Molecular dynamics simulations of liquid silica crystallization

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Silica is one of the most abundant minerals on Earth and is widely used in many fields. Investigating the crystallization of liquid silica by atomic simulations is of great importance to understand the crystallization mechanism; however, the high crystallization barrier and the tendency of silica to form glasses make such simulations very challenging. Here we have studied liquid silica crystallization to β-cristobalite with metadynamics, using X-raydiffraction (XRD) peak intensities as collective variables. The frequent transitions between solid and liquid of the biased runs demonstrate the highly successful use of the XRD peak intensities as collective variables, which leads to the convergence of the free-energy surface. By calculating the difference in free energy, we have estimated the melting temperature of β-cristobalite, which is in good agreement with the literature. The nucleation mechanism during the crystallization of liquid silica can be described by classical nucleation theory.

Silicon dioxide, also known as silica, is one of the most abundant minerals and is widely used in many fields, from engineering to microelectronics and pharmaceutical industries. The basic structural element of silica is the SiO$_4$ tetrahedron. There are many possible ways of connecting SiO$_4$ tetrahedra, resulting in a very large number of silica polymorphs (1). Among all silica polymorphs, β-cristobalite directly crystallizes from liquid silica at around 2,000 K (2, 3) under equilibrium conditions. In β-cristobalite SiO$_4$ tetrahedra are arranged into a cubic diamond lattice (Fig. 1A), while in liquid silica the distinctive SiO$_4$ units persist but are arranged into a disordered network (Fig. 1B).

In material science, geophysics, and technology, understanding the crystallization process of β-cristobalite from liquid silica is of great importance. In general, experiment can give only a very limited insight into the crystallization of silica. This difficulty is compounded by the high crystallization temperature. Thus, more than in other systems, computer simulations are indispensable for understanding its microscopic crystallization mechanism (4). In the case of liquid silica only one simulation has been reported (5). However, in this case, crystallization was induced by supercooling the system at the pressure of 44.0 GPa. Under these conditions, a transition to the stishovite polymorph was observed. This is rather different from the behavior of silica at ambient pressure where the liquid at the melting temperature makes a transition to the β-cristobalite phase (2, 3).

The simulation is not without difficulty. On the one hand, the timescale is longer than what can be reached in a direct simulation (4). On the other hand, the tendency of liquid silica to form glasses (6, 7) and the large variety of silica polymorphs can hamper observing crystallization to the thermodynamically stable phase if one tries to accelerate the simulation by using, say, very deep quenches. This makes the use of an enhanced sampling method mandatory. Such a method should be efficient in accelerating crystallization, yet gentle enough not to induce unwanted transformations. Among the many enhanced sampling methods (8–10) suggested in recent decades, the metadynamics method (9) has proved to have these qualities. However, like other methods (8, 10) it relies on the choice of an appropriate set of collective variables (CVs). Finding appropriate CVs for this problem is therefore key.

Here we take the point of view that a CV that can be related to an experimental quantity is to be preferred to other choices. For this reason we use the X-raydiffraction (XRD) pattern as the CV. This quantity has many of the properties that are needed; i.e., it is simple and physically meaningful and can distinguish between different states. Ideally, in the future, one could imagine using this experimental information directly to construct useful CVs, when the structure into which the system is going to crystallize is not known.

Methods

Before discussing the crystallization calculation, we briefly introduce the XRD peak intensity-based CV. In an XRD experiment the scattering intensity as a function of the scattering vector $\mathbf{Q}$ is given by

$$I(\mathbf{Q}) = \sum_{i=1}^{N} \sum_{j=1}^{N} f_i(Q) f_j(Q) e^{-\mathbf{Q} \cdot (\mathbf{R}_i - \mathbf{R}_j)},$$

where $f_i(Q)$ and $f_j(Q)$ are the atomic scattering form factors and $\mathbf{R}_i$ and $\mathbf{R}_j$ are the position vectors of atom $i$ and atom $j$, respectively. $f_i(Q)$ and $f_j(Q)$ are functions of the scattering-vector modulus $Q$ and depend on the atomic species (11). The sum goes over all of the atoms in the system. When spherically

Significance

Silica is one of the most abundant minerals in Earth’s crust and since the dawn of civilization its use has accompanied mankind’s technological evolution. Understanding crystallization is crucial in many industrial processes as well as in geology. Although experiments and simulations are difficult, we are able to perform an atomistic simulation of the β-cristobalite crystallization using an enhanced sampling method that uses as input only the intensity of the highest X-raydiffraction peak of β-cristobalite.

