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Effect of instantaneous and continuous quenches on the density of vibrational modes in model glasses

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Computational studies of supercooled liquids often focus on various analyses of their “underlying inherent states”—the glassy configurations at zero temperature obtained by an infinitely fast (instantaneous) quench from equilibrium supercooled states. Similar protocols are also regularly employed in investigations of the unjamming transition at which the rigidity of decompressed soft-sphere packings is lost. Here we investigate the statistics and localization properties of low-frequency vibrational modes of glassy configurations obtained by such instantaneous quenches. We show that the density of vibrational modes grows as ω^β with β depending on the parent temperature T_0 from which the glassy configurations were instantaneously quenched. For quenches from high temperature liquid states we find $\beta \approx 3$, whereas β appears to approach the previously observed value $\beta = 4$ as T_0 approaches the glass transition temperature. We discuss the consistency of our findings with the theoretical framework of the soft potential model, and contrast them with similar measurements performed on configurations obtained by continuous quenches at finite cooling rates. Our results suggest that any physical quench at rates sufficiently slower than the inverse vibrational time scale—including all physically realistic quenching rates of molecular or atomistic glasses—would result in a glass whose density of vibrational modes is universally characterized by $\beta = 4$.

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Introduction. Instantaneous quenches of high-temperature configurations into their so-called “underlying inherent states” are a prevalent practice in computational studies of disordered materials [1–6]. One conspicuous example of this methodology is found in the large body of numerical work dedicated to the unjamming scenario (see, e.g., [7], and references therein), in which simple models of soft repulsive spheres are regularly employed. In these studies, packings of soft spheres at zero temperature are conventionally generated by instantaneous quenches from some random, high-energy disordered states, and later subjected to various structural analyses [8–11] and/or perturbations [12,13].

A similar methodology is also extensively utilized in computational investigations of the glass transition [1–4], whose structural origin remains a highly debated topic in condensed-matter physics [14,15]. Instantaneous quenches that map an equilibrium configuration to a zero-temperature glassy state were first put forward by Stillinger and Weber [16], and subsequently utilized by many others [1–4], with the general assumption that the structural properties of the inherent states are indicative in some quantitative way of the dynamics of the supercooled configurations from which they are mapped.

A clear advantage of analyzing the structure of glassy inherent states over equilibrium configurations is the ability to cleanly and quickly extract structural observables while avoiding the difficulties that stem from thermal-fluctuations-induced noise, and from the broad spectrum of relaxation times that characterizes these systems. Instantaneous quenches are considered to be unrealistic idealizations of the physical cooling process by which glasses are formed. However, it is regularly assumed that *generic* properties of the resulting glasses remain unaffected by such protocols. This uncontrolled assumption overlooks the potential physical artifacts involved

in performing instantaneous quenches in computational studies of the structural properties of glassy materials.

In this Rapid Communication we question the common practice of investigating glassy states that were instantaneously quenched from high-temperature configurations, and subsequently deducing conclusions about generic glasses formed via physically realistic protocols. We focus, in particular, on the statistical and structural properties of low-frequency vibrational modes measured in ensembles of inherent states created by an instantaneous quench of configurations equilibrated at various parent temperatures T_0 . Recent studies of several structural glass-forming models [11,17,18] (see additional comments about the relation between [17] and the present work in [19]) identified a population of quasilocalized low-frequency glassy vibrational modes whose density $D(\omega)$ grows from vanishing frequencies $\omega \rightarrow 0$ as $D(\omega) \sim \omega^4$. These modes are either measured below the lowest Goldstone modes’ frequency [17,18], or identified by classifying vibrational modes according to their degree of localization [11]. Similar findings for a three-dimensional Heisenberg spin glass in a random field were put forward in [20]. Here we show that the *functional form* of the density of low-frequency vibrational modes can be affected by instantaneous quenches, and, under some conditions, displays deviations from the ω^4 law. We contrast our findings with measurements performed in ensembles of inherent states created by a continuous quench at a cooling rate \dot{T} through our model systems’ glass transition temperature. We find that the ω^4 law is robust to very rapid but not overdamped quenches, suggesting that inertia plays a key role in the self-organizational processes that occur as systems tumble down the multidimensional potential energy landscape during their quench into a glassy solid.

