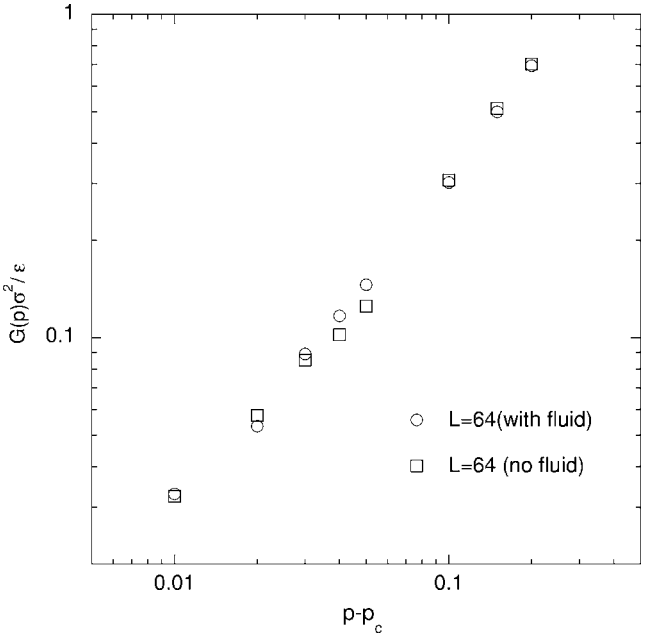


FIG. 4. The shear modulus for $L=64$ for the cases of spanning cluster only and spanning cluster plus fluid. The discrepancy between the two sets of data is a measure of the statistical error.

for a finite system is not zero and there are notable finite-size effects visible in the data. Conversely, when the fluid is retained, the pressure increases by only 2% over the range $p=0.7-0.52$. Therefore, the total system, although the area is fixed, is essentially isobaric. We note that the behavior of the pressure seems to be model dependent: Farago and Kantor [5] simulated a system of hard disks and tethers and found an increasing pressure as $p \to p_c$ and a negative pressure at high $p$. This is an indicator that in their model the contribution of the tethers dominates over that of the hard cores.

We now discusss the behavior of the shear modulus as function of $p$. In Fig. 4 we display $G(p)$ as function of $p-p_c$ for $L=64$ for the two cases of fluid and no background fluid. The two sets of data are essentially identical indicating that the shear modulus is entirely due to the percolating cluster and that the internal pressure and consequent compression of the spanning cluster is irrelevant. We have also calculated the modulus for the two situations for $L=32$ and found the same behavior.

We next display, in Fig. 5, the data for the shear modulus of the spanning cluster for $L=32$, 64, and 128 together with lines representing the functions $G(p) \sim (p-p_c)^{1.3}$ and $G(p) \sim (p-p_c)^{d\nu}$ where $\nu=4/3$ is the correlation length exponent for percolation. It is evident from the data that there are strong finite-size effects and that if $G(p) \sim (p-p_c)^t$ then $t$ is much closer to 1.3 than to $d\nu=8/3$. A simple way of correcting for finite size effects is the finite-size scaling method in which it is assumed that $G(p,L)=L^{-t/\nu}\Phi(L/\xi(p)) = L^{-t/\nu}\Phi((p-p_c)^\nu L)$ where $\Phi$ is a universal function. We plot $L^{t/\nu}G(p,L)$ for the three values of $L$ in Fig. 6, using $t=1.3$ and the known value $\nu=4/3$. The collapse of the data, while not spectacular, is quite reasonable and very much better than with the choice $t=d\nu$. For the choices $t=1.2$ and 1.4 one already sees a systematic separation of the data according to system size and we therefore conclude that $t=1.3\pm0.1$ for this model. For large values of the argument $x$ of the scaling function, the required behavior is $\Phi(x) \sim x^{t/\nu}$ and this line is also shown in the figure. Because the exponent $\beta=5/36$ that controls the probability that a given particle is a member of

