Entropic Elasticity at the Sol-Gel Transition

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Abstract

The sol-gel transition is studied in two purely entropic models consisting of hard spheres in continuous three-dimensional space, with a fraction $p$ of nearest neighbor spheres tethered by inextensible bonds. When all the tethers are present ($p = 1$) the two systems have connectivities of simple cubic and face-centered cubic lattices. For all $p$ above the percolation threshold $p_c$, the elasticity has a cubic symmetry characterized by two distinct shear moduli. When $p$ approaches $p_c$, both shear moduli decay as $(p - p_c)^f$, where $f \simeq 2$ for each type of the connectivity. This result is similar to the behavior of the conductivity in random resistor networks, and is consistent with many experimental studies of gel elasticity. The difference between the shear moduli that measures the deviation from isotropy decays as $(p - p_c)^h$, with $h \simeq 4$. 82.70.Gg, 62.20.Dc, 61.43.-j, 05.10.-a
Gels are macroscopically large networks, formed when short polymeric units in a solution (sol) are randomly cross-linked. The transition from sol to gel is a second order phase transition from fluid to solid during which the viscosity of the system diverges and shear elasticity (rigidity) develops. Frequently, the geometry of the gels is modeled by percolation [1], when the monomers are represented by the vertices of some lattice, while the random chemical bonds are modeled by bonds joining the vertices with probability \( p \). The gel point is identified with the percolation threshold \( p_c \), the critical bond concentration above which a spanning cluster is formed. Close to \( p_c \) quantities like the average cluster size or the gel fraction have power law dependence on \( (p - p_c) \) with exponents independent of the details of the lattice. Experimental measurements [2] of the geometric features of gels confirm the correspondence with the percolation model. Therefore, we expect that model systems whose geometry is described by percolation will produce a correct description of the physical properties of gels, such as elasticity. In this work, we study the elastic properties of a purely entropic percolation model of gels, and compare the results with experimental measurements of elasticity near the sol-gel transition, as well as with the predictions of approximate theories.

Close to \( p_c \) the shear modulus of a gel follows a power law: \( \mu \sim (p - p_c)^f \). Since the polymeric network forming the gel is tenuous and floppy, the dominant contribution to its shear modulus is of entropic origin: Upon distortion of the system, the available phase space, namely entropy, of the gel decreases, leading to an increase of the free energy, and to a restoring force. De Gennes suggested that the exponent \( f \) should be equal to the exponent \( t \) describing the conductivity \( \Sigma \) of random resistor networks near \( p_c \): \( \Sigma \sim (p - p_c)^t \) [3]. The equality \( f = t \) can be proved rigorously for a phantom network [without excluded volume (EV) interactions] of Gaussian springs each having the energy \( E = \frac{1}{2}Kr^2 \), where \( r \) is the spring length [4]. It describes the entropic elasticity of most phantom networks since the latter exhibit an effective Gaussian behavior on sufficiently large scales (provided that they are not strongly stretched) [5,6]. It is an open question whether the equality \( f = t \) is also valid in the presence of EV interactions. It does, according to some theories which claim
that EV interactions primarily influence the bulk (compression) modulus rather than the shear (rigidity) modulus of the system, as if the gel is a phantom network embedded into a “pressure producing” fluid medium [7]. However, a different approach based on scaling arguments concludes that the elastic moduli of a gel are of the order of $kT/\xi^d$, where $\xi$ is the percolation correlation length that diverges as $(p - p_c)^{\nu}$, and $d$ is the dimensionality. Consequently, the relation $f = d\nu$ is obtained [8].

