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Communication: Broken-ergodicity and the emergence of solid behaviour in amorphous materials

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Using a combination of theory and molecular dynamics simulations, we show how solid behaviour emerges in amorphous materials from microscopic considerations. The effect on the systems response to a sudden change in strain, upon entering the history dependent glass state, is focused on. An important symmetry that is always present in a fluid state, is shown to be broken for a simulated history dependent amorphous solid. Details of how this applies to a single sample and an ensemble of independent samples are discussed, along with the dependence on the time scale the system is monitored on. © 2011 American Institute of Physics. [doi:10.1063/1.3650323]

The glass transition is often studied in terms of how the dynamics of a supercooled liquid slow down so dramatically as vitrification is approached, e.g., see. Ref. 1. While this approach is important for understanding how super-cooled liquids approach the glass transition, it provides little insight about the mechanical response of the glass state. This is because glass is not in equilibrium and its microscopic distribution function is different to that of any equilibrium ensemble. The glass state may be viewed as a transient state which is evolving extremely slowly. Often to such an extent that it appears stationary on the longest time scale being monitored.

There are many amorphous solids or glasses which show the macroscopic phenomenology of a structural solid. This may be viewed in terms of the constitutive relation for a solid

$$\Delta S_{xy} = G_0 \Delta \gamma, \quad (1)$$

where $\Delta \gamma$ is the change in strain, G_0 is the zero frequency shear modulus, and ΔS_{xy} is the resulting change in stress after the system has relaxed. However, if we simply apply this to a glass, it may evolve some small but significant amount on the same time scale that it relaxes from the change in strain. This can make the determination of G_0 ambiguous and leaves an important question to be answered from microscopic considerations. How is it that the macroscopic behaviour of an ordinary equilibrium solid emerges in a glass, which is in a history dependent nonequilibrium state? As it turns out something very closely related to Eq. (1) emerges in the time dependent linear response for the glass. This allows the solid character of the glass to be determined at short times, on which the glass does not evolve significantly, and alleviates problems arising from the fact that given enough time a solid material may flow.²

First we define precisely how we classify a solid and a fluid. Consider a system which is initially in equilibrium. If the system is a fluid, its average stress will be zero. If we subject it to a change in strain and then allow it to relax, it will relax to equilibrium with zero average stress and there will be no change in free energy. In contrast, after a change in strain

(which is not too large) a solid relaxes to a new equilibrium with a different average stress and usually a different free energy. If the change in strain is small enough this change in stress can be calculated as a linear perturbation on the initial equilibrium. When a fluid has a nonzero stress it is out of equilibrium, in a way that can not be described using an equilibrium perturbation. For a fluid one must consider a nonequilibrium perturbation such as that developed by Kubo.³ For a solid the equilibrium stress can change and for a small change in strain we may compute this as an equilibrium perturbation. After this change the solid will take some time to reach the new perturbed equilibrium. When the system is relaxing this underlying equilibrium change will be present in the formula for the nonequilibrium response. However, treating a glass as being initially in equilibrium is too simplistic. Because a glass is not in equilibrium, whether it appears to be a liquid or a solid by this type of classification is dependent upon how the averages are formed. Later we will consider two types of averages representative of an ensemble and a time average.

To treat a glassy solid (as well as crystalline solid materials with nonequilibrium defects) we consider broken-ergodicity in quasi-equilibrium⁴⁻⁶ (for examples of related approaches see Refs. 7-9). Here the $6N$ dimensional phase space is divided into N_D different domains (or regions). Within each domain the system is equilibrated, between domains the system is not. Recently we have developed the probability distribution for a classical system with broken-ergodicity in quasi-equilibrium.^{5,6} The microscopic probability density within the α th phase space domain is given by

$$f_\alpha(\Gamma) = s_\alpha(\Gamma) \frac{\exp[-\beta H(\Gamma)]}{Z_\alpha}, \quad (2)$$

$$Z_\alpha = \int d\Gamma s_\alpha(\Gamma) \exp[-\beta H(\Gamma)],$$

where $\Gamma(\mathbf{q}, \mathbf{p})$ is the $6N$ dimensional phase space vector representing all the positions $\mathbf{q}$ and momenta $\mathbf{p}$, $s_\alpha(\Gamma)$ is a switch that is set to unity when Γ is in the α th domain and zero otherwise, $\beta = 1/(k_B T)$ is the inverse temperature, and $H(\Gamma) = \mathbf{p} \cdot \mathbf{p}/(2m) + \Phi(\mathbf{q})$ is the Hamiltonian