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Fig. 1. Structure models of (A) an idealized unit cell of \( \beta \)-cristobalite and (B) liquid silica. \( \beta \)-Cristobalite is constructed by corner-bonded SiO\( _4 \) tetrahedra with a cubic diamond framework. In reality the tetrahedra are constantly tumbling. A liquid silica structure model is obtained by melting \( \beta \)-cristobalite, which is composed mostly of SiO\( _4 \) tetrahedra with a small amount of defects.

averaged, as done in a powder diffraction experiment, one gets the Debye scattering function (12)

\[
I(Q) = \sum_{i=1}^{N} \sum_{j=1}^{N} f_i(Q) f_j(Q) \frac{\sin(Q \cdot R_{ij})}{Q \cdot R_{ij}},
\]

where \( R_{ij} = |\vec{R}_i - \vec{R}_j| \) is the distance between atoms \( i \) and \( j \).

We could have used the static structure factor as the CV; however, in the spirit of this work in which we want to use an experimentally measurable quantity as the CV, we prefer to use Eq. 2. This also provides a simple recipe for obtaining a one-dimensional CV in a multicomponent system. One could also use the neutron scattering pattern which is simply obtained by replacing \( f_i(Q) \) with the corresponding neutron scattering form factor. We prefer to derive our CVs from the most easily available XRD patterns. Furthermore, \( f_i(Q) \) provides a cutoff to the range of \( Q \) that needs to be considered.

Since we are dealing with a finite simulation box, there is an upper limit \( R_c \) to the \( R_{ij} \) distances that can be included in Eq. 2. Such a sharp cutoff introduces a spurious effect typical of any truncated Fourier expansion. To limit this artifact we use a window function (13, 14):

\[
W(R_{ij}) = \frac{\sin(\pi R_{ij}/R_c)}{\pi R_{ij}/R_c}.
\]

Thus, we use as CV the final expression for our estimation of the scattering intensity normalized by the total atoms \( N \), which is

\[
I(Q) = \frac{1}{N} \sum_{i=1}^{N} \sum_{j=1}^{N} f_i(Q) f_j(Q) \frac{\sin(Q \cdot R_{ij})}{Q \cdot R_{ij}} W(R_{ij}).
\]

Each \( Q \) gives rise to a different CV. Since one can deal only with a limited number of CVs, it is necessary to select a few \( Q \) values. It is natural to select those values of \( Q \) that appear more prominently in the XRD spectrum (Fig. 2). To drive the simulation we chose as CV the scattering intensity evaluated at the \{111\} peak:

\[
s_1 = I(Q_{\{111\}}).
\]

To analyze the results and only for this purpose we use also the second-largest peak \{022\}:

\[
s_2 = I(Q_{\{022\}}).
\]

We are encouraged in the choice of the first peak of \( I(Q) \) as CV by the Ramakrishnan–Yussouff theory (16) of crystallization that suggests the highest peak of the structure factor as a suitable freezing order parameter.

**Computational Setup**

We performed an isothermal–isobaric molecular dynamics (MD) simulation. All MD simulations were performed with large-scale
atomic/molecular massively parallel simulator (LAMMPS) (17) patched with a development version of a plugin for molecular dynamics (PLUMED 2) (18). The integration of the equations of motion was carried out with a time step of 2 fs. We used the stochastic velocity rescaling thermostat with a relaxation time of 0.1 ps (19). The target pressure of the Parrinello–Rahman barostat (20) was set to the standard atmosphere value and a relaxation time of 10 ps was used. We used the interatomic potentials reported in ref. 21 for our MD simulations, which can describe both β-cristobalite and liquid silica. To determine the free-energy surface (FES) $G_s(s)$ as a function of CVs, we used well-tempered metadynamics (WTMetaD) (22). We set the bias factor of the WTMetaD ensemble equal to 100. The WTMetaD bias in the potential space was constructed by depositing Gaussians every 1 ps with width 5 CV units and a height of 40 kJ/mol.

