

Entropic Elasticity of Two-Dimensional Self-Avoiding Percolation Systems

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The sol-gel transition is studied on a purely entropic two-dimensional model system consisting of hard spheres (disks) in which a fraction p of neighbors are tethered by inextensible bonds. We use a new method to measure directly the elastic properties of the system. We find that over a broad range of hard sphere diameters a the rigidity threshold is insensitive to a and indistinguishable from the percolation threshold p_c . Close to p_c , the shear modulus behaves as $(p - p_c)^f$, where the exponent $f \simeq 1.3$ is independent of a and is similar to the conductivity exponent in random resistor networks.

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In the gelation process, monomers or short polymers in a fluid solution are randomly cross-linked. At a certain moment during the reaction, a macroscopically large network, *the gel*, spans the system. At this point, the system changes from a fluidlike (sol) to a solidlike (gel) phase which has a finite shear modulus. Percolation [1] is frequently used to describe the geometry of gels [2]. On a lattice, a percolation problem is described by randomly occupying a fraction p of the bonds or the sites. Usually, the gel point is identified with the percolation threshold p_c , above which a spanning cluster is formed. Close to p_c , the shear modulus is expected to follow a power law: $\mu \sim (p - p_c)^f$. In random resistor networks, near p_c , the effective conductivity scales as $(p - p_c)^t$, where t depends only on the dimensionality of the system. De Gennes [3] used an analogy between gel elasticity and conductivity of random resistor networks and conjectured that $f = t$. While de Gennes's conjecture was supported by several experiments [4], other experimental works measured very different values of the exponent f [5]. Numerical studies of elasticity at vanishing temperature T showed that the *energetic* elastic behavior of percolation systems depends on the details of the interaction: For nonstressed central force networks the rigidity threshold p_r is larger than p_c [6]. If bond bending forces are present, then p_c and p_r coincide, but the exponent f is considerably larger than t [7,8].

Near the sol-gel transition typical polymer clusters are very large, tenuous, and floppy. Elastic properties of such systems are primarily determined by the *entropy*, i.e., distortions of a sample barely modify its energy, but they decrease the available phase space (decrease entropy) and, thus, increase the free energy. Models of energetic elasticity may, therefore, be less relevant for studying the critical elastic behavior of gels. In this work we consider a purely entropic system—a network of hard spheres, connected by “tethers” [9], that have no energy but simply limit the distance of a connected pair to be smaller than some value b . No exact theory or direct numerical measurement are presently available for the entropic elasticity problem with excluded volume (EV) interactions. The entropic elastic behavior of *phantom* networks (i.e., without EV) is, on the

other hand, well understood. Phantom entropic networks are often modeled as networks of Gaussian springs having the energy $E = \frac{1}{2}Kr^2$, where r is the length of the spring. The quantities that characterize the elastic behavior are the stress tensor σ_{ij} and the elastic constants C_{ijkl} . They are the coefficients of the expansion of the free energy density: $f(\{\eta\}) = f(\{0\}) + \sigma_{ij}\eta_{ij} + \frac{1}{2}C_{ijkl}\eta_{ij}\eta_{kl} + \dots$, in η_{ij} , the components of the Lagrangian strain tensor [10]. In Ref. [11] we proved that for phantom Gaussian networks (PGNs) (i) the expansion of $f(\{\eta\})$ includes only linear terms in η_{ij} and, therefore, $C_{ijkl} = 0$, and (ii) the stress tensor is *equal* to the conductivity tensor of an equivalent resistor network in which each spring with a force constant K is replaced by a resistor of conductance K . Neither result depends on the temperature or the topology of the network. Close to p_c , percolation networks “forget” the details of the lattice and behave like isotropic systems, and, therefore, the stress tensor $\sigma_{xx} = \sigma_{yy} \equiv -P$, where P is the pressure. Isotropic systems have only three *different* nonvanishing elastic constants [12]: $C_{11} \equiv C_{xxxx} = C_{yyyy}$, $C_{12} \equiv C_{xxyy} = C_{yyxx}$, and $C_{44} \equiv \frac{1}{2}(C_{xyxy} + C_{xyyx}) = \dots$, which are related by $C_{11} = C_{12} + 2C_{44}$. Frequently, one finds it more useful to describe the elastic behavior in terms of the *shear* modulus $\mu \equiv C_{44} - P$ and the *bulk* modulus $\kappa \equiv \frac{1}{2}(C_{11} + C_{12})$ [for two-dimensional (2D) systems]. For isotropic PGNs we find that $\mu = -P = \Sigma$, where Σ is the conductivity of the equivalent resistor network [11]. Thus, $f = t$ within the PGN model. It is believed that phantom networks which are not strongly stretched exhibit an effective Gaussian behavior on sufficiently large scales, independently of the detailed shape of the microscopic potential. For linear polymers this is a consequence of the central limit theorem, while for more complicated systems this can be demonstrated numerically [9,13]. Thus, $f = t$ is expected to be valid for most phantom systems. Recently, this result was indeed demonstrated by Plischke *et al.* in a numerical study of phantom central force percolation networks at $T \neq 0$ [14].

