Elastic Properties of a Network Model of Glasses

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A standard model of glasses is shown to exhibit unexpected and remarkably simple elastic properties. For a sequence of networks of decreasing degree or coordination z, the number of zero-frequency vibrational modes (also called "degrees of freedom") increases as $e^{-z/\zeta}$. A simple statistical model is given which illuminates this behavior. In addition, the elastic constant c_{44} decreases as $(z-z_0)^{\nu}$; in certain cases other elastic constants also exhibit this behavior. These simple functional relationships appear to hold accurately for all $z > z_0$, where z_0 is the critical average degree at which the elastic constants vanish.

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Glasses and amorphous materials are tremendously varied and complex. Yet many such materials can be modeled simply as networks of atoms and bonds [1]. Phillips [2] and Thorpe [3] suggested that the elastic properties of such networks depend primarily on a single variable z, the average atomic coordination (e.g., $z=4$ for diamond). They predicted a transition from rigid behavior, for $z > z_0$, to "floppy" behavior for $z < z_0$, with $z_0=2.4$. The behavior of such networks has been extensively studied in the critical regime ($z \approx z_0$); but surprisingly little is known about the dependence of the elastic properties upon z in the regime most relevant to glasses and amorphous materials, where z is significantly larger than z_0 and the material is macroscopically rigid.

Here we show that, for a standard model of network glasses, the important elastic properties depend on z in an unexpected and very simple way. As z decreases, the number of zero-frequency vibrational modes increases as $e^{-z/\zeta}$, and a simple statistical model sheds light on this behavior. At the same time, c_{44} (and in certain cases other elastic constants) decreases as $(z-z_0)^{\nu}$. Remarkably, both of these forms superficially resemble critical behavior, as discussed below, yet they persist far beyond the critical regime.

We first recall the basic features of network models. A network consists of a set of *vertices*, and a set of *edges* (vertex pairs). The number of edges incident to a given vertex is called the *degree* of the vertex. Here the vertices represent atoms, the edges represent bonds, and the degree corresponds to the atomic *coordination*, i.e., the number of bonds formed by the corresponding atom.

In the simplest model appropriate for glasses, the energy of the system depends on the lengths of the edges, and on the angles between edges. (This is sometimes referred to as the "bond-bending model.") Although network rigidity has been studied extensively in both mathematics and physics for more than a century, most studies have focused on the simpler "central-force model," in which the angular forces are omitted [4]. However, this simpler model is not directly relevant to glasses, or to covalent materials generally.

There are two principal measures of elastic behavior. First, the *elastic constants* describe the macroscopic stiffness. Second, the *number of zero-frequency modes* (ZFMs) in the vibrational spectrum provides a complementary measure of local rigidity. The elastic constants are defined as $c_{\mu\nu}=\partial^2 E/\partial\varepsilon_\mu\partial\varepsilon_\nu$, where E is the energy and ε_μ is a uniform strain. ZFMs correspond to eigenvectors of the dynamical matrix $\mathbf{D}$ having eigenvalue zero; they form a complete orthonormal basis for the set of displacements which cost no energy. Here $D_{ij}=\partial^2 E/\partial x_i\partial x_j$, and x_i and x_j are any of the $3N$ variables specifying the positions of the N vertices of the network.

To describe the energetics, we use a Keating potential [5] which can be written as

$$E=\alpha\sum_{ij}(\mathbf{d}_{ij}\cdot\mathbf{r}_{ij})^2+\beta\sum_{ijk}(\mathbf{d}_{ij}\cdot\mathbf{r}_{ik}+\mathbf{d}_{ik}\cdot\mathbf{r}_{ij})^2. \quad (1)$$

Here $\mathbf{r}_{ij}$ is the vector from vertex (atom) i to vertex j in the undistorted (minimum-energy) structure; $\mathbf{d}_{ij}$ is the change of $\mathbf{r}_{ij}$ in the distorted network; sums are over all i, and all $j\neq k$ sharing an edge with i; and α and β are bond-stretching and bond-bending force constants, respectively. We use values of α and β appropriate for carbon (diamond).