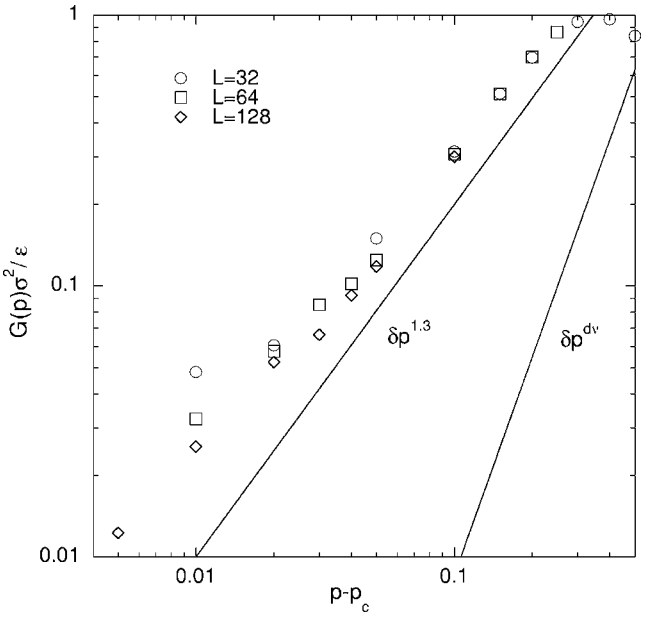


FIG. 5. The shear modulus generated by the spanning cluster as a function of $p-p_c$ for $L=32$, 64, and 128. The straight lines correspond to the critical behavior $G \sim (p-p_c)^t$ with $t=1.3$ (de Gennes) and $t=d\nu$.

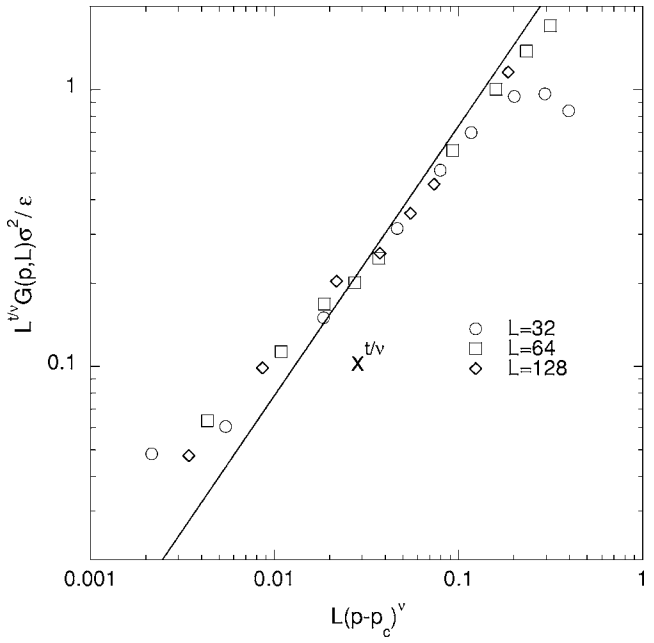


FIG. 6. $L^{t/\nu}G(p,L)$ plotted as a function of $x=L(p-p_c)^\nu$ for various $L$. The straight line is the function $x^{t/\nu}$ which is the required form of the scaling function for large values of the argument.

