

## Effect of Lennard-Jones Potential Softness on Crystallization of Colloidal Particles

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**Abstract:** Crystal nucleation phenomena have practical relevance to applications as broad as pharmaceutical manufacturing, climate modeling, and flow assurance in petroleum transportation (Sosso *et al.* Chem. Rev. **116**, 7078-7116, 2016). Molecular simulations are a vital tool for uncovering the microscopic mechanisms of this process but require interaction models that accurately capture the behavior of the system under study. The Lennard-Jones (LJ) potential is a popular choice to represent generic repulsion and attractive dispersion forces. In condensed phases, the repulsion is expected to dominate the structural and dynamical properties (Chandler, Weeks, and Andersen. Science. **220**, 787-794, 1983), so the effects of modifying the repulsion are of interest. Here, we examine the effects on the nucleation kinetics and mechanism caused by softening the repulsion and attraction of the LJ potential. Crystal nucleation rates are calculated using molecular dynamics simulations combined with the advanced sampling technique called forward flux sampling (FFS) (Allen, Frenkel, and ten Wolde. J. Chem. Phys. **124**, 024102, 2006). We investigate two potentials: one is the classical 12-6 LJ potential, and the other is the softer 7-6 potential. By softer, it is meant that the forces of attraction and repulsion are lower in magnitude at close interparticle distances. The nucleation kinetics of the two potentials are compared within the framework of classical nucleation theory (CNT). Thermodynamic and kinetic properties of the liquid and crystal phases are needed to make this comparison: namely, the chemical potential difference, the surface free energy, and the attachment rate to the nucleus. The chemical potential difference is obtained from thermodynamic integration. The surface free energy and attachment rate are extracted from simulations of the liquid seeded with crystalline nuclei (Espinosa *et al.* J. Chem. Phys. **144**, 034501, 2016). With these properties, CNT predicts similar rates for the two potentials, while the rates from FFS are nearly identical. Since FFS samples many nucleation events, we have a means to analyze the mechanism in detail. It is revealed that the softer potential shifts the phase composition of nuclei towards higher fractions of body-centered cubic structure, as opposed to the thermodynamically stable face-centered cubic structure. Therefore, while it appears that the softness of the potential does not affect the rate of crystal nucleation at the same undercooling, the structures found along the nucleation pathways are different. The results presented here provide an understanding of the interplay of intermolecular interactions and crystal nucleation. This has implications in processes such as colloidal assembly, where the interactions can be tuned by particle structure and external fields, and development of force field parameters for molecular simulations.