

Atomistic modeling of heterogeneous nucleation of ice

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An accurate description of clouds in climate models requires solid knowledge about their properties, but formation of ice clouds, in particular, is not well understood. Ice crystals may form in the atmosphere either by homogeneous or heterogeneous ice nucleation. The latter process, initiated by an aerosol seed particle at relatively high temperatures, is not understood at the molecular level. Different nucleation modes (immersion-, contact- and deposition nucleation) are active in the atmosphere at different temperature and water supersaturation ranges.

We have developed an atomistic model of ice crystal formation using a continuum of methods from density functional theory (DFT) to large-scale classical molecular dynamics (MD). We are looking at kinetic and thermodynamic factors controlling nucleation at different conditions and in the presence of different surfaces that represent aerosol particles with varying lattice match with ice, surface corrugation and interactions, both for ideal test systems and for feldspar, AgI and black carbon that are active as heterogeneous nucleation seeds. In particular, we are looking at features that deviate from predictions of classical nucleation theory (CNT), such as Stranski–Krastranov growth seen with large system sizes, which is in contrast to both CNT and simulations done with small systems.

Simulations with the mW potential (Molinero and Moore, 2009) show that surface geometry can largely explain the high nucleation activity of AgI, whereas K-feldspar, considered an important ice nucleation agent in the atmosphere (Atkinson *et al.*, 2013), shows very weak activity in mW simulations, without considering the real surface chemistry of the material, studied with DFT.

We also show the importance of the effect of feldspar microstructure – interface between alternating orthoclase and albite layers and defects due to lattice mismatch. In addition to studying nucleation dynamics with MD, we are looking at accurate energetics with quantum chemical DFT, utilizing the ORCA code with the BP86 functional with D3BJ dispersion. Comparison of water layer adsorption on SiO₂ versus K-feldspar is helping us understand the difference in nucleation activity between these materials.

Contact nucleation mode simulations show nucleation activity at higher temperatures than immersion, in agreement with experiments, due to rotational freedom of water at the open surface.

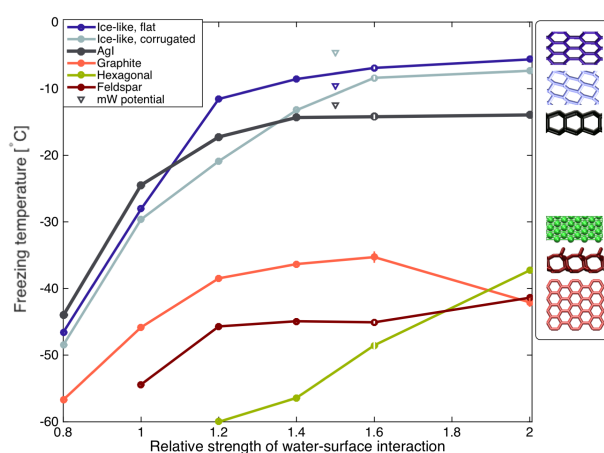


Figure 1. Surfaces with a good lattice match with hexagonal ice nucleate ice effectively in MD. This result with the monatomic water (mW) potential shows that the high nucleation activity of AgI can be explained by surface geometry alone, whereas for feldspar the specific surface chemistry of the material needs to be considered. The inset on the right side of the figure shows the surface geometries of the studied surfaces.

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Molinero, V. and Moore E. B. (2009) *J. Phys. Chem. B* **113**, 4008.

Atkinson, J. D. *et al.* (2013) *Nature* **498**, 355.