

Multistep Nucleation from Vapor-to-Solid in Molecular Dynamics Simulations

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It is often observed that droplets formed from vapor are supercooled liquids in nature and experiments, although crystallization is expected to occur at temperature below the triple temperature. This phenomenon is known as an example of Ostwald's step rule in which a metastable phase appears first before a stable phase. We performed MD simulations of homogeneous vapor-to-solid phase transition of Lennard-Jones molecules, which shows multistep nucleations of formation of liquid-like particles (first step nucleation) and crystallization in those (second step nucleation). During a long direct NVE (constant number of molecules, volume and energy) integration up to 200 million steps ($= 4.3 \mu s$), the nuclei of supercooled liquid appear and growth. Crystal structure is identified using the Common Neighbor Analysis (CNA) method implemented in LAMMPS. The crystallizations of many large supercooled nano-clusters are observed after the liquid particles growth to a size (800 molecules at 60K). Some of them crystallize quickly and almost completely. We found all crystallized clusters lose a few % of their mass at freezing and every mass loss of this kind is associated with crystallization. The mass loss is caused by evaporation, since the latent heat from freezing heats up the cluster. The crystallized clusters composed of (1000-5000) atoms show various structures in our simulations. The crystallized clusters have characteristic structures for nano-particles, i.e., isosahedral (Ih), decahedral (Dh), face-centered cubic (fcc), and hexagonal close-packed (hcp). These several kinds of clusters are present in the same size range. In the simulations, once a liquid-like particle freezes, the crystal structure was kept during the growth of the crystal with the size up to 5000 molecules. Our results imply that the solid-solid transition does not occurs easily because of the energy barrier between different structures.

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