#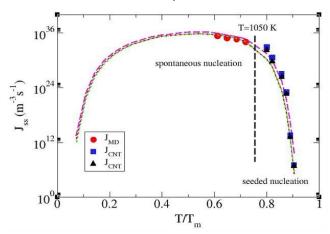 Nucleation kinetics in supercooled ZnSe: Computer simulation data corroborate the validity of the Classical Nucleation Theory

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Understanding and controlling the liquid to crystal transformation is a central topic for numerous natural phenomena and technological applications. The first step of crystallization is the birth of critical nuclei. Their size, structure and rate at which critical nuclei appear and grow are fundamental parameters for understanding and controlling crystallization. Although nucleation rates can be measured experimentally in a few systems due to the very small nucleus size (nm) and either a too short or too long lifetime, it is extremely difficult to understand and describe the microscopic mechanism of nucleation, which remains elusive. To this end, computer simulation techniques provide, in principle, a suitable tool to dig deeper into this process. At least three main methods are available to obtain crystal nucleation rates via molecular dynamics simulation: 1) the mean lifetime method, 2) enhanced-sampling methods and 3) the seeding method. The Classical Nucleation Theory (CNT) is one of the most well-known models to describe the nucleation process. This theory assumes that the formation of crystal nuclei takes place as a result of thermal fluctuations in a supercooled liquid (SCL). If an embryo overcomes a certain threshold size, it becomes a critical nucleus that spontaneously grows until it meets other growing crystals and the liquid solidifies. According to this theory, the interplay between the supercooled liquid/nucleus interfacial free energy, γ, and the difference between the chemical potentials of the crystal phase and the supercooled liquid describes the thermodynamics of crystal nucleation. The third key property is the effective diffusion coefficient, which controls the atomic transport rate at the liquid/crystal interface. The independent determination of these three quantities allows CNT calculations and comparison with experimentally determined or simulated nucleation rates. Owing to the scarcity of direct measurements of these properties, often questioned the validity and accuracy of the CNT. In this work, we were able to deeply supercool Zinc Selenide (ZnSe), and determine spontaneous homogeneous steady-state nucleation rates by molecular dynamics simulations (MD) using the mean lifetime method. At moderate supercoolings, where the nucleation rates are much smaller, we used the seeding method to compute the nucleation rates by the classical nucleation theory formalism, J_{CNT}, without any fitting parameter, using the physical properties obtained by MD simulations: the melting temperature, density, melting enthalpy, diffusion coefficient, and the critical nucleus size, combined with two expressions for the thermodynamic driving force. The values of γ calculated by the CNT expression using the MD simulation data, via both the seeding method and the mean lifetime method at moderate and deep supercoolings show a weak temperature dependence, which is in line with the Diffuse Interface Theory. The extrapolated values of γ, from the spontaneous nucleation regime to the seeding nucleation region cover the range of values of γ calculated via the seeding method and the CNT formalism. Finally, the J_{CNT} extrapolated from moderate supercoolings to deep supercoolings are in good agreement with the J_{MD}. These results confirm the validity of the CNT.