It has been suggested that EV interactions primarily influence the system by introducing osmotic pressure [15].

Thus, the true problem may be approximated by a mixture of PGN and “pressure producing fluid.” This reduces the self-avoiding system to an *energetic* “scalar” elasticity model [15,16], which is equivalent to the PGN, and leads to the conclusion that $f = t$. On the other hand, a heuristic approach to the problem [17] leads to the conclusion that f is significantly larger than t . A semimicroscopic theory of the somewhat related problem of vulcanization transition [18] yields the exponent $f = 3$, predicted by the classical theory [19]. (This is also the value of the conductivity exponent in the upper critical dimension of the percolation model.) One of the explanations for the large range of experimental and theoretical values of f is the difficulty to separate the energetic and entropic contributions to the shear modulus. In Ref. [14], for instance, the authors used central force systems, for which at $T = 0$ energetic rigidity appears at $p > p_r > p_c$, and argued that even at $T \neq 0$ the energetic contribution to μ , just above p_c , should be minor. A way to bypass the problem of mixing of entropic elasticity with the energetic contribution is to measure the elastic moduli of *purely entropic* systems. The system whose elastic properties are studied in this paper, a network of hard spheres connected by tethers [9], is a simple example of such a system. Recently, we have devised a method very well suited for numerical calculation of the stress tensor and the elastic constants of such “hard-spheres-and-tethers” systems [20]. Within the method, σ_{ij} and C_{ijkl} are measured *directly* from the probability densities of contacts between spheres and the probability densities of having stretched tethers.

The topology of the network was defined by considering the bond percolation problem of a triangular lattice ($p_c = \frac{\pi}{9} \approx 0.349$), with a fraction p of bonds present. Each site of the lattice was replaced by a sphere of diameter a , while each present bond was replaced by a tether of maximal extension b , where the lattice spacing $b_0 \equiv 1$. Once the (quenched) topology was defined, the system was allowed to move in a *continuous* 2D space. Figure 1 depicts a part of a typical equilibrium configuration. In our Monte Carlo (MC) simulations we used a 52×60 site lattice (that has an aspect ratio very close to 1). Periodic boundary conditions were applied in order to fix the area of the systems. We generated the MC configurations using a new updating scheme [21], in which the conventional Metropolis single atom steps are replaced by collective steps of chains of atoms. At each MC time unit we made a number of move attempts (with acceptance probability ~ 0.5) equal to the number of atoms. We measured σ_{ij} and C_{ijkl} over a broad range of concentrations p above p_c . As p approached p_c , we needed to simulate more quenches because of the increasingly broader distribution of the values of μ between the different samples. For the system closest to p_c we used 40 quenches, while for the systems distant from p_c , four quenches sufficed. Close to p_c , the relaxation time τ becomes very large. To estimate τ , we used the expression $\tau = 2kTL^2\rho/(\pi^2\mu s^2)$, where

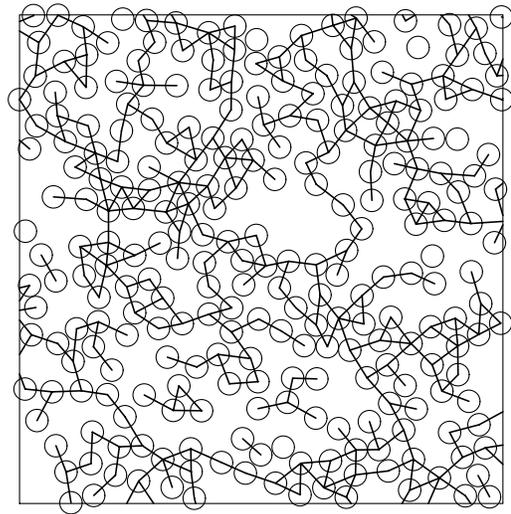


FIG. 1. Equilibrium configuration of the system with $a = 0.7$, $b = 1.05$, and $p = 0.405$. Only part of the system is shown.

