Experimental final states in a density matched, polydisperse hard sphere polymer mixture

Thomas Palberg¹*, Richard Beyer¹, Eckhard Bartsch²

¹ Institute of Physics, University Mainz, D-55128 Mainz, Germany
² Institute of Physical Chemistry, University Freiburg, D-79104 Freiburg, Germany

*palberg@uni-mainz.de

For monodisperse hard sphere polymer mixtures of size ratio around 0.1 theory and simulation predict pronounced phase behaviour. Starting with the hard sphere volume fractions of melting, $\Phi_M = 0.545$ and freezing $\Phi_F = 0.495$ and adding polymer, at first leads to marginal changes of the coexistence region, but for polymer reservoir packing fractions of 0.3 and larger, it considerably widens to give rise to a coexistence of a compressed solid of $\Phi_s \cong 0.74$ and a very dilute fluid (or gas) of $\Phi_F < 0.05$. Experimentally, this behaviour has been confirmed using e.g. polymethyl methacrylate spheres in organic solvents, though a gelation of the samples occurred shortly after the widening of the coexistence region, due to gravitational effects. In the present study, we instead use very well density matched polystyrene micro-gel spheres suspended in 1-Ethynaphtalene. These are polydisperse with a polydispersity index of 0.07. The packing fraction behaviour we observed at low polymer concentration is consistent with previous experiments and theoretical expectations. At large polymer concentrations, however, the system phase separates into a highly compressed crystal of $\Phi_{\text{crystal}} = 0.73$ and a fluid of $\Phi_{\text{fluid}} = 0.5$. We argue that polydispersity hinders the dilution of the remaining fluid by suppressing sufficient crystal formation. This occurs through a fractionation mechanism required for crystal formation at such large polydispersity. The gas phase is further absent, as there is no macroscopic separation of particle rich and particle depleted regions due to gravity in our finely density matched system, which could give rise to bubble nucleation. In summary, we see the onset of the expected phase separation, but its completion is hindered by two different kinetic effects.