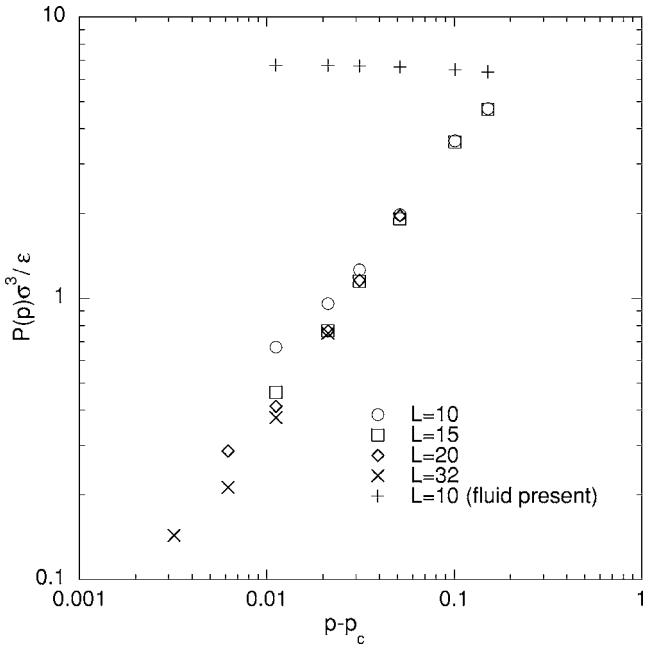


FIG. 7. The dimensionless pressure in three dimensions as a function of $p$ for $L$ ranging from 10 to 32 when only the spanning cluster is present and for $L=10$ (upper branch) where the pressurizing fluid is retained. In this case, the pressure incrases by roughly 5% in the range $p=0.4-0.26$.

the spanning cluster is so small, this probability rises very rapidly, and already at $p=0.7$ more than 99% of the original particles remain after cross-linking and removal of finite clusters. This is undoubtedly one of the reasons that only a rather narrow region of clear power law behavior is seen in Figs. 5 and 6.

The two-dimensional data are clearly inconsistent with the renormalization group prediction $t=d\nu$ [9]. However, two-dimensional systems are somettimes special and we therefore also carried out the three-dimensional calculations that we next discuss.

### B. Three dimensions

In three dimensions, we are limited by computational resources to systems of size $N=32^3$ particles or smaller. We begin, as in the previous subsection, with a discussion of the pressure that is depicted in Fig. 7. In the presence of fluid, the pressure increases slightly (5%) over the range of $p$ $0.4 \geqslant p \geqslant 0.26$ shown. The raw data for the shear modulus are displayed in Fig. 8 for the four values of $L$ with only the spanning cluster present and for $L=10$ in the pressurized case. As in two dimensions, the shear modulus is the same in the pressurized case as when only the spanning cluster is retained. There are evident finite-size effects which set in quite far from the critical point. Also shown on this graph are the functions $(p-p_c)^t$ with $t=1.9$ and $t=d\nu=2.64$. Neither provide a particularly good fit to the data but it is clear that the smaller power represents the data much better. We have used $t=1.9$ rather than $t=2.0$ because in the finite-size scaling analysis shown in Fig. 9 a slightly better collapse of the data is obtained with the smaller exponent. Using the same criteria as in two dimensions, we conclude that $t=1.9\pm0.15$ for the three-dimensional model.

Although the data in both two and three dimensions are plagued by large fluctuations, the conclusion that the de Gennes conjecture is closer to reality (at least for this model) than the scaling hypothesis $t=d\nu$ seems inescapable. We will discuss this further in the next section.

