Mechanical Properties of Glass Forming Systems

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We address the interesting temperature range of a glass forming system where the mechanical properties are intermediate between those of a liquid and a solid. We employ an efficient Monte-Carlo method to calculate the elastic moduli, and show that in this range of temperatures the moduli are finite for short times and vanish for long times, where ‘short’ and ‘long’ depend on the temperature. By invoking some exact results from statistical mechanics we offer an alternative method to compute shear moduli using Molecular Dynamics simulations, and compare those to the Monte-Carlo method. The final conclusion is that these systems are not “viscous fluids” in the usual sense, as their actual time-dependence concatenates solid-like materials with varying local shear moduli.

Traditionally the term “glass-transition” refers to the spectacular increase in viscosity when the temperature $T$ of a liquid is lowered within a relatively narrow temperature range. Some authors even proposed to call an amorphous medium a “glass” when its viscosity increases above $10^{12}$ Pa s [1]. For sufficiently high temperatures such glass-former are liquids with a finite viscosity. For sufficiently low temperatures these systems are solids, although they fail to exhibit any crystalline order. Here we address the range of temperature in between, and attempt to clarify the state of matter that is observed there. Over the years a qualitative picture seems to have emerged: already Goldstein in 1969 [2] proposed that in the intermediate temperature range the potential energy surface exhibits various minima separated by relatively high potential barrier (with respect to $k_B T$). Stillinger and Weber expounded this further, discussing the existence of “inherent states”. The dynamics is trapped for a while in an inherent state and then hops, via a saddle, to another “inherent state” [3]. Demonstrations of such events were presented for example in [8]. The aim of this Letter is to explore the nature of these “inherent states” from the point of view of their mechanical properties. We will offer a complementary point of view focusing on the elastic moduli of the material. An accepted notion of a liquid is a medium that cannot support shear, and thus by definition has a zero shear modulus. In this Letter we propose that it is advantageous to study the shear moduli in glass formers, since the notion of viscosity loses its usual meaning as a local descriptor of the state of flow in this range of temperatures, as is explained below.

In contradistinction, the shear moduli lend themselves to accurate measurement also locally in time throughout the temperature range. Moreover, the typical jamming that occurs at low temperatures can be overcome when computing the shear moduli by employing an efficient Monte Carlo method [4] as is described below. Using this point of view we will be able to present in this Letter accurate calculations showing that there exists an interesting temperature range where the elastic moduli are finite when computed for short times, but tending to zero when computed for longer and longer times. The appropriate length of time should be quantified with respect to the statistics of the (relatively rare) relaxation events in which the system jumps from one state to the other. We reiterate that viscosity in the local sense does not exist.

For concreteness and in order to be able to check our calculations with respect to others we chose to work here on the well studied glass former obtained from a two-dimensional binary mixture of discs interacting via a soft $1/r^2$ repulsion with a “diameter” ratio of 1.4 [6, 7]. The particles have the same mass $m$, but half of the particles are ‘large’ with ‘diameter’ $\sigma_2 = 1.4$ and half of the particles are ‘small’, with ‘diameter’ $\sigma_1 = 1$. The three pairwise additive interactions are purely repulsive:

$$u_{ab} = \epsilon \left( \frac{\sigma_{ab}}{r} \right)^{12}, \quad a, b = 1, 2,$$

where $\sigma_{aa} = \sigma_a$ and $\sigma_{ab} = (\sigma_a + \sigma_b)/2$. The cutoff radii of the interaction are set at $4.5\sigma_{ab}$. The units of mass, length, time and temperature are $m$, $\sigma_1$, $\tau = \sigma_1 \sqrt{m/\epsilon}$ and $\epsilon/k_B$, respectively, with $k_B$ being Boltzmann’s constant.

Ref. [3] found, using molecular dynamics simulations in the isothermal-isobaric ($NPT$) ensemble, that for temperature $T > 0.5$ the system is liquid and for lower temperatures dynamical relaxation slows down. A precise glass transition had not been identified in [3]. In [6, 7] it was argued on the basis of statistical mechanics that there exists a typical length scale that grows exponentially fast when the temperature decreases. Associated with this fastly growing scale there exists a fastly growing relaxation time, such that below a certain temperature the system is jammed for all practical purposes. Here we will shed further light on this phenomenon.

