87h Computing Solid-Fluid Coexistence for Molecular Systems Using a Pseudo-Supercritical Path Sampling Method

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The problem of constructing melting curves for compounds using molecular simulation techniques has been approached several ways. Direct methods based on heating/cooling of a pure phase to achieve phase transition or simulation of coexisting phases are straightforward but suffer timescale and system size problems. More rigorous free-energy based methods have a stronger theoretical basis but suffer drawbacks common to free energy methods. Methods based on determining absolute free energies of the two phases suffer the additional problem of defining a solid phase reference state with an analytic free energy. The direct methods are easily applicable to molecular systems while the reference system approaches become increasingly difficult for complex molecular systems. Recently we outlined a free-energy based method which eliminates the need for absolute reference states by constructing a pseudo-supercritical path that reversibly transforms between the solid and liquid phases. By integrating along this path, the free energy difference between the solid and liquid phases can be found directly. This method was demonstrated for Lennard-Jones and NaCl systems. Here we present the application of this method to molecular systems. The changes to the transformation path needed for molecular crystals are described along with modifications that can increase the efficiency of the method. Results are presented for two molecular potential models and it is shown that crystal structure and solid-liquid coexistence curves are very sensitive to the force field and can be indicators of the predictive ability of a potential model.