Vibration Modes and Characteristic Length Scales in Amorphous Materials

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The numerical study of the mechanical responses of amorphous materials at the nanometer scale shows characteristic length scales that are larger than the intrinsic length of the microstructure. In this article, we review the different scales appearing upon athermal elastoplastic mechanical load and we relate it to a detailed study of the vibrational response. We compare different materials with different microstructures and different bond directionality (from Lennard–Jones model materials to amorphous silicon and silicate glasses). This work suggests experimental measurements that could help to understand and, if possible, to predict plastic deformation in glasses.

INTRODUCTION

Amorphous materials are widely present in our environment, but their mechanical properties, although very interesting, are still poorly understood because of the lack of periodicity in their atomic structure. These materials have no intrinsic structural length scale despite the interatomic distance, as can be probed by measuring its static structure factor¹ or, equivalently, pair correlation function. It includes amorphous semiconductors like silicon,^{2,3} oxide glasses like silica and silicate glasses,⁴ metallic glasses,⁵ and other disordered assemblies like colloidal glasses.⁶ These materials are brittle at large scale but ductile at small scale.⁷ Their mechanical response is characterized by a very high strength with localized deformation.⁸ It is thus very important to understand the origin and the organization of plastic rearrangements, and if possible, to prevent plastic damage. One unsolved question concerns the connection between plastic rearrangements and structural defects. Also important is the search of visualization tools to measure local rearrangements and to prevent further plastic damage. Nanoindentation experiments and direct visualization through transmission electron microscopy, for example, need relevant interpretation tools; the former is sensitive to the loading geometry⁹ and the latter is distorted by the scattering due to structural disorder.¹⁰ In this context, vibrational spectroscopy and anelastic neutron and x-ray experiments are interesting and

well-controlled methods to infer the mechanical properties of glasses. Indeed, vibrational spectroscopy was already successful to identify vibrational anomalies like the Boson peak in glasses¹¹ and was proposed to quantify plastic deformation at the micrometer scale.¹² Brillouin spectroscopy was used to measure the low-frequency sound velocities and thermally activated processes.¹³ Anelastic neutron and x-ray scattering was used to measure dynamical structure factors, Boson peak, and mean-free paths,¹⁴ as well as relaxational processes with the help of time-resolved photon correlation measurements.¹⁵ In situ deformations give access to the strain tensor at the micrometer scale.¹⁶ However, nanometric heterogeneities make the interpretation of the measurements always difficult,¹⁷ and it is necessary first to obtain an insight into the elementary processes responsible for vibrational dynamics and local plastic rearrangements in glasses. Elementary processes responsible for plastic deformation in glasses were identified 30 years ago as shear transformation zones¹⁸ and were compared with free volume theory.¹⁹ Evidence of local nanometric rearrangements was found recently in different systems with the help of atomistic simulations.^{20,21} However, the location of the center of the rearrangements and its composition dependence is still a matter of debate.²² At the same time, it was shown that in the elastic reversible regime, displacement field already shows large-scale correlations that have a signature in the vibrational response.²³

In this article, we review first the different length scales identified numerically in glasses upon elastoplastic loading and discuss their composition dependence. We then look more accurately on the vibrational response and its sensitivity to mechanical deformation and structural changes resulting from plastic deformation. Finally, we show examples of the possible signature of these characteristic lengths and associated structural rearrangements in spectroscopic measurements.

ELASTICITY VERSUS PLASTICITY IN AMORPHOUS MATERIALS

Amorphous solids can be obtained experimentally and numerically by quenching very quickly a liquid drop in order to avoid the crystallization, as explained in Fig. 1. The crystallization is avoided kinetically, giving rise to a disordered solid after the atomic motion was strongly damped probably due to trapping below the glass transition temperature. The material is quenched into a liquid-like structure²⁴ without volume variation. The very high quenching rate ($>10^{11} \text{ K s}^{-1}$) used in atomistic simulations is far larger than the largest experimental quenching rate ($\sim 10^6 \text{ K s}^{-1}$). However, the numerically obtained equilibrium structure is very close to the experimental one⁴ at least for small-scale order as measured by the pair correlation function, suggesting that the classic empirical interatomic interactions used for the calculation implicitly accelerate the relaxational dynamics.²⁵ This is why a comparison between classic molecular

dynamics and experimental measurements is not hopeless and can be used to emphasize the role of the local structure on the mechanical properties. In this article, we will take examples from different model amorphous materials obtained in this way and constructed with different empirical interatomic potentials: Lennard–Jones interactions as an example of two-body interactions,²³ Stillinger–Weber potentials with a set of variable parameters to tune the bond directionality (three-body interactions),³ and BKS potential with effective Coulomb interactions and two different species that are used to model silica glasses.⁴ The variety of these interactions will allow us to underline the role of composition on the elementary processes of the mechanical response.

