Droplet nucleation and crystallization in large-scale molecular dynamics simulation

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Phase transitions play important roles in many areas of science and technology. Despite the familiarity of the process, serious unreliability remains in model predictions for nucleation rates, because the properties of the small nuclei of the new phase are poorly understood. The classical nucleation theory (CNT) is a very widely used model for describing nucleation and provides the nucleation rates as a function of temperature, supersaturation ratio, and macroscopic surface tension of a condensed phase. However, several studies have found that the CNT fails to explain the nucleation rates observed in laboratory experiments and numerical simulations of molecular dynamics (MD) simulations, for example, the error is the order of $10^{10\text{-}20}$ for argon [1]. MD simulations are able to directly resolve details of the nucleation process and provide useful test cases for nucleation models. Recently, we presented large-scale MD simulations of homogeneous vapor-to-liquid nucleation of (1-8)$\times 10^9$ Lennard-Jones atoms [2-4]. The simulations cover a wide range of temperature and supersaturation ratios. We have resolved nucleation rates as low as 10^{17}cm^{-3}s^{-1} (in the argon system) and succeeded in quantitatively reproducing argon nucleation rates at the same supersaturations, and temperature as in the argon experiment. The liquid supercooled nano-droplets forming naturally out of the vapor also allow us to study droplet crystallization. Here we present the results of droplet crystallization in the MD simulations of vapor-to-liquid nucleation. During a long time integration (116 million steps=2.5μs), the crystallization of many large (>800 atoms) supercooled nano-clusters is observed. Some of them crystallize quickly and almost completely. The solid clusters lose at least 2 % of their mass at freezing. The mass loss is caused by evaporation, since the latent heat from freezing heats up the cluster. The solid clusters composed of 1000-4500 atoms show various structures: icosahedral, decahedral, fcc, and hcp. The comparison with the classical nucleation theory shows the consistency between the results of MD simulations and the theory including the size dependent interfacial energy.

[1] Tanaka et al. *J. of Chem. Phys.* 134, 204313, 2011 [2] Diemand et al. *J. of Chem. Phys.*139, 074309, 2013 [3] Angelil et al. *J. of Chem. Phys.* 140, 074303,2014 [4] Tanaka et al. *J. of Chem. Phys.* 140, 194319, 2014