Models and methods. Here we briefly review the models and methods used in this work; a detailed description of

our model, methods, and preparation protocols can be found in the Supplemental Material (SM) [21]. We employ a binary mixture of pointlike particles in three dimensions (3D) that interact via a purely repulsive inverse-power-law potential. In what follows, physical observables (temperatures, frequencies, lengths, etc.) are understood as expressed in terms of the relevant microscopic units as defined in the SM. For visualization purposes alone we rescale frequency axes by a scale ω_0 (see figure captions). We chose to simulate systems of $N=2000$ particles for which the linear size of the box is slightly larger than the localization length of low-frequency glassy modes (estimated in our model at about ten particle diameters [17]), but still small enough such that Goldstone modes are sufficiently suppressed, allowing ample exposure of vibrational modes that occur below the lowest Goldstone mode frequency [17].

Ensembles of inherent states were created by collecting a large number of independent equilibrium configurations from each parent temperature T_0 , and evolving each one of these forward in time under fully overdamped dynamics $\dot{\vec{x}} \propto -\frac{\partial U}{\partial \vec{x}}$ until convergence, where \vec{x} denotes particles' coordinates and U the potential energy. We have also created ensembles of continuously quenched glasses, starting from independent equilibrium configurations at $T=1.00$, followed by a quench at a prescribed quench rate \dot{T} . Each of the constructed ensembles consists of 10000 glassy samples, which ensures statistical convergence (see SM for further details).

Results. Our model system exhibits the conventional phenomenology of computer glass-forming models. In Fig. 1 we demonstrate the slowing down in the relaxational dynamics upon supercooling of our model by monitoring the stress autocorrelation function $c(t) \equiv N \langle \sigma(t) \sigma(0) \rangle$ measured at various equilibrium runs at temperatures T . Here $\sigma \equiv \frac{1}{V} \frac{\partial U}{\partial \gamma}$, V is the volume of the simulation cell, U is the potential energy, and γ is a simple shear strain. The angular brackets denote an average over the time-translationally invariant signals of the stress from our equilibrium simulations. The inset of Fig. 1 shows the relaxation time τ_α vs $1/T$; relaxation times are

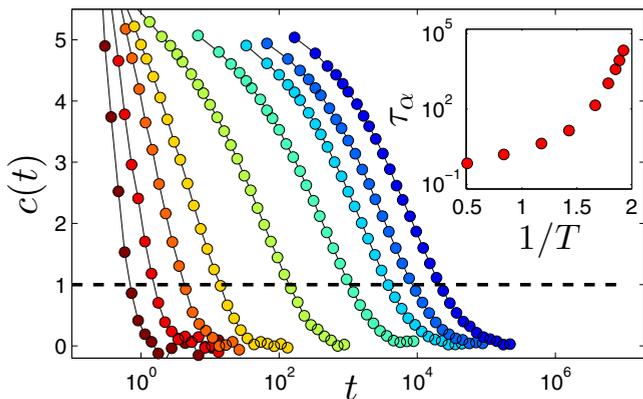


FIG. 1. Stress autocorrelation function (see text for definition) measured in equilibrium simulation runs at temperatures $T=2.00, 1.20, 0.85, 0.70, 0.60, 0.56, 0.54, 0.53$, and 0.52 , decreasing from left to right. Inset: the relaxation times τ_α vs $1/T$, determined by $c(\tau_\alpha)=1$, as indicated by the dashed horizontal line of the main panel.

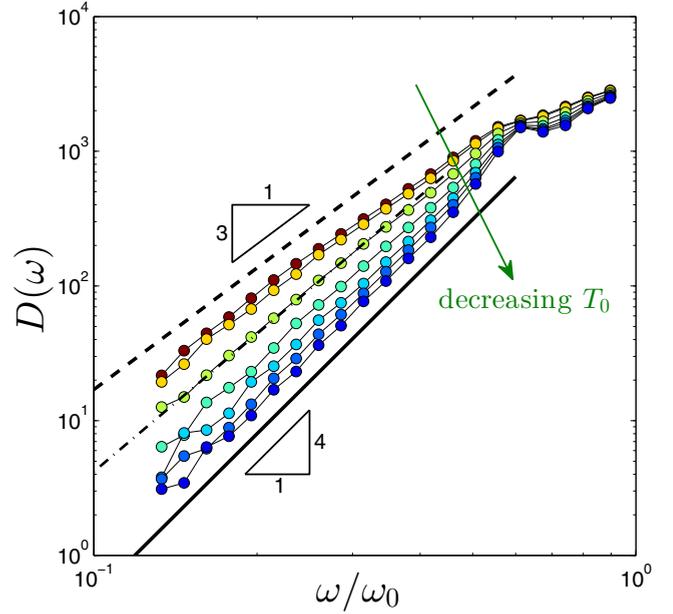


FIG. 2. Density of vibrational modes $D(\omega)$ measured in the ensembles of glassy samples quenched from the parent temperatures $T_0=2.00, 0.70, 0.60, 0.56, 0.54, 0.53$, and 0.52 , decreasing from top to bottom. The frequency axis is scaled by $\omega_0=3.0$ for visualization purposes. The dash-dotted line fitted to the $T_0=0.60$ data set corresponds to $D(\omega) \sim \omega^{3.4}$.

estimated via $c(\tau_\alpha)=1$, as indicated by the horizontal dashed line. The computer glass transition temperature of our model is estimated at $T_g \approx 0.5$, where the relaxation time $\tau_\alpha(T_g) \approx 10^5$.