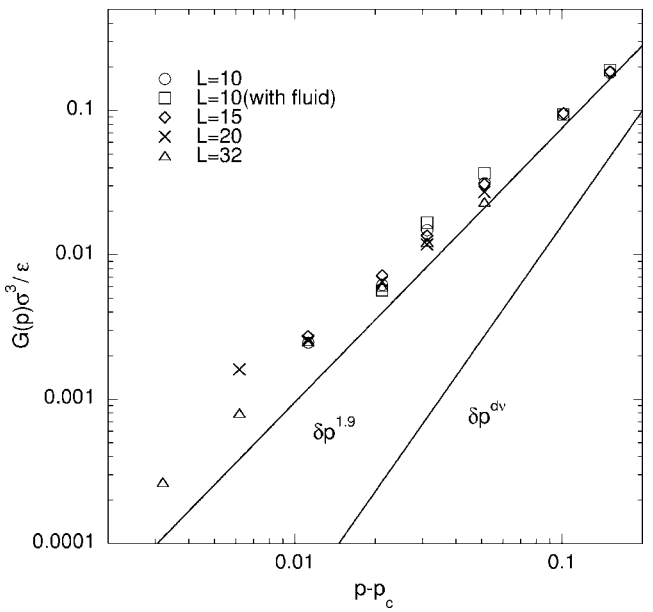


FIG. 8. The three-dimensional shear modulus for several values of $L$ as function of $p$. The data for $L=10$ with fluid present are indistinguishable from those obtained for the spanning cluster only.

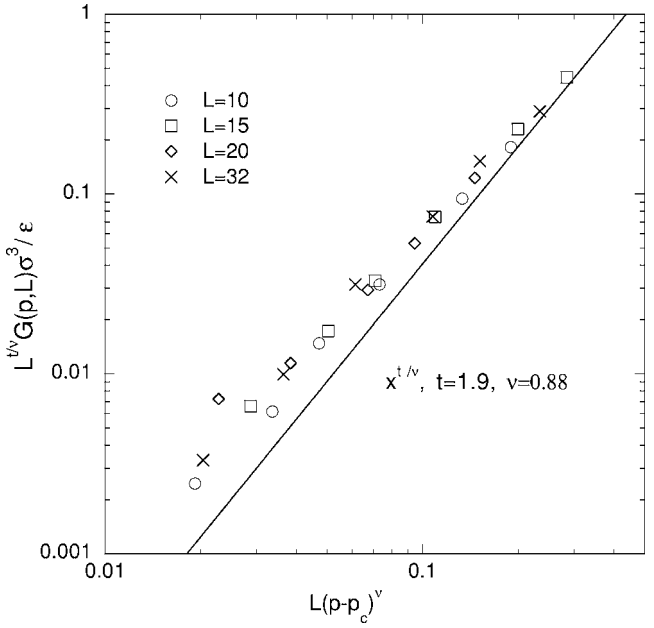


FIG. 9. The rescaled data for the shear modulus plotted as a function of $L/\xi$, using $t=1.9$ and $\nu=0.88$. The collapse is much worse if $t=d\nu$ is used instead. The solid line is the required behavior $(L/\xi)^{t/\nu}$ in the region $L \gg \xi$.

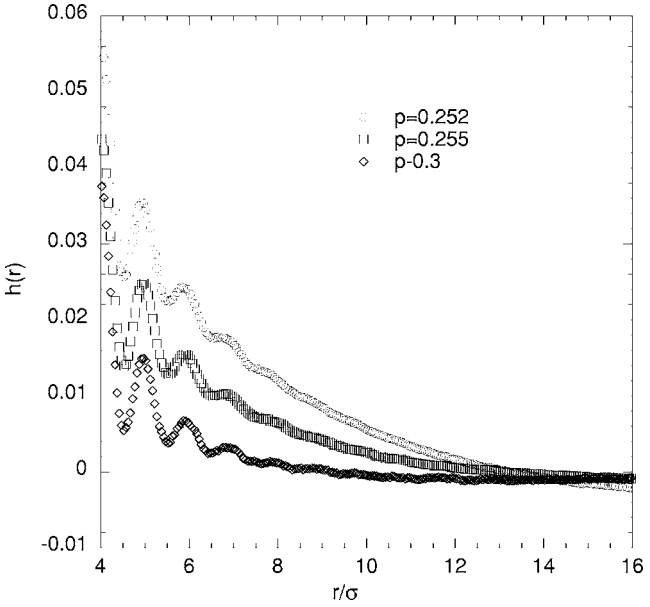


FIG. 10. The density-density correlation function for $L=32$ of the fluid component of the system for (top to bottom) $p=0.252$, 0.255, and 0.3.

