Rigidity in Condensed Matter and Its Origin in Configurational Constraint

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Motivated by the formal argument that a nonzero shear modulus is the result of averaging over a constrained configuration space, we demonstrate that the shear modulus calculated over a range of temperatures and averaging times can be expressed (relative to its infinite frequency value) as a single function of the mean squared displacement. This result is shown to hold for both a glass-liquid and a crystal-liquid system.

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Glasses are rigid and liquids are not. The difficulty with any distinction of two phases based solely on rigidity is that the property is not an equilibrium one. Over 45 years ago, Lebowitz [1] and Ruelle [2] pointed out that, in the thermodynamic limit, the free energy of a phase cannot depend on the shape of the sample, so the equilibrium value of the shear modulus must vanish for all phases—crystals as well as glasses—in the limit of a large N. Rationalizing the obvious point that rigid materials do in fact exist, a number of researchers [3] have concluded that a nonzero shear modulus is a property of a metastable state, and hence rigidity is observable only for observation times shorter than the lifetime of that state. Since the observation of a nonzero shear modulus depends crucially on this lifetime, it would seem that any theoretical treatment of the mechanical properties of a material will depend on solving the onerous problem of slow relaxation in a condensed phase. Williams and Evans [4], acknowledging this difficulty, suggested that the shear modulus be formally calculated as an equilibrium average over a constrained space of configurations. This perspective suggests the attractive possibility that the magnitude of the shear modulus might be expressed as an explicit function of the magnitude of the configurational constraint applied, a relation that includes a threshold degree of constraint, below which rigidity vanishes. In this Letter we establish just such a relationship between the shear modulus and the configurational constraint, measured here by the mean squared displacement, for both a glass-liquid and a crystal-liquid system.

The Squire-Holt-Hoover expression [5] for the (constrained) equilibrium shear modulus G_{eq} of a solid is

$$G_{\mathrm{eq}} = G_\infty - \beta V[\langle\sigma^2\rangle - \langle\sigma\rangle^2], \tag{1}$$

where σ is the shear stress, $\beta = 1/k_B T$, V is the volume, and G_∞ is the infinite frequency (or Born) shear modulus given by [6]

$$G_\infty = \frac{N}{V}k_B T - \frac{1}{2V}\sum_i\sum_{j\neq i}\left\langle\left(y_{ij}^2 F_{ij}\left[1-\frac{x_{ij}^2}{r_{ij}^2}\right] - \frac{d^2\phi}{dr_{ij}^2}\frac{x_{ij}^2 y_{ij}^2}{r_{ij}^2}\right)\right\rangle, \tag{2}$$

where $F_{ij} = -(1/r_{ij})(d\phi/dr_{ij})$ and $\phi(r)$ is a spherically symmetric interparticle potential. Note that the shear modulus G_{eq} is reduced, relative to the high frequency value, by an amount associated with variance of the shear stress fluctuations. In the context of elastic theory, these fluctuations correspond to nonaffine contributions to the modulus [7]. What is measured in a typical experiment is the stress relaxation function $G(t) = \sigma(t)/\gamma$, where γ is an applied strain and $\sigma(t)$ is the resulting time dependent shear stress. The relation between $G(t)$ and G_{eq} is given by the following expression [8]:

$$G(t) = G_{\mathrm{eq}} + \beta V[\langle\sigma(0)\sigma(t)\rangle - \langle\sigma\rangle^2], \tag{3}$$

where the shear stress autocorrelation function $\langle\sigma(0)\sigma(t)\rangle$ equals $\langle\sigma^2\rangle$ when $t = 0$ and $\langle\sigma\rangle^2$ in the limit $t \to \infty$. It follows from Eq. (3) that G_{eq} represents a lower bound to the observed modulus $G(t)$ with $\lim_{t\to\infty} G(t) = G_{\mathrm{eq}}$. This long time limit refers only to the *explicit* time dependence arising from the shear stress autocorrelation function. It does not include any *implicit* time dependence associated with the observation time used to construct the averages in G_{eq} [see Eq. (1)]. So, the averages $\langle\cdots\rangle$ in Eqs. (1)–(3) are understood to be taken over some constrained configuration space. In the absence of a constraint, $\langle\sigma\rangle = 0$ and $G_\infty = \beta V\langle\sigma^2\rangle$ [9], so that $G_{\mathrm{eq}} = 0$.

