Probing equilibrium glass flow up to exapoise viscosities

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Glasses are out-of-equilibrium systems aging under the crystallization threat. During ordinary glass formation, the atomic diffusion slows down, rendering its experimental investigation impractically long, to the extent that a timescale divergence is taken for granted by many. We circumvent these limitations here, taking advantage of a wide family of glasses rapidly obtained by physical vapor deposition directly into the solid state, endowed with different “ages” rivaling those reached by standard cooling and waiting for millennia. Isothermally probing the mechanical response of each of these glasses, we infer a correspondence with viscoelasticity along the equilibrium line, up to exapoise values. We find a dependence of the elastic modulus on the glass age, which, traced back to the temperature steepness index of the viscosity, tears down one of the cornerstones of several glass transition theories: the dynamical divergence. Critically, our results suggest that the conventional wisdom picture of a glass ceasing to flow at finite temperature could be wrong.

Significance

“Does the glass cease to flow at some finite temperature?” Answering this question—of pivotal importance for glass formation theories—would require ridiculously long observation times. We circumvent this infeasibility relating the (directly inaccessible) ultraviscous flow of a liquid to the elastic properties of the corresponding glass, which we measure as a function of its age. The older the glass, the lower the temperature at which viscosity can be determined. Taking advantage of physical vapor deposition, we rapidly obtain a wide spectrum of ages rivaling those of millenary amber, enabling viscosity determinations at values as large as those pertaining to the asthenosphere. Our result ultimately rules out the finite-temperature divergence of the molecular diffusion timescale in a glass.

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configurations (28, 32, 33). Specifically, for a given deposition rate, coming from the high-temperature side, the (relatively large) surface mobility grants that the glass is “assembled” in equilibrium with its liquid, i.e., each layer of molecules is equilibrated before new molecules arrive in the deposition process. Within this regime, the lower the temperature, the lower the entropy of the system and the higher the stability. Below a given temperature the mobility is so slow that the structure is no longer in equilibrium with the liquid, and the system becomes increasingly unstable. Because the shape of the inherent structures of the energy landscape defines the vibrational properties, a question arises on the possible connection between mechanical response and glass stability, in connection with recent experimental evidence in amorphous depositions and naturally aged glasses (17, 37, 38). Specifically, previous studies (39) of IMC obtained by PVD reveal a sound velocity dependence on local substrate temperature which, in turn, has been shown to relate to the onset temperature of enthalpy release measured in calorimetry upscans (40). To address this issue we first studied the acoustic properties of the most ultrastable deposition by a combination of time-domain pump–probe optical spectroscopy and frequency-domain inelastic X-ray scattering (IXS). The former technique is a broadband version (41, 42) of picosecond photoacoustics (BPA) (43), which we recently developed to efficiently generate and detect longitudinal acoustic wavepackets in sub-μm-thick transparent layers. Specifically, by using white light pulses (450–650 nm), the energy dispersion and mode attenuation of the vibrational excitations have been simultaneously investigated in the frequency range 10–20 GHz. IXS, on the other hand, allows the study of the high-frequency limit (THz), where the characteristic excitation wavelengths approach the average interparticle distance and the structural disorder becomes of crucial importance. Further details on both the techniques are given in Materials and Methods. The dispersion curve as determined by BPA in the low-frequency regime, and by IXS in the mesoscopic regime, is reported in Fig. 2, along with the photoinduced differential reflectivity oscillations map and IXS spectra at fixed exchanged momenta (Fig. 2, Insets A and B), from which the dispersion is obtained.

