Homogeneous Crystal Nucleation in Deeply Supercooled Glass-forming Liquids – Open Issues

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Abstract

We summarize the classical nucleation theory (CNT) and discuss selected experimental tests and MD simulations that were performed since the fifties with metallic, polymer and inorganic glass-formers. Some oxide system show internal (homogeneous) nucleation rates in laboratory scales even without the addition of nucleating agents. We demonstrate that their nucleation rates show a rather remarkable pattern: i) the maximum values always occur at a temperature T* _˜ Tg12 (Tg12 = glass transition temperature). And, ii) for these substances, the structural order of the network modifier cations of the parent liquids is very similar to that of their isochemical crystal phases!
The CNT describes quite well the experimental nucleation rates with a fitted (2-parameter) temperature dependent surface energy, s(T), for T > T*, but there is always a substantial discrepancy for T < T*. We investigate some reasonable possibilities to explain this break at T*, for instance: can the diffusion coefficient that controls nucleation be replaced by the viscosity via the Stokes-Einstein equation; what is the effect of internal stresses in the nucleation rates at deep undercoolings? What is the role of dynamic heterogeneities that exist in the liquid? We also dwell on other unusual problems, such as the possibility to measure or estimate the average time for formation of the first crystalline nucleus.
We conclude by showing that, despite some yet unexplained phenomena and other shortcomings, the CNT has been successfully used for different purposes. For instance, to distinguish glasses that nucleate homogeneously from those which only show heterogeneous nucleation, to predict nucleation rates and induction times, to explain why some glasses, such as albite and B2O3, "never" crystallize, and for the development of novel or improved glass-ceramics with higher fracture strength and toughness or optical transparency.

Keywords: nucleation, crystal, surface energy, viscosity, crystallization, glass, ceramic

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