The model liquid used in this study is a 2D system of soft disks with a pair interaction potential, $\phi_{ij}(r) = \epsilon(a_{ij}/r)^{12}$, between species i and j. In the case of the binary equimolar mixture, we use $a_{11} = 1.0$, $a_{22} = 1.4$, and $a_{12} = 1.2$—with all particles having unit mass—a model that has been extensively studied [10] in the context of the glass transition. The temperature is reported in units of ϵ/k_B and the time in units of $\tau = \sqrt{ma_{11}^2/\epsilon}$. Molecular dynamics simulations were carried out under constant NVT

conditions using LAMMPS [11] with a Nose-Hoover thermostats at reduced densities 0.7468 (binary mixture) and 1.398 (single component) with a potential cutoff distance of $6.3a_{11}$. The system consisted of a total of $N = 1024$ particles in the case of the binary mixture and $N = 1400$ for the single component system. Previously [12], we established that these values of N were sufficient for an accurate calculation of the stress fluctuations. At low temperatures, the trajectories are nonergodic for all accessible values of the averaging time t. In order to fairly sample the configuration space at these low temperatures, we have averaged trajectories over statistically distinct initial configurations. For the binary mixtures, 51 uncorrelated configurations were generated by cooling a liquid, equilibrated at $T = 0.60$ to $T = 0.30$ at a cooling rate of 5×10^{-5}, then minimizing the potential energy of the resulting $T = 0.30$ liquid by conjugate gradient minimization. The minima, referred to as inherent structures (ISs), were statistically independent as established by the average shear stress (at $T = 0$) of the inherent structures equaling zero. To calculate G_{eq} and G_∞ at a given temperature T, we randomly assigned momenta from the Boltzmann distribution consistent with a temperature T to the particles in each of the n IS configurations and then determined the moduli for each individual IS using Eqs. (1) and (2), respectively, by averaging over a trajectory run for a time interval t. To obtain our final values of G_{eq} and G_∞, we averaged the moduli for the individual IS configurations over all 51 IS configurations. In the case of the single component system, this protocol was modified as follows. For the crystal phase we only used a single inherent structure, that of the perfect crystal. For the liquid phase data we simply carried out averages over molecular dynamics trajectories of the equilibrated liquid.

In Fig. 1 we plot the values of G_{eq} and G_∞ as a function of T for a binary mixture of soft disks in 2D at a fixed density. We find that G_∞ increases linearly with T and shows no significant variation with the averaging time t. [Note that the infinite frequency modulus referred to experimentally is not G_∞ but the value of $G(t)$ in the plateau region.] The equilibrium modulus G_{eq}, in contrast, exhibits a strongly nonlinear decrease with increasing temperature, finally vanishing at a sufficiently high temperature. The family of curves presented in Fig. 1 is evidence of the significance of the time t used to calculate the statistics of the stress fluctuations.

A number of papers [13–15] have discussed the loss of rigidity of a glass as characterized by the disappearance of G_{eq} on heating in the context of a possible thermodynamic instability, analogous to the softening in a superheated crystal [13,14], or as an unjamming transition associated with the thermal expansion of the amorphous solid [15]. (We remind the reader that our calculations have been carried out at a fixed density, so the latter proposal is not directly relevant here.) While the role of the observation time is discussed in Ref. [14], it is the temperature that is treated as the essential control parameter for the transition. Following from our opening discussion, we shall explore the idea that this decrease of the equilibrium shear modulus, through increasing either T or the observation time, is most fundamentally expressed as a result of the changing degree of the configurational constraint associated with the averaging.

To begin we note that the temperature dependence of G_∞ is not associated with the configurational constraint since, by construction, the infinite frequency modulus depends only on the sampling of the local curvature of the potential energy surface. The increase in G_∞ with temperature at constant volume demonstrated in Fig. 1(b) is directly associated with the increase of the virial pressure with T under the constant volume constraint [see the inset of Fig. 1(b)]. To eliminate this additional temperature dependence we shall therefore consider the reduced modulus G_{eq}/G_∞. Next, we need a measure of the configurational constraint. The simplest such measure is the particle mean squared displacement

