Molecular Mechanism for the Cross-Nucleation between Polymorphs

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Understanding and controlling in which structure (or polymorph) a molecule crystallizes are complex and long-standing issues.[1] In many cases, a process yields crystals of more than one polymorph at the same time, making the control of polymorphism even more challenging.[2] Several mechanisms have been proposed to account for this phenomenon, known as concomitant polymorphism. It has been attributed either to competing processes of homogeneous nucleation of different polymorphs[2-4] or to solvent-mediated conversion of one polymorph into another[5] or, more recently, to the heterogeneous nucleation (or cross-nucleation) of one polymorph on another.[6-8] In this work, we use molecular dynamics simulations to study the early stages of crystallization in a supercooled liquid of spherical particles. We observe the onset of concomitant polymorphism and demonstrate that this phenomenon results from the cross-nucleation of a metastable polymorph on the stable polymorph. We also show that cross-nucleation is selective since it only takes place between polymorphs of almost equivalent free energy. Our simulations provide detailed insights into the molecular mechanism underlying concomitant polymorphism and cross-nucleation.

We choose the Lennard-Jones potential to model the spherical particles because it is an excellent candidate to study concomitant polymorphism. The free-energy difference between the stable polymorph, the face-centered cubic (fcc) structure, and one of the metastable polymorphs, the hexagonal close-packed (hcp) structure, is very small[9] and should favor the onset of concomitant polymorphism.[1] However, previous studies[10,11] on crystal nucleation in this system only reported the formation of crystal nuclei consisting of fcc particles and of particles of a polymorph of higher free energy, the base-centered cubic (bcc) structure. As we shall see, concomitant polymorphism takes place well after the nucleation stage and in crystallites much larger than the critical nuclei.

We study a Lennard-Jones liquid at a reduced pressure of 5.68 and a reduced temperature of 0.86 (22% below the melting temperature).[12] In this paper, we use the conventional system of reduced units for the Lennard-Jones fluid.[13]

We first induce the formation of a critical nucleus. We perform molecular dynamics simulations together with an umbrella sampling bias potential on a system of 4000 particles. This bias potential[10] allows the system to overcome the free-energy barrier of nucleation. It imposes a fixed value of the global order parameter Q_6 to the system[14] (this bias potential does not favor the formation of a specific polymorph since Q_6 takes similar values for the fcc, hcp, and bcc polymorphs). By gradually increasing the imposed value for Q_6, we are able to grow a crystal nucleus. Using local bond order parameters,[9,13] we analyze the structure of the nucleus throughout nucleation (we detail in the Supporting Information how we carry out this analysis). The system follows Ostwald's rule of stages. Nucleation first proceeds into the bcc metastable polymorph with the formation of small bcc nuclei. As the nucleus grows, it steadily evolves toward the stable fcc structure. The critical nucleus contains 339 ± 45 particles and can be described as a fcc core
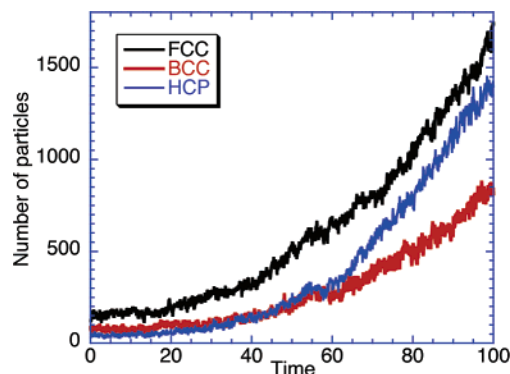
Figure 1. Evolution of the number of fcc, bcc, and hcp particles during the growth of the crystal nucleus ($t = 0$ denotes the time at which the bias potential is switched off and the system starts to evolve freely).

wetted by bcc particles (the free-energy barrier of nucleation is of 22.6 ± 1.0 k_BT). These findings are consistent with those from previous work.[10,11] The number of hcp particles is still negligible at this point.

Once we have formed the critical nucleus, we propose to study its evolution in the absence of the bias potential by (i) embedding the system of 4000 particles containing a critical nucleus in a supercooled liquid of 28000 particles, (ii) equilibrating the new system of 32 000 particles while still applying the bias potential on the central subsystem of 4000 particles, (iii) storing a configuration of the system every 10 time units during the equilibration run, and (iv) switching off the bias potential and letting each of these configurations evolve freely during a molecular dynamics (MD) trajectory at fixed temperature and pressure. We generated 15 MD trajectories. We observed the dissolution of the nucleus in the surrounding liquid for 7 of them and the growth of the nucleus in the remaining 8 MD trajectories. The 7:8 ratio, close to the ideal 5:5 ratio, expected for a critical nucleus, demonstrates that the crystal nuclei we have formed are critical nuclei.

During the growth of the crystal nuclei, we monitor the increases in the number of fcc (N^{fcc}), hcp (N^{hcp}), and bcc (N^{bcc}) particles. We present the results obtained for one of the MD trajectories in Figures 1 and 2 (all 8 trajectories gave qualitatively similar results).