In the low-frequency region, the linear energy dispersion indicates the existence of propagating vibrational excitations corresponding to a single longitudinal acoustic-like phonon branch. Remarkably, the propagating nature of these excitations lingers up to the THz frequency regime. The presence of structural disorder, indeed, strongly attenuates acoustic modes at the nanometer scale. Nevertheless, the existence of a well-defined first sharp diffraction peak mimics a first pseudo-Brillouin zone and, although the vibrational eigenmodes are no longer plane waves, a well-defined dominant wavevector still exists up to a zero-group velocity point corresponding to half of the pseudo-Brillouin zone boundary (44). The obtained sound velocity (the \( q = 0 \) derivative of the best sinusoidal fit to IXS data, dashed line in Fig. 2) is in excellent agreement with BPA data in the 10-GHz range and with previous single- (lower) frequency determination (37). The existence of a well-defined dispersion at any lengthscales within

![Fig. 1. Fictive temperature of PVD glasses as function of the substrate temperature during deposition, determined from DSC upscans, directly relates to the enthalpy content, hence quantifying the glass stability (see Materials and Methods for more details). Typical values obtained for conventional glasses for two different cooling rates are also indicated (dashed lines).](https://www.pnas.org/ cgi/doi/10.1073/pnas.1423435112)
a pseudo-Brillouin zone suggests the potential sensitivity of the acoustic properties to the local topology of the inherent structures visited by the glass. Given their capability to access a sizable portion of the dispersion curve, determining sound velocity with superior accuracy (down to 0.1%, about one order of magnitude better than ordinary Brillouin light scattering), BPA measurements have been extended to the other PVD samples as shown in Fig. 3A and B. During the experiments the temperature was kept constant at $T = 295$ K, i.e., well below $T_g$ and above the $T_f$ of the different depositions, to ensure that the glass state is arrested on the laboratory timescale.

A clear inverse correlation between sound velocity and $T_f$ arises. BPA experiments also enable determination of the hypersonic attenuation $\Gamma$ with an accuracy of tenths of GHz, and, accordingly, determination of the frequency dependence of the lifetime of the vibrational excitations. As an example, the frequency dependence of $\Gamma$ for $T_f = 281$ and 301 K is reported (pink and blue, respectively) in Fig. 3C. Aiming to unravel any link with $T_f$, we integrated the attenuation over the explored frequency range and calculated the excess relative (and normalized) to the most ultrastable glass ($T_f = 281$ K), as reported in Fig. 3D. The relative attenuation shows, similarly to the sound velocity, a clear but opposite (direct) correlation with $T_f$. Acoustic attenuation in disordered materials is ruled by different physical mechanisms (42). In the GHz regime, where a crystal-like picture of vibrational excitations holds, the attenuation is expected to be due to the anharmonicity of the interparticle interaction. The decrease of sound attenuation toward the lowest $T_f$s discussed above, therefore, corroborates the idea that lower energy basins are more harmonic in nature.

**Discussion**

The distinct thermomechanical correlation reported in this study has important implications for the validity of those paradigms which can be uniquely benchmarked at the liquid side of the glass transition, because equilibration times dramatically increase below $T_g$ preventing direct explorations. Fragility, in particular, quantifies the steepness of the liquid viscosity (or equivalently the relaxation time, through Maxwell’s relation $\eta = G'\tau$) at $T_g$, and it has a pivotal role in controlling physical properties of the supercooled phase (2, 3). The provocative idea that fast degrees of freedom characterizing glass dynamics well below $T_g$ can be predictors for slow dynamical properties of the liquid state, such as the structural relaxation time and hence fragility, is rapidly gaining consensus (4, 45–48). Whereas density fluctuations completely decorrelate in a liquid, as a consequence of the ergodic sampling of different basins in the energy landscape, in a glass a residual correlation exists, uniquely determined by the entire spectrum of vibrational eigenstates of the energy minimum where the system is trapped. This is the so-called nonergodicity factor (NEF), the long-time limit of the density–density autocorrelation function. Of interest here, it has been shown that the liquid fragility $m$ can be determined by the low-temperature behavior of the NEF, $f_2(T)$ (46, 47). The NEF can be quantified in different ways among them by the relative sound velocity jump occurring at the glass transition (49, 50), namely,