**Results and Discussion**

Using $s_1$ (Eq. 5) as the CV we performed several WTMetaD simulations at different temperatures. We can see in Fig. 3 that the transition between liquid and solid phases is well described. The frequent reversible transitions between the two phases, especially above 2,500 K, indicate the high effectiveness and efficiency of the XRD peak intensity as the CV. From Fig. 3 we can also note that the transitions between liquid and solid become less frequent as the temperature is lowered. One of the culprits is of course the increase in viscosity of silica as the temperature is lowered (23).

Since the transition is reversible, the FES can be estimated accurately. Following the reweighting procedure (24), we obtained the FES at different temperatures as a function of $s_1$ and $s_2$ (Fig. 4). These pictures clearly show two minima. The top right basin with higher CV values refers to the solid phase, while the bottom left refers to liquid silica. The dominant phase changes from solid at 2,300 K to liquid as the temperature increases. At 2,300 K the two phases are separated by a free-energy barrier of ~12 kBT. This justifies calling the transition a rare event even at this relatively small system size.

From our calculations, we can also derive the difference in free energy $\Delta G_{\text{S} \rightarrow \text{L}}$ between β-cristobalite and liquid at different temperatures as

$$\Delta G_{\text{S} \rightarrow \text{L}} = -\frac{1}{\beta} \log \frac{\int_s dse^{-\beta G_s(s)}}{\int_s dse^{-\beta G_L(s)}}$$

where $s$ is the CV, $G(s)$ is the FES, and the integrals are restricted to solid and liquid basins. After the simulations reach convergence, we can obtain the difference in free energy $\Delta G_{\text{S} \rightarrow \text{L}}$ as a function of temperature (Fig. 5). As expected, $\Delta G_{\text{S} \rightarrow \text{L}}$ shows a linear relationship with temperature above 2,500 K. The melting temperature $T_m$ of β-cristobalite can be calculated from $\Delta G_{\text{S} \rightarrow \text{L}}(T_m) = 0$. Our estimated melting temperature is $T_m = 2,342 \pm 15$ K, in agreement with the result (2,400 K) reported in ref. 21 by using the same interatomic potential. We note that the error bars in the $\Delta G_{\text{S} \rightarrow \text{L}}$ curve decrease with increasing temperature as a consequence of increased rate of transitions between the liquid and solid basins.

Once the temperature dependence of $\Delta G_{\text{S} \rightarrow \text{L}}$ is determined, the difference in entropy between β-cristobalite and liquid,
Configuration snapshots of one typical crystallization process of liquid silica to \(\beta\)-cristobalite at 2,300 K with 5,136 atoms (512 Si atoms) in the system. From A to F, the snapshots are extracted from the biased run at an interval of 40 ps. Only crystal-like Si atoms are shown, while liquid-like Si atoms and O atoms appear transparent. The black square shows the simulation box with periodic boundary conditions. The color scale refers to the local entropy values of crystal-like Si atoms. The lower the local entropy value, the higher the atom is ordered.

\[ \Delta S_{c\rightarrow L}, \text{ can be calculated from the thermodynamic relation} \ \Delta S_{c\rightarrow L} = -\left(\frac{\partial G}{\partial T}\right)_{P}, T \ \text{at melting temperature is around 14.6 J K}^{-1} \text{ mol}^{-1}. \]  

We can compare this value with the reported difference in entropy between \(\beta\)-cristobalite and amorphous silica of 4.5 J K\(^{-1}\) mol\(^{-1}\) (25) that has been experimentally determined at 2,000 K. Considering the fact that the entropy content of the liquid state is higher than that of the amorphous state, our estimate appears to be in the ballpark.

The FES in Fig. 4 seems to imply that the crystallization process is possibly well described by classical nucleation theory (CNT). Also in ref. 5 it was suggested that CNT applies to the high-pressure transition at 2,300 K with 5,136 Si atoms. However, the use of deep quenches might change the nature of the transition. We thought it useful to investigate in detail whether CNT applies also here.

