Irradiation-Induced Topological Transition in SiO₂: Structural Signature of Networks' Rigidity

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By affecting the connectivity of atomic networks, composition, temperature, or pressure can induce topological transitions between the three atomic states of rigidity — flexible, isostatic, and stressed-rigid. However, no clear structural signature of such transitions has been elucidated thus far. Here, based on realistic molecular dynamics simulations of irradiation-induced damage in quartz, we report the first evidence of a rigid-to-flexible rigidity transition controlled by structural variations only. This topological transition is shown to arise from the simultaneous loss of atomic eigenstress and onset of network flexibility, and features a well-defined structural signature in the medium-range order of the atomic network.

I. INTRODUCTION

Since originally proposed by Phillips [1], topological constraint theory (TCT, or rigidity theory) has been widely used to predict the compositional trends of various properties in glasses, e.g., glass transition temperature, viscosity, or hardness [2–5]. Indeed, by reducing complex atomic networks into simple mechanical trusses, TCT captures the important atomic topology, while filtering out less relevant details that ultimately do not affect macroscopic properties [6]. Specifically, the rigidity of a network is assessed by determining the number of topological constraints per atom, n_c , which comprises the radial bond-stretching (BS) and angular bond-bending (BB) chemical atomic bonds, and comparing this metric to three, the number of degrees of freedom per atom. According to Maxwell's stability criterion [7], atomic networks can be (1) flexible ($n_c < 3$), showing floppy internal modes of deformation [8], (2) stressed-rigid ($n_c > 3$), featuring eigenstress due to mutually incompatible constraints [9], or (3) isostatic ($n_c = 3$), being rigid but free of eigenstress.

Rigidity transitions, e.g., flexible-to-rigid, can be induced by variations of composition [4, 10, 11] or thermodynamic conditions, as, e.g., temperature tends to thermally break constraints [12], whereas pressure tends to create constraints by increasing coordination numbers [13]. While such rigidity transitions are associated with anomalous behaviors in thermodynamics [14], dynamics [15], or mechanical properties [16], structural signatures of rigidity transitions have remained elusive thus far [17]. In addition to composition and thermodynamic conditions, atomic structure itself should also affect rigidity. For example, although α -quartz is stressed-rigid [4, 18], glassy silica, despite having the same composition, is iso-

static on account of the breakage of Si–O–Si BB constraints [10, 11]. However, no continuous rigidity transition based on structural changes only has been reported thus far.

Here, based on molecular dynamics (MD) simulations of irradiation-induced damage in α -quartz, we report the first evidence of a purely structural rigidity transition, that is, at constant composition and thermodynamic conditions. Starting from the stressed-rigid atomic network of quartz, irradiation is shown to induce the progressive disordering of the network associated with the breakage of a fraction of weak BB constraints, which, ultimately, results in the formation of a disordered flexible network. As they are not affected by any compositional effect, pressure-induced stress, or temperature-induced disordering, these results constitute the first example of an “intrinsic” rigidity transition. This allows us to clearly isolate a medium-range structural signature of the rigidity transition, and to identify the onsets of eigenstress and internal flexibility in the network.

II. SIMULATION DETAILS

A. RADIATION SIMULATION METHODOLOGY

To establish our conclusions, we rely on realistic simulations of irradiation-induced damage in α -quartz based on a well-established methodology [19, 20]. An $8 \times 9 \times 7$ supercell of α -quartz with 4536 atoms is chosen as the starting structure. The radiation simulation requires larger system size to avoid potential self-interaction during the ballistic cascade due to the periodic boundary conditions. To choose the initial system size, the dis-

tance traveled by a bullet atom in randomly chosen directions is estimated. The dimensions of the supercell in each of the directions are chosen as twice the maximum distance traveled by the initial bullet atom. To simulate neutron irradiation, an atom in the structure is randomly selected based on the probabilities calculated from the concentration of each element and their experimentally determined neutron cross-sections. This atom is then accelerated with a given kinetic energy determined by the energy of the simulated colliding neutron, 600 eV herein, thereby simulating the energy transfer from the radiation. The trajectory of the atom is tracked to locate the first collision, around which a cascade of collisions would be initiated. A spherical zone is then set up around this region, inside which the temperature is not controlled, in order to avoid any spurious effect that might affect the dynamics of the atoms. Outside this zone, however, a thermostat is used to maintain the temperature at 300 K, thus allowing the dissipation of the generated thermal energy to be properly simulated. After each collision, the system is equilibrated at 300 K and ambient pressure and, thereby, is free to feature some changes in density. By repeating such ballistic events, damage, e.g., atomic displacements and associated structural relaxations, accumulates in the quartz structure, which eventually leads to complete amorphization.