To measure elastic moduli at any temperature one employs the relation between the strain fluctuations and the elastic properties of a system. In the frame of the isothermal-isobaric ensemble the strain simultaneous correlation functions are given by:

$$< \epsilon_{ij} \epsilon_{kl} > = \frac{\int \epsilon_{ij} \epsilon_{kl} \exp(-\Delta G) d\epsilon_{xx} d\epsilon_{yy} d\epsilon_{xy}}{Z},$$

where $Z$ is the following partition function:

$$Z = \int \exp(-\Delta G) d\epsilon_{xx} d\epsilon_{yy} d\epsilon_{xy}$$

and $\epsilon_{ij}$ are the components of the strain tensor. $\Delta G$ is the difference of Gibbs free energy between the strained and
the reference state. In the linear elastic approximation for a 2-dimensional system it takes on the form [3]:
\[
\frac{\Delta G}{A_0} = \frac{1}{2} \left[ \lambda (\epsilon_{xx} + \epsilon_{yy})^2 + \mu' (\epsilon_{xx} - \epsilon_{yy})^2 + 4\mu\epsilon_{xy}^2 \right],
\]
(4)
where \(\lambda, \mu\) and \(\mu'\) are the elastic moduli, and \(A_0\) is the area of the system in the reference state with respect to which the free energy is computed. With this form of the free energy Eq. (2) reduces to simple Gaussian integrals yielding the wanted relations [10, 11]. Here we are interested mostly in the shear modulus \(\mu\) which is defined by:
\[
\mu = \frac{1}{4} \frac{T}{<\epsilon_{xy}^2> A_0},
\]
(5)

The strain fluctuation in (4) can be evaluated using numerical simulations. An efficient Monte Carlo method aimed at calculating this quantity in NPT ensemble was described in [3]. In essence, the method introduces strains into the simulation box by first defining a square box of unit area where the particles are at positions \(s_i\). Then one defines a linear transformation \(h\), taking the particles to positions \(r_i\) via \(r_i = hs_i\). The area of the system becomes the determinant \(|h|\). In order to prevent rotations of the simulation box, the matrix \(h\) should be symmetric. After the application of the transformation one performs \(n\) standard Monte-Carlo steps, after which the transformation \(h\) changes according to
\[
h_{ij}^{new} = h_{ij}^{old} + \Delta h_{max}(2\xi_{ij} - 1),
\]
(6)
where \(\Delta h_{max}\) is the maximum allowed change of a matrix element and \(\xi_{ij}\) is a random number uniformly distributed between 0 and 1. At this point one performs additional \(n\) standard Monte Carlo steps etc. The strain tensor in this procedure is calculated by [12]:
\[
\epsilon = \frac{1}{2} (h_0^{-1}hhh_0^{-1} - I),
\]
(7)
where \(h_0 = <h>\) is the reference box matrix which is obtained from averaging \(h\) until the time of evaluation, and \(I\) is the unit matrix. In our calculation we chose \(n = 100\) for the number of Monte-Carlo steps between strain transformations. Note that the strain \(\epsilon\) depends on time both due to \(h\) itself and due to (the possibly slowly convergent) time dependent \(h_0\).

In Fig. 1 we present the results of our calculations for the shear modulus \(\mu\). We have used 1024 particles in the 2-dimensional simulation cell. After an initial run of 5000 \(n_0\) sweeps (undisplayed in Fig. 1), these quantities were measured as a function of the number of times \(n_h\) of \(h\) sweeps, for the five temperatures \(T = 0.1, 0.2, 0.3, 0.4\) and 0.5 and the pressure \(P = 13.5\) (in units of \(\sigma^2\)). Clearly, for \(T = 0.1\) the shear modulus converges to a time-independent value, indicating the existence of a real solid. For \(T = 0.4\) and \(T = 0.5\) the shear modulus converges to zero, indicating the existence of a fluid. For \(T = 0.2\) and 0.3 the shear modulus did not converge, continuing to decrease as a function of \(n_h\), possibly approaching zero asymptotically, but maybe stabilizing at a finite value after a very long time.