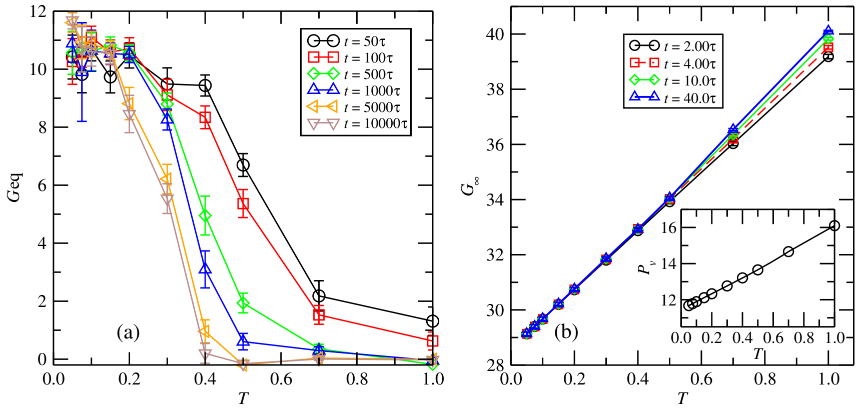

FIG. 1. Plot of (a) G_{eq} and (b) G_∞ vs T for the binary mixture over different averaging times. Note the significant effect of the averaging time in the case of G_{eq}, in contrast to G_∞, where the influence of averaging time has saturated within a short time of ~40τ. [Inset of (b)] The virial pressure $P_v = -(1/4V)\langle \sum_i \sum_{j \neq i} r_{ij}(d\phi/dr_{ij})\rangle$ as a function of T.

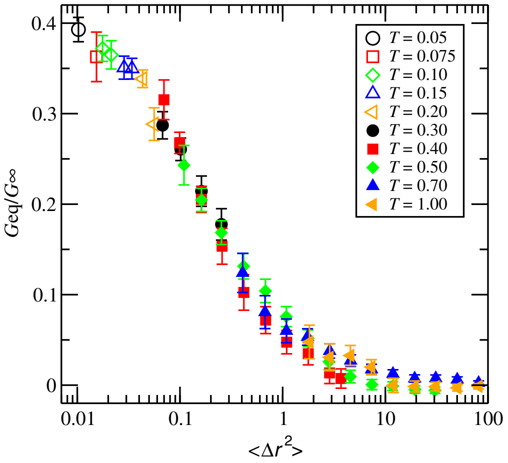

FIG. 2. Plot of G_{eq}/G_∞ vs $\langle\Delta r^2\rangle$ for the binary mixture. In each case, the mean squared displacement is calculated over the same time interval as that used to evaluate G_{eq}.

$$\langle\Delta r^2(t)\rangle = \frac{1}{N}\sum_i \langle|\vec{r}_i(0) - \vec{r}_i(t)|^2\rangle, \tag{4}$$

where the time t here is the same as the observation time used to calculate the stress averages and, in the case of a binary mixture, the average is over both species.

In Fig. 2 we plot G_{eq}/G_∞ vs $\langle\Delta r^2\rangle$, where we have used the data from Fig. 1 for a range of temperatures and observation times. We find that all of the data from Fig. 1 collapses onto a single curve. This result provides strong support for the twin propositions of this Letter, i.e., that the (reduced) shear modulus is simply a consequence of the configurational constraint and that the mean squared displacement provides a useful measure of this constraint.

A glass forming liquid is convenient for our purposes because it can access the entire range of G_{eq} without encountering a thermodynamic singularity. Our argument relating shear modulus and configurational constraint, however, should apply equally to crystallizing liquids. To demonstrate this point, we consider a single component soft disk liquid in 2D which crystallizes readily into a triangular lattice. In Fig. 3 we plot the values of G_{eq} and $\langle\Delta r^2\rangle$ for the system as a function of T, using an observation time $t = 199\tau$. The presence of the first order freezing at $T = 5.0$ is clearly evident in both quantities. In Fig. 4 we plot G_{eq}/G_∞ vs $\langle\Delta r^2\rangle$ for a range of temperatures (using crystal and liquid configurations for T below and above the two phase region in Fig. 3, respectively) and a range of observation times. Again, we find the data collapsed onto a common curve, this in spite of the discontinuity of the modulus and $\langle\Delta r^2\rangle$ with respect to temperature. It is worth noting the striking difference in the low T limit of G_{eq}/G_∞ for the crystal (Fig. 4) and the glass (Fig. 2). The reason for the considerable softening of the glass relative to G_∞, even at $T = 0$, is due to (i) the higher density of the crystal and (ii) the large nonaffine motions