Some features of the elastic behavior can be readily understood within the mean-field theory of Phillips and Thorpe [2,3]. Given a network of N vertices, each having degree two or more, one can show [3,6]

$$N_{\mathrm{ZFM}}\geq(6-\tfrac{5}{2}z)N, \quad (2a)$$

where N_{ZFM} is the number of ZFM's. Mean-field theory treats (2a) as an equality, except that there are always three rigid translations, so

$$N_{\mathrm{ZFM}}\geq 3. \quad (2b)$$

(We use periodic boundary conditions as discussed below, so for a connected network there are no free rigid rotations.) The crossover from floppy to rigid behavior, i.e., from Eq. (2a) to (2b), occurs at an average degree

$z_0 = \frac{12}{5} - 6/5N$, or $z_0 = 2.4$ for $N \to \infty$.

Numerical studies [6,7] show that these predictions are remarkably accurate for $z < z_0$. However, the same studies show that in reality, as z approaches z_0 from above, N_{ZFM} increases smoothly, although it remains small until $z \approx z_0$. Thus for $z > z_0$, the mean-field theory is not sufficient to explain the behavior of N_{ZFM}; moreover, mean-field theory is silent on the behavior of the elastic constants [8].

To gain insight into the elastic properties for $z > z_0$, we therefore resort to numerical experiments similar to those of He and Thorpe [7]. We generate networks of decreasing z by removing edges (bonds) at random from a diamond-structure network with periodic boundary conditions. Such "bond-depleted" networks have become a standard model for glasses and disordered materials, because they permit the construction of a sequence of structures distinguished only by the average degree z. Of course, this model is intended to describe behavior which is generic to random networks. Some glasses may in addition exhibit behavior which is peculiar to their particular structure.

We begin by considering the elastic constants $c_{\mu\nu}$. To ensure consistent numerical precision even for $z \approx z_0$, where relaxation methods become less efficient, we employ a direct algebraic approach, using the fact [9] that

$$c_{\mu\nu} = \frac{\partial^2 E}{\partial \bar{\varepsilon}_\mu \partial \bar{\varepsilon}_\nu} - \sum_m \frac{B_{\mu m} B_{\nu m}}{\lambda_m} . \quad (3)$$

Here $\bar{\varepsilon}_\mu$ refers to a strain applied only to the lattice vectors which define the periodic boundary conditions, with the coordinates of vertices within the cell kept fixed; λ_m is the mth eigenvalue of the dynamical matrix $\mathbf{D}$; and $B_{\mu m} = \sum_j \mathbf{S}_{jm} \partial^2 E / \partial \bar{\varepsilon}_\mu \partial x_j$, $\mathbf{S}$ being the matrix of orthonormal eigenvectors of $\mathbf{D}$.

Our results for three elastic constants are shown in Fig. 1; c_{11}, c_{44}, and the shear constant $c_s \equiv (c_{11} - c_{12})/2$ are plotted against the average degree z. These results represent an average over nine independent values of each constant for each z, corresponding to the three orientations of each of three randomly generated samples with $N = 216$. The elastic constants vanish near 2.4, as expected.

Figure 1(b) shows the elastic constants versus $z - z_0$ in a log-log plot. Each data set closely follows a straight line, which indicates that

$$c \propto (z - z_0)^\nu . \quad (4)$$

For each set, a line with slope $\nu = 1.40$ falls nearly within the error bars over 2 orders of magnitude. In particular, c_{44} is described almost perfectly by Eq. (4). This accurate power-law behavior is quite remarkable. We did not expect it, since it was not observed in previous studies [7].

We have further examined whether the results depend on the parameters of the potential (1). Note that, except for an overall constant, the energy depends only on the ratio $\gamma \equiv \beta/\alpha$. We have repeated our calculations for values of γ ranging over 4 orders of magnitude, from $10\gamma_C$ to $\gamma_C/1000$, where γ_C is the value for carbon (diamond). Here we only summarize the results of these extensive studies.