In Fig. 2 we plot the actual evolution of \(\epsilon_{xy}\) in the Monte-Carlo simulations as a function of \(n_h\). Upper panel: \(T = 0.1\). Middle panel: \(T = 0.3\). Lower panel: \(T = 0.5\).
we invoke some exact results from statistical mechanics. Two important results are due to Zwanzig \cite{13} and to Wallace \cite{14}, relating the shear modulus to other computable objects. The first object is the so-called “infinite frequency shear modulus” \( \mu_{\infty} \) which is defined as
\begin{equation}
\mu_{\infty} \equiv \frac{\rho}{A_0} \frac{T}{\sigma_{xy}}
\end{equation}
where the microscopic shear stress is given by:
\begin{equation}
\sigma_{xy}(t) = \frac{1}{A_0} \left( \sum_i p_{i,x} \cdot p_{i,y} \frac{m_i}{\rho} + \sum_i r_{i,x} \cdot F_{i,y} \right),
\end{equation}
where \( p_{i,\alpha} \) is the \( \alpha \) component of the momentum of particle \( i \) and \( F_{i,\alpha} \) is the \( \alpha \) component of the force exerted on particle \( i \) \cite{15}. Zwanzig had considered a different quantity, which is referred to by the same name “infinite frequency shear modulus” but which is only appropriate for liquids, denoted here \( \mu_{L\infty} \). In two dimensions this object reads
\begin{equation}
\mu_{L\infty} \equiv \rho T + \frac{1}{8A_0} \sum_{i<j} \frac{1}{r_{ij}} \frac{\partial}{\partial r_{ij}} \left( r_{ij}^3 \frac{\partial\phi(r_{ij})}{\partial r_{ij}} \right)
\end{equation}
For interparticle potentials of the form \( 1/r^n \) (\( n=12 \) in \cite{11}) the expression \cite{10} yields:
\begin{equation}
\mu_{L\infty} = \rho T + \frac{n-2}{4} (P - \rho T).
\end{equation}
Wallace obtained in 2000 the remarkable result (apparently uncited even once) \cite{14}:
\begin{equation}
\mu = \mu_{L\infty} - \mu_{\infty},
\end{equation}
where the shear modulus \( \mu \) is the same as defined by \cite{4}. We thus learn that statistical mechanics provides us an indirect way to measure the shear modulus as the difference between the exactly calculable \cite{11} (in our case with \( n = 12 \)) and the simulationally accessible \( \mu_{\infty} \) Eq. \cite{8}.

We performed Molecular Dynamics simulations in the canonical (NVT) ensemble with \( N = 256 \) particles in a square simulation box. The equations of motion were integrated using a third order Gear predictor-corrector...
algorithm, a constant temperature was preserved using a velocity rescaling method [16], at each temperature the density was chosen in accordance with the simulations results in NPT ensemble as described in [7]. We also followed this reference in correcting the shear modulus for the frozen-in stress. Our results and the results obtained in [7] are presented in Fig. 3. We see that as long as the system is liquid ($T > 0.4$), the Zwanzig calculation agrees exactly with our simulation of $\mu_\infty$, predicting zero shear modulus, as expected. For smaller values of $T$, $\mu_\infty$ deviates from the liquid value, and the difference is the Molecular Dynamics estimate for the shear modulus.

As before, in the interesting region of temperatures this method indicates a finite value of the shear modulus, but this again depends on the simulation time, and still needs to be interpreted.

To understand what is the state of matter that is behind these results we present in Fig. 4 the actual trajectory of the Molecular dynamics simulations in the stress-energy plane for three different temperatures and for the same simulation time. We see that at $T = 0.2$ the system fluctuates around one distinct state, giving us a non-zero value of $\mu_\infty$ as computed from [3]. For all that one can judge we have a solid with a finite value of its shear modulus. Changing the temperature to $T = 0.3$ we recognize that the system fluctuates around one such “solid-like” state, and then another such state; for this time of the simulation one resolves at $T = 0.3$ three states each of which would have given us a sharply defined shear modulus for the time of life of that state. Upon averaging over longer periods we get contributions from different “solid-like” states and the shear modulus becomes dependent on the time of averaging, as seen in Figs. 1 and 3. For $T = 0.4$ the trajectory now fills up an extended region in the stress-energy plane, and one can see why the shear modulus must average to zero for longer averaging times (see also Fig. 2). Anyway we look at the dynamics the emerging picture is the same: between real solid and real liquid the system is locally not a “viscous fluid”. Rather, the trajectory concatenates relatively long periods of times where the system behaves like a solid, interconnected by relatively short period of times where the system flows between these states. Clearly, a viscous fluid behaves very differently, responding to stress by a viscous flow, be it as sluggish as one wishes. Here, most of the time, the system does not respond to stress, except in the narrow corridors of flow which become rare when the temperature goes down and more common when the temperature warms up. Of course this does not mean that in the sense of long time averaging the notion of viscosity cannot be resurrected, but locally in time this is impossible.

The question that remains is how to describe macroscopically this state of matter. In our opinion a promising approach was described in [14], where all the accessible stationary points of the potential energy surfaces $\mathcal{V}(r_1 \cdots r_N)$ for all the $N$ particles were obtained by solving the $3N$ nonlinear equations $\partial \mathcal{V} / \partial r_i = 0$. Having a complete enumeration of the accessible minima, the saddles and the eigenvalues of the Hessian matrix at the saddle (cf. [16] for details) one can hope to analyze the relative length of time that the system might stay in each of its “solid-like” minima. In that case one can attempt to answer the question whether a long time average would yield a finite or a zero shear modulus or at any rate describe the mechanical behavior of the system for a finite time. Such a program is becoming more and more realistic with the increase in computer power, and appears unavoidable if one wants to make real progress in understanding the interesting range of temperatures between liquid and solid in amorphous glass-formers.

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