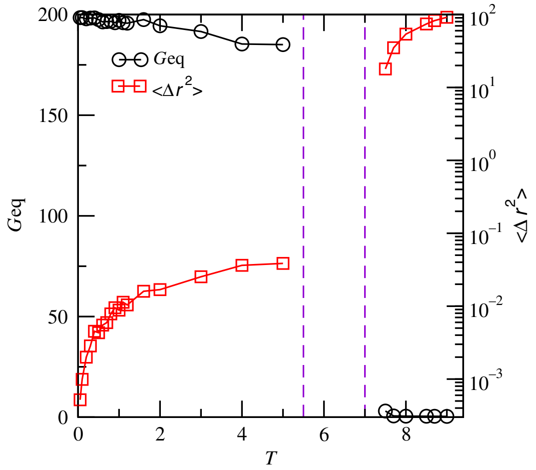

FIG. 3. The temperature dependence of G_{eq} and $\langle\Delta r^2\rangle$ (both averaged over a time 199τ) for the single component 2D soft disk system. Because of the constant density constraint, there is a range of temperatures corresponding to a two phase coexistence, indicated by the two vertical dashed lines. The freezing transition is marked by a steplike change in the modulus and the mean squared displacement.

[7] in the glass relative to those in the crystal. The presence of nonaffine motions in the amorphous phase and their effective absence in the crystal is due to the absence of inversion symmetry in the local structure of the amorphous phase and its presence in the crystal [16].

The dependence of the reduced shear modulus G_{eq}/G_∞ on $\langle\Delta r^2\rangle$ is found, empirically, to be well described by the following relation:

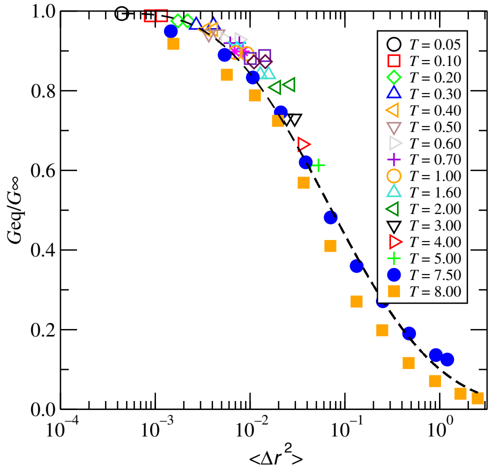

FIG. 4. The dependence of G_{eq}/G_∞ on $\langle\Delta r^2\rangle$ for the single component crystal and liquid. As for Fig. 2, each point corresponds to a choice of T and the averaging time. Liquid state data, i.e., $T > 5.0$, are represented by filled symbols and crystal data by open symbols. The curve corresponds to a fit of Eq. (5) to the single component data with $\alpha = 2.9$ and $q = 0.0061$.

$$\frac{G_{\mathrm{eq}}}{G_\infty} = \frac{G_{\mathrm{eq}}}{G_\infty}\bigg|_{T=0.05} \exp\left(-q\ln^\alpha\left[\frac{\langle\Delta r^2\rangle}{\langle\Delta r^2\rangle|_{T=0.05}}\right]\right). \quad (5)$$

The success of this functional fit is shown in Fig. 5 for the glass forming mixture with the fitted values $\alpha = 2$ and $q = 0.08$. Equation (5) also provides an excellent fit to G_{eq}/G_∞ vs $\langle\Delta r^2\rangle$ for both the crystal and liquid phases of the single component system (see Fig. 4), but with different parameters, $\alpha = 2.9$ and $q = 0.0061$. Viewed as an emergent property of restricted particle fluctuations, the derivation of the dependence of G_{eq}/G_∞ on the degree of configurational constraint must represent a problem of fundamental importance.

