Binary hard-sphere mixtures re-visited: depletion and the elusive fluid-fluid phase transition

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In tackling the statistical mechanics of highly size-asymmetric mixtures it is usually efficacious to integrate out the degrees of freedom of the smaller species to obtain an effective Hamiltonian for the larger species. We describe the results of a set of detailed (classical) density functional theory (DFT) calculations, based on fundamental measure theory, and Monte Carlo simulations, using i) staged particle insertion and ii) the geometrical cluster algorithm, of the effective (depletion) potential between a pair of big hard spheres immersed in a reservoir of much smaller hard spheres. The size disparity is measured by the ratio of diameters $q = \sigma_s/\sigma_b$. We focus on the regime $q < 0.1$ where previous work suggested (metastable) fluid-fluid phase separation might occur. Agreement between DFT and simulation is generally very good for packing fractions of the reservoir up to about 0.35. By calculating the second virial coefficient associated with the effective potential we make new estimates[1] for the onset of this elusive fluid-fluid phase transition. Knowledge of the latter is important for interpreting dynamical observations on colloidal mixtures, such as where in the phase diagram gelation or glassiness might set in.

We also describe recent experimental work[2] on a colloid-polymer mixture studied above the theta temperature of the non-adsorbing polymer (polystyrene).Increasing temperature increases the radius of gyration of the polymer thereby increasing the polymer-colloid size ratio. We find i) onset of gelation occurs very close to the (metastable) fluid-fluid critical point estimated from the Asakura-Oosawa depletion potential and ii) enhancement of the crystallization rate occurs in the neighbourhood of this critical point.

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[1] 1. D.J.Ashton, N.B.Wilding , R.Roth and R.Evans , Phys.Rev.E. 84, 061136 (2011).

[2] 2. S.Taylor, R.Evans and C.P. Royall , J.Phys.Condens. Matt. (to appear).