

## Reorganization and Growth of Metastable $\alpha$ -N<sub>2</sub> Critical Nuclei into Stable $\beta$ -N<sub>2</sub> Crystals

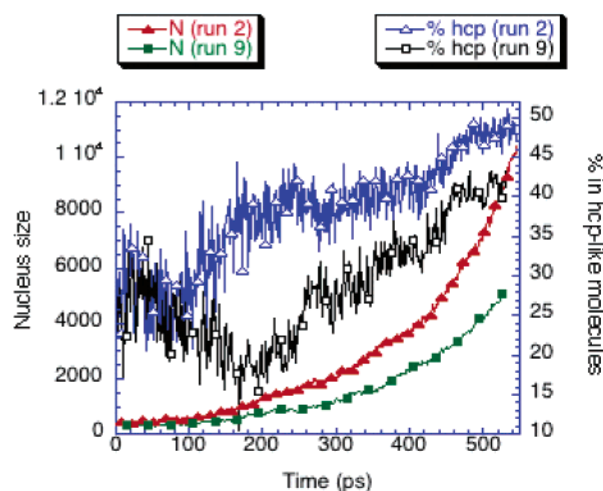
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Despite many experimental and theoretical studies, it still remains impossible to predict which crystalline variety or polymorph will form upon cooling a liquid or a solution.<sup>1,2</sup> This issue is of both fundamental and technological interest. Since polymorphs may have very different physical properties (e.g., solubility in water), it is of great importance, e.g., for the pharmaceutical industry to know which polymorph of a drug molecule will be obtained. In this work, we show that the crystallization of N<sub>2</sub> takes place in accord with the empirical Ostwald's rule of stages.<sup>3</sup> This rule summarizes the interplay between kinetics and thermodynamics in a polymorphic system and indicates that the crystallization process starts with the appearance of the least stable form and finishes with the most stable form. Indeed, our results demonstrate that the structure of the critical nucleus is essentially that of metastable  $\alpha$ -N<sub>2</sub> and that subsequent growth occurs concomitantly with a structural transition toward stable  $\beta$ -N<sub>2</sub>. Our simulations also shed light on the microscopic mechanisms accounting for this transition. In contradiction with the commonly assumed mechanism,<sup>4</sup> we show that the transition results from a faster growth rate for the stable form rather than from the dissolution of the metastable form.

We consider the example of liquid nitrogen for the following reasons: (i) there are two well-identified polymorphs (the metastable fcc-like  $\alpha$ -N<sub>2</sub> and the stable hcp-like  $\beta$ -N<sub>2</sub>) with similar free energies for the state point investigated,  $T = 76.6$  K and  $P = 2203$  bar (this corresponds to a realistic degree of supercooling of 25%); (ii) a reliable potential model is available;<sup>5</sup> and (iii) simulations with large system sizes can be performed on this molecule (this is absolutely necessary to avoid artifacts arising from the use of periodic boundary conditions<sup>6</sup>). In a preliminary study,<sup>7</sup> we used molecular dynamics simulations together with the umbrella sampling technique<sup>8</sup> and observed the formation of a critical nucleus of  $\alpha$ -N<sub>2</sub>. We showed that, in accord with Ostwald's rule of stages,<sup>3</sup> nucleation proceeded in metastable  $\alpha$ -N<sub>2</sub> rather than in stable  $\beta$ -N<sub>2</sub>. Building on these results, we have further assessed the reliability of these results: for two system sizes of 3000 and 4000 molecules, we obtained a free energy barrier of nucleation of  $36.9 \pm 1.0 k_B T$  and a critical nucleus of  $\alpha$ -N<sub>2</sub>, containing  $344 \pm 61$  molecules (the ( $\alpha$ ) fcc-like or ( $\beta$ ) hcp-like character of each molecule and the structure of the nucleus were identified by analyzing the distributions of local bond order parameters<sup>9</sup>). Using this criterion,<sup>10</sup> we found that, on average,  $71 \pm 5\%$  of the molecules within a critical nucleus were fcc-like ( $29 \pm 5\%$  were hcp-like). We then studied the evolution of the critical nucleus. We proceeded as follows: (i) a system of liquid N<sub>2</sub> containing 40 000 molecules was first equilibrated; (ii) a chunk of liquid was removed and replaced by the 4000-molecule system containing a critical nucleus, leading to a system of a total of 39 851 molecules; and (iii) the resulting system was subsequently equilibrated. During this equilibration, the harmonic bias potential, used in the umbrella sampling technique to fix the value of the  $Q_6$  order parameter, was still applied to the subsystem of 4000

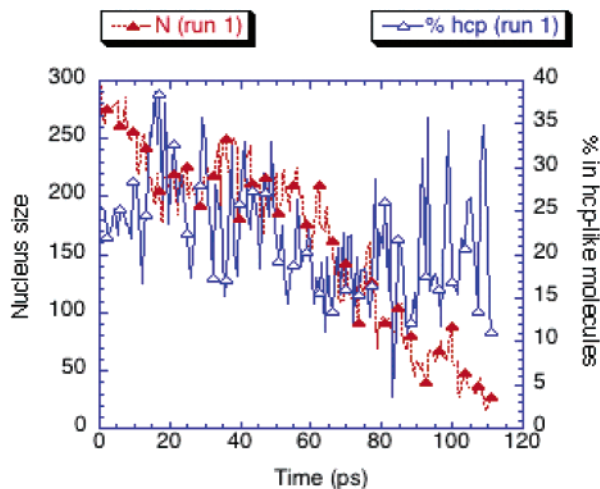


**Figure 1.** Evolution of the number of particles belonging to the nucleus (nucleus size  $N$ ) and of the fraction of hcp-like molecules (noted as % hcp) in the nucleus for two trajectories leading to crystal growth.