We have argued here that the value of G_{eq} (relative to G_∞) is a consequence of constraint. This is the opposite of the account provided within harmonic models of solids in which the elastic constants (or the bond force constants) are prescribed in the model and the mean squared displacement is determined as a consequence. The latter treatment, however, is only possible because of the implicit configurational constraints (i.e., assumed elasticity, unbreakable harmonic bonds, etc.) on which such models rely. For the harmonic solid, $G_{\mathrm{eq}}\langle\Delta r^2\rangle/T = \mathrm{constant}$ (at a fixed density). As shown in the Fig. 5 inset, this relation holds only for $\langle\Delta r^2\rangle < 0.1$, a result that underscores the inclusion of anharmonic effects in the empirical relations demonstrated in Figs. 4 and 5. Yoshino and Zamponi [17] have recently derived a power law relationship between the shear modulus and the mean squared displacement in a granular model that applies within a metabasin, a restricted range of configuration space corresponding, roughly, to $0.01 \leq \langle\Delta r^2\rangle \geq 0.2$.

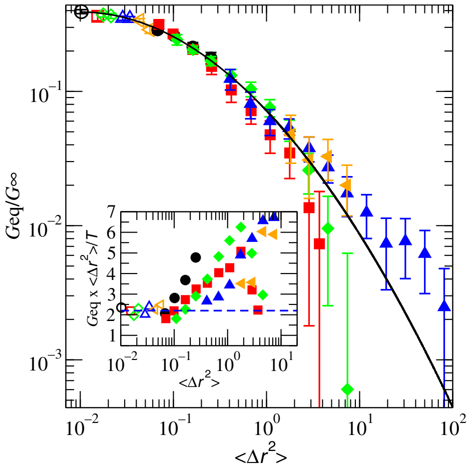

FIG. 5. A log-log plot of G_{eq}/G_∞ vs $\langle\Delta r^2\rangle$ for the binary mixture. (The correspondence between symbols and temperatures is the same as in Fig. 2.) The expression in Eq. (5) (solid curve) provides a good description over the entire range of $\langle\Delta r^2\rangle$, with $\alpha = 2.0$ and $q = 0.08$. (Inset) The quantity $G_{\mathrm{eq}}\langle\Delta r^2\rangle/T$ vs $\langle\Delta r^2\rangle$. The harmonic approximation, indicated by a constant value (dashed line), breaks down for $\langle\Delta r^2\rangle \geq 0.1$.

In conclusion, we have verified that our two propositions—(1) the degree of configurational constraint determines the magnitude of the shear modulus (relative to the infinite frequency modulus), and (2) the mean squared displacement provides a useful measure of this constraint—do indeed represent a consistent physical picture for both a glass forming liquid and one that undergoes freezing. This result represents a fundamental unification of the physical basis of rigidity. The presence of a nonzero shear modulus is not, we argue, the consequence of a low temperature, a high frequency measurement or even the presence of long-range order. Rather, each of these factors is important only in as far as it contributes to an implicit constraint on the volume of the configuration space that can be explored by stress fluctuations. It is this constraint, however it is achieved, that determines the value of the equilibrium shear modulus. This is a powerful result with a number of interesting consequences. First, accounts of the temperature dependence of the shear modulus of metallic glasses [18] have relied on the language of anharmonic effects borrowed from crystal physics. In the picture we present here, the decrease in the glass modulus on heating is associated with the increase in $\langle\Delta r^2\rangle$ by harmonic or anharmonic motions (along with any decrease in G_∞ associated with thermal expansion when a constant pressure is employed, as in Ref. [14]). Second, we have argued that the shear modulus should be regarded as a mechanical manifestation of restricted motion. Couple this idea with a description of the role that elastic behavior plays in determining the rate of particle motion (e.g., the shoving model of Dyre [19]) and there is the possibility of a self-consistent theory in which the modulus is, itself, a consequence of the very particle mobilities that it acts to constrain. Third, these results suggest a reassessment of the empirical Lindemann criterion [20], i.e., the observation that crystal order is lost once the mean squared displacement exceeds some threshold value. Our results here suggest that it is rigidity, not structure, *per se*, that vanishes as the mean square displacement increases. Finally, since our account of rigidity places no special condition on how the configuration space is accessed, it is possible that nonthermal contributions to particle mobility such as the nonaffine motion due to applied strain should result in an analogous reduction in G_{eq}/G_∞ [21].

In this Letter we have established that a collection of factors—time, temperature, and order—associated with the observation of rigidity in a dense phase can be replaced by a single tangible length that characterizes the degree of configurational constraint. While we have established that $\langle\Delta r^2\rangle$ provides a workable measure of this constraint length, further work is required to establish whether there is a better measure of this constraint and whether we can derive from first principles the mathematical relationship between this measure and the shear modulus.

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