We next turn to the investigation of the statistics and properties of vibrational modes in the different ensembles of instantaneously quenched glasses. Each such ensemble was obtained by an instantaneous quench of independent configurations that were equilibrated at some parent temperature T_0 . In Fig. 2 we show the low-frequency tails of the density of vibrational modes $D(\omega)$ measured in all the ensembles of glassy samples that were instantaneously quenched from parent temperatures as indicated by the figure caption. We find that $D(\omega) \sim \omega^\beta$ with $3 < \beta \leq 4$ for all ensembles, and $\beta \rightarrow 4$ as $T_0 \rightarrow T_g$. These data demonstrate that it is not only that the high T_0 inherent states possess more soft glassy vibrational modes, but that the actual functional form of the vibrational modes' distribution function depends explicitly on T_0 , at least up to the vicinity of the accessible equilibrium temperatures using conventional simulation methods. We emphasize at this point that our goal is not to accurately estimate the precise numerical value of the scaling exponents that characterize the density of vibrational modes. Our aim is rather to identify trends in the observed exponents upon systematically varying the preparation protocol of the glassy samples.

In Fig. 3 we show the means and the second to ninth deciles of the participation ratio e binned over frequency ω . The participation ratio of a vibrational mode $\hat{\Psi}$, defined as $e \equiv [N \sum_i (\hat{\Psi}_i \cdot \hat{\Psi}_i)^2]^{-1}$, is a simple measure of the degree of localization of a mode: the more localized a mode is, the smaller its participation ratio is expected to be. In [17,18] it has been shown that the participation ratio of low-frequency glassy

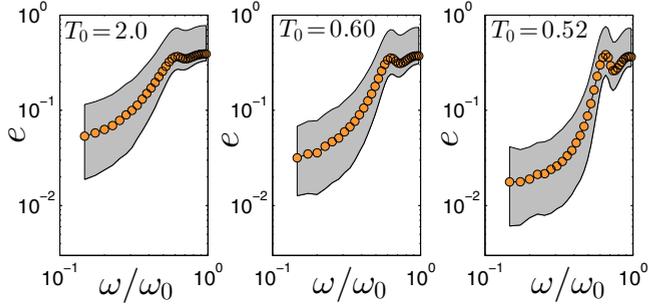


FIG. 3. Participation ratio e of vibrational modes vs frequency ω , for glassy samples instantaneously quenched from a parent temperature T_0 as indicated in the figure. The shaded gray areas cover the second through ninth deciles of data, and the circles represent the mean participation ratio binned over frequency. The frequency axes are scaled by $\omega_0 = 3.0$ for visualization purposes. Stronger localization is observed as $T_0 \rightarrow T_g$.

modes scales as N^{-1} , indicating that they are quasilocalized [22]. Figure 3 here shows that the degree of localization of low-frequency glassy modes increases for deeper supercooling, consistently with the findings of [17] that show a decrease in the participation ratio of low-frequency glassy modes for slower cooling rates. The data indicate that the transition of the mean participation ratio from the Goldstone modes' value to the low-frequency plateau (shown clearly for a much larger data set in [18]) is faster in ensembles created by an instantaneous quench from deeply supercooled solids. Furthermore, the rapid crossover in the localization properties of modes with increasing frequencies suggests that the exponent β can only be read off $D(\omega)$ below frequencies that are roughly a third of the lowest Goldstone mode frequency (see, e.g., the data in Fig. 4 below). We note that the crossover from quasilocalized, glassy modes at low frequencies to the first Goldstone modes is broader for smaller N ; this can be seen, for instance, in Fig. 1 of Ref. [18]. In the SM we show that increasing the system size does not, however, appear to have a substantial effect on our results, which reinforces the statement that the crossover broadening in our systems of $N = 2000$ does not affect our conclusions.

