518b Mixed Lamellae of Symmetric Diblock Copolymer Thin Films

Dong Meng and Qiang Wang

For symmetric diblock copolymers confined between two flat and homogeneous surfaces, three morphologies (parallel, perpendicular, and mixed lamellae) have been obtained in experiments. The effects of surface preference (for one of the two blocks) and film thickness D (compared to the bulk lamellar period L_0) on the thin-film morphology are well understood. Less studied is the copolymer chain conformation near a hard (impenetrable) surface, referred to as the "hard-surface effect". It is this effect that favors the formation of perpendicular lamellae between two neutral surfaces over parallel lamellae, at *all* film thicknesses. It also leads to the possible formation of mixed lamellae between asymmetric surfaces (not antisymmetric ones where the two surfaces prefer different blocks with the *same* strength).

While the mixed lamellae have been observed in Monte Carlo simulations[1] and various experiments, theoretical predictions on their formation are contradictory: Both using lattice self-consistent field calculations in 2D, Tang[2] and Fasolka *et al.*[3] studied symmetric diblock copolymer thin films of $D=L_0$ between asymmetric surfaces, and reached contradictory conclusions regarding whether the mixed lamellae are a stable phase (over parallel and perpendicular lamellae) or not. This morphology between asymmetric surfaces was not *numerically* examined by Matsen in his continuum self-consistent field calculations in 2D, where he assumed that mixed lamellae, if they were to occur, would be most stable between either identical or antisymmetric surfaces[4].

In this work, we use the self-consistent field theory in continuum to study the morphology of mixed lamellae in both 2D and 3D. A parallel algorithm is used to solve the SCF equations in real space with high accuracy. Results under different boundary conditions (zero-density *vs.* non-flux) are compared to examine their influence on the copolymer chain conformation near the surface and on the free energy of mixed lamellae. We also study in detail the chain conformation at the T-junction in this morphology. The conditions under which the mixed lamellae are a stable phase are determined quantitatively. We finally compare our SCF calculations with available experimental and simulation results.

References:

[1] *Q. Wang, et al.*, **J. Chem. Phys., 112**, 450 (2000)

[2] *W. H. Tang*, **Macromolecules, 33**, 1370 (2000)

[3] *M. J. Fasolka, et al.*, **Macromolecules, 33**, 5702 (2000)

[4] *M. W. Matsen*, **J. Chem. Phys., 106**, 7781 (1997)