Investigating the Nucleation Behavior of Diblock Copolymers During an Order-disorder Transition to Complex Spherical Phases

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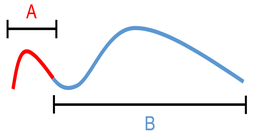
Goals

- Understand the nucleation pathway for a disordered (DIS) to body-centered cubic (BCC) phase transition in an AB diblock copolymer system
- Calculate critical nucleus size and energy barrier height for the DIS-BCC transition

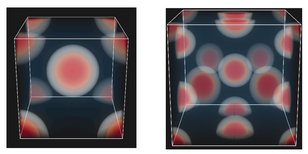
AB Diblock System

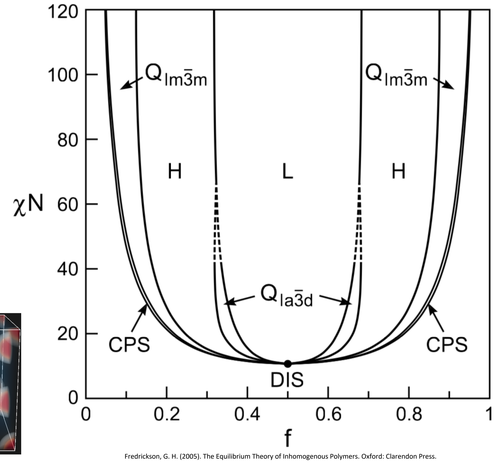
Self-assembly of Block Copolymers

Block copolymers are polymers made up of different monomer types. The simplest block copolymer is a linear AB diblock, where one chain of A-type monomers is covalently linked to one chain of B-type monomers. By carefully selecting the polymer chemistry and geometry. Diblock copolymers can be made to self-assemble into complex phases.



$$f = \frac{N_A}{N_A + N_B}$$





Fredrickson, G. H. (2005). The Equilibrium Theory of Inhomogenous Polymers. Oxford: Clarendon Press.

Some of these phases include spherical packing phases, such as BCC, where lattice sites are occupied by spherical clusters of polymers and are on the order of ten nanometers. Understanding the kinetic pathway and details of how these phases form can have great implications in polymer processing and material design.

Self-consistent Field Theory (SCFT) of Diblock Copolymers

SCFT is an equilibrium mean-field theory that remarkably captures the behavior of diblock copolymer melts.

$$H[w_+^*, w_-^*] = \rho_0 \int dr \left[\left(\frac{1}{\chi_{AB}} \right) w_-^{*2} - i w_+^* \right] - n \ln Q[w_A^*, w_B^*]$$

How can we study kinetic transitions of diblock self-assembly from DIS to BCC even though SCFT is an equilibrium theory?

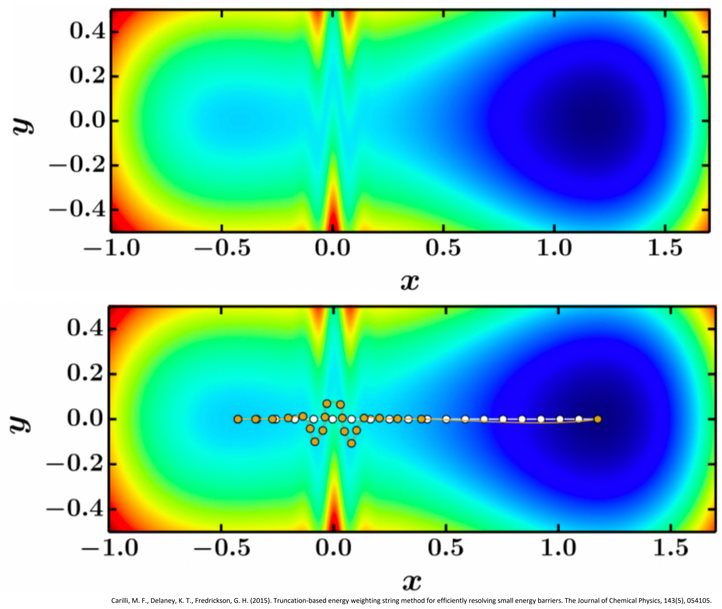
String Method Can Map Kinetic Pathways

String Method

The string method maps a minimum energy path between two metastable states by evolving a string of images between them. The images are evolved until the normal force along the path is zero, given by the following equation:

$$(\nabla V)^{\perp}(\phi(\alpha)) = 0$$

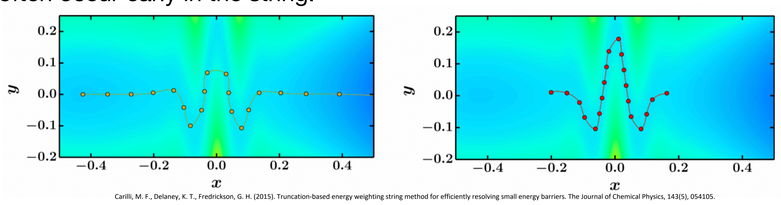
Example: $V(x,y) = -x^2 - x^3 + x^4 + \left(a\left[y - be^{-(cx)^2}\cos(dx)\right]\right)^2$; $(a, b, c, d) = (2, 0.2, 10, 40)$



Carilli, M. F., Delaney, K. T., Fredrickson, G. H. (2015). Truncation-based energy weighting string method for efficiently resolving small energy barriers. The Journal of Chemical Physics, 143(5), 054105.

Truncation-based Energy-weighting (TBEW) Improved String Method

TBEW improves the string method by discarding physically uninteresting regions of a string using an energy cutoff, E_C, and zooms in on critical regions. This is useful for examining nucleation, because critical regions often occur early in the string.



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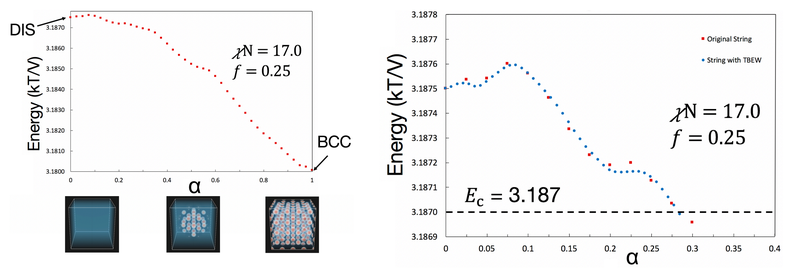
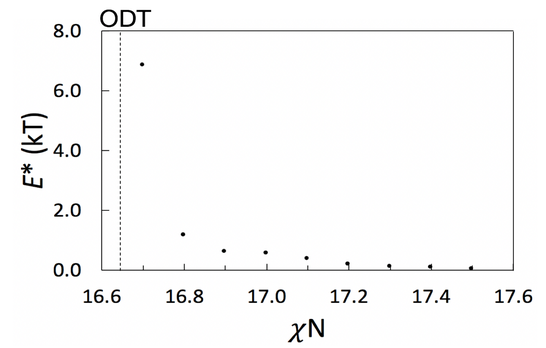
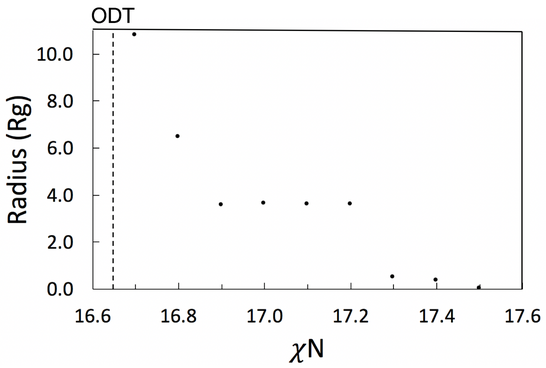
String Method and TBEW in the DIS-BCC Transition



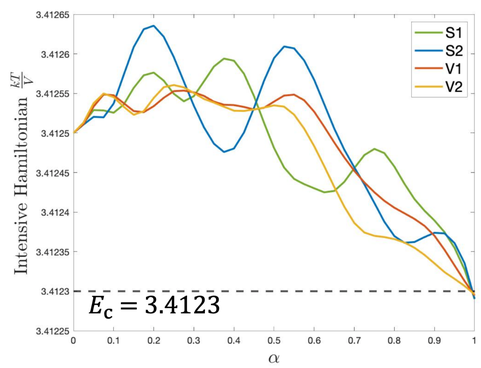
Results

Critical Nucleus Size and Energy Barrier Height Grow Near the Order-disorder Transition (ODT)





Preliminary Results for A15 Phase



$\chi N = 18.20$

- String calculations show that nucleation site matters in the A15 phase: the strings have drastically different shapes and energy barrier heights for different nucleation sites, denoted by S1, S2, V1, and V2.