Note that such simulations require a realistic inter-atomic potential that (1) correctly describes both the pristine and disordered structures with a constant set of parameters, (2) offers a realistic description of high-energy events (at low inter-atomic distances), and (3) is able to accurately handle over- and under-coordinated atoms (i.e., irradiation-induced damage observed in quartz [20]). To this end, we use the ReaxFF reactive potential [21], as it can successfully reproduce the structure of α -quartz and glassy silica [22–24] and features sophisticated potential forms that can dynamically adjust potential energy based on local atomic environments. The simulations are carried out using the LAMMPS package [25].

B. CONSTRAINTS ENUMERATION METHODOLOGY

Elucidating the effect of irradiation on the rigidity of the atomic network requires to enumerate the number of topological constraints acting between the atoms, without relying on any unproven guesses. For a fully connected homogeneous network, for example Ge–Se glasses, the constraints enumeration is straightforward and depends only on the coordination number, r_i of each of the species. Thus, each species will have $(r_i/2)$ BS constraints, each constraint being shared by two atoms, and $(2r_i - 3)$ BB constraints, which corresponds to the number of independent angles required to define a polyhedra. Thus, the total number of constraints per atom n_c is:

$$n_c = \bar{r}/2 + 2\bar{r} - 3 \quad (1)$$

where $\bar{r}$ is the average coordination number of the atoms. The isostatic state corresponds to $n_c = 3$, where the number of constraints is equal to the number of degrees of freedom.

In contrast, constraints enumeration for a complex system like an irradiated mineral is complicated due to the following difficulties. (1) The coordination number (CN) could vary for each species present in the system [20]. For example, Si can have a coordination number of 3 or 4; O can have a coordination of 1, 2 or 3. Accordingly, the number of constraints associated with these atoms vary. (2) The weak angular constraints, for example Si–O–Si bonds in quartz, which are associated with lower energies, are progressively broken by energy deposited due to irradiation. This process is reminiscent of the weak constraints broken at room temperature (300 K) due to thermal energy [12, 26]. As such, enumeration of constraints requires a closer look at the evolution of the atomic structure.

To tackle these issues, we rely on MD simulations, as they provide access to the trajectories and dynamics of individual atoms. Exploiting the so obtained atomic trajectories, a method has been developed for constraints enumeration, which has been widely applied to chalcogenide and oxide glasses [11] and, more recently, to atomic-scale models of cement pastes [4]. This method is based on an inverse approach, wherein the motion of an atom is used to deduce the number of active constraints associated with it. The basic idea of this method is that: an active constraint would maintain bond lengths or angles fixed around their average values, whereas a broken or missing constraint would allow large atomic motion. Thus, to obtain the number of BS and BB constraints associated with a central atom, we estimate the radial and angular excursions of each neighbor, respectively. A broken constraint corresponds to a large radial or angular excursion, while an intact constraint restricts the motion around its mean value.

To count the number of BS constraints, we calculate the pair distribution functions (PDFs) of oxygen and silicon atoms and the contributions of each neighbor 1, 2, ..., 6, where the latter are identified according to their respective distances to the central atom. The choice of 6 is arbitrary, while ensuring that the number of neighbors considered is large enough to count all the constraints. Further, the second moment of the distribution is calculated, which corresponds to the radial excursion of the neighbor atom. Such radial excursions, as computed in quartz, are plotted as a function of neighbor number in Fig. 1. We observe that there is a clear jump in the radial excursion after a neighbor number of 4 and 2 for Si and O atoms, respectively, which corresponds to their coordination number. As such, the number of intact and broken BS constraints can be clearly discriminated by ensuring that the BS constraints are accounted only if (1) the mean distance d belongs to the first coordination shell [27], and (2) σ is low. A similar method is applied for BB constraints. Note that the limit between in-

FIG. 1. (color online). Radial excursions with respect to a central Si and O atom of each neighbor. Note that intact and broken BS constraints are associated with significantly different (low and high, respectively) radial excursions.

tact and broken constraints has been found to be around $\sigma/d = 7\%$ [26], which is fairly close to the Lindemann criterion [28, 29]. We note, however, that the σ of intact and broken constraints typically significantly differ from each other (see Figs. (1-2)), so that the enumeration only weakly depends on the value of this threshold.