L is the linear size of the system, s is the (average) distance an atom moves in one MC time unit, $\rho = 2/(\sqrt{3}b_0^2)$ is the number density of atoms, and k is the Boltzmann constant [22]. The value of μ in the expression for τ was taken, *a posteriori*, from the simulations. For each individual quench, the total duration of the MC run was *at least* 30 times larger than τ . The increase of the fluctuations in the value of μ and the larger relaxation times close to p_c effect the error estimates. The error bars appearing in the graphs correspond to 1 standard deviation of the average.

Figure 2 depicts the pressure and the bulk and shear modulus for a range of values of p for $a = 0.7$ and $b = 1.05$. The pressure and the bulk modulus do not vanish at p_c . The pressure decreases monotonically with p due to the increasingly larger negative contribution of the tethers to P . At $p \approx 0.46$, the contribution of the tethers

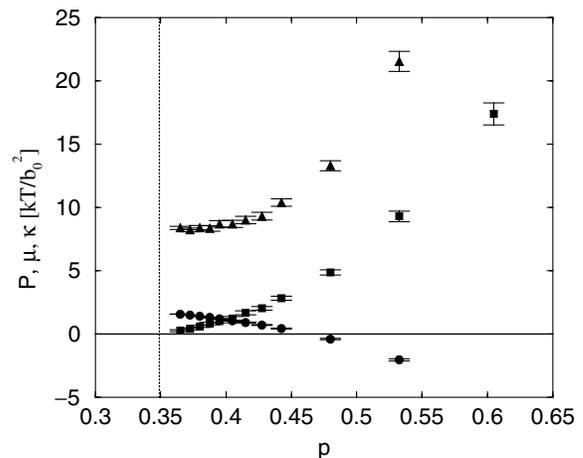


FIG. 2. Pressure P (circles), shear modulus μ (squares), and bulk modulus κ (triangles) as a function of the bonds concentration p , for percolation networks with $a = 0.7$ and $b = 1.05$. Results are in kT/b_0 units. The vertical dotted line marks p_c .

to the pressure overcomes the positive contribution of the hard spheres, and P becomes negative. The point of vanishing P depends on a and b . The bulk modulus does not change significantly near p_c , while at larger values of p it increases rapidly. The shear modulus becomes extremely small at p_c , signaling the sol-gel transition. (The elastic constants C_{ijkl} do not vanish near p_c .) In the presence of EV interactions it is not self-evident that the transition from liquid (sol) to solid (gel) behavior appears at p_c . In the absence of tethers ($p = 0$), the behavior of the system depends on the diameter of the disks a , or rather the reduced density $d = \rho a^2$, as indicated near the vertical axis of Fig. 3. The maximal possible packing is $d = 2/\sqrt{3} \approx 1.15$. At slightly smaller densities the system is a 2D solid with quasi-long-range order. At $d \approx 0.91$ the solid melts into a phase whose nature is controversial. Some numerical works [23] suggest that it is an hexatic phase with quasi-long-range orientational order, as predicted by the Kosterlitz-Thouless-Halperin-Nelson-Young theory [24]. Other works [25] favor a fluid-solid coexisting phase (i.e., the usual first order transition), as proposed, for instance, by Chui [26]. At $d \approx 0.89$, the system becomes a homogeneous liquid. For the purpose of our work, it is important to realize that close to $d \approx 0.89$, corresponding to $a \approx 0.88$, finite size effects make it difficult to distinguish between the phases, and, therefore, the largest a used in our simulations is $a = 0.85$, as indicated by the full circle in Fig. 3. (The open circle in Fig. 3 indicates the smaller density $d \approx 0.57$, corresponding to $a = 0.7$, used in our simulations.) In the absence of EV interactions, the onset of rigidity is obviously at p_c . One might expect