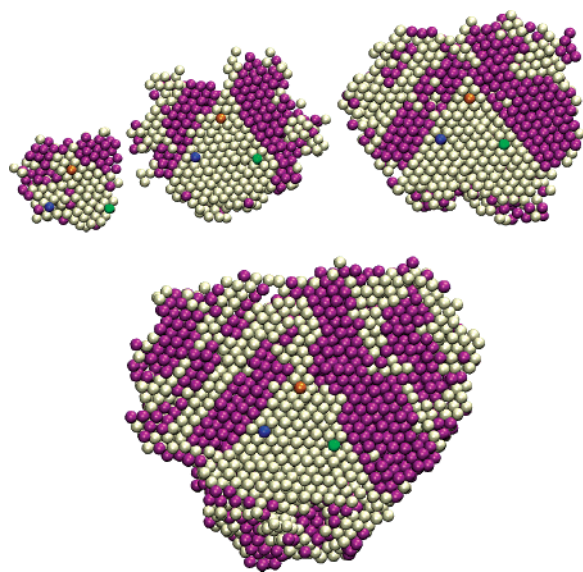
molecules containing the critical nucleus. We selected a set of 10 configurations over a period of 135 ps. Each of these configurations was then used as a starting point for an unbiased molecular dynamics simulation in the NPT ensemble. Therefore, the system was allowed to evolve freely during the simulation. Out of these 10 runs, 3 have resulted in melting of the nucleus and 7 have led to crystal growth. This 3:7 ratio shows that the procedure we used gives a correct description of a critical nucleus for a system of 39 851 N<sub>2</sub> molecules, since it is close to the ideal 5:5 ratio. A summary of the typical behaviors observed in this work is presented in Figures 1 and 2.

We observed for the seven trajectories leading to the growth of the nuclei that this growth is always accompanied by an increase in the fraction of ( $\beta$ ) hcp-like N<sub>2</sub> molecules in the nucleus, which is the thermodynamically stable crystalline phase for the state point investigated. As can be seen in Figure 1 for the results from the second trajectory (run 2), the earlier the increase in the hcp-like fraction takes place, the faster the nucleus grows. On the contrary, when the fraction of hcp-like molecules remains of the same order or lower than the value obtained for the critical nucleus (29%), the nucleus either grows very slowly (see run 9 in Figure 1 for times shorter than 250 ps), until the fraction of hcp-like molecules finally increases, or quickly melts as shown in Figure 2 (and as observed within 150 ps from the start of the simulation for the three trajectories for which melting was observed).

These results show that the crystallization process essentially occurs in accord with Ostwald's rule of stages. First, nucleation proceeds to a metastable phase ( $\alpha$ -N<sub>2</sub>), i.e., the crystalline phase closest to the liquid phase in terms of free energy and associated with the lowest free energy barrier. Second, growth of the crystallite



**Figure 2.** Evolution of the nucleus size and of the fraction of hcp-like molecules for a trajectory leading to melting of a nucleus.



**Figure 3.** Cross sections showing the evolution of a post-critical nucleus (purple, hcp-like molecules; white, fcc-like molecules). Three fcc-like particles (colored in blue, orange, and green), delimiting the initial critical nucleus, are chosen as reference points throughout the growth process to indicate the orientation of the cluster.

occurs concomitantly with a structural transition of the nucleus toward the thermodynamically stable phase ( $\beta$ -N<sub>2</sub>).

We now examine the mechanism underlying the growth process. Successive snapshots of a growing nucleus are presented in Figure 3 (only the centers of mass appear as spheres in this plot). Nuclei are actually composed of a block of fcc-like molecules, slowly growing on the initial critical nucleus, and of blocks of hcp-like molecules growing at a faster rate on this fcc block. The growth process differs from that generally assumed:<sup>4</sup> there is no dissolution

of the metastable form since we clearly see that the fcc-like core of the critical nucleus remains intact throughout the process. Actually, blocks of the metastable form still keep on appearing at a very slow rate. The increase in the overall hcp-like character of the nucleus results mostly from the fact that the hcp-like blocks grow faster than the fcc-like blocks. Because the crystallization process occurs through the formation of blocks, we observe some faceting, and all nuclei were rather of an ellipsoidal shape, as observed experimentally on colloidal crystallization.<sup>2</sup> Finally, we note that the fcc and hcp blocks are bounded by (111) hexagonal planes common to these two structures. This observation is reminiscent of the findings of O'Malley and Snook,<sup>11</sup> who studied crystal nucleation in the hard-sphere system and obtained similar blocks of fcc-like and hcp-like particles. There is, however, a major difference with this work: they did not observe any structural change during the growth process, and their nuclei retained a strong fcc-like character (57%) throughout the growth process.

Two main conclusions can be drawn from our results. First, the crystallization process obeys Ostwald's rule of stages,<sup>3</sup> as observed in experiments<sup>4</sup> and in simulations:<sup>8</sup> kinetics leads initially to the formation of a critical nucleus of a metastable form, and thermodynamics then induces a transition to the stable form during crystal growth. Second, the observed structural transition is due to the faster growth of the stable form rather than to a dissolution of the metastable form as generally assumed<sup>4</sup> (the metastable form actually continues to grow at a slow rate).

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**Supporting Information Available:** Definitions of the local bond order parameters and how these parameters are used to determine which molecules are fcc-like or hcp-like. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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