Liquid-state theory of polymer-nanoparticle composites

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By making use of a liquid-state (integral equation) framework, the effect of hard fillers on the thermodynamics, phase behavior, and electrical properties of polymer blends and diblock copolymers is analyzed. The theory combines the Sanchez–Lacombe equation of state for compressible polymer mixtures with a self-consistent treatment of correlation functions between polymer species and fillers. This formulation enables evaluation of excess thermodynamic functions induced by fillers, as well as polymer-mediated interactions between them.

Analysis of the structure factors shows that correlations in polymer blends arise from two distinct mechanisms: finite compressibility and spatial variations in local composition. The latter generates a significant non-osmotic contribution to the polymer-mediated interaction between fillers, which dominates over the conventional osmotic contribution in dense blends. In athermal systems, size asymmetry between polymer components further enhances these interactions through an additional entropic contribution. Moreover, asymmetric polymer–filler interactions produce a complex interaction landscape, leading to both effective attraction and repulsion between fillers depending on composition and thermodynamic conditions.

Building on these results, the effect of fillers on the thermodynamic stability and miscibility of compressible polymer blends is examined. The spinodal transition temperature is calculated as a function of blend composition, interaction parameters, filler size, and filler volume fraction using the developed thermodynamic framework. For blends exhibiting low critical solution temperature (LCST) behavior, neutral (non-adsorbing) fillers increase stability, shifting the spinodal temperature upward due primarily to osmotic effects. In contrast, for upper critical solution temperature (UCST) systems, fillers reduce stability and shift the spinodal temperature downward. Extension of the Sanchez–Lacombe lattice-fluid model to filled systems allows derivation of the spinodal condition, which reduces in the low-compressibility limit to a simple analytical expression obtained self-consistently. The approximate and exact results agree closely, with deviations in the spinodal temperature below 4K, and both are consistent with experimental observations.

Finally, as a practical application, the electrical response of insulating polymer blends and diblock copolymers filled with conductive particles is investigated. Using the filler distributions predicted for phase-separated systems, the effective electrical conductivity of the composite is evaluated. The results provide a direct link between thermodynamic structure and macroscopic transport properties, and are in quantitative agreement with experimental data.