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

Lerner, E.; Bouchbinder, E.

DOI
10.1103/PhysRevE.96.020104

Publication date
2017

Document Version
Final published version

Published in
Physical Review E

Citation for published version (APA):
Effect of instantaneous and continuous quenches on the density of vibrational modes in model glasses

Edan Lerner$^1$ and Eran Bouchbinder$^2$

$^1$Institute for Theoretical Physics, University of Amsterdam, Science Park 904, 1098 XH Amsterdam, The Netherlands
$^2$Chemical Physics Department, Weizmann Institute of Science, Rehovot 7610001, Israel

(Received 2 May 2017; revised manuscript received 14 July 2017; published 28 August 2017)

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 $\omega^\beta$ with $\beta$ 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 $\beta$ 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 $\beta = 4$.

DOI: 10.1103/PhysRevE.96.020104

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 $\omega \to 0$ 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 $\omega^4$ 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 $\omega^4$ 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 \( \omega_0 \) (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 \( \ddot{x} \propto -\partial U/\partial x \) until convergence, where \( \ddot{x} \) 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 \( T \). 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 \( c(t) \equiv \langle \sigma(t) \sigma(0) \rangle \) 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 \( \gamma \) 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 \( \tau_\alpha \) vs \( 1/T \); relaxation times are estimated via \( c(\tau_\alpha) = 1 \), as indicated by the horizontal dashed line. The computer glass transition temperature of our model is estimated at \( T_0 \approx 0.5 \), where the relaxation time \( \tau_\alpha(T_0) \approx 10^3 \).

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 \( \beta \to 4 \) as \( T_0 \to T_g \). 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 \( \omega \). The participation ratio of a vibrational mode \( \Psi \), defined as \( e \equiv \left[ N \sum (\Psi_j, \Psi_j)^2 \right]^{-1} \), 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
We find the rapid crossover in the localization properties of modes with instantaneous quench from deeply supercooled solids. Furthermore, data set in [18]) is faster in ensembles created by instantaneous to the low-frequency plateau (shown clearly for a much larger the mean participation ratio from the Goldstone modes' value for slower cooling rates. The data indicate that the transition of in the participation ratio of low-frequency glassy modes for systems quenched at rates $\dot{T}$ indicates by the dashed line.

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 $D(\omega)$ 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 $\omega^4$ 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 $\beta$ 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 $\rho$. 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 $\beta$ 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 $\rho$. 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 $\beta$ 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 $\rho$. 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 $\beta$ 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.
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 the energy in that subsystem, this framework suggests that the energy in the vicinity of $s = 0$ satisfies $U(s) \approx U(0)$, then $D(\omega)$ is expected to grow as $\omega^\beta$. 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 $\beta$ 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.

Acknowledgments. We thank G. Düring, E. DeGiuli, and M. Wyart for fruitful discussions.

[21] See Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevE.96.020104, which includes Refs. [36,37,17], for a detailed description of the models and numerical methods employed in our work, a discussion about finite size effects, and the statistical convergence of our data.
[22] The term quasilocalized is used to describe low-frequency glassy modes since their amplitude has been shown [17] to decay as a power law away from their core.