MAR14-2013-001863

Abstract for an Invited Paper
for the MAR14 Meeting of
the American Physical Society

Microscopic Theories of Diffusion, Tube Localization and Slow Relaxation in Polymer Nanocomposites

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Dynamics in polymer nanocomposites is rich and complex but poorly understood due to the presence of multiple length scales, excluded volume effects and other factors. We have developed new statistical mechanical theories at the level of forces for particle and polymer motion in flexible and rigid polymers. This talk presents an overview, including quantitative comparisons to simulations and experiments. First, by combining Brownian motion, polymer physics and mode coupling ideas, a self-consistent theory for the non-hydrodynamic diffusion of a spherical nanoparticle in melts has been constructed. Three competing mechanisms are predicted: sieving-like diffusion through unentangled regions, reptation-driven constraint release in entangled melts, and activated hopping through entanglement meshes. The controlling mechanism depends on particle size, tube diameter and entanglement density. The approach can also treat soft fillers, nonspherical particles, adsorption, solutions and networks. Second, a self-consistent microscopic theory for the slow dynamics of a needle fluid in a matrix of static spheres has been developed which exactly enforces inter-needle topological uncrossability and needle-sphere impenetrability constraints at the two-body level. The rich dependences of the effective tube diameter and anisotropic diffusion constants on filler-needle aspect ratio, polymer concentration and particle volume fraction has been established. Due to steric blocking of longitudinal motion by obstacles, a literal localization transition is predicted that is controlled by the particle to tube diameter ratio. For a restricted window of parameter space, needles are predicted to diffuse via a "renormalized" reptation dynamics where compression of the tube and suppression of longitudinal diffusivity enter in a manner that depends on all system variables. Generalization of the approach to treat mobile fillers, flexible chains and nonrandom microstructure is possible.