

Large molecular dynamics simulations of the vapor-to-liquid nucleation of water

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Phase transitions play important roles in many areas of science and technology. The classical nucleation theory (CNT) is the most widely used model for describing homogeneous nucleation and provides the nucleation rate as a function of the supersaturation ratio and the surface tension of a condensed phase. However, many studies have reported that the CNT fails to describe experimentally obtained results. In the case of water, the deviations between the nucleation rates predicted by the classical nucleation theory and the experimental values are several order of magnitude.

Molecular dynamics (MD) simulations are able to directly resolve details of the nucleation process, and provide useful test cases for nucleation models. Until now, many MD simulations examining the nucleation process of water molecules have been carried out [1-3]. Tanaka et al. [3] performed MD simulations of the nucleation of water vapor in order to test nucleation theories with 4000 water molecules. The results showed that the classical nucleation theory (CNT) and the modified classical nucleation theory (MCNT) overestimate the nucleation rates in all cases. On the other hand, the semi-phenomenological model, which corrects the CNT prediction using the second virial coefficient of a vapor, reproduced the formation free energy of a cluster within 10% and the nucleation rate J within one order of magnitude. The sticking probability of the vapor molecules to the clusters was also determined from the growth rates of the clusters. The sticking probability rapidly increases with the supersaturation ratio S , which is similar to the Lennard-Jones system. For such low- S cases, we must estimate the sticking probability precisely for the evaluation of J .

Previous typical MD simulations of homogeneous nucleation use 10^3 - 10^4 atoms. At low vapor densities, and therefore low supersaturations, a single nucleation event becomes unlikely to occur within reasonable computational timeframes. Simulations with larger number of molecules allow for the occurrence of such rare nucleation events, and enable us to measure these low rates. Recently, we started the large-scale MD simulations the SPC/E rigid water model with LAMMPS (Large-scale Atomic/Molecular Massively Parallel Simulator). In the simulations, the particle numbers are 1 to 120 million atoms (324000-4116000 molecules). We assumed NVT (constant volume and temperature) ensembles and used a three-dimensional periodic boundary condition with different parameters of temperature T and initial supersaturation ratio S . Here, first results for the large-scale simulations are presented. We obtained the smaller nucleation rates by 4-5 order of magnitude than the previous studies.

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