$$m = \gamma \cdot \left( f^{-1}(T_g) - 1 \right) \approx 140 \frac{c_0^2}{c_{\infty}^2} - \frac{c_\infty}{c_0}. \quad [1]$$

where $c_0$ and $c_{\infty}$ are the liquid and glass sound velocity values, respectively, and $\gamma \approx 140$ expresses the above-discussed correlation with fragility $m$ (46), verified in ordinary IMC glass (51). Critically, $c_0$ is an equilibrium property of the liquid, whereas $c_{\infty}$ is shown here to depend upon the very stability of the corresponding glass. This advocates the extension of the fragility concept to a temperature-dependent steepness index (11) $I(T)$ such that $I(T_f) = m$, which we use here to obtain the equilibrium viscosity below $T_g$. The mechanical response of a glass of a given stability, indeed, determines the viscosity of its liquid at the corresponding $T_f$ via the dependence $I(T = T_g) = I(c_{\infty}(T_f))$ in Eq. 1, reported in Fig. 4A.

Integrating this latter (see Eq. 11 in Materials and Methods), an Arrhenius plot can ultimately be obtained, shown in Fig. 4B. The super-Arrhenius behavior documented in IMC above $T_g$ (52) is reported as a dashed line representing a Vogel–Fulcher–Tamman (VFT) function. For $T > T_g$, a remarkable deviation is observed: The apparent fragility $I(T)$ is larger than $m$, but falls below the VFT expectation, and decreases with the glass stability, signifying a fragile-to-strong transition, quantified in Fig. 4A. This result verifies the predictions of Kovacs and Adam–Gibbs–Vogel models from aged IMC (27) and rationalizes very recent work in naturally long-time–aged amber (17), which set an upper bound to the temperature dependence of the dynamics below $T_g$. It is also in line with the conclusion against the VFT extrapolations in the glass (11, 53), and relates to the observation of an additional non-Arrhenius equilibration process in polymers (54). Moreover, the simultaneous decrease of both the acoustic attenuation and generalized fragility reported here at low $T_f$s validates recent molecular dynamic simulations (55) which put forward a direct correlation between kinetic fragility $m$ and the degree of anharmonicity of the interparticle interaction potential.

All together, these evidences syncretize on the scenario schematically depicted in Fig. 4, establishing a firm link between the hypsometric characterization of the energy landscape and basin-specific vibrational properties. Crucial to technological applications, the mechanical approach advanced here to assess stability is a nondestructive one, as opposed to calorimetric determinations of $T_f$. Most important, we demonstrate that the state of the glass is totally identified by $T_f$ and $T_g$, and once the nonergodicity parameter is calculated by the sound velocity jump at $T_f$, it is possible to determine the relaxation time from Eqs. 1 and 11, as shown in Fig. 4. The emerging protocol provides...
a unique way to capture essential features of a liquid attaining the structural arrest away from \( T_g \), up to relaxation times beyond 10\(^7\) s, corresponding to exapoise viscosities. In conclusion, we circumvented here the major hindrances to probe equilibrium content compared with the glasses cooled at ordinary rates. The fictive temperature of ultrastable glasses signify a smaller enthalpy rate and directly reflects the structural state of the glass. The lower values of the extrapolated value of the fictive temperature does not depend on the heating liquid line extrapolated according to a quadratic fit (32). Notably, the exchangeable momentum \( \Gamma = 266 \text{ K} \) and de-

The dynamic structure factor, \( S(q,\omega) \), contains information about the sound dispersion on the THz regime (51, 58).

\[ S(q,\omega) = S(q) \frac{1}{\omega} \frac{\Omega(q)\Gamma(q)}{1-e^{\hbar q^2/(2k_B T)}} e^{i\hbar \omega q^2/(2k_B T)} \]  

where the Bose factor accounts for the quantum nature of the probed excitations. The two terms in Eq. 2 represent the elastic and the inelastic components of the spectra, respectively. Eq. 2 was fitted to the experimental data and a correction was applied to the small difference in IXS sound velocity measurement of the ordinary glass reported in Fig. 3B accounts for a 0.8% positive dispersion occurring in the THz regime (31, 58).

