The role of ice III in crystal nucleation

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In 1975, Kanno, Speedy, and Angell [1], investigated experimentally homogeneous ice nucleation (i.e., in the absence of surfaces and impurities) for pressures up to 2000 bar. By measuring the temperature at which microscopic emulsified water drops freeze when cooled at a rate of a few Kelvin per minute, they established the so-called homogeneous nucleation line (HNL), whose slope is negative and larger than that of the melting line. Thus, they found that whereas water remains liquid for temperatures down to -38 °C at ambient pressure, at high pressures it is possible to have liquid water at temperatures as low as -92 °C. Therefore, applying pressure significantly increases the range of temperatures at which liquid water may exist. This important experimental result is the basis of state-of-the art coolers used for the preservation of biological samples [2, 3]. Despite its importance, the experiment by Kanno *et al.* has long remained unexplained.

The HNL is a line in the pressure-temperature plane where the ice nucleation rate, or the number of growing ice clusters nucleated per unit time and volume, remains constant [4]. Thus, computing the HNL for a given ice polymorph requires obtaining the nucleation rate as function of temperature for different pressures. We suggest the kink in the experimentally measured HNL [2] is due to a change in the nucleation path from ice Ih to ice III.

To test our hypothesis, we perform Molecular Dynamics simulations using a technique called *seeding* [5, 6]. This technique consists in embedding a crystalline cluster of a certain size of the desired stable phase (ice III in this work) in the metastable phase (liquid). The temperature at which this cluster is critical is then obtained and using the Classical Nucleation Theory (CNT) we can obtain both the interfacial free energy and the nucleation rate. Three different cluster sizes are investigated and the HNL of ice III is computed and compared with the one of ice Ih (computed in [4]). We observe that the crossing point of these curves coincides with the kink in the HNL obtained experimentally.

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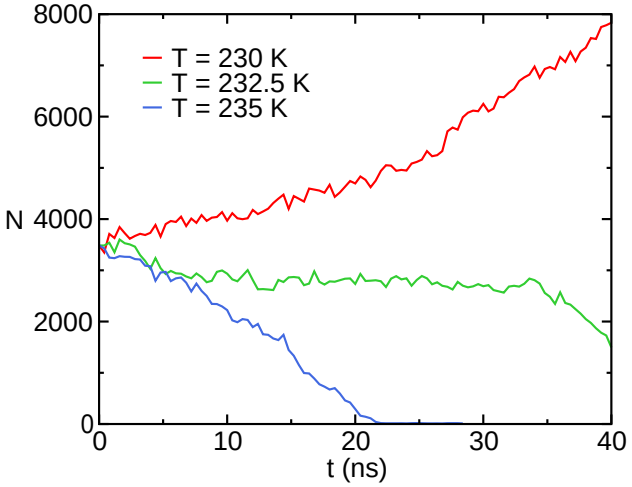

Fig. 1. Evolution of the number of particles of the cluster N as a function of time t for different temperatures and for one cluster size. Lower temperatures make the cluster to grow while high temperatures make the cluster to shrink.