Reconciliation of Cahn-Hilliard predictions for spinodal decomposition lengthscales in polymer blends

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Spinodal decomposition (SD) of partially miscible polymer blends can yield well-defined nanostructures with prescribed lengthscales and connectivity, and applications ranging from membranes and scaffolds to photovoltaics. Cahn-Hilliard-Cook (CHC) theory estimates the initial, dominant SD wavenumber to be $q_m = \sqrt{\frac{G''}{4k}}$, where G'' is the second derivative of the free energy of mixing with respect to concentration and k is a structural parameter which can be computed from the segment lengths and volumes of monomer units. Tuning G'', with quench depth into the two phase region, for instance, should thus provide a facile and precise means for designing polymeric bicontinuous structures. The fulfillment of this potential rests on the thermodynamics of available polymer systems, coarsening kinetics, as well as engineering constraints. We extensively review experimental measurements of G'' in both one- and two-phase blend systems, and critically examine the accuracy of this fundamental prediction against achievements over the past 4 decades of polymer blend demixing. Despite widespread misconceptions in detecting and describing SD, we find the CHC relation to be remarkably accurate and conclude with design considerations and limitations for polymer nanostructures via SD, reflecting on John Cahn's contributions to the field.