Role of Liquid Polymorphism during the Crystallization of Silicon

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S *Supporting Information*

ABSTRACT: Using molecular simulation, we establish the pivotal role played by *liquid* polymorphs during the crystallization of silicon. When undercooled at a temperature 20% below the melting point, a silicon melt is under the form of the highly coordinated, high-density liquid (HDL) polymorph. We find that crystallization starts with the formation, within the HDL liquid, of a nanosized droplet of the least stable *liquid* polymorph, known as the almost tetracoordinated low-density liquid (LDL) polymorph. We then show that the crystalline embryo forms within the LDL droplet, close to the interface with the surrounding HDL liquid, thereby following a pathway associated with a much lower free energy barrier than the direct formation of the crystalline embryo from the HDL liquid would have required. This implies that, for substances exhibiting liquid polymorphs, theories, like the classical nucleation theory, and empirical rules, like Ostwald's rule, should be modified to account for the role of liquid polymorphs in the nucleation process.

Crystallization is a complex phenomenon, central to many applications in chemistry, biology, and materials science.[1,2] Crystal nucleation often starts with the formation of an embryo of a metastable crystalline polymorph, rather than yielding directly the stable crystalline polymorph. This behavior results from a competition between kinetics and thermodynamics, summarized in the well-known Ostwald's step rule.[3−5] The physical interpretation of this rule is that the formation of a metastable crystalline polymorph from the melt is generally associated with a lower free energy barrier than the direct formation of the stable crystalline polymorph. While polymorphism had long been thought to pertain only to crystals,[4] some substances have been shown recently to also exhibit a liquid polymorphism.[6−11] For instance, in the case of silicon,[8,12−14] two distinct liquid phases, of different structures and densities, are found to be metastable below the melting point. Liquid polymorphism essentially increases the number of metastable states available to the system and, as a result, could possibly alter the nucleation pathway described in Ostwald's step rule. Determining if (and how) liquid polymorphism plays a role during crystal nucleation is the aim of this work.

When cooled below its melting temperature, silicon has been shown to present two liquid phases,[8,12−14] a low-density liquid (LDL) phase, which is almost tetracoordinated, and a high-density liquid (HDL) phase, which is more highly coordinated. The widely used classical empirical potential proposed by Stillinger and Weber[15] (SW) reproduces well these features. Using this potential, Sastry and Angell[8] determined the temperature of the transition

between the LDL and HDL phases to be 1060 K (LDL being the low-temperature phase). In this work, we perform molecular dynamics simulations[16−21] to study the crystal nucleation process in a moderately undercooled liquid of silicon, modeled with the SW potential. We simulate the crystallization process at ambient pressure and at a constant temperature of 1333 K, that is, at a temperature 20% below the melting point of silicon.[22−25] Under those conditions,[8] liquid silicon is in the form of the HDL polymorph since the LDL polymorph only becomes more stable than the HDL polymorph below 1060 K.

Throughout nucleation, we closely look for any local variation of the properties of the liquid to detect the formation of an inhomogeneity. More specifically, we focus on the local variations of the two components of the SW interaction potential, (i) the attractive two-body term, which ensures cohesion, and (ii) the repulsive three-body term, which promotes tetrahedral ordering. We divide the liquid into slabs of a 1.4 nm thickness and determine the two-body and three-body energy profiles over these slabs. We present in Figure 1 the energy scans obtained before the formation of a crystalline embryo. Both plots show a circular domain of the fluid, with a local increase in the two-body energy and a local decrease in the three-body energy. We emphasize that, at this stage, there is no trace of crystalline order as revealed by an analysis based on local order parameters[26−28] (see the Methods in Supporting Information) and as confirmed by the structural analysis presented in the next paragraph. This means that the circular domain identified in Figure 1 is a *liquid* droplet. The three-body energy scan, shown in Figure 1 (bottom), offers the best contrast and allows us to determine the diameter of the liquid droplet to be approximately equal to 1.2 nm.