Similar methodology is adopted for the counting of BB constraints, wherein the distribution of angles around a central atom is calculated. Counting the number of angles formed by the central atom with 6 nearest neighbors, we obtain 15 angles ($N(N-1)/2$). The second moment of these distributions gives the angular excursion corresponding to each angle as plotted in Fig. 2. Similar to the BS constraints, we observe that there is a clear demarcation between intact and broken BB constraints, which makes the constraint enumeration straightforward. Thus, the method completely relies on the dynamics of each species present in the system and hence presents a rigorous method to enumerate the number of constraints. A detailed discussion on the methodology has been presented in Ref. [26].

III. RESULTS

A. IRRADIATION-INDUCED DAMAGE

Upon irradiation, we observe that the density of quartz decreases and eventually converges to a value comparable to that of glassy silica. As shown in Fig. 5, a similar trend and degree of swelling are observed experimentally [30–33], although we note that different experimental conditions prevent direct comparisons based on mere knowledge of the dosage.

In addition, as expected, we observe a progressive dis-

FIG. 2. (color online). Angular excursions around central Si and O atoms. Note that, as in the case of BS constraints, the angular distributions associated to intact and broken BB constraints significantly differ.

FIG. 3. (color online). Pair distribution function (PDF) calculated from pristine and irradiated quartz, showing the loss of long-range order after irradiation. PDF of glassy silica is also plotted for comparison.

ordering of the quartz structure (see the snapshots in Fig. 5), in agreement with electron diffraction measurements [34]. More specifically, Fig. 3 shows the PDF of irradiated quartz. We note that the atomic network of irradiated quartz retains some degree of short-range order, but largely loses the longer-range structural correlations present in the crystal. Such features are typically observed in the atomic networks of glasses, i.e., when the disordering of the network arises from rapid quenching from the liquid state rather than irradiation, which suggests that the structure of irradiated quartz is close to that of glassy silica.

FIG. 4. (color online). Si-O-Si bond angle distribution calculated for pristine and irradiated quartz. Values have been normalized by the total number of angles.

However, as shown in Fig. 3, the short-range structure of irradiated quartz significantly differs from that of glassy silica (note that both systems were simulated using the same inter-atomic potential[22]). In details, the PDF of irradiated quartz shows (1) broader peaks and (2) an additional peak centered around 2 Å. While (1) suggests an overall higher degree of disorder in the network, (2) arises from the presence of coordination defects[35]. Indeed, as detailed in Ref. [20], we observe upon irradiation the formation and accumulation of a small amount of coordination defects that are not observed in glassy silica — around 0.8 % of tricluster O atoms and 1.5 % of non-tetrahedral Si species. Finally, the disordering of the network also manifests itself in the Si-O-Si partial bond angle distribution (PBAD), as shown in Fig. 4. The broadening of the PBAD upon irradiation observed here indicates the loss of rigidity of the inter-tetrahedral angle (see Sec. IIIB). Altogether, to the best of our knowledge, these results constitute the first realistic atomistic description of the irradiation-induced amorphization of quartz.

B. EVIDENCE OF A RIGIDITY TRANSITION INDUCED BY IRRADIATION

We now focus on assessing the effect of irradiation on network rigidity. To this end, we rely on the MD-based methodology presented in Sec. IIB, which allows us to unambiguously discriminate active from inactive constraints and, as such, enumerate the number of constraints per atom n_c . The irradiation-induced variation of network rigidity is presented in Fig. 6. First, we note that the constraints enumeration for quartz is in agreement with the results expected for fully connected networks, that is, each atom undergoes $r/2$ and $2r - 3$ BS

FIG. 5. (color online). Evolution of the density of irradiated quartz as a function of deposited irradiation energy (bottom axis), compared with experimental data (top axis). The experimental values are represented by orange circles [30], blue diamonds [30], green squares [32], and purple triangle [31]. The insets show three snapshots of the atomic structures after selected deposited energies.