**Picosecond Photoacoustics.** Time-domain measurements of longitudinal sound velocity and acoustic damping in the hydrodynamics limit were performed by broadband picosecond photoacoustics. This pump-and-probe technique is based on the generation and detection of coherent vibrational excitations by means of ultrashort laser pulses. The setup is built on a regeneratively amplified Ti:sapphire laser producing 50-fs, 4-mJ pulses at 800 nm with 1-kHz repetition rate. The output is split to generate both the pump and the probe beams; the former, after passing through a delay line, is focused onto the sample on an heating rate, \( \mu \sin \theta = 190, 210, 236, 266, 285, \) and 290 K) and coated by a 15-mm-thick layer of Ni. As the pump impinges on the sample, it is partially absorbed by the metallic coating, which thermally expands, launching in the underlying glass very short strain pulses, i.e., longitudinal acoustic wave packets with a characteristic spectrum extending from a few to hundreds of GHz (43). The photogenerated acoustic wavepacket travels inside the sample along the pump propagation direction. When the acoustic pulse is reflected at the metallic surface, whereas the transmitted component interferes with the light scattered from the traveling density fluctuation associated with the acoustic wavepacket. By monitoring transient differential reflectivity (with and without the pump pulse) \((\Delta R(t))/R\) as a function of the time pump–probe time delay, information can be gained on the phonon spectrum. Specifically, at any given probe wavelength \( \lambda \), the phonon frequency is set by the Bragg condition corresponding to a stimulated Brillouin scattering event:

\[ \nu = \frac{\nu}{2T} \sqrt{\frac{2\nu}{\lambda} n^2 - \sin^2 \beta}, \]

where \( \nu \) is the longitudinal sound velocity, \( q \) the exchanged momentum, \( n(\lambda) \) the index of refraction of the glass, and \( \beta \) is the incident angle with respect to the metallic coating. In our realization, the probe pulse consisted of a broadband white light continuum, generated from 2-mm-thick sapphire crystal plate and filtered to select wavelengths in the range of 450-450 nm. The broadband probe pulse’s reflection was dispersed by a 150-g/mm grating and monitored by a CCD, such that a number of two-color pump-and-probe experiments were simultaneously recorded. Transient reflectivity data were first reduced by subtraction of an exponential thermal background. Each channel achieves a sensitivity up to \( \Delta R/R = 10^{-5} \). To get rid of an independent determination of the refractive index \( n \), required in Eq. 2, the measurements were repeated at different scattering angles from 0° to 30°. A plot of the reflectivity oscillations as a function of time and probe wavelength is reported in the color map in Fig. 2 together with the signals at selected wavelengths. The signal was modeled with the dashed harmonic oscillator
Temperature dependence is from ref. 37. In Fig. 5 we sketch the evolution of the sound velocity, $c(T)$, as a function of the exchanged momentum $q$ exhibits a strong direct correlation with the kinetic fragility in the low-temperature limit, a dimensionless steepness index can be introduced:

$$f_0(T) = \frac{1}{1 + \alpha T}$$

where the notation $c_m(T)$ explicitly indicates the above-mentioned dependence on ficitive and measurement temperatures, respectively. It is worth mentioning that the $T$ dependence in Eq. 10 (i.e., on the very temperature where the sound velocity jump is evaluated) is negligible compared with the $T_T$ dependence brought about by the glass sound velocity. Once integrated in $1/T$, Eq. 10 provides the relaxation time below $T_T$ through

$$\log_{10}(1/T) = \alpha \log_{10}(1/T_m) + T_f \int T^{-1}d(1/T),$$

with $c(T) = 1.354 m/s$ estimated by Brillouin light scattering (61), and the $c(0)$ dependence is from ref. 37. In Fig. 5 we sketch the evolution of the sound velocity as function of temperature across the glass transition, for two glasses of different fictive temperature.

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