## IV. DISCUSSION

As mentioned in the Introduction, our results in both two and three dimensions are consistent with those of Farago and Kantor [5,6] for a different central force model, but not with those of Ref. [8]. These authors measure the mean square fluctuation of the radius of gyration of the percolating cluster $\langle \Delta R_g^2 \rangle = \langle (R_g - \langle R_g \rangle)^2 \rangle$ and conjecture that $G \sim 1/\langle \Delta R_g^2 \rangle$. We are not aware of any derivation of this connection, except in the case of a simple spring in a heat bath. Moreover, since the radius of gyration is a relatively straightforward quantity to measure, we have done so in both two and three dimensions and find that it is not proportional to the modulus of our model in either case. As well, there is a strong indication in the work of Farago and Kantor [6] that there is more than one relevant exponent in the case where the underlying symmetry for the case $p=1$ is cubic: The difference between the two independent shear moduli of a system with cubic symmetry also vanishes at $p_c$ with a power law behavior $(p-p_c)^h$ with $h \approx 4$. Therefore, we are doubtful that measuring the fluctuations of the radius of gyration captures the critical behavior of the elastic constants.

Our results are also inconsistent with the conclusions of Xing *et al.* [9] who carried out a field theoretic renormalization group calculation and concluded that $t=d\nu$ to all orders in $\epsilon=6-d$. The underlying assumption in their work is that near $p_c$ there is only a single relevant length, namely, the percolation correlation length $\xi(p)$. We have measured the density-density correlation function $h(r)=\langle \rho(r)\rho(0)\rangle/\langle \rho \rangle^2 - 1$ of the *fluid* component of the system as a function of $p$ in both two and three dimensions. We show this function for $L=32$ in three dimensions in Fig. 10 for three values of $p$ reasonably close to the percolation point. While the data are too limited to permit an accurate determination of a correlation length, it seems clear that as $p \to p_c$ the decay of $h(r)$ as a function of $r$ becomes slower and this may indicate the emergence of a second nontrivial length.

The situation is clearer in two dimensions where we can measure the density-density correlation function over much longer distances. There is a range of $r$ over which $h(r)$ seems to decay exponentially as $\exp[-r/\xi_h(p)]$ where $\xi_h$ is the correlation length associated with $h$. This is depicted in Fig. 11 where $\ln(h)$ is plotted as a function of $r$. While it is possible

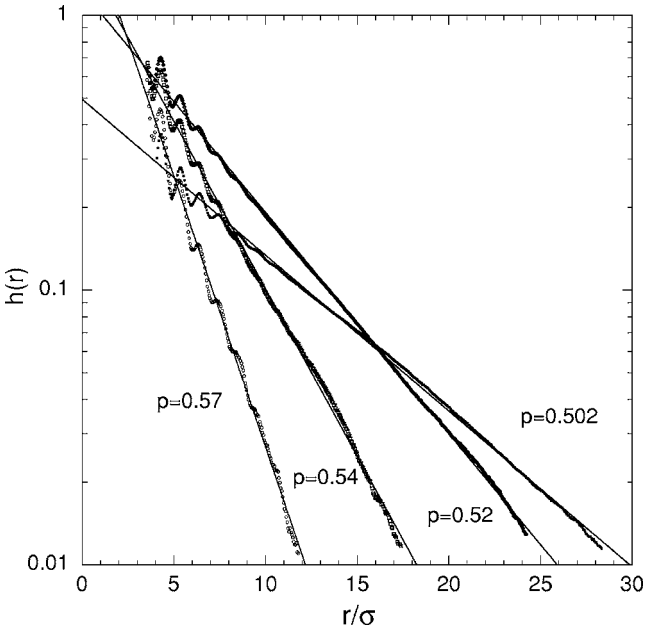


FIG. 11. The density-density correlation function $h(r)$ as function of $r$ for several values of $p$ close to $p_c$. The straight lines are fits to the form $h(r)=a\exp(-r/\xi_h)$.

