Interdiffusion Coefficients and the Intermediate Scattering Function for Glass-Forming Liquids

Peter Daivis C.S, Stephen Hannam and Gary Bryant

Physics, School of Science, RMIT University, Melbourne, Vic, Australia
peter.daivis@rmit.edu.au

We have computed the coherent intermediate scattering functions over a range of wavevectors at different compositions leading up to the freezing point and in the metastable region up to the glass transition for bimodal model colloidal suspensions and for water-sugar solutions. We observe strong similarities between the two systems, even though they are qualitatively different. In the case of the bimodal colloidal suspensions, diffusive transport can be described in terms of the two eigenvalues of the matrix of ternary diffusion coefficients, one corresponding to the decay of fluctuations in the total concentration at constant composition while the other corresponds to the decay of fluctuations in the composition at fixed total concentration. We find that the rate of decay of composition fluctuations decreases dramatically as the total packing fraction increases, leading to structural arrest and characteristic glassy behavior. In this case, the glass transition can be attributed to the inability of the composition to relax to the equilibrium crystal composition within the accessible timescale. In the sugar-water solutions, it is the mutual diffusion coefficient that decreases dramatically as the glass transition is approached from the equilibrium liquid state. While a unimodal colloid almost always crystallizes before the glass transition is reached (unless the quench rate is extraordinarily high), the water-sugar solution forms a glass more easily. We show that factorizing the diffusion coefficient into its kinetic and thermodynamic contributions allows us to analyze and propose reasons for this contrasting behavior.