and BB constraints, respectively, where r is the coordination number. For quartz, this leads to $n_c = 11/3$, i.e., stressed-rigid, in agreement with the present results [4, 18]. Second, we observe that, upon irradiation, n_c decreases towards $n_c = 3$, which is the value expected for glassy silica, due to the breakage of the Si-O-Si BB constraints – a consequence of the high glass transition temperature of silica [10, 11]. Third, n_c is noted to cross the value of three at about 13 eV/atom deposited energy, which effectively separates a stress-rigid from a flexible domain. To the best of our knowledge, this constitutes the first evidence of irradiation-induced rigidity transition. As shown in the inset of Fig. 6, this transition mostly arises from the decrease of the number of angular BB constraints per atom upon irradiation, which results from the breakage of Si-O-Si, as well as a small fraction of O-Si-O BB constraints. This suggests that irradiation preferentially affects these weaker angular constraints [4], while it has little, if any, effect on the stronger radial Si-O BS constraints.

IV. DISCUSSION

A. IDENTIFICATION OF A STRUCTURAL SIGNATURE OF NETWORK'S RIGIDITY

Having demonstrated the existence of an irradiation-induced rigidity transition, we now focus on identifying a potential structural signature thereof. This is moti-

FIG. 6. (color online). Evolution of the number of constraints per atom n_c in irradiated quartz as a function of deposited radiation energy. Data are fitted by a decreasing exponential function. The red dashed line indicates the position of the rigidity transition ($n_c = 3$), which effectively separates the stressed-rigid from the flexible domain (grey area). The inset shows the re-partition of radial BS and angular BB constraints.

vated by the fact that, here, as opposed to conventional topological transition induced by composition, temperature, or pressure, the shift of rigidity is entirely controlled by the structure itself. As such, this example constitutes an ideal system to seek for a structural signature of the rigidity transition. First, we note that no anomalous behavior of the short-range order structural features – bond length, angles, coordination numbers – is found at the rigidity transition. Rather, the rigidity transition appears to be encrypted in the medium-range order (MRO) structure of the network. To characterize the MRO, the neutron structure factors ($S_N(Q)$) are computed through the Fourier transform of the pair distribution functions, at different radiation energy dosages. Special focus is placed on the first sharp diffraction peak (FSDP) of $S_N(Q)$ [36–38], which captures the structural correlations in the MRO.

In glassy silica, the FSDP is found at around $Q = 1.5 \text{ \AA}^{-1}$ [39]. Note that, from the Debye scattering equation, a structural feature with a spatial frequency of r results in a most intense peak at $Q = 7.72/r$, where 7.72 is the first maximum of the spherical Bessel function [17, 40]. As such, in real space, the position of the FSDP is associated with a typical repetition distance of $5.1 \text{ \AA}$, which is thought to be related to the distribution of interstitial voids in the network [41]. Similarly, the full width at half maximum (FWHM) of the FSDP is associated, in real space, with a coherence length L . L has been reported to be indicative of an average rigid cluster size, following the Scherrer equation for microcrystals, which connects the width of a Bragg peak with the average size of the microcrystals [15, 17].

FIG. 7. (color online). Six-member Si–O–Si ring structure and associated $\{10\bar{1}0\}$ and $\{\bar{1}011\}$ lattice planes in quartz illustrated with a $1 \times 2 \times 2$ supercell.

As shown in Fig. 8, the position of the FSDP decreases upon irradiation. We note that, eventually, the fully amorphized quartz shows an FSDP centered at around $1.6 \text{ \AA}^{-1}$, similar to that of glassy silica. Although the FSDP is ill-defined for crystals, we note that the FSDP of irradiated quartz is reminiscent of a peak centered at around around $1.85 \text{ \AA}^{-1}$ in pristine quartz, which arises from the $\{10\bar{1}0\}$ and $\{\bar{1}011\}$ reflections. As presented in Fig. 7, the $\{10\bar{1}0\}$ and $\{\bar{1}011\}$ lattice planes in α -quartz are directly associated with individual six-member Si–O rings. Due to thermal vibrations and finite system size, reflections from these two planes broaden and merge into a single peak in the structure factor computed herein, which eventually emerges as the FSDP after the irradiation. The decrease of the position of this peak upon irradiation suggests that the atomic structure becomes more open, which is associated with an increase in the ring size. Such a feature appears to be the main driver of the observed decrease in density (see Fig. 5). In addition, as shown in Fig. 8, the FWHM of the FSDP increases upon irradiation.

