Calculating the Free Energy of Self-Assembled Structures by Thermodynamic Integration

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We discuss a method for calculating free energy differences between disordered and ordered phases of self-assembling systems utilizing computer simulations. Applying an external, ordering field, we impose a pre-defined structure onto the fluid in the disordered phase. The structure in the presence of the external, ordering field closely mimics the structure of the ordered phase (in the absence of an ordering field). Self-consistent field theory or density functional theory provide an accurate estimate for choosing the strength of the ordering field. Subsequently, we gradually switch off the external, ordering field and, in turn, increase the control parameter that drives the self-assembly. The free energy difference along this reversible path that connects the disordered and the ordered state is obtained via thermodynamic integration or expanded ensemble simulation techniques. The application of this technique to the order-disorder transition in symmetric diblock copolymers [1] and defect structures in copolymer [2] and lipid systems are illustrated.

[1] M. Müller and K.Ch. Daoulas, J. Chem. Phys. 128, 024903 (2008)
[2] M. Müller, K.Ch. Daoulas, and Y. Norizoe, Computing free energies of interfaces in self-assembling systems, preprint 2008 S