Phases and Phase Transitions of Block Copolymers

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Spontaneous formation of ordered structures from amphiphilic molecules has attracted tremendous attentions in the last decades. Among the many different amphiphilic systems, block copolymers with their rich phase behaviour and ordering transitions have become a paradigm for the study of structural self-assembly. For the simplest case of diblock copolymers, which are linear polymers composed of two different sub-chains (A and B blocks), a variety of ordered bulk phases, including lamellae, hexagonally-packed cylinders, body-centered-cubic spheres and a bicontinuous network structure called gyroid, are observed. Theoretical studies of block copolymer phase behavior have been mostly within mean-field approximation, which is capable of describing many of the observed phases. In my talk I will present our studies of the kinetic pathways of the order-order transitions.

It is well know that a phase transition can proceed via two mechanisms, spinodal decomposition or nucleation and growth. In order to determine which mechanism is operating, Gaussian fluctuations in the mean-field solutions are used to study the stability of, and the kinetic pathways between, the ordered phases. The Gaussian fluctuation theory allows the study of spinodal lines, fluctuation modes, and scattering functions of the ordered phases.

When the system is in a metastable region, phase transitions proceed via nucleation and growth process. The nucleation of a droplet of stable phase from a metastable phase is examined theoretically. The free energy for an interface of arbitrary orientation separating the two phases is computed. This interfacial free-energy is anisotropic, leading to non-spherical nucleus. Typical values for the critical nucleus size are obtained. The region where the nucleation barrier is significant ($> 10\ k_BT$) is calculated. Examples of lamellar-to-cylindrical and spherical-to-cylindrical transitions will be shown and our results will be compared with relevant experiments and previous theoretical treatments.