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with Φ the interparticle potential. For the entire ensemble we then have

$$f_{qe}(\mathbf{\Gamma}) = \sum_{\alpha=1}^{N_D} w_{\alpha} f_{\alpha}(\mathbf{\Gamma}), \quad (3)$$

$$\sum_{\alpha=1}^{N_D} w_{\alpha} = 1,$$

where w_{α} is the nonequilibrium weight.⁵ The utility of this development is that it allows one to bring the Liouville equation to bear on broken-ergodic/quasi-equilibrium statistical mechanics.⁵ Previously we have used this to compute the linear response of a glass to a change in strain.⁶ The quasi-equilibrium perturbation then appears in the nonequilibrium response, in a way which is analogous to how the equilibrium perturbation appears in the nonequilibrium response of an ergodic solid.¹⁰

Consider the case of planar shear where the system undergoes a step change in the strain, $\gamma(t) = \gamma_0 \Theta(t)$, where $\Theta(t)$ is the Heaviside step function and γ_0 is a small change in strain. For a fluid that is in equilibrium at times $t < 0$ the shear stress will initially be zero, $S_{xy} = -\langle P_{xy} \rangle_{eq} = 0$, where P_{xy} is the xy element of the pressure tensor and $\langle \dots \rangle_{eq}$ represents an equilibrium ensemble average. The step change drives the system out of equilibrium which then relaxes back to zero stress as given by linear response theory¹¹

$$S_{xy}(t) = -\langle P_{xy}(t) \rangle = \beta V \gamma_0 \langle P_{xy}(t) P_{xy}(0) \rangle_{eq} + \mathcal{O}(\gamma_0^2), \quad (4)$$

where V is the system volume. Given time the equilibrium correlation function relaxes, $\langle P_{xy}(t) P_{xy}(0) \rangle_{eq} = 0$, and the fluid once again falls into equilibrium with zero stress.

If we now subject a solid to the same procedure we observe qualitatively different behaviour. We will consider the more general case of broken-ergodicity. The special case of an ergodic equilibrium solid is obtained if we specify that all the ensemble members are in the same domain, *i.e.*, there is only one domain, $N_D = 1$ and $w_1 = 1$. Using the results from⁶ for the case of a step change we have

$$\begin{aligned} \langle P_{xy}(t) \rangle_{ne,\alpha} &= \langle P_{xy} \rangle_{\alpha} - \beta V \gamma_0 \langle P_{xy}(t) P_{xy}(0) \rangle_{\alpha} \\ &\quad - \gamma_0 \langle g_{\infty} \rangle_{\alpha} + \beta V \gamma_0 \langle P_{xy}^2 \rangle_{\alpha} \\ &\quad + \mathcal{O}(\gamma_0^2), \end{aligned} \quad (5)$$

where $\langle \dots \rangle_{\alpha}$ represents a quasi-equilibrium average over the α th domain, $\langle B(t) \rangle_{ne,\alpha}$ is the nonequilibrium average of the phase variable B over the α th domain at time t , and g_{∞} is the infinite frequency response.⁶ Equation (5) may be combined with Eq. (3) to obtain the ensemble averaged response,

$$\begin{aligned} \langle P_{xy}(t) \rangle_{ne} &= \langle P_{xy} \rangle_{qe} - \beta V \gamma_0 \langle P_{xy}(t) P_{xy}(0) \rangle_{qe} \\ &\quad - \gamma_0 \langle g_{\infty} \rangle_{qe} + \beta V \gamma_0 \langle P_{xy}^2 \rangle_{qe} \\ &\quad + \mathcal{O}(\gamma_0^2), \end{aligned} \quad (6)$$

where, $\langle \dots \rangle_{ne}$ represents the nonequilibrium average and $\langle \dots \rangle_{qe}$ represents the quasi-equilibrium ensemble average obtained using Eq. (3).

It is important to note that Eq. (5) can result in a stress that is unable to relax back to its initial value $\langle P_{xy} \rangle_{\alpha}$ even when the correlation function decays to zero. We have previously shown this very clearly for the case of a defect free face centre cubic crystal.¹⁰

If we change the shape of the boundary, which contains a fluid in equilibrium, while holding the volume fixed, the free energy of the fluid does not change. This means that for a fluid we always have the equilibrium average $\langle P_{xy} \rangle_{eq} = 0$, and as a consequence we must have^{6,12}

$$\langle g_{\infty} \rangle_{eq} = \beta V \langle P_{xy}^2 \rangle_{eq}. \quad (7)$$