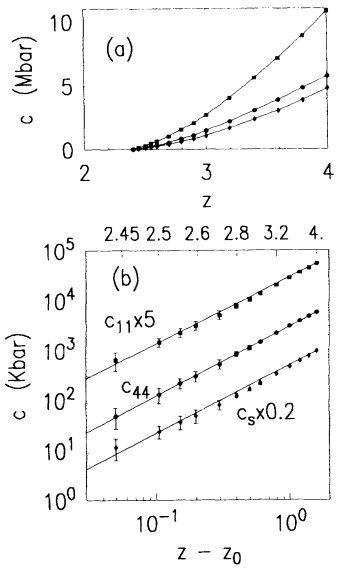

FIG. 1. Elastic constants c_{11} (top curve, squares), c_{44} (middle curve, circles), and $c_s = (c_{11} - c_{12})/2$ (bottom curve, diamonds). (a) Plotted vs average degree z on a linear scale. Solid curve is spline fit to guide the eye. (b) Plotted vs $z - z_0$ on a logarithmic scale, where $z_0 = 2.394$. (Top scale gives z.) In (b), squares have been multiplied by 5, and diamonds by 0.2, to separate data for clarity. Error bars give rms scatter among nine data averaged for each point.

For this entire range of γ, c_{44} obeys the power law, Eq. (4), to within our numerical accuracy. The value of the exponent ν ranges from approximately 1.35 for $\gamma = 10\gamma_C$ to 1.89 for $\gamma = \gamma_C/1000$. We know of no reason *a priori* to believe that c_{44} obeys Eq. (4) exactly; and for the largest values of γ, there were deviations from Eq. (4) which might be numerically significant. Nevertheless, our results are consistent with a power-law behavior of c_{44} for *all* values of the potential parameters.

The other elastic constants exhibit more complex behavior. For either very small or very large γ, c_{11} deviates considerably from power-law behavior. Also, c_s deviates for large γ; but it obeys Eq. (4) closely for small γ.

It seems particularly intriguing that for parameters appropriate for carbon, all three elastic constants obey Eq. (4) so accurately over 2 orders of magnitude, with a single value of the exponent ν. It is difficult to believe that such behavior can be a coincidence. In particular, the power-law behavior of c_{44} over the entire range of γ strongly suggests the existence of an underlying principle. We emphasize that this is not critical behavior, which would give a power law with ν independent of γ. Moreover critical behavior is not expected except very near z_0, and not in such a small sample. Understanding the basis

of the power-law behavior here should lead to deeper insight into the elastic properties of glasses.

We now turn to the second elastic property of interest, N_{ZFM}, the number of zero-frequency modes of a network. The presence of small numbers of ZFMs in macroscopically rigid networks ($z > z_0$) is of considerable importance in understanding heat capacity, and the scattering of phonons and photons. Yet to our knowledge the number and nature of the ZFMs for $z > z_0$ has never been examined [10]. In large part, this is because with tractable cell sizes, for $z > z_0$ there are too few ZFMs to analyze quantitatively.

N_{ZFM} should depend only on the network topology [11], and not on geometry or on α and β. Recently, one of us introduced a new combinatorial algorithm for estimating the number of ZFMs directly from network topology [6]. This algorithm permits the treatment of systems too large to handle with standard algebraic methods; and though not exact, it gives a lower bound on the number of ZFMs which is considerably more accurate than the mean-field estimate. Here we have used it to examine systems of size $N = 4096$.

The results are shown in Fig. 2. For $z \gtrsim z_0$ there is a tail in N_{ZFM}, as in previous results for smaller samples [6,7]. Here, with our large cell size, we can examine this tail over 2 orders of magnitude. In the logarithmic plot of Fig. 2(b), we see that the tail closely obeys a surprisingly simple relationship,