It is natural to contrast our results for instantaneously quenched glasses with similar measurements in glassy samples formed by a continuous quench into solids at finite quench rates. In Fig. 4 we show the density of vibrational modes of systems quenched at rates \dot{T} as described in the legend. Each such quench was performed from initial equilibrium configurations at temperature $T = 1.00$ (see SM for details). We find $\beta = 4$ at rates $\dot{T} < 10^{-2}$, as shown by the continuous lines. For higher rates, β appears to decrease, and for an infinitely fast quench from $T = 1.00$ we find $\beta \approx 3.3$ as indicated by the dashed line.

In Fig. 5 we plot the average potential energy per particle of the ensembles of instantaneously quenched and continuously quenched glassy samples. Interestingly, we find that the mean energy per particle of glasses quenched at the highest continuous rate for which $\beta = 4$ is observed ($\dot{T} = 10^{-3}$; see Fig. 4) is the same as for instantaneously quenched samples from the parent temperature $T_0 = 0.60$, up to less than a percent.

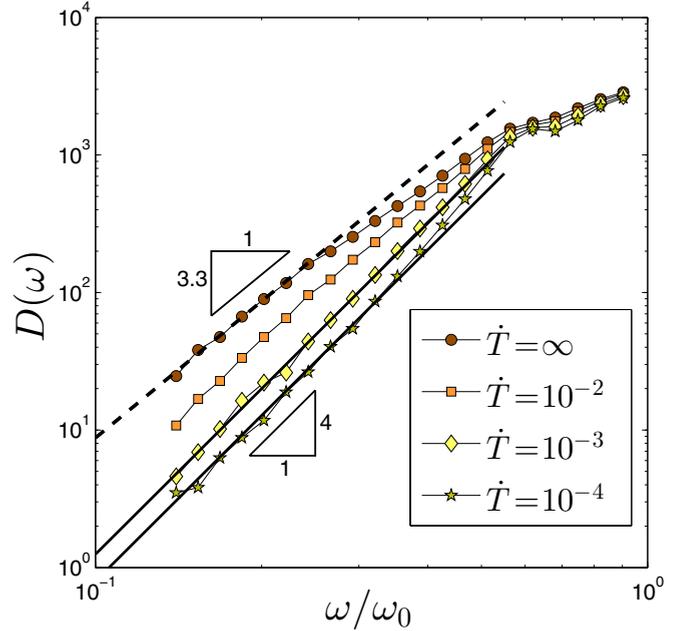


FIG. 4. Density of vibrational modes $D(\omega)$ measured in ensembles of glassy samples quenched continuously at rates as indicated by the legend, starting from equilibrium configurations at $T = 1.00$. Both continuous lines correspond to the ω^4 law. The frequency axis is scaled by $\omega_0 = 3.0$ for visualization purposes.

However, in the latter ensemble we clearly find $\beta < 4$ (see dash-dotted line in Fig. 2). This observation of two ensembles with the same inherent state energies but different β indicates that inertia that is present during the continuous quenches, but absent in the instantaneous quenches, plays an important role in the self-organizational processes that determine the fine details of the microstructure of the resulting glasses.

In order to explore the implications of our results for realistic glasses, we cast our reported observables into dimensionless numbers. We start with forming an atomistic time scale by considering the shear-wave speed $c_s \equiv \sqrt{\mu/\rho} \approx 4$, with an athermal shear modulus [23] $\mu \approx 15$ and a mass density

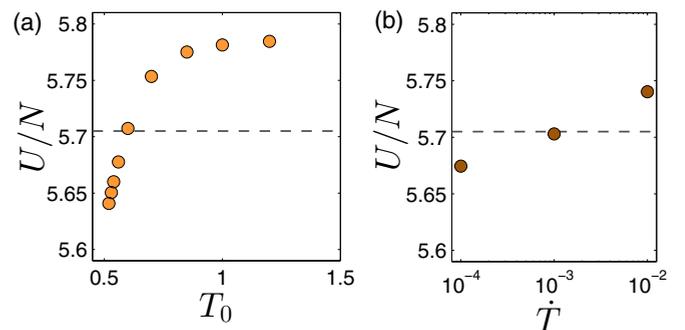


FIG. 5. Potential energy per particle of glassy samples averaged over (a) ensembles created by instantaneous quenches from the parent temperature T_0 , and (b) ensembles created by continuous quenches at quench rates \dot{T} . The dashed horizontal line shows that the $T_0 = 0.60$ ensemble and the $\dot{T} = 10^{-3}$ ensemble have very similar energies per particle (see text for further discussion).

