Molecular dynamics simulations of liquid silica crystallization

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Contributed by Michele Parrinello, April 11, 2018 (sent for review March 5, 2018; reviewed by C. Richard A. Catlow and Sidney Yip)

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 \( \beta \)-cristobalite with metadynamics, using X-ray diffraction (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 \( \beta \)-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.

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 \( \beta \)-cristobalite crystallization using an enhanced sampling method that uses as input only the intensity of the highest X-ray diffraction peak of \( \beta \)-cristobalite.

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

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

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

1 Contributed by Michele Parrinello, April 11, 2018 (sent for review March 5, 2018; reviewed by C. Richard A. Catlow and Sidney Yip)
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)

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

[2]

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):

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

[3]

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

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

[4]

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:

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

[5]

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

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

[6]

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) $G(s)$ 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 $\sim 12 k_B T$. 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 $\Delta G_{S \rightarrow L}$ between β-cristobalite and liquid at different temperatures as

$$\Delta G_{S \rightarrow L} = -\frac{1}{\beta} \log \frac{\int_{s_1} dse^{-\beta G(s)}}{\int_{s_2} dse^{-\beta G(s)}}$$

[7]

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 $\Delta G_{S \rightarrow L}$ as a function of temperature (Fig. 5). As expected, $\Delta G_{S \rightarrow L}$ shows a linear relationship with temperature. Furthermore, the melting temperature $T_m$ of β-cristobalite can be calculated from $\Delta G_{S \rightarrow L}(T_m) = 0$. 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 $\Delta G_{S \rightarrow L}$ curve decrease with increasing temperature as a consequence of increased rate of transitions between the liquid and solid basins.

Once the temperature dependence of $\Delta G_{S \rightarrow L}$ is determined, the difference in entropy between β-cristobalite and liquid,
\[ n_c = \frac{4\pi\rho^3}{3\rho} N_t, \]

where \( L \) is the box edge, and \( N_t \) is the total number of atoms, in our case the total Si atom number \( N_s \). Thus, in Eq. 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 \( \Delta \mu = \Delta \mu(S - T \cdot n) \). For \( T = 2,300 \) K one gets \( \Delta \mu = 0.032 k_B T \cdot mol^{-1}(0.579 \text{ kJ mol}^{-1}) \), while the fit yields \( \sigma = 2.6 k_B T \cdot mol^{-1} \). 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 \( n^* \) will be around 160,000 and 3,700 Si atoms, respectively. To observe such clusters would require simulating impractically large systems.

Fig. 7. Configuration snapshots of one typical crystallization process of liquid silica to \( \beta \)-cristobalite at 2,300 K with 1,536 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.

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.

ACKNOWLEDGMENTS. H.N. is grateful to Dan Mendels and Yixiao Chen for useful discussions. This research was supported by the National Center for Computational Design and Discovery of Novel Materials (MARVEL), funded by the Swiss National Science Foundation, and European Union Grant ERC-2014-Adg-670277/VARMET. The computational time for this work was provided by the Swiss National Supercomputing Center (CSCS) under Project mr3. Calculations were performed in CSCS cluster Piz Daint.