The experimental values of $f$, measured for different gel systems, are divided between the above two approaches. In one group of experiments [9], done on materials like gelatin and silica gels, the measured exponent is close to the conductivity exponent $t \simeq 2$ in three dimensions [10]. Another group consists of experiments in materials like polyester and PVC, where the exponent varies from 2.5 to 3.0, and seems to agree with $f = d\nu \simeq 2.7$ [11]. The gels formed by the materials in both groups of experiments are floppy, and the dominance of the entropic contribution to their elastic properties is fairly expected. Thus, the division of experimental works into these two groups is based on the values of the measured exponents rather than on the nature of the investigated materials. The origin of the discrepancy between the experimental results is not clear, and we can only list several possible reasons: In some cases the topology of the system does not correspond to three-dimensional (3D) percolation model of gels, but is somewhere between gel (cross-linking of monomers or short polymeric units) and rubber (cross-linking of a melt of long polymers) [12]. Additional reasons are related to experimental difficulties, such as the imprecise determination of concentration of cross-links, or the difficulty to extract the static shear modulus from measurements of the low frequency behavior of the dynamic complex modulus. A more fundamental reason for the wide range of experimental results is the energetic contribution to gel elasticity which mixes with the entropic contribution and influences the “effective” exponent. Energetic bending elasticity is characterized by a much larger exponent, $f \simeq 3.8$ [13]. Such an exponent is measured only when the entropic contribution to elasticity is negligible, e.g, in the experiments in sintered metallic powders [14]. When both energetic and entropic contributions coexist, we expect the elastic behavior near the gel point to be
dominated by the latter, since the critical exponent of entropic elasticity (according to both approaches to entropic elasticity) is smaller than that of bending elasticity. However, the dominance of entropic elasticity near the transition may be limited to a very narrow regime, in which the shear modulus is small and difficult to measure.

In the present work we bypass the problem of mixing of the entropic and elastic contributions and investigate the elastic behavior of purely entropic systems: We consider a system consisting of hard spheres, connected by “tethers” that have no energy but simply limit the distance of a connected pair to be smaller than some value $b$. We apply a new method in which the stress tensor $\sigma_{ij}$ and the elastic constants $C_{ijkl}$ of such “hard-spheres-and-tethers” systems are measured from the probability densities of contact between spheres and the probability densities of having stretched tethers [15]. The stress and elastic constants are the coefficients of the expansion of the free energy density in the components of the Lagrangian strain tensor, $\eta_{ij}$: $f(\{\eta\}) = f(\{0\}) + \sigma_{ij} \eta_{ij} + \frac{1}{2} C_{ijkl} \eta_{ij} \eta_{kl} + \ldots$. In this paper we study systems whose elastic properties posses a cubic symmetry under uniform external pressure $P$. Such systems have a diagonal stress tensor: $\sigma_{ij} = -P \delta_{ij}$, and only three different non-vanishing elastic constants: $C_{11} \equiv C_{xxxx} = C_{yyyy} = C_{zzzz}$; $C_{12} \equiv C_{xxyy} = C_{yyxx} = C_{yyzz} = \ldots$; and $C_{44} \equiv \frac{1}{2}(C_{xyxy} + C_{xyyx}) = \ldots$ [16]. Cubic systems have two shear moduli $\mu_1 = C_{44} - P$ and $\mu_2 = \frac{1}{2}(C_{11} - C_{12}) - P$.