$\rho = 0.82$, and dividing it by an atomistic length $a_0 \approx 1.0$ to find $c_s/a_0 \approx 4$. We next take $T_g \approx 0.5$ as a characteristic temperature scale, such that a dimensionless quench rate is formed as $\frac{\dot{T}a_0}{T_g c_s}$. Our findings suggest that for dimensionless quench rates lower than a crossover value 10^{-3} , or alternatively, for quench rates $\dot{T} \lesssim 10^{-3} T_g c_s / a_0$, the density of vibrational modes exhibits the ω^4 law. To compare to physical glasses, e.g., metallic glasses, we take $T_g \approx 500$ K, $c_s \approx 10^3$ m/s, and $a_0 \approx 10^{-9}$ m [24], from which we conclude that glasses quenched at rates $\dot{T} \lesssim 10^{11}$ K/s would exhibit the ω^4 law. The fastest rates that these materials can be quenched are typically on the order of 10^7 K/s (for quasi-2D ribbons; for bulk glasses the fastest cooling rates are slower), some four decades slower than our estimated crossover rate. This comparison essentially implies that any laboratory glass formed by quenching a melt would follow the ω^4 law.

Summary and discussion. In this Rapid Communication we have shown that the low-frequency tails of the density of vibrational modes of computer glasses created by an instantaneous quench have qualitatively different features compared to glasses created by a continuous quench. Our results suggest that the presence of inertia is important for the structural relaxation that occurs during quenches which leads to more stable glassy structures with less low-frequency vibrational modes. This suggestion is consistent with the results of Salerno *et al.* [25], who showed that upon reducing the inertia in the microscopic dynamics of sheared model glasses, the nature of avalanches of plastic activity, which depends in turn on the abundance of soft glassy modes, can change dramatically. Similar findings were reported in [26]. If indeed the presence of inertia in the microscopic dynamics is key in determining the low-frequency spectra, it would be of interest to observe whether overdamped glasses such as emulsions or foams, or computer glasses generated in simulations that employ Brownian dynamics, exhibit observable qualitative differences in their spectra compared to their inertial counterparts.

Our results call for caution when attempts are made to establish general conclusions about glassy solids from studies of model glasses that are created by instantaneous quenches from high-temperature liquid states. For instance, it is common practice in studies of the unjamming point to create packings of soft spheres by instantaneous quenches. While the qualitative features of the scaling of most mechanical observables with respect to the distance to the unjamming point do not seem to depend on the protocol with which packings are generated, our results suggest that the density of vibrational modes of those

packings might not be representative of the spectra of glasses created by physical quenches.

It is interesting to attempt to relate our findings to the predictions of the soft potential model [27–30]. This theoretical framework assumes that a glass can be decomposed into small subsystems, each possessing a quasilocalized soft glassy mode. Focusing on such a typical subsystem, and assuming that particles are displaced a distance s along the soft mode associated with that subsystem, this framework suggests that if the energy in the vicinity of $s=0$ satisfies $U(s) \geq U(0)$, then $D(\omega)$ is expected to grow as ω^4 . However, relaxing this constraint results in a different prediction, namely, that $D(\omega) \sim \omega^3$ [30]. The condition that the energy only grows in the vicinity of $s=0$ can be viewed as a stability condition; in instantaneously quenched glasses the overdamped nature of the quench makes it possible to form barely stable glasses that would possess local soft potentials $U(s)$ that have deeper minima at $s \neq 0$ compared to $U(0)$, e.g., asymmetric double-well potentials [29]. Creating such unstable structures in slowly quenched glasses is much less likely. According to the discussed framework, one may hypothesize that $\beta = 3$ should be observed in glasses created by an instantaneous quench; we indeed find β very close to 3 in samples that were instantaneously quenched from very high temperatures (see Fig. 2).

In this work we followed the simple approach of [17] and investigated the density of vibrational modes in small, three-dimensional model glasses, in which Goldstone modes are sufficiently suppressed to expose a population of quasilocalized soft glassy vibrational modes. This approach is, however, still limited in terms of the range of soft glassy modes' frequencies that can be probed, due to hybridizations with extended Goldstone modes at higher frequencies, as can be seen in Fig. 3. It is therefore of interest to investigate these issues using frameworks that overcome the issue of hybridization with Goldstone modes, e.g., [18,20,31–33], allowing one to probe the density of quasilocalized excitations up to higher frequencies.

A key question to be addressed in future research is whether extremely slow quench rates can result in glasses with $\beta > 4$. Recent developments [34,35] in the computational research of structural glasses allow one to equilibrate a particular model glass well below what is possible using conventional molecular dynamics or Monte Carlo methods. The new methodology introduced in [34,35] will be certainly useful in addressing this question.

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