Critical Phenomena and Crossovers in Colloidal Dispersions

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Colloidal dispersions are often described in terms of an effective colloid-colloid interaction, which results from averaging over many degrees of freedom, be they internal to the macroparticles, or related to other constituents of the dispersion. One of the most interesting characteristic of these effective potentials is their tunability. By acting on the dispersion parameters, one can thus change the interaction profile and study how this affects the properties of the system, a possibility which does not occur in atomic fluids. Compared to the investigation of the overall shape of the phase diagram, the critical behavior has so far received little attention in this context. The hierarchical reference theory (HRT) is very suited to this investigation, because it combines the realistic treatment of the universal features of criticality given by the renormalization group with the description of the nonuniversal properties offered by microscopic liquid-state theories. Here we consider three examples, namely the Asakura-Oosawa (AO) model of a colloidal dispersion under the influence of polymer-induced attractive depletion forces; a fluid where the short-ranged interparticle attraction is followed by a longer-ranged repulsion due e.g. to electrostatic interactions or nonideal depletant agents; a solution of star-polymers whose pair potential presents both an attractive well and a repulsion at shorter distances, the latter being much softer than its atomic counterpart because of the mutual penetrability of the stars. In the first case, the interaction range is controlled by the size asymmetry between polymer and colloid: as the asymmetry increases, the interaction range gets shorter, and the crossover to the asymptotic Ising-like critical behavior takes place farther from the critical point than in atomic fluids. In the second case, the competition between attraction and repulsion favors particle clustering, which strongly enhances the large-density fluctuations and causes a steep crossover in the isothermal compressibility, with a very large effective critical exponent. Finally, star-polymer solutions show mean-field-like critical behavior in a very wide range of reduced temperatures.