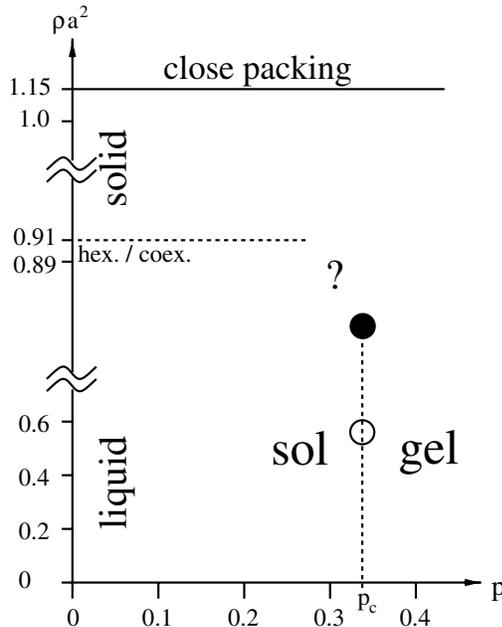


FIG. 3. The phase diagram of the system. The horizontal and vertical axes represent the concentration of the tethers and the reduced density of the spheres, respectively.

that the line separating the sol and the gel phases should move towards lower p with increasing a . However, within the accuracy of our simulations we were unable to distinguish between the rigidity threshold p_r and p_c . Thus, the sol and the gel are separated by essentially a vertical line depicted in Fig. 3 at p_c .

In Fig. 4 we depict our results for μ as a function of $(p - p_c)$ for the two values of a . As expected, larger EV interactions correspond to larger values of shear modulus. However, both graphs exhibit similar power laws with $f = 1.3 \pm 0.1$ for $a = 0.7$ and $f = 1.3 \pm 0.2$ for $a = 0.85$. This value of f is close to the value of the conductivity exponent $t = 1.310 \pm 0.001$ in 2D [27], which is expected for phantom networks ($a = 0$) whose elastic behavior is Gaussian. We therefore conclude that f is independent of a over the entire range $a \leq 0.85$. Note that our result is inconsistent with an *indirect* estimate $f = 2.7 \pm 0.1$, which was obtained by Del Gado *et al.* [28]. Their simulations were performed on a discrete lattice, where the phase diagram differs from the one in Fig. 3, and used slightly correlated bond topologies.

In this work we analyzed the elastic behavior of purely entropic systems. The fact that the numerical value of the exponent f found in our simulations is (within error bars) equal to the exponent t of the conductivity lends credibility to qualitative theories which treat the system as if it is a PGN with added pressure. However, we must note that formal exact identity between the elasticity and conductivity problems cannot exist in the same simple sense as it exists between the true PGN problem and conductivity. While in 2D we can only suspect that p_r may be lower than p_c in dense systems, in three dimensions topological entanglements reduce p_r below p_c [29]. (Unfortunately, the decrease in p_r due to topological entanglements is very small and cannot be investigated in the context of elasticity.) This and additional possible EV effects bring

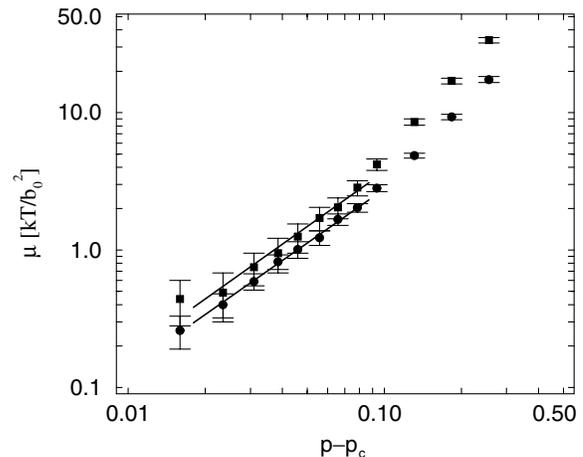


FIG. 4. Logarithmic plot of the shear modulus μ as a function of $(p - p_c)$, for systems with $a = 0.7$ (circles) and $a = 0.85$ (squares). For both systems $b = 1.05$.

p_r strictly below p_c , and, therefore, a simple mapping between the random resistor model and elasticity problem is impossible (unless it is used in some generalized sense). The fact that the exponent f is much smaller than the exponent predicted by the energetic bending elasticity model implies that at finite T in the presence of bond bending forces, sufficiently close to rigidity threshold, the elastic behavior will be entropy dominated. The lack of importance of central force elasticity for systems of this kind was already discussed in Ref. [14].

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