In the solid state, the departure from the homogeneous and isotropic mechanical behavior of glasses can be quantified by looking either at the nonaffine displacements²³ or at the micromechanical properties like the local elastic moduli.²⁶ The nonaffine displacements are defined on each atom as the difference between the actual displacement of the atom during one elementary strain step and the displacement it would support in a purely isotropic and homogeneous medium for the same kind of external deformation.²³ Examples of nonaffine displacements are shown in Figs. 2 and 3. These figures were obtained during athermal quasi-static mechanical shear load; the configurations are equilibrated with fast energy minimization after each applied elementary strain step (the effect of shear rate will be discussed below). This kind of

Fig. 1. Preparation of a SiO₂ glass from an initial cristobalite sample. The sample is heated up to 5200 K and then quenched with a quenching rate of $5.2 \times 10^{12} \text{ K s}^{-1}$. The crystallization is avoided kinetically.

Fig. 2. Simple shear of a silica glass sample: (a) shear stress versus shear strain, (b) simple shear deformation, and (c) nonaffine displacement field during reversible step. For the visibility, the displacements are magnified 5000 times. (d) Nonaffine displacement field for an elementary plastic rearrangement. Displacements are magnified by a factor 50.

Fig. 3. (a) Nonaffine reversible displacement field in a two-dimensional Lennard-Jones glass. The large-scale rotational structure is clearly visible, and STZ forms at the intersection between vortices. d = first-neighbor interatomic distance. (b) Effect of the composition, here for SW interactions with $\lambda = 19$. Vortices are clearly visible. (c) Nonaffine reversible displacement field for SW interactions with $\lambda = 21$. For higher bond directionality, the vortices appear chopped, which reveals a smaller length scale. Simulations were obtained with athermal quasi-static mechanical load.

measurement allows isolating the role of structural disorder on the energy landscape. Nonaffine displacements show mesoscopic rotational structures in the elastic reversible regime for low applied strain,²³ and they localize along Eshelby-like

deformations during elementary irreversible processes²⁷ that is at the onset of local plasticity. The stress–strain relationship (Fig. 2a) results from the alternation of such reversible and irreversible steps. The plastic rearrangements organize progressively

Fig. 4. Comparison between the boson peak and elastic heterogeneities in a two-dimensional Lennard-Jones glass: $(\omega/cq)^2$ as a function of the wavelength $\lambda = 2\pi/q$ for different system sizes (ω is the frequency, q is the wavevector, and c is the sound wave velocity obtained from macroscopic elastic constants), and average local shear modulus $G(\Lambda)$ divided by the macroscopic shear modulus G , as a function of the coarse-graining scale Λ (and for different system sizes). Lennard-Jones units. Error bars are the relative fluctuations of the local shear modulus.²⁶

upon mechanical load to give rise to macroscopically measured plasticity. This organization depends strongly on the composition and on the interatomic interactions,³ and it affects the elastic background²⁶ and thus the vibrational properties.²⁸ At this stage, it is very important, and unfortunately not always clearly mentioned in the literature, to distinguish large-scale elastic correlations and localized plastic rearrangements. As can be seen in Figs. 2c and 3, elastic reversible motion involves a continuous set of large-scale vortices spread across the entire system. It is not easy to determine the size of these vortices. From our knowledge, the best way is to look at the local elastic moduli and to identify the scale above which the behavior of the system becomes elastically homogeneous.²⁶ The corresponding size ξ is about $\xi \approx 20$ interatomic distances. Such a typical size appears as well as a characteristic wavelength for the convergence of the vibrational eigenfrequencies to those of the isotropic and continuous material (see Fig. 4). Conversely, in general localized plastic rearrangements are isolated (Fig. 2d) in the athermal regime (below the glass temperature T_g). They appear only at the spinodal limit when a bifurcation occurs at the onset of plasticity and, thus, are marginally relevant for harmonic vibrations, as will be discussed later. They are positioned at the border of a vortex²⁹ and the corresponding local strain is very large ($\geq 10\%$). They can be identified as a large amplitude local maximum of the nonaffine displacement field,³ and the size of the core of the plastic event can be measured with an exponential fit of the small distance decay of its amplitude. The size W of the athermally driven plastic event is of the order of five interatomic

distances (Fig. 3a). The unfolding of this size upon strain depends on the shear rate.³⁰ In the athermal quasi-static limit, its average value appears maximum at the tensile stress³⁰ just before plastic flow.