The topologies of the networks were defined by considering bond percolation problems on simple cubic (SC) and faced-centered cubic (FCC) lattices, with a fraction $p$ of bonds present. Each site of the lattice was occupied by a sphere of diameter $a$, while each present bond was replaced by a tether of maximal extension $b$, which was larger than the nearest-neighbor distance $b_0$. Once the topology (connectivity) was defined, the systems were allowed to move in a continuous 3D space. For both types of topologies we set the volume fraction of the spheres to be 0.2 and the ratio $b/a \sim 1.6$. We measured the elastic behavior as a function of $p$. It should be noted that even in the absence of tethers a dense system solidifies into FCC solid. In such a case we have a first order phase transition, where the liquid-solid coexisting phase appears at volume fraction of spheres 0.494, and the system becomes solid at volume
fraction 0.545. The topologies of the SC and the FCC systems are quite different: In the latter the number of nearest-neighbor lattice sites is larger and, consequently, the percolation threshold is smaller: \( p_c \approx 0.12 \) and \( p_c \approx 0.249 \) for the FCC and SC topologies, respectively. Thus, highly connected rigid regions are formed more rapidly (at lower \( p \)) in FCC networks. It has been suggested (see, e.g., Devreux et al. in Ref. [9]) that in real gels the creation of such rigid blobs tends to enhance the contribution of energetic bending elasticity and, thus, makes the entropy-dominated regime near \( p_c \) narrower. Therefore, it seems interesting to compare the SC and the FCC topologies in a purely entropic model. In our Monte Carlo (MC) simulations we used box sizes \( L = 18b_0 \) and \( L = 12\sqrt{2}b_0 \) for the SC and FCC topologies, respectively, with periodic boundary conditions. Figure 1 depicts a typical equilibrium configuration of the FCC system. We measured \( \sigma_{ij} \) and \( C_{ijkl} \) over a broad range of concentrations above \( p_c \). Strictly speaking, the rigidity threshold \( p_r \) is lower than the percolation threshold \( p_c \) due to effects of entanglements [18] (and, perhaps, also due to additional EV effects). However, the two thresholds are so extremely close that they are practically indistinguishable in experiments and numerical studies. Therefore, we treat \( p_r \) and \( p_c \) as identical. The number of quenched topologies and the length of the MC run of each individual topology increased as we approached \( p_c \). For systems close to \( p_c \) we needed to average the relevant quantities over 10 different topologies, while far from \( p_c \), 2–3 sufficed. Close to \( p_c \) the duration of the MC runs is about 500 times larger than the relaxation time \( \tau \) of the simulations (see an approximate expression for \( \tau \) in Ref. [6]). During each MC run the systems were sampled several million times.

The networks studied in this work posses a cubic symmetry since their topologies are defined on cubic lattices. Therefore, their elastic behavior is described by two distinct shear moduli rather than one, as in isotropic systems. This property does not exist in experiments where the networks are isotropic because of randomness. Figure 2 depicts the two shear moduli, \( \mu_1 \) and \( \mu_2 \), as a function of \( (p - p_c) \) for the SC and FCC systems. For each type of connectivity, its own \( p_c \) is used. The error bars appearing in Figs. 2 and 3 correspond to one standard deviation of the averaged quantities. For both systems close to \( p_c \), \( \mu_1 \) and \( \mu_2 \)
are practically indistinguishable, suggesting that the systems become isotropic. The shear moduli can be approximated by the power laws \( \mu_1 \simeq \mu_2 \sim (p - p_c)^f \) with \( f = 2.0 \pm 0.1 \) for the SC system, and \( f = 2.1 \pm 0.1 \) for the FCC system. Within numerical uncertainty both values are similar and consistent with recent estimates of the conductivity exponent in 3D, \( t \simeq 2.0 \) \cite{10}. We already found that \( f \simeq t \simeq 1.3 \) in two dimensions \cite{19} and, therefore, we expect that \( f \simeq t \) at any dimension. As we have mentioned earlier in the text, the equality \( f = t \) is expected for a phantom network \((a = 0)\) and can be explained by the Gaussian nature of its elastic response close to \( p_c \). Our results indicate that a similar picture may apply to systems with EV interactions.