Interestingly, both the position and FWHM of the FSDP feature a break of slope at the vicinity of the rigidity transition. This constitutes the first clear evidence of a structural signature of a topological transition and offers the following atomistic picture of rigidity. (1) Starting from the stressed-rigid domain, irradiation results in a loss of rigidity, thereby decreasing the size of the rigid clusters, i.e., domains of atoms fully connected via rigid constraints, which is captured by the decrease in the coherence length. (2) The rigid-to-flexible transition enables the network to suddenly open, as captured by the decrease of the position of the FSDP. As noted below, this opening is associated with a release of eigenstress. (3) Eventually, the coherence length reaches a value of around $3 \text{ \AA}$, that is, the typical length of Si tetrahedra, which are left as the last rigid structures of the network

FIG. 8. (color online). Position (Q_{FSDP} , left axis) and full width at half maximum (FWHM, right axis) of the first sharp diffraction peak of the neutron structure factor (shown in the inset) as a function of the deposited radiation energy. The grey area indicates the extent of the flexible domain.

due to the breakage of the Si–O–Si BB constraints.

B. ONSET OF STRESS AND FLEXIBILITY

The atomic structure — and its evolution over time — also embeds some signatures of the flexibility of the network. Indeed, in addition to their break of slope, we note that both the position and FWHM of the FSDP feature a significant increase in their variability upon irradiation (see Fig. 8). As shown Fig. 9, the standard deviation of the FSDP position, as calculated from 15 sequential frames, significantly increases in the flexible domain. As such, in the stressed-rigid domain, irradiation creates local damages, e.g., point defects and local tetrahedron rearrangements [20], but does not significantly impact the rest of the network over large scales. In contrast, once in the flexible domain, each new irradiation-induced ballistic cascade strongly affects the MRO of the whole network. This suggests that the standard deviation of the position of the FSDP can be seen as a metric of network flexibility, which arises at $n_c < 3$.

Finally, we focus on the onset of internal stress in the stressed-rigid domain, which effectively prevents any flexibility of the network. To investigate the presence of such eigenstress, we assess the stresses applied on each atom in the irradiated structures, using the virial definition of stress [42]. To account for the structural effect only, the kinetic contribution of the virial stress is removed by relaxing the configurations to zero temperature by energy minimization before any atomic stress is calculated. The diagonal elements of the stress tensor of each atom are then averaged to obtain its stress state. It is worth noting that, although the stress per atom does not correspond to any macroscopic stress in the network, it provides a good indication of the internal stress distribution within

FIG. 9. (color online). Local eigenstress per Si atom (right axis) and relative standard deviation of the position of the first sharp diffraction peak (a metric of flexibility, right axis) as a function of the deposited radiation energy. The grey area indicates the extent of the flexible domain.

the structure. We find that, for both quartz and glassy silica, the stresses are distributed in the atomic structures such that Si atoms are systematically under tension, whereas O atoms are under compression, so that, overall, they mutually compensate each other. As such, the average stress applied, e.g., on Si atoms acts as a measure of the internal eigenstress present in the structure, and is shown in Fig. 9. In agreement with the idea that n_c corresponds to a stressed-to-flexible transition, we observe that the eigenstress decreases upon irradiation, and eventually nearly vanishes in the flexible domains. The onsets of flexibility and eigenstress for n_c lower and larger than three, respectively, unambiguously support the existence of an irradiation-induced rigidity transition in quartz.

V. CONCLUSIONS

Altogether, it is remarkable that dynamic properties (the radial and angular motion used as a basis for constraints enumeration), static structural properties (the FSDP of the structure factor), and interaction forces (eigenstress) are all correlated with each other and offer a consistent representation of the irradiation-induced rigidity transition at the atomic scale. Although these features might not be found for conventional composition-driven rigidity transition, as, e.g., a variable composition would affect the structure factor at constant rigidity, these results suggest that the state of rigidity of a network is intrinsically encrypted into the local stress and medium range order structure.

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