Depending on the composition (and on the pressure applied), the core of the plastic events can be either shear like or compression like, thus changing the corresponding constitutive laws. We have shown in Stillinger-Weber samples that the size W depends strongly on the bonds directionality and can be used as the analog of the size of dislocations core to infer the value of the tensile stress (Peierls stress).³ The general dependence is a decay of W with bonds directionality. In Fig. 3, we see that bond directionality affects the shape of the vortices in the elastic response: Higher bond directionality yields to a screening of the vortices that appear chopped and the corresponding increased fluctuations in the displacement field affect the acoustic scattering processes (see the “Vibration Modes” section).

Small-size plastic rearrangements locate at a place and a scale where mechanical strain is ill defined.²⁶ When looking at the mechanical functions coarse-grained at a slightly larger scale, we saw that they can be predicted by the statistical analysis of the local elastic moduli.^{26,28} Heterogeneous elasticity and plastic rearrangements are thus closely linked, and the latter could be revealed by an appropriate analysis of the vibration modes. We will now describe the resonant vibrations of amorphous materials.

VIBRATION MODES

Disordered solids are isotropic and homogeneous at a large scale. Plane waves with wavelengths larger than ξ are only slightly distorted by structural disorder.²³ The vibrational eigenmodes $\{\mathbf{u}_i\}$ are given by the eigenvectors of the dynamical matrix $\mathbf{D}$. They are the solutions of the dynamical harmonic equation

$$\sqrt{m_i}\omega^2 u_i^\alpha = \sum_{\beta j} \sqrt{m_j} D_{\alpha i, \beta j} u_j^\beta \quad (1)$$

where ω is the eigenfrequency (ω^2 is the corresponding eigenvalue of $\mathbf{D}$), m_i is the mass of atom i , and u_i^α is the displacement of atom i in the direction α . It is possible to find numerically the eigenfrequencies and the eigenvalues of $\mathbf{D}$. The geometrical description of the vibrations can then be created with the help of a projection on the plane waves²³ or by looking at different quantities like the participation ratio.³¹ In all the systems we have studied, the vibrational eigenmodes can be regrouped into three different vibration families (Fig. 5):

- At low frequencies (below $2\pi c/\xi$ where c is the velocity of transverse waves), plane waves coexist with *soft modes* that are the precursors of plastic instabilities. The number of soft modes depends

Fig. 5. Vibration modes in a SiO_2 glass at (a) 21 cm^{-1} (soft mode), (b) 103 cm^{-1} (rotons), and (c) 898 cm^{-1} (multifractal mode) and in a-Si (SW interactions with $\lambda = 21$) at 0.795 THz (soft mode), 7.663 THz (rotons), and 17.451 THz (multifractal mode).

on the proximity to a plastic rearrangement,²⁸ on the quenching rate, and on the composition of the glass. For example, contrary to Lennard–Jones glasses, silica glasses contain many soft modes at rest and this number increases with the pressure applied. Plane waves are not purely plane waves but contain a small amount of nonaffine displacements whose amplitude is increasing when approaching the frequency $2\pi c/\xi$. In this case, these modes are also called quasi-localized modes.³²

- At intermediate frequencies, between $2\pi c/\xi$ and the frequency characterizing the transition between propagating (or diffusing³³) acoustic modes and localized optic modes, vibration modes show a rotational structure (rotons) analog to the non-affine displacement field observed in the athermal elastic regime (Fig. 3).
- Finally, at the transition between acoustic and optic modes (which can be identified either by the saturation of the dispersion relation measured by the dynamical structure factor or by the decay in the vibrational density of states (VDOS) possibly followed by a deep increase), the vibration modes show a multifractal structure similar to the one observed in Anderson localization.³⁴

These categories are of course very crude because, for example, in the intermediate frequency domain, each type of glass has its own Raman signature (with very

specific active bands that are not described here). However, these categories can be retrieved by looking at the dynamical structure factor,³³ which shows a transition from propagative acoustic modes to slightly scattered, strongly scattered (diffusons), and then optic modes. These categories appear as well in the VDOS. After normalized by the Debye density of states,³⁵ the VDOS in amorphous materials shows a peak at a frequency that is low compared to the Debye frequency. This peak is called the Boson peak. We have seen³⁶ that it is approximately located at the transition frequency $2\pi c/\xi$. It is shown in Fig. 6a that the position of the maximum of this peak depends indeed on the composition, as for example on the bond directionality.³⁷ When the bond directionality is increased in Stillinger–Weber-like systems, the primary peak located at a wave vector $2\pi c/\xi_1$ (with $\xi_1 \approx 25 \text{ \AA}$) is progressively replaced by a secondary peak located at a smaller length scale $\xi_2 \approx 7 \text{ \AA}$. The transition occurs for a parameter $\lambda = 21$ corresponding to the description of amorphous silicon. The change in this characteristic length scale can be compared with the small-scale fluctuations appearing in the nonaffine fields of Fig. 3, suggesting a scattering on smaller entities due to the bond directionality. Note that ξ_2 is associated to a common maximum in the participation ratio of the vibration modes in all samples (Fig. 6b), and thus it cannot be related to a localized mode.

