Modelling the out-of-equilibrium dynamics of colloids by Monte Carlo simulations

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Colloids have a striking relevance in a wide spectrum of industrial formulations, spanning from personal care products to protective paints. Their behaviour can be easily influenced by extremely weak forces, which disturb their thermodynamic equilibrium and dramatically determine their performance. Motivated by the impact of colloidal dispersions in fundamental science and formulation engineering, we have designed an efficient Dynamic Monte Carlo (DMC) approach to mimic their out-of-equilibrium dynamics.

Our recent theory, which provided a rigorous method to reproduce the Brownian motion of colloids by MC simulations [1, 2], is here generalised to reproduce the Brownian motion of colloidal particles during transitory unsteady states, when their thermodynamic equilibrium is significantly modified [3]. In particular, we have recently proposed a DMC algorithm to investigate the Brownian motion of pure systems [1] and mixtures [2] of colloidal particles in isotropic, nematic and smectic liquid crystal phases. By rescaling the MC time step with the acceptance ratio of particle displacements and rotations, we demonstrated the existence of a unique MC time scale that allows for a direct comparison with BD simulations.

In the present work, we extend our theoretical framework to the case in which an external stimulus perturbs the thermodynamic equilibrium of a colloidal system conmsisting of monodisperse or bidisperse rod-like particles. From a steady-state condition of dynamic equilibrium, where all the observables, including the above mentioned acceptance ratio A, are independent of time t, the system undergoes a transitory unsteady state taking it to a new equilibrium configuration. We apply our DMC simulation technique to simulate the effect of an external field forcing an isotropic phase of rod-like colloidal particles to reorient along a common direction and thus form a nematic liquid crystal. We also study the behaviour of the system once the external field is removed and show that, even when $A = A(t)$, our DMC simulations, which are in excellent quantitative agreement with BD simulations, can be employed to extract reliable dynamical information also from out-of-equilibrium systems.

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