Invited Contribution from AIChE Area 1a

Predicting Solid State Phase Diagrams Using Multistate Reweighting and Jacobian Mapping

Michael Shirts [C, S], Natalie Schieber and Nathan Abraham
Department of Chemical and Biological Engineering, University of Colorado Boulder, Boulder, CO, U.S.A.
michael.shirts@colorado.edu

Eric Dybeck
Department of Chemical Engineering, University of Virginia, Charlottesville, VA

In materials with multiple metastable crystalline packings (polymorphs), the specific polymorphic phase affects many properties of the material. These include optical properties of dyes, charge transport in semiconductors, detonation properties of energetic materials, and bioavailability in small molecule organic pharmaceuticals. For this reason, effective prediction of the solid state phase diagrams of small molecules is important in the efficient development of materials. In this study, we present a new approach for predicting solid phase diagrams, Successive Interpolation of Multistate Reweighting (SIMR). This method can be easily adapted to also determine the relative Gibbs free energy of metastable polymorphs at a range of temperatures and pressures. Multistate reweighting is used to calculate free energy differences between temperature and pressure points within a polymorph. These results are then combined with a reference Gibbs free energy obtained with a pseudo-supercritical path (or other method) to obtain a Gibbs free energy difference surface between polymorphs at each point. Determining the line of intersection of these surfaces, which can be done by several different adaptive methods, gives the coexistence lines in the phase diagram and the most stable polymorph in each region. With this method, the uncertainty in each coexistence point returned by the method can be also efficiently and reliably estimated. We show the feasibility of SIMR for both the phase diagram of Lennard-Jones solids and of benzene. To increase the efficiency by decreasing the number of sampled states required, we have also used configuration mapping to increase the overlap between configurational states. Configuration mapping involves applying a post-simulation coordinate transformation between any two ensembles that partially compensates for the differences in the ensembles, essentially breaking the problem into two: an analytically free energy of the mapping, and a simulation-based correction to account for the remaining unknown differences in configurational ensembles. This approach allows for improved spacing of temperatures and pressures, significantly increasing the computational efficiency, sometimes by a factor of 20-30. We also analyze the efficiency of this method for system size scaling. Poor system size scaling has been proposed as a weakness of multistate reweighting approaches in the past. We find in analytical models and with number of test systems, this method scales slightly better than O (*N*), where *N* is the size of the system.