In Fig. 2 we observe that the values of \( \mu_1 \) and \( \mu_2 \) gradually deviate from each other far from \( p_c \) because at large \( p \) the systems “remember” the lower (cubic) symmetry of their connectivities. For the FCC connectivity \( \mu_1 > \mu_2 \), while for the SC case \( \mu_2 > \mu_1 \). (The definitions of the shear moduli \( \mu_1 \) and \( \mu_2 \) depend on the orientation of the axes of the reference system, which in our study were taken along the edges of the conventional cubic unit cell.) Figure 3 shows that the difference \( \Delta \mu \equiv |\mu_1 - \mu_2| \), follows, in both cases, quite similar power laws \( \Delta \mu \sim (p - p_c)^h \) with \( h = 3.95 \pm 0.15 \) for the SC case and \( h = 4.15 \pm 0.15 \) for the FCC case. Because of the similarities of the values of \( h \) in SC and FCC systems, it is reasonable to assume that \( h \) is a new universal critical exponent which characterizes deviation from isotropic elastic behavior. While the power law dependence of \( \Delta \mu \) is not surprising due to the self-similar nature of the large percolation clusters, we could only support this assumption by numerical data of limited accuracy. We verified the validity of the power law dependence on \( (p - p_c) \) by attempting (unsuccessfully) to fit the data to other functional forms.

We already saw that the exponent \( f \) (describing the leading critical elastic behavior) is very similar for self avoiding (SA) and phantom percolating systems. Therefore, it is interesting to check whether this similarity applies to the exponent \( h \), as well. For this purpose we measured \( \Delta \mu \) for a phantom FCC bond percolating network with the same values of \( b \) and \( b_0 \), but with \( a = 0 \) \cite{20}. The results of these simulations are also plotted in
Fig. 3, revealing a power law with $h = 4.15 \pm 0.15$, as in the SA FCC case. The phantom Gaussian model which predicts that $f = t$, cannot be used to predict the value of $h$ since it gives $\Delta \mu \equiv 0$ at any bond concentration $p$ [4,21]. Hence, $\Delta \mu$ represents deviation from a purely Gaussian behavior which originates in the non-Gaussian form of the tether potential and (in the SA case) EV interactions. Our results for the exponent $h$ imply that the similarity between the critical elasticity of phantom and SA percolating systems may not be restricted to the leading Gaussian behavior.

In conclusion, we have studied the entropic elasticity of 3D purely entropic percolating systems. Our study shows that the critical behaviors of the shear moduli of phantom and SA percolation systems are characterized by similar critical exponents which are very close to the conductivity exponent. (For phantom systems the elasticity exponent actually coincides with the conductivity exponent.) This result agrees with many experimental studies of gel elasticity. It corresponds to heuristic theories which assume that the finite clusters (1) do not contribute directly to the shear modulus (i.e., behave like a fluid medium) and (2) effectively screen out EV interactions in the elastic network. Further support to this theoretical description is given by our result for $\Delta \mu$ which is also described by similar exponents in phantom and SA systems. The exponent $h$ that characterizes the decay of $\Delta \mu$ seems to be universal, namely independent of the lattice on which the geometry of the system is defined, but this point should be established more carefully by studying other lattice connectivities, and by measuring $h$ for two dimensional (phantom and SA) percolation systems.

We thank M. Kardar for numerous discussions of the problem. This work was supported by the Israel Science Foundation through Grant No. 177/99. The numerical simulation were performed on SGI Origin2000 supercomputer and Beowulf cluster at the High Performance Computing Unit at the Inter University Computation Center of Israel. We thank G. Koren for his support in conducting the numerical work.
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FIG. 1. A part of an equilibrium configuration of the FCC bond percolating system with $p = 0.1975$. For clarity the spheres are shown as $\frac{1}{3}$ of their actual diameter.
FIG. 2. Logarithmic plot of the shear moduli $\mu_1$ (solid symbols) and $\mu_2$ (open symbols) as a function of $(p - p_c)$, for FCC (circles) and SC (squares) bond percolating systems. For each topology, its percolation threshold is used ($p_c \simeq 0.12$ for FCC, and, $p_c \simeq 0.249$ for SC). For both systems the volume fraction is 0.2 and $b/a \sim 1.6$. 
FIG. 3. Logarithmic plot of the difference between the shear moduli $\Delta \mu$ as a function of $(p - p_c)$, for SA FCC (solid circles), SA SC (squares) and phantom FCC (open circles) bond percolating systems.