This symmetry is always present in a macroscopic equilibrium fluid, but not in an amorphous solid. If we now specify that there is only one domain, $N_D = 1$ and $w_1 = 1$, then Eq. (5) reduces to equilibrium. Under these conditions, upon applying Eq. (7) to Eq. (5) with $\langle P_{xy} \rangle_0 = 0$ we obtain Eq. (4). The infinite frequency response may be obtained in terms of the Born expression,^{6,13–15}

$$g_{\infty} V = \sum_{i=1}^N \frac{p_{yi}^2}{m_i} - \sum_{i=1}^N \sum_{j=1}^N \frac{\partial F_{xi}}{\partial q_{xj}} q_{yi} q_{yj}, \quad (8)$$

where p_{yi} is the y component of the i th particles momentum, m_i is the mass of the i th particle, F_{xi} is the x component of the interparticle force acting on the i th particle, and q_{xi} is the x coordinate of the i th particle. For the case of a broken-ergodic solid, in the α th domain we have

$$G_{0,\alpha} = \langle g_{\infty} \rangle_{\alpha} - \beta V (\langle P_{xy}^2 \rangle_{\alpha} - \langle P_{xy} \rangle_{\alpha}^2), \quad (9)$$

where $G_{0,\alpha}$ is the zero frequency modulus in the α th domain. This shows how the difference in response between the fluid and the solid is closely related to Eq. (1).

So we have two qualitatively different expressions for the response to a step change in the strain. The first of these, Eq. (4) is applicable to an equilibrium liquid and the second, Eqs. (5) and (6), is a generalisation that is applicable to solid materials. This includes history dependent glassy solids on a time scale where they do not evolve significantly (say a decade less than the alpha time of the stress auto-correlation function). These expressions apply to the average response in some form. It is important to appreciate the details of how such averages may be constructed. For an ordinary ergodic fluid the ensemble averaged equilibrium correlation function appearing in Eq. (4) is equivalent to a time average obtained from an experiment or computer simulation. The response may also be measured directly, and for a reasonably large system the variance between different independent trials will often be negligible. However, under some circumstances (e.g., for small or soft systems) there will be significant variance in the measured response. We must then repeat the measurement, averaging a number of independent trials, in order to reduce the variance. When we consider a glassy solid, a time average on a single system may be representative of the average over a single domain, Eq. (5). Such behaviour will be predicated on a clear separation of time scales in the glassy dynamics. We can also obtain an ensemble average by measuring a large number of different samples, pre-

pared by the same macroscopic protocol (*i.e.*, the same history dependence). This ensemble of measurements may then be described using Eq. (6). Note that Eq. (6) is such that an ensemble average may be obtained by direct measurement without referring to the weights, w_α , which appear in Eq. (3).

In principle we may arrange to measure any system on a short enough time scale that it appears nonergodic. However, for a glassy system there are two relevant points: the relaxation time becomes longer than the longest time scale we are able to monitor and there is a separation of time scales. Consequently the system appears to be in a state of quasi-equilibrium.⁵ If we looked at an ordinary liquid (which does not have this separation of time scales) on a short enough time that it appeared to be nonergodic, then it would not be in a state of quasi-equilibrium, it would be out of equilibrium and Eqs. (5) and (6) would not work. This leaves us with four cases

1. The system is ergodic (*i.e.*, $N_D = 1$ upon constructing an ensemble of independent experiments using the same macroscopic protocol) and obeys Eq. (4) upon being subjected to a step change in strain. The system is a fluid.
2. The system is ergodic and obeys Eq. (5) but not Eq. (7). The system is an ergodic solid or a constrained ergodic metastable solid (e.g., a crystal polymorph which may not visit any polymorphs of lower free energy). See Ref. 10.
3. The system is nonergodic (*i.e.*, $N_D > 1$) and obeys Eq. (6) for the observed time after the step change. The system is a broken-ergodic solid (a glass).
4. The system obeys neither Eq. (4) nor Eq. (5) or (6) over the entire observation time. The system is out of equilibrium and out of quasi-equilibrium on this time scale. Given sufficiently more time to relax it will fall into one of the three criteria listed above.

We now apply the above considerations to molecular dynamics computer simulations.

We study a binary glass former featuring the Weeks-Chandler-Andersen potential as we have used previously.^{5,6} Our previous constant pressure simulations on this system identified a nominal glass transition at a density of $\rho = 1.25$ and $T_g \simeq 0.435$ based on diffusion data.⁵ This value is only indicative of the transition location for what follows. Here we will consider isochoric simulations with the number of particles, $N = 108$, using the Gaussian isokinetic thermostat¹¹ at the temperature of $T = 0.435$ at the three different densities $\rho = 1.25, 1.27$, and 1.3 . The units are in terms of parameters from the potential for the species *A* interparticle interaction. The length unit is σ_{AA} the energy unit is ϵ_{AA} and the time unit is $\sqrt{m\sigma_{AA}^2/\epsilon_{AA}}$. We consider two different preparative protocols, the first representative of a single sample and the second representative of an ensemble of independently prepared samples. In both cases we start with an ergodic liquid at $T = 0.5$ that has been allowed to reach a state of (metastable) equilibrium. For the first case (*single sample simulations*) there is one starting configuration, for the second (*ensemble simulations*) there are 100 independent starting configurations. The system is then instantaneously quenched to a temperature of $T = 0.45$ and run for a duration of 8000 time units.

