

MAR07-2006-007143

Abstract for an Invited Paper
for the MAR07 Meeting of
the American Physical Society

PE Crystallization and Rotator Phases.

SCOTT MILNER, ExxonMobil Research and Engineering, Annandale NJ 08801

Recent work on crystallization of polyethylene (PE) implicates a metastable rotator phase as the nucleating phase. This claim invites the questions: what is the structure of this phase, what is the free energy difference ΔF driving nucleation, and what is the surface free energy Σ of the phase in contact with the melt? Related proposals for critical nuclei in polymer crystallization (“fringed micelles”) were dispensed with long ago, with estimates of ΔF and Σ that were unduly pessimistic. With more recent theoretical tools, we can revisit PE nucleation, comparing crystalline and rotator phase nuclei. To do so requires a model that can describe the bulk and surface free energy of both phases. To compare bulk free energies, we use a 6-state generalized Potts model, in which the disordered phase represents the rotator phase. Using a multiscale approach, coupling constants are obtained from solid-state simulations of domain walls between six degenerate crystalline orderings. The surface free energies, dominated by entropic penalties of melt segments near the nucleus surface (the “fringe”), are calculated using methods developed in the context of polymer brushes. Combining these ingredients, we can make a more enlightened comparison of the nucleation barrier for crystalline and rotator phase nuclei.