Modeling Relaxation Processes for Fluids in Porous Materials Using Dynamic Mean Field Theory: An Application to Partial Wetting

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Abstract We review a recently developed dynamic mean field theory for fluids confined in porous materials and apply it to a case where the solid-fluid interactions lead to partial wetting on a planar surface. The theory describes the evolution of the density distribution for a fluid in a pore that has contact with the bulk during a quench in the bulk chemical potential. In this way the dynamics of adsorption and desorption can be studied. By focusing on partial wetting situation we can investigate influence of a weaker surface field on the mechanisms of capillary condensation and desorption. We have studied the dynamics of pore filling in a quench of the chemical potential between two states either side of the pore filling step, tracking the density distributions during the process. The pore filling process features an asymmetric density distribution where a liquid droplet appears on one of the walls. The droplet spreads and grows in size and this is followed by the appearance of a liquid bridge between the pore walls (for longer pores two liquid bridges are seen). The density distributions obtained in the dynamics resemble those obtained from static mean field theory in the canonical ensemble for an infinite pore without contact with the bulk.

Keywords Porous materials · Wetting · Dynamic mean field theory

1 Introduction

Adsorption/desorption experiments for gases such as nitrogen in mesoporous materials (materials where pore sizes lie in the range from 2 nm to 100 nm) at temperatures significantly below the bulk critical temperature frequently exhibit hysteresis between the adsorption/desorption branches of the isotherm. Hysteresis is an indication of failure by the system to equilibrate and under such circumstances the nature of the relaxation dynamics in the system becomes of some interest.
Classical density functional theory (DFT’s) has contributed much to our understanding of the molecular level behavior of fluids confined in porous materials [17, 20]. DFT allows us to calculate the free energy and density distribution for fluids inside porous materials yielding an important route to understanding confinement effects on fluids in porous materials. DFT also permits the study of metastable states associated with hysteresis loops in adsorption/desorption isotherms [6, 7, 22, 28, 29, 48]. In developing a theory of the dynamics of adsorption and desorption in mesoporous materials it is worthwhile to focus on approaches that have built into them a description of the thermodynamics from DFT.

The idea of building dynamical theories of systems with phase transitions based upon free energy functionals that give a physically realistic picture of the equilibrium behavior is an old one and goes back to the work of Cahn [10] who incorporated the Cahn-Hilliard square gradient free energy functional [9, 11, 12] into a diffusion equation and used the resulting equation to describe the early stages of spinodal decomposition. This idea has had enormous impact in many fields, ranging from polymer phase separation dynamics [19] to colloidal dynamics [4, 27]. Two lines of recent development in this field are of particular interest. One of these focuses on the incorporation of more quantitatively accurate descriptions of the free energy functional as well as the derivation of the dynamical equations from the atomic level equations of motion, typified by the dynamic density functional theories (DDFT’s) [2–5, 25, 26, 39, 52]. Another line of development has focused on incorporating a more realistic description of the relationship between the mobility and the density distribution in the system [21, 30, 43]. This latter problem is of particular importance in considering the time evolution of fluid states in porous materials in the neighborhood of capillary condensation due to the rapid evolution of interfacial structure with time in these systems.

The approach we take here is to develop a theory of the time dependent molecular density distribution in the system [37]. We then consider the dynamic evolution of this distribution in terms of the probabilities of transitions between states of the system governed by a master equation. In this sense the approach can be regarded as a theory of the dynamics produced in a dynamic Monte Carlo simulation. The result of the analysis is a differential equation for the local density in the system based on a mean field approximation for the transition probabilities. The transition probabilities can be related to the chemical potential from DFT and the density distribution approaches the distribution from DFT for long times. The theory can also be analyzed as a theory of diffusion or as a dynamic density functional theory. We refer to the approach as mean field kinetic theory (MFKT) or dynamic mean field theory (DMFT).

Our approach makes use of lattice gas models to describe confined fluids. Monte Carlo simulations and theories of such models have been widely used in recent years [1, 8, 13, 14, 16, 17, 22, 28, 29, 35, 40–42, 49] because they are simple to implement and computationally efficient yet qualitatively realistic. Applications have included wetting transitions [16, 41] as well as the properties of fluids in porous materials [8, 22, 28, 29, 48, 49]. The dynamic behavior for such models can be studied in dynamic Monte Carlo simulations and one approach is to use Kawasaki dynamics, which generates dynamics via nearest neighbor hopping processes [13, 23, 35, 44, 47, 48]. The present theory provides an approximation to the average of the time dependent density distribution resulting from an ensemble of Kawasaki dynamics trajectories. The novelty of this approach primarily arises from the context in which we