University of Fribourg / Faculty of Science and Medicine / Department of Physics

New approaches to classical (dynamical) density functional theory by including inhomogeneous two-body correlation functions

Salomée Tschopp

We start our journey with the study of inhomogeneous two-body correlations for the three-dimensional hard-sphere model. Using Rosenfeld's fundamental measure theory, we provide analytic formulae for the Hankel and Legendre transforms of the inhomogeneous two-body direct correlation function as explicit functionals of the density. When combined with the inhomogeneous Ornstein-Zernike equation these results then allow for rapid calculation of inhomogeneous hard-sphere density correlations in real-space, for the special cases in which the density has either planar or spherical symmetry. This first study not only provides information about the packing structures of the hard-sphere system, but also forms an essential building-block for (i) constructing perturbation theories of realistic models and (ii) developing better dynamical theories for the description of inhomogeneous fluids out-of-equilibrium.

Moving to attractive systems, we then develop and implement a first-principles `Barker-Henderson density functional'. This study has its roots in the Barker-Henderson perturbation theory, bedrock of liquid-state physics, which provides quantitative predictions for the bulk thermodynamic properties of realistic model systems but has not been exploited for the study of inhomogeneous systems before. The Barker-Henderson density functional provides a robust and quantitatively accurate theory for classical fluids in external fields. We present numerical results for the hard-core Yukawa model in three dimensions. Our predictions for the density around a fixed test-particle and between planar walls are in very good agreement with simulation data. The density profiles for the free liquid vapour interface show the expected oscillatory decay into the bulk liquid as the temperature is reduced towards the triple point, but with an amplitude much smaller than that predicted by the standard mean-field density functional.

Finally, we focus on classical many-body systems subject to Brownian dynamics and develop a first-principles superadiabatic dynamical density functional theory (DDFT) for the description of inhomogeneous fluids out-of-equilibrium. By explicitly incorporating the dynamics of the inhomogeneous two-body correlation functions we obtain superadiabatic forces directly from the microscopic interparticle interactions. We demonstrate the importance of these nonequilibrium forces for an accurate description of the one-body density by numerical implementation of our theory for three-dimensional hard-spheres in time-dependent planar potentials. These have been chosen to probe distinct aspects of structural relaxation in dense, strongly interacting liquid states. Nonequilibrium density profiles predicted by the superadiabatic theory are compared with those obtained from both adiabatic DDFT (namely the standard DDFT and the new force-DDFT developed in the same chapter) and event-driven Brownian dynamics simulation. Our findings show that superadiabatic-DDFT accurately predicts the time-evolution of the one-body density.

Jury:
Prof. Dr. Joseph M. Brader (thesis supervisor)
Prof. Dr. Robert Evans (external co-examiner)
Dr. Benjamin Goddard (external co-examiner)
Prof. Dr. Philipp Werner (internal co-examiner)
Prof. Dr. Christian Bernhard (president of the jury)