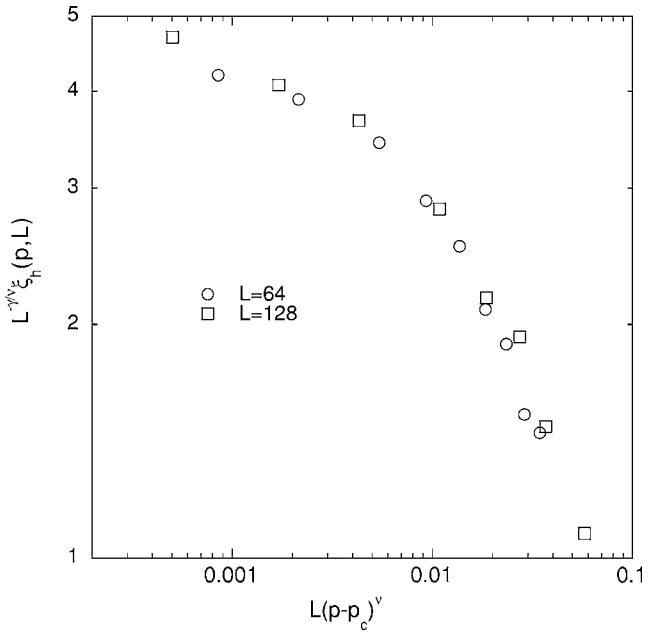


FIG. 12. Finite-size scaling plot of the correlation length for $L=64$ and 128. The value of the exponent $\gamma$ used in this plot is 1.15.

that at larger length scales or closer to the critical point a power law decay will emerge, we see no indication of that. As well, although it is obvious that interactions between fluid particles and those on the percolating cluster are responsible for the emergence of $\xi_h$, it seems that $\xi_h(p)$ is not proportional to the percolation correlation length $\xi(p)$. Evidence for this is presented in Fig. 12 where a finite-size scaling plot of the correlation length is given. While the data are not free of noise, our best estimate of the exponent $\gamma$ in the equation $\xi_h(p) \sim (p-p_c)^{-\gamma}$ is $\gamma \approx 1.15$. While this is not very different from $\nu=4/3$, that value of $\gamma$ yields a considerably worse collapse of the data. Therefore, it seems plausible that the theory of [9] is incomplete. At this point we have no clear picture of how a second length scale could be generated. However, Fig. 2 demonstrates that the finite clusters significantly distort the spanning cluster and it seems plausible that other lengths such as the chemical length [12] that are not proportional to $\xi(p)$ could play a role.

The present results, together with our earlier results [3,4] as well as those of Farago and Kantor [5,6], are consistent with the conjecture that there is a single universality class that describes the critical behavior of entropic rigidity. On the other hand, experimental values of the critical exponent $t$ do fall into two rather widely separated groups [10,11]. To date all the simulations that we are aware of have been done for central force networks for which there is a range of $p$ in which entropy dominates. It would be of interest to include bond-bending forces in a model and such calculations are presently in progress [15]. In this case, $p_r=p_c$ and at $T=0$ the critical exponent $t \approx 4$. We would expect that at finite temperature the entropic contribution would dominate at least very close to the critical point because at large length scales the angular piece of the microscopic interaction should renormalize to zero. However, it is certainly possible that this is not the case or that there is a large crossover regime in which the effective exponent is larger than the conductivity exponent.

## ACKNOWLEDGMENTS

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[13] It is always necessary to be careful about equilibration in systems with long time scales. For sample systems close to $p_c$, we have increased the equilibration time by a factor of 4 relative to the standard quoted in the text and checked that there were no changes in the values of the modulus. Moreover, for all values of the parameters, we calculted a time series for $G$ after the equilibration period and checked that there was no drift toward higher or lower values. Because of the fixed connectivity of the clusters, one should not expect to see the kind of aging found in glassy systems.
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