Fig. 6. (Top) Density of vibrational states (VDOS) rescaled by the Debye prediction for SW interactions with different values of the parameter λ . The horizontal axis is the rescaled frequency $q^* = \omega/c_T$. The boson peak is clearly visible. Two characteristic length scales appear: a large length scale $\xi_1 = 2\pi q_1^* \approx 25$ Å for low directionality and a smaller length scale $\xi_2 = 2\pi q_2^* \approx 7$ Å for $\lambda > 21$. (Bottom) Participation ratio (PR) of the vibrational eigenmodes as a function of the rescaled frequency $q^* = \omega/c_T$ and for different values of λ . The local maximum at PR = 0.55 occurs for the same value of $q^* \approx 7.5$ nm $^{-1}$ whatever λ , that is at ξ_2 .

The boson peak can be measured in glasses with different spectroscopic techniques (Raman and Brillouin spectroscopy, x-ray and neutron scattering). We will now look at a different signature of the mechanical deformation in vibrational spectroscopy.

SPECTROSCOPIC MEASUREMENTS

Scattering measurements of the mechanical response can be regrouped into two different groups: scattering on the atomic positions (light, x-ray, and neutron scattering) versus scattering due to temporal variation of the local optical polarizability resulting from atomic motion (Raman and Brillouin scattering). The former will allow to get the dispersion relation and the acoustic mean-free paths in the boson peak frequency range,¹⁴ whereas the latter will be more sensitive to local vibrations and structural changes.³⁸

To take into account the large-scale correlations in the vibration modes, it is possible to perform

Fig. 7. Comparison between the semiclassically computed Raman spectrum and experimental data on SiO $_2$ glass at $T = 300$ K.

semiclassical calculations of Raman spectra, with an empirical description of the local polarizability.^{39,40} The classic vibration modes are computed from the diagonalization of the dynamical matrix of the samples at rest (relaxed to a local energy minimum). The temperature ($T \approx 300$ K) determines the Bose factor in the Raman amplitude.³⁹ The bond polarizability approximation³⁹ assumes that only the vibrations of the first neighbors will contribute to the Raman tensor. A comparison between the semiclassically computed spectrum and experimental results in silica glass is shown in Fig. 7. The peak characteristics of a silica glass are recovered⁴⁰ and the computed spectrum is quite good in comparison with ab initio calculations.⁴¹

It is possible to test the sensitivity of the semi-classical spectrum to mechanical loads. Figure 8 shows the effect of the simple shear plastic flow described in Fig. 2b. In Fig. 8, “basic” configurations are obtained prior to loading, and “shear” configurations are taken arbitrarily in the quasi-static plastic plateau shown in Fig. 2a, where irreversible structural changes occur. Thanks to numerical data, the numerically observed increase in the high-frequency Raman intensity for irreversibly strained configurations can be compared with the computed VDOS and to the description of the vibrational modes. In silica glasses, it is shown that after shear, the computed vibrational modes tend to localize in the 700–1000 cm $^{-1}$ frequency range. In this same frequency range, the VDOS increases. This increase has been identified with an increased mobility of oxygen atoms in the stretching direction,⁴⁰ which is the signature of structural changes. It is interesting to note that the permanent structural changes observed affect mainly the vibrational response close to the localization transition from acoustic to optic modes that appears unexpectedly to be the most sensitive to shear. Note that the Raman activity is constant during the plastic flow and thus could be used as a stress sensor,⁴² as already proposed for hydrostatic compression.

◀Fig. 8. (a) Shear sensitivity of HH Raman spectrum of SiO₂. (b) Shear sensitivity of the participation ratio of the vibration modes. (c) Shear sensitivity of the VDOS and separate contribution of oxygen and silicon atoms to the VDOS of a silica glass. (d) Separate contribution of bonding, rocking, and stretching modes and shear sensitivity in the same silica glass.

CONCLUSION

Quasi-static athermal atomistic simulations helped to identify two characteristic length scales in the nonaffine displacement field of amorphous materials submitted to a mechanical load. These length scales are related respectively to the elastic and to the plastic deformation of athermally driven amorphous materials and can be inferred from the analysis of elastic constants at the nanometer scale. Consequently, they have a signature in the vibrational response and vibrational spectroscopy measurements. Elastic deformation acts as a scatterer and contributes to the boson peak. Irreversible plastic structural changes can be probed with Raman spectroscopy. Among other perspectives, the detailed analysis of the vibration modes and of their sensitivity to mechanical load strongly encourages researchers to evaluate a spectroscopic signature of the soft modes that are the precursors for the plastic instability and could be used to predict plastic deformation.

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