

Dynamical Phenomena in Molten, Crosslinked and Quenched Polymer-Nanoparticle Hybrid Materials

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Polymer nanocomposites are hybrid materials composed of nanoparticles and macromolecules that display diverse microstructures and unique viscoelastic properties. Their rich, but poorly understood, particle and polymer dynamics in the liquid phase is a consequence of the simultaneous presence of multiple length and time scales, excluded volume forces, geometric confinement, and topological entanglements. The physics underlying this complexity is also relevant to polymer motion in quenched porous media, and in diverse biological contexts such as entangled networks of stiff cytoskeleton biopolymers in cells, protein and vesicle diffusion in crowded environments, and drug delivery. We have recently developed new microscopic statistical mechanical theories for spherical particle and polymer (flexible and rigid) motion, and this talk presents an overview including comparisons to simulation and experiment. The mobility of isolated nanoparticles in polymer liquids exhibits three distinct non-hydrodynamic regimes that typically result in a massive failure of the Stokes-Einstein relation. Our predictions for hard particles are in good agreement with recent simulations and experiments in polymer melts and concentrated DNA solutions. Intermittent activated hopping transport can control diffusion in crosslinked networks and heavily entangled liquids in certain system parameter regimes, and is very sensitive to particle softness. At higher particle concentrations, polymer dynamics is deeply modified in a manner that depends sensitively on polymer/particle size ratio, degree of entanglement, and nanoparticle loading and mobility. Examples of these new phenomena for both rod and chain polymer nanocomposites will be presented with a focus on how slowly moving hard spherical particles modify entanglements and the anisotropy of polymer diffusion. In the quenched particle limit, rigid rod polymers can become dynamically arrested.