X-ray photon correlation spectroscopy studies of nanoparticle motion in glassy polymer melts and entangled polymer solutions
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Microrheology, in which colloids suspended in a complex fluid probe the mechanical environment, can provide unique information on the microscopic length scales characterizing the fluid’s hierarchical structure. We describe x-ray photon correlation spectroscopy (XPCS) studies tracking the nanometer-scale motion of dilute suspensions of gold nanoparticles in low-molecular-weight polystyrene melts and in high-molecular-weight polystyrene solutions. In the melts, the high-temperature nanoparticle dynamics are diffusive with a rate that tracks the melt viscosity. Close to the glass transition, a hyper-diffusive process that we identify with heterogeneous strain in the melts supersedes the diffusion. Following a quench, the hyper-diffusive dynamics display characteristics of aging. Similar slow, heterogeneous strain has been observed in a range of soft glassy materials such as colloidal gels and emulsions. The apparently universal nature of the phenomenon hence provides a link between the microscopic processes of aging in hard and soft glassy systems. In contrast, the nanoparticle motion in the high-molecular-weight solutions reveals qualitatively different behavior. Over displacements from nanometers to tens of nanometers, the particles undergo anomalous subdiffusion in which the particle mean-squared displacement grows as a power law in time with power-law exponent in the range 0.3 to 0.5 depending on solution conditions. Scaling behavior of the nanoparticle mobility with respect to temperature and polymer concentration and molecular weight indicates that the subdiffusive motion results from the temporal evolution of the entanglement mesh in the immediate vicinity of the particles. The results thus provide novel microscopic characterizations of the structural dynamics in the melts and entangled solutions and more broadly demonstrate the ability of XPCS-based microrheology to interrogate the nanoscale mechanical behavior of polymer materials.