Thesis for the Degree of Doctor of Philosophy in Physical Chemistry

Structure, phase behavior, and dynamics of colloidal systems characterized by strong, short- and moderate-range attractions:
a computational study

Bodil Ahlström

UNIVERSITY OF GOTHENBURG

Structure, phase behavior, and dynamics of colloidal systems characterized by strong, short- and moderate-range attractions: a computational study

Bodil Ahlström

Abstract

Attractions between colloidal particles are often so strong that non-equilibrium behavior results. However, dissolved non-adsorbing polymer can be added to give a weak attraction between particles so that equilibrium phase transitions appear at moderate polymer concentrations. At higher polymer concentrations and small polymer-colloid size ratios non-equilibrium effects like gelation occur, for which a complete understanding is lacking.

Monte Carlo and Monte Carlo-like computer simulations have been used to investigate the role of many-body effects and the structures that colloidal particles adopt under influence of a polymer-induced depletion attraction. The phase diagram proves difficult to determine for these systems by direct application of the Gibbs ensemble Monte Carlo method, especially for small polymer-colloid size ratios that correspond to short-range attractions. However, a sequential equilibration scheme is shown be able to give equilibrated fluid-fluid coexistence data where usual application of the method fails. The dynamics of colloidal particles along this fluid-fluid coexistence curve is studied by a Brownian dynamics algorithm, corrected for the use of a large time step. The dynamics slows down as the particle and polymer concentrations are increased, but the systems appear to reach equilibrium for the cases studied. This is in contrast to what is found by applying mode coupling theory; it predicts glass-like transitions already at modest polymer concentrations for short-range attractive systems, which is an issue that is investigated to some extent. In addition, a number of approximate theories have been developed and tested against the results from the computer simulations.