We recall that in CNT, the cost of forming a cluster of the new phase is expressed as

\[ \Delta F(n) = -\Delta \mu n + \sigma n^{2/3}, \]  

in which \(n\) is the number of atoms in the cluster and one assumes that the clusters are spherical, \(\Delta \mu\) is the difference in chemical potential between the new phase and the liquid phase (super-saturation), and \(\sigma\) is an effective interfacial energy. The first term represents the free-energy gain in going into the more thermodynamically stable phase whereas the second term expresses the energetic cost of forming an interface between the two phases. At a critical cluster size \(n^*\), \(\Delta F(n^*)\) has a maximum and clusters larger than \(n^*\) will grow spontaneously and form the new phase.

By using the recently proposed local entropy fingerprint (26), we identify crystal-like atoms in the samples (SI Appendix, Fig. S1). In our case only Si atoms are selected to calculate the local entropy fingerprint. In evaluating \(\Delta F(n)\) we encountered very strong finite-size effects. This is a reflection of the fact that for the systems simulated here the critical size exceeds the box volume. Thus, for sizes larger than a certain value \(n_c\) a cluster can interact with its own images and crystallize much earlier than it would otherwise in an infinite system. A rough estimate of \(n_c\) that assumes that the clusters are spherical is

\[ n_c = \frac{4}{3} \pi \left(\frac{L}{2}\right)^3 N_s, \]

where \(L\) is the box edge, and \(N_s\) is the total number of atoms, in our case the total Si atom number \(N_{Si}\). Thus, in Fig. 6 we calculate \(\Delta F(n)\) up to the value \(n_c\) that is appropriate to each system size. It can be seen that even before \(n = n_c\) there are significant deviations from CNT. However, it is reassuring to see that at lower \(n\) all of the different curves overlap with one another. From this part of the \(\Delta F(n)\) curves we can fit the value of \(\sigma\) in Eq. 8, after having evaluated \(\Delta \mu\) from the thermodynamic relation \(\Delta \mu = \Delta S^\ast (T - T_m)\). For \(T = 2,300 K\) one gets \(\Delta \mu = 0.032 k_BT\text{ mol}^{-1}(0.579 kJ\text{ mol}^{-1})\), while the fit yields \(\sigma = 2.6 k_BT\text{ mol}^{-1}\). Assuming that \(\sigma\) is constant at different temperatures, we can estimate the critical nucleus size at different temperatures. For instance, at temperatures 2,300 K and 2,200 K, the critical cluster sizes \(n^*\) would be around 160,000 and 3,700 Si atoms, respectively. To observe such clusters would require simulating impractically large systems.

Configuration snapshots (Fig. 7) illustrate the homogeneous nucleation process at 2,300 K. Several clusters with different sizes are shown; some of these disappear and some grow steadily into a larger size. Even though the system size is smaller than the critical cluster size, our results can shed light on the nucleation mechanism of \(\beta\)-cristobalite. The continuous nucleation-growth process indicates that the structural unit SiO\(_4\) tetrahedra in silica rearrange themselves into the cubic diamond framework of \(\beta\)-cristobalite.

Conclusions

Understanding crystallization of liquid silica is of great importance for both theoretical and practical reasons. In this paper we have shown crystallization of liquid silica to \(\beta\)-cristobalite can be studied in atomic simulations using XRD peak intensities as CVs. The results demonstrate the power of using an XRD pattern as CVs in atomistic simulations.

The transition rate between \(\beta\)-cristobalite and liquid in the biased runs significantly depends on temperature, which is in agreement with the experimental observation that silica viscosity increases exponentially with temperature decreasing. The FES along with the difference in free energy between \(\beta\)-cristobalite and liquid as a function of temperature has been evaluated. The estimated melting temperature from the difference in free energy shows good agreement with the literature. The estimated difference in entropy between \(\beta\)-cristobalite and liquid at melting temperature is around 14.6 J K\(^{-1}\) mol\(^{-1}\). Furthermore, we have also investigated the nucleation mechanism and have found the nucleation process can be described by CNT. The crystallization of liquid silica shows a continuous nucleation and growth process.

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