At first ($t < 50$), the mechanism of growth can be summed up as follows. The crystal nucleus always retains a fcc core, wetted by bcc and hcp particles. The bcc and hcp particles progressively convert into fcc particles and contribute to the growth of the fcc core (see the first two snapshots in Figure 2). As shown in Figure 1, N^{fcc}, N^{hcp}, and N^{bcc} steadily increase. Not surprisingly, N^{fcc} grows the fastest (with the volume of the nucleus) while N^{hcp} and N^{bcc} grow at a slower rate (with the surface of the nucleus). N^{hcp}, initially very small in the critical nucleus, grows faster than N^{bcc} and becomes larger than N^{bcc} around $t = 40$.

Between $t = 50$ and $t = 60$, we observe a plateau in N^{hcp}. The third snapshot in Figure 2 shows that this plateau corresponds to
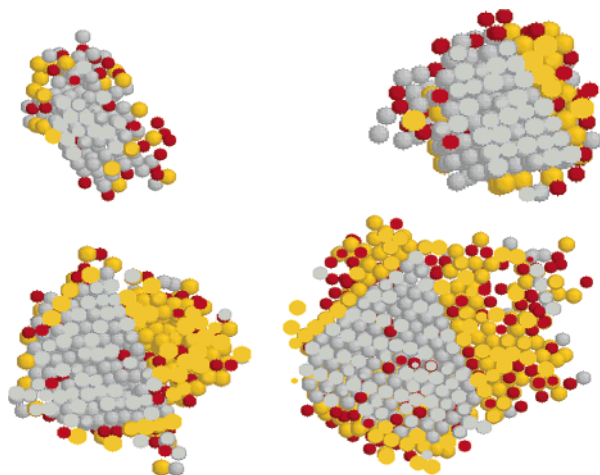
Figure 2. Cross sections showing the evolution of a crystal nucleus (gray for fcc, yellow for hcp, and red for bcc) after a time of 10, 30, 50, and 70 (in reduced units).

the formation of a cluster of hcp particles on the (111) plane of fcc particles. We are therefore able to observe the cross-nucleation of an hcp crystal on an fcc crystal. Once the cluster of hcp particles forms, the growth rate of N^{hcp} steeply increases for $t > 57$ and becomes larger than that of N^{fcc}. Eventually, for $t > 80$, N^{hcp} and N^{fcc} have comparable growth rates. Throughout the MD trajectory, N^{bcc} retains a steady growth rate, indicating that the bcc particles always play the same role, that is, scattered on the surface of the fcc and hcp crystals before converting to either fcc or hcp. We do not observe any cross-nucleation of the least stable polymorph bcc on any of the hcp or fcc crystals.

Cross-nucleation has only been observed in three systems[6−8] so far. Our simulations demonstrate that cross-nucleation also occurs in a system of spherical molecules and indicate that the phenomenon of cross-nucleation between polymorphs is much more general.

We show that cross-nucleation is mostly governed by kinetics. First, we observe the nucleation of a metastable polymorph (hcp) on a crystal of the stable polymorph. Moreover, cross-nucleation takes place because the metastable polymorph (hcp) grows at a faster rate than the stable polymorph (fcc), as shown in Figure 1 for $t = 57$. These two findings are supported by the experimental results from Yu et al.[8] In their study of cross-nucleation, they show that metastable polymorphs may nucleate on stable polymorphs. Besides, they conclude that the new polymorph formed grows faster than (or at least as fast as) the one initially present.

However, while cross-nucleation is essentially controlled by kinetics, our results also show that the relative stability of the polymorphs plays an important role. We only observe cross-nucleation between polymorphs of almost equivalent free energies. If the free energy of a polymorph is notably larger, as it is the case for bcc here, particles of this polymorph may appear, but they quickly convert into one of the more stable polymorphs before a large cluster forms. This shows that cross-nucleation is selective.

This also accounts for the fact that cross-nucleation between some polymorphs could not be observed experimentally.[8]

Cross-nucleation of the hcp cluster takes place on the structurally compatible (111) surface of the fcc nucleus. Like any nucleation event, cross-nucleation is an activated process. The fact that we observe this phenomenon on several MD trajectories indicates that the free-energy barrier of cross-nucleation is much lower than that of homogeneous nucleation and can be easily overcome by the collective fluctuations in the fluid.[15] This is in accord with what one would expect for any heterogeneous nucleation event.

Our simulation results show that the pathway to crystallization is extremely complex, even in a model liquid of spherical particles. Crystal nucleation occurs in accord with Ostwald's rule of stages, as the small metastable (bcc) clusters form and then grow into larger and predominantly stable (fcc) crystallites. Then, cross-nucleation takes place between the stable (fcc) polymorph and a metastable (hcp) polymorph, of almost equivalent free energy, with bcc particles wetting both the fcc and hcp crystals. We do not observe any cross-nucleation of the least stable polymorph bcc on any of the hcp or fcc crystals.

These findings show that controlling polymorphism can be extremely difficult when concomitant polymorphism takes place. For instance, seeding the liquid with small crystals of the stable (fcc) polymorph, a strategy often used in practical applications to control polymorphism, will not prevent the formation of hcp crystals.

Supporting Information Available: Definitions for the local bond order parameters, how we use these parameters to analyze the structure of the crystal nuclei, and how the critical nuclei are embedded in large systems of liquid are detailed. This material is available free of charge via the Internet at http://pubs.acs.org.

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