What is the nature of this liquid droplet? The local decrease in the three-body energy indicates that there is an enhanced tetrahedral ordering within this droplet, suggesting that this might be a droplet of the LDL polymorph. To test this hypothesis, we perform a structural analysis of the liquid droplet and of the surrounding liquid. Figure 2 shows $N(r)$, the number of silicon atoms within a distance r of a central atom, $G(r)$, the pair distribution function, as well as the distribution function for the atomic tetrahedral order parameter[27,28] q_v, for both regions of the fluid. We also include in Figure 2 the structural properties of the HDL and LDL polymorphs. The overlap between the data for the liquid droplet and for the LDL polymorph demonstrates that the liquid droplet, identified in Figure 1, is indeed a LDL droplet. Furthermore, the overlap observed between the structural data for the liquid surrounding the droplet and the HDL polymorph shows that, throughout the formation of the LDL droplet, the rest of the liquid has remained in the HDL form. This result
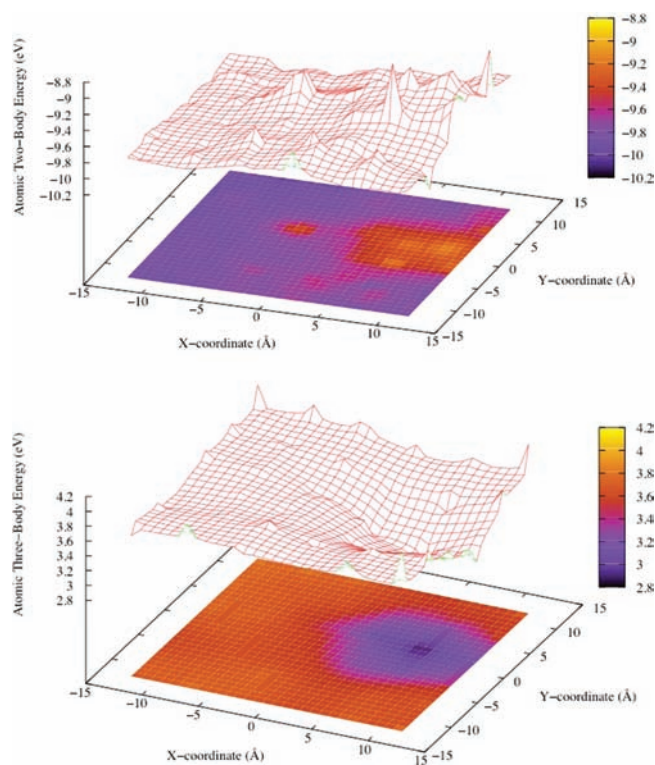
Figure 1. Spatial variations of the two-body energy per silicon atom (top) and of the three-body energy per silicon atom (bottom). These profiles are averaged over a slab of liquid silicon, taken perpendicularly to the *z*-axis, and with a thickness of 1.4 nm. The liquid droplet appears on the right of both plots.
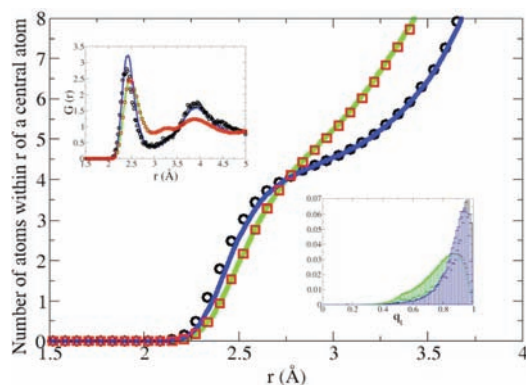

Figure 2. Structural analysis of the liquid droplet. Central plot: variation of the number of atoms within a distance *r* of a central silicon atom as a function of *r*. Upper left corner: radial pair distribution function $G(r)$. Lower right corner: distribution function for the atomic tetrahedral parameter q_t. Properties for the silicon atoms belonging to the liquid droplet are shown using black symbols (circles or histograms), while the properties for the atoms located outside the liquid droplet are shown in red (circles or histograms). Properties for the LDL and HDL polymorphs are shown in blue and green, respectively.

establishes that, prior to the formation of a crystalline embryo, a nanosized droplet of the least stable liquid polymorph, that is, the LDL polymorph, has developed in a small and localized region of the HDL liquid.

We now turn to the connection between the formation of the LDL droplet and the nucleation of a crystalline embryo. For this
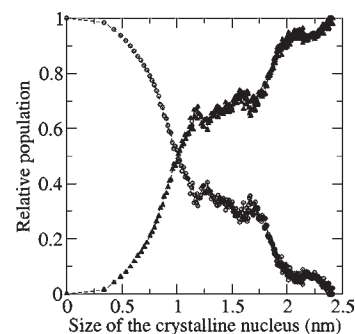

