

The homogeneous nucleation of a crystal phase is one of the most interesting phenomena of molecular fluids. Although it has been the subject of extensive experimental and theoretical study, the microscopic mechanism of crystal nucleation still remains poorly understood. It is even more a mystery in chain molecule systems because the chain connectivity could produce very different crystal nucleus conformations, which are important factors in determining the subsequent crystal growth process and the properties of the final product. For example, people observed anomalously low undercooling for homogeneous nucleation of *n*-alkane from C₁₆ to C₃₂ [1], which has been proposed to be a result of the change in nucleus conformation. However, experiments were not able to examine the exact conformations of the crystal nuclei, especially for the critical nuclei.

In this work we report the results of molecular simulations to study crystal nucleation of *n*-octane from the melt. A realistic united atom force field was employed for *n*-octane. The melting behavior was first determined by ramping temperature in a set of molecular dynamics simulations. The adiabatic nucleation trajectory was then sampled using the Monte Carlo umbrella sampling technique. The surface energy of the crystal nuclei was calculated assuming a spherical nucleus model and compared with previous studies to validate our numerical definition of a crystal nucleus. We were also able to calculate the end and side surface free energies of a cylinder nucleus model from the simulation data without making further assumption. This method can be extended to study longer *n*-alkane molecules and the change of nucleus conformation as *n* increases.

[1]. Turnbull, D. and R.L. Cormia, *Kinetics of Crystal Nucleation in Some Normal Alkane Liquids*. The Journal of Chemical Physics, 1961. **34**(3): p. 820-831.