Theoretical Model of Crystallization through Homogeneous Nucleation in Water Droplets

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The crystallization process of water droplets is not only fundamentally important, but is also climate-sensitive and hence relevant to urgent problems such as climate change. However, water crystallization in environments such as cirrus clouds is difficult to explore by conventional experimental approaches. Analytical models of the crystallization process can assist our understanding of ice nucleation and predict the crystallization processes in environments that cannot be replicated in the laboratory. Experimentally, micrometer-sized droplets are known to crystallize at approximately 235 K, regardless of cooling rate and experimental method. However, the crystallization temperature of smaller (nanometer-sized) droplets suddenly drops at high cooling rates (~10^5 K/s). At very high cooling rates (10^{6-7} K/s), liquid water droplets vitrify rather than crystallize. A model that explains all of these characteristics is thus far lacking. Motivated by this knowledge gap, we construct a new model of water-droplet crystallization that evolves the homogenous nucleation and crystal growth in water droplets during cooling (Tanaka & Kimura, PCCP, 21, 2410, 2019). The crystallization process depends on the surface energy at the liquid–solid interface (which determines the liquid-to-sold nucleation rate) and the activation energy of molecular diffusion through the liquid. The model extends our previous model (Tanaka et al. J. Crystal Growth, 310, 1281, 2008) by incorporating the droplet size-dependence of the crystallization process. Especially, smaller droplets begin crystallizing later than larger droplets because they are less likely to form a nucleating center in a given time. We also try two diffusion coefficients: the diffusivity of amorphous ice (ASW) and the diffusivity of supercooled liquid (SCL) water. The model well replicated the results of previous laboratory experiments, especially, the different responses of the crystallization temperatures of the micrometer- and nanometer-sized particles as functions of cooling rate. At low cooling rates, the ASW and SCL diffusivities gave the same results for micrometer-sized particles, because these particles crystallize at temperatures around the homogenous nucleation temperature (235 K), where both diffusivities are identical. However, for nanometer-sized particles, the crystallization temperature is lower and the SCL diffusivity is more accurate than the ASW diffusivity. Calculations on small droplets also provide low-temperature information at high cooling rates, which are sparsely acquired in experiments. The critical cooling rate of vitrification was predicted as 10^{7-8} K/s with SCL diffusivity, consistent with the experimental rates.

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