Figure 3. Relative populations in the region identified as a LDL droplet during the formation of the crystalline embryo. The two relative populations shown here are (i) the fraction of atoms from the LDL droplet having converted to crystal-like (filled triangles) and (ii) the fraction of atoms from the LDL droplet remaining liquid-like (circles).
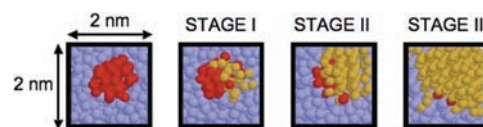

Figure 4. Enlarged views of a subpart of the system, centered on the LDL droplet. The first cross section (starting from the left) shows this subpart before the crystalline embryo forms (the atoms belonging to the LDL droplet are shown in red while the atoms belonging to the surrounding HDL are shown in blue). The next three cross sections (Stages I, II and III) show the formation of the crystalline embryo. In these snapshots, atoms identified as crystal-like are shown in yellow.

purpose, we closely follow the evolution of the region of the fluid identified in the previous paragraph as the LDL droplet. We plot in Figure 3 the fraction of atoms that initially belonged to the LDL droplet and have turned into crystal-like atoms against the diameter of the growing crystalline nucleus. Figure 3 also shows the fraction of atoms from the LDL droplet that has remained liquid-like atoms, as a function of the diameter of the crystalline nucleus. In the rest of the discussion, we refer to the fraction of crystal-like atoms as f_C and to the fraction of liquid-like atoms as f_L. In the early stages of the formation of the embryo (Stage I, up to a diameter of about 1.1 nm), f_C steeply increases with the diameter of the nucleus, thereby demonstrating that the crystalline embryo develops within the LDL droplet. This is confirmed by the sharp drop in f_L observed during Stage I. A closer look at the formation mechanism reveals that the crystalline cluster actually forms at the interface between the LDL droplet and the surrounding HDL (see the Stage I snapshot in Figure 4). This means that, because of the prior formation of the LDL droplet, the formation of the crystalline embryo is essentially a heterogeneous process, which occurs at the LDL−HDL interface. Given that the presence of an interface reduces the free energy barrier of nucleation,[2] the nucleation pathway determined here is much more favorable than the direct formation of a crystalline embryo from a uniform HDL. To further establish this point, we plot in Figure 5 the free energy profile, as a function of the size of the nucleus. The free energy barrier obtained here ($15\ k_BT$) is lower than what is typically expected for a homogeneous nucleation process under similar conditions ($20-25\ k_BT$).[17] This confirms that the crystal nucleation process is favored by the presence of the HDL−LDL interface. We finally summarize the end of the conversion of the LDL droplet into a completely crystalline region. During Stage II (up to a diameter of 1.7 nm), both f_C and f_L vary
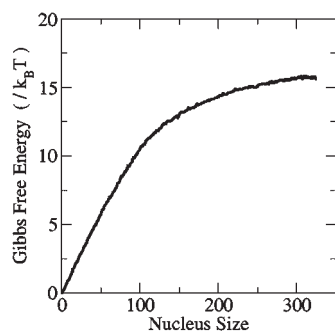
Figure 5. Free energy profile, as a function of the nucleus size (in number of atoms).

more slowly. This is merely due to the fact that the crystalline embryo starts to expand outside of the droplet (see the Stage II snapshot). Then, as shown in Stage III, f_C quickly rises to reach a value of 1 (and f_L reaches a value of 0) as the crystalline embryo overcomes the formerly LDL droplet.

These results establish the pivotal role played by liquid polymorphism, through the formation of the LDL droplet, during the crystal nucleation process. This suggests that Ostwald's step rule should be extended to include the role of liquid polymorphism during crystallization. As shown here, the liquid polymorphism exhibited by silicon allows for the formation of a droplet of an intermediate metastable structure (LDL), which shares similarities with both its parent phase (HDL) and crystalline silicon. A nucleation pathway, connecting the undercooled HDL liquid to crystalline silicon and involving, as an intermediate metastable state, a droplet of the LDL polymorph, is therefore very reasonable. We add that the formation of transient LDL droplets in the HDL parent phase at equilibrium naturally occurs as a result of fluctuations. For instance, the simultaneous and transient occurrence of the LDL and HDL phases was very recently reported for water.[29] We therefore anticipate that the role played by liquid polymorphs during the crystallization, illustrated here on the example of silicon, is applicable to other systems exhibiting liquid polymorphism.[7,9–11] Among those systems, water stands out as an example waiting to be investigated.

■ ASSOCIATED CONTENT

ⓢ Supporting Information. A description of the simulation methods, order parameters and structural analyses. This material is available free of charge via the Internet at http://pubs.acs.org.

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