$$N_{ZFM} \propto e^{-z/\zeta}, \tag{5}$$

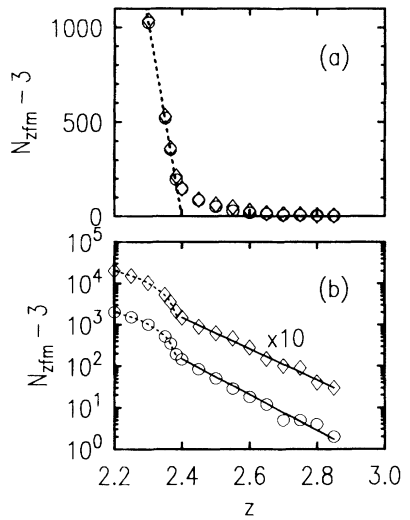

FIG. 2. (a) Number of ZFMs (minus three uniform translations) vs average degree z, calculated as described in text. Circles and diamonds correspond to two different randomly generated networks. (b) Same results on a logarithmic scale. [One data set (diamonds) has been multiplied by 10 to separate the two sets for clarity.] The dotted line corresponds to the mean-field estimate (2), while the solid line, corresponding to an exponential dependence on z, is fitted by eye to the data for $z > z_0$.

over the entire range $z > z_0$. The crossover from linear to exponential behavior at $z = 2.4$ is strikingly abrupt. Results of both trials are well described by Eq. (5), with similar values of ζ (0.10 and 0.11 in the respective trials).

Although we cannot yet fully explain this remarkable behavior, a simple statistical model is quite illuminating. In this model, we assume that the presence of ZFMs for $z > z_0$ is due mainly to statistical fluctuations in the local average degree in subregions of the network. We assume that there is some characteristic size $\hat{N}$ such that the mean-field estimate holds in any subregion of the network of size $\hat{N}$. (We later address the dependence of $\hat{N}$ upon z.) To evaluate these fluctuations, for a given average degree z, we randomly sample a large number of sets of vertices, of size $\hat{N}$, from our $N = 4096$ network. We let A_{ZFM} denote the average number of ZFMs per vertex, obtained by applying Eq. (2) to each set of $\hat{N}$ vertices. [Equation (2b) becomes $N_{ZFM} \geq 0$ for each subnetwork.]

The results are shown in Fig. 3(a), with the data of Fig. 2 superimposed for comparison. Clearly, for any *fixed* $\hat{N}$, this model fails to capture the qualitative behavior of N_{ZFM}, and shows no transition at $z = z_0$. However, intuitively we expect that $\hat{N}$ is closely related to the size of the "floppy" subregions, which should be small for $z \gg z_0$, becoming quite large as $z \to z_0$.

In fact, if we compute the value of $\hat{N}$ which must be *assumed* for each z to reproduce the data of Fig. 2, we

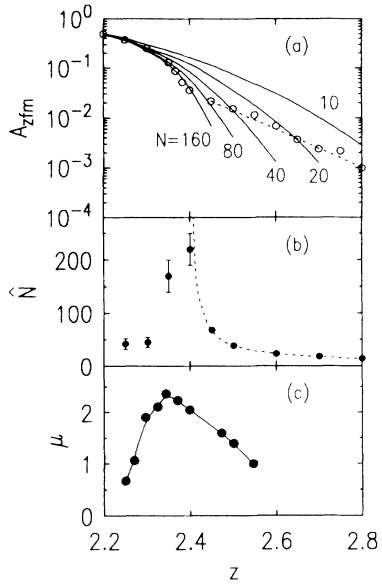

FIG. 3. (a) Number of ZFMs per vertex, A_{ZFM}, vs average degree z, for the statistical model described in text. Each line corresponds to the indicated value of $\hat{N}$. Circles are results of Fig. 2, for comparison. Dotted line is result obtained with $\hat{N} = 7(z - z_0)^{-0.75}$ [see (b)]. (b) Value of $\hat{N}$ which must be assumed, for each z, to reproduce the results of Fig. 2. Error bars reflect statistical uncertainty due to our finite sampling. Dotted line is a fit with power law, $\hat{N} = 7(z - z_0)^{-0.75}$. (c) Measure μ of the delocalization of the ZFMs [12], see text.

find that the inferred value of $\hat{N}$ accurately obeys a power law for $z > z_0$. The inferred value of $\hat{N}$ is shown as a function of z in Fig. 3(b); the dotted line, corresponding to $\hat{N} = 7(z - z_0)^{-0.75}$, provides a nearly perfect fit to the data for $z > z_0$. This power-law divergence of the characteristic size scale at $z = z_0$ is precisely what would be expected for critical behavior. However, it is surprising that the power law holds over such a wide range of z.