In the *single sample* case 2000 independent simulations are now spawned off with the same position coordinates but different random velocities selected from the Boltzmann-Gibbs distribution, $P(p_i) \sim \exp(-\beta p_i^2/(2m))$. In the *ensemble* case 20 independent simulations are spawned off from each of the 100 independent configurations. The temperature is then instantly quenched to the final value of $T = 0.435$ and the simulations are run for an additional duration of 6000 time units. This point in time is now labelled zero, $t = 0$.

We now apply a step change of $\gamma = 0.025$ and obtain the response over the next 800 time units. The step change is arranged to be consistent with the SLLOD equations of motion, see Ref. 11. In addition we run the simulations from the same initial conditions without subjecting them to the step change in shear strain and compute the stress auto-correlation function and the infinite frequency response, Eq. (8). Thus we obtain three separate estimates of the response to the step. The first is obtained directly by subjecting the simulations to the step and the second and third is obtained using the appropriate response theory, Eq. (4) or (6).

The results from the *ensemble simulations* are shown in Fig. 1. At the density of $\rho = 1.27$ it can be seen that both the liquid linear response theory Eq. (4) and the quasi-equilibrium linear response theory Eq. (6) give essentially the same result, which shows strong agreement with the directly simulated data. This shows how the system at this density may be accurately modelled as an ergodic fluid. We now increase the density very slightly to the value of $\rho = 1.3$ and ob-

FIG. 1. Response to the step change at the densities of $\rho = 1.27$ and 1.3 for the *ensemble simulations*. The symbols (NEMD) show the response which is obtained by directly simulating the process. Also shown is the response which has been predicted from simulations which have not been subject to the step. These predictions are from liquid linear response theory (liquid theory) Eq. (4) and quasi-equilibrium linear response theory (QE theory) Eq. (6).

FIG. 2. Similar to Fig. 1 but for the *single sample simulations* at the densities of $\rho = 1.25$ and 1.27 . *QE theory* now refers to Eq. (5).

serve a very different outcome. The agreement between the directly simulated response and the quasi-equilibrium linear response theory remains very strong. However, the liquid linear response theory has broken down and no longer represents the directly simulated response. Note that Eqs. (4) and (6) differ by a time independent constant. If we add the zero frequency modulus less the residual stress term, i.e., $G_0\gamma_0 - \beta V\gamma_0 \sum_{\alpha=1}^{N_D} w_{\alpha} \langle P_{xy} \rangle_{\alpha}^2$, to the liquid response we obtain the quasi-equilibrium response. The nonzero value of this time independent term is due to the emergence of the constitutive relation of a solid.

The results from the *single sample simulations* are shown in Fig. 2 for the respective densities of $\rho = 1.25$ and 1.27 . There are two important observations here. *First*: whether the results from Eq. (4) appear above or below the directly simulated results (for single sample simulations) depends on how much residual stress is trapped in the sample. The

data in the figure, for $\rho = 1.27$, happens to have a less than typical residual stress and as a result the value of $\langle P_{xy}^2 \rangle_{\alpha} = \langle \Delta P_{xy}^2 \rangle_{\alpha} + \langle P_{xy} \rangle_{\alpha}^2$ is less than it would be in equilibrium. *Second*: the *single sample simulations* appear to be a nonergodic solid at a lower density, $\rho = 1.27$, than is the case for the *ensemble of simulations*. This is illustrative of how, for a real *single sample* case ergodicity will be determined by the duration of the time averaging. In contrast the apparent ergodicity of the *ensemble simulations* will be determined by the ageing time which has elapsed since the quench protocol was completed. Thus, if we construct an ensemble of independent samples, and then wait for a long enough time for it to relax, we obtain a response which is consistent with a fluid, Eq. (4). However, if we then apply the response theory to a single one of these relaxed samples, for it to appear ergodic we must time average for a very long time, otherwise it will appear as a solid, Eq. (5). This is so regardless of whether the ensemble has been allowed to relax before we begin measuring the single sample or not. To view a single glass sample behaving as an extremely slow liquid we must observe it over an extremely long time, much longer than is practically feasible. Clearly such a description is not relevant, we can only observe the glass for a limited amount of time, and thus it behaves as a broken-ergodic solid. On the longest time scale we are able to access, glass behaves as a solid material in a way that is qualitatively different to an extremely slow liquid.

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