350f Deliquescence, Diffusion, and Crystal Nucleation in Levitated Polyethylene Oxide

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Polymer crystallization is a first order phase transition that is complicated by severe kinetic frustration, a metastable endpoint, and inclusion of single molecules in multiple crystallites. The conditions under which a polymer crystallizes affect the resulting morphology, and thus the mechanical, optical, and transport properties of the material. An instrument has been developed for inducing phase transitions in polymers by thermal and solvent processing of micron sized particles that are levitated in an electrostatic field. Working with levitated microscopic particles eliminates container surfaces, increases the probability of observing material without solid impurities, and facilitates rapid equilibration of diffusive processes so that repeated experiments can be carried out in a short period of time. The apparatus features mass measurement with picogram resolution and precise control of temperature (+/- 0.1 K) and relative humidity (+/- 0.1% RH). Angular scattering of laser radiation is also recorded since it is strongly dependent upon particle size, shape, and refractive index uniformity. The dynamics associated with melting, dissolution, and crystallization are monitored through changes in sample mass and/or optical properties.

Polyethylene oxide is a semicrystalline polymer that is water soluble and biocompatible. Deliquescence is observed when polyethylene oxide particles are exposed to an increasing ramp in humidity -- the semicrystalline material spontaneously absorbs water to become an amorphous polymer solution. Equilibrium water content as a function of RH can thus be measured for both the semicrystalline and amorphous states. Levitated particles enable access to highly supersaturated solutions so that metastable states persist as RH is decreased until homogeneous nucleation enables crystallization. A single particle can be cycled repeatedly through strictly controlled conditions to capture the statistical nature of homogeneous crystal nucleation. Metastability in partially dissolved polyethylene oxide has also been discovered. Thus, the population of crystallites that remains in the partially dissolved material does not spontaneously nucleate additional crystallization.