If we then calculate A_{ZFM} from the statistical model, assuming this power law for $\hat{N}$, the result agrees very well with the full calculation [dotted line in Fig. 3(a)]. Moreover, the exponential behavior is robust: If the power-law exponent for $\hat{N}$ is reduced by 25%, the exponential behavior of A_{ZFM} survives, with ζ merely increased from 0.11 to 0.13. Thus this simple model confirms our intuition that the behavior of N_{ZFM} can be understood in terms of two effects: statistical fluctuations in the local average degree, and the progressive delocalization of the ZFMs as $z \to z_0$.

A striking feature of Fig. 3 is that the inferred value of $\hat{N}$ peaks at z_0, then decreases as z decreases further. Presumably the sets of vertices that can move independently with zero energy become smaller as z decreases toward 2, accounting for the decrease in $\hat{N}$. We can in fact confirm that the ZFMs become most delocalized near $z = z_0$, by direct examination of the eigenmodes in a smaller sample ($N = 216$), where direct diagonalization of the dynamical matrix $\mathbf{D}$ is feasible. Adapting a standard measure of localization (the "participation ratio") to the case at hand, we have defined a measure $\mu(z)$ of the delocalization of the ZFMs as a function of z [12].

The results for μ vs z are shown in Fig. 3(c). The ZFMs clearly become most delocalized near $z = z_0$, supporting the statistical model with its inferred behavior of $\hat{N}$. (While μ does not peak as sharply as does $\hat{N}$, and is slightly displaced from z_0, this can be attributed to the smaller cell size, and to the fact that the definition of μ is not unique.)

In conclusion, our numerical studies have uncovered two surprising new relationships between the elastic properties of a network and its average degree z, i.e., the atomic coordination. The number of ZFMs depends exponentially on z, Eq. (5), and the elastic constant c_{44} obeys a power law in z, Eq. (4). The power law (4) also describes other elastic constants well, over a limited range of parameters of the potential.

These equations are in effect "experimental" results, and we do not claim that they are exact. Nevertheless, the behavior is quite striking, and is intuitively reasonable. Moreover, the exponential behavior of the ZFMs can be understood within a simple statistical model, in which the characteristic size $\hat{N}$ has a power-law divergence at z_0. We believe that these results illuminate an important aspect of the behavior of network models which has not been previously recognized, and we hope that these results will provide guidance in developing a fuller understanding of the elastic properties of disordered materials.

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[9] This formula follows from $c_{\mu\nu} = \partial^2 E/\partial\varepsilon_\mu \partial\varepsilon_\nu$. The atomic relaxations are determined by applying a strain $\bar{\varepsilon}_\mu$, and solving $\partial E/\partial x_i = 0$ for all i. In the sum over m, if $\lambda_m = 0$ then $c_{\mu\nu} = 0$, unless $B_{\mu m} B_{\nu m} = 0$, in which case that term does not contribute.

[10] The number of ZFMs for $z > z_0$ has, however, been examined in a very different model, a central-force network in two dimensions *under tension*: H. Yan, A. R. Day, and M. F. Thorpe, Phys. Rev. B **38**, 6876 (1988). In that study, vertices of degree one are allowed, leading to a simple (but very different) behavior at large z.

[11] This is strictly true if the vertex positions are algebraically independent variables, see Ref. [4]. Geometry intrudes in special cases such as 180° bond angles.

[12] Since the ZFMs share a common eigenvalue, only the subspace spanned is unique. We therefore first define a measure of the delocalization of this subspace, whose behavior accords with our intuition: $M \equiv \sum \rho_i / \sum \rho_i^2$, where the sums are over all vertices i. Here $\rho_i = \sum_j |\mathbf{a}_{ij}|^2$, where the sum over ZFMs j excludes the three uniform translations; and $\mathbf{a}_{ij}$ is the amplitude vector of the jth ZFM on site i, normalized so that $\sum_i |\mathbf{a}_{ij}|^2 = 1$. The measure $\mu(z)$ is defined as dM/dN_{ZFM}, N_{ZFM} depending implicitly on z.