Relaxational dynamics of microscopic films. Spectral methods for the equations of classical density-functional theory.

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ABSTRACT

Classical density functional theory (DFT) is a formulation of statistical mechanics in which the relevant equations are expressed in terms of the spatially varying number density of the fluid. It can be applied to molecular fluids and their mixtures, colloids and even certain biological systems. Given the intermolecular and external potentials in the fluid, a DFT model is essentially free from any additional assumptions.

Consider an argon-like fluid adsorbed on a Lennard-Jones planar wall. First, we obtain a set of phase diagrams corresponding to the equilibrium adsorption and compare our results obtained from different approximations to the hard sphere part of the free energy functional. Using principles from the theory of sub-critical dynamic phase field models, we formulate the time-dependent equations which describe the evolution of the adsorbed film. Through dynamic considerations we interpret the phase diagrams in terms of their stability. Simulations of various wetting and drying scenarios allow us to rationalize the dynamic behavior of the system and its relation to the equilibrium properties of wetting and drying.

We also propose a novel numerical scheme based on the Chebyshev pseudo-spectral collocation method for solving the integral and integral-differential equations of DFT and its dynamic extension. The convolution-like integrals typical of DFT models are computed in real space. We demonstrate the exponential convergence of our scheme, which typically requires much fewer discretization points to achieve the same accuracy compared to conventional methods. This discretization scheme can also incorporate the asymptotic behavior of the density, e.g. in the vicinity of a substrate or far from it, which can be of interest in the investigation of open systems. Our scheme is complemented with a numerical continuation algorithm and an appropriate time stepping algorithm, thus constituting a complete tool for the efficient and accurate calculation of phase diagrams and associated dynamic phenomena.