

Dynamic Mean Field Theory for Fluids in Mesoporous Materials

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Application of classical density functional theory (DFT) has led to dramatic improvements in our understanding of the thermodynamics of fluids confined in mesoporous materials. DFT allows us to calculate the free energy and density distribution for fluids inside porous materials for equilibrium states of the system. In this way it provides an important route to understanding confinement effects on fluids in porous materials. A testament to the success of DFT has been its incorporation in computer software for commercial adsorption analysis equipment. DFT also permits the study of

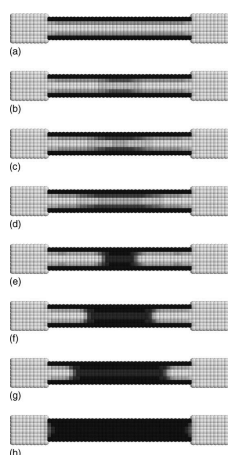


Figure 1. Visualizations from DMFT of states during the dynamics of capillary condensation for a model of a fluid in a slit pore in contact with the bulk.

metastable states associated with hysteresis loops in adsorption/desorption isotherms. The phenomenon of hysteresis is an indication that the fluid confined inside the porous material is not at equilibrium for a range of states. It then becomes of particular interest to understand the dynamics of the system in addition to the equilibrium behavior. We have recently developed [1-3] theory of the dynamics (DMFT) of adsorption and desorption of fluids in mesoporous materials that incorporates the mean field DFT description of the thermodynamics. The theory predicts the evolution of the density distribution in the porous material after a step change in the bulk state. It can also be used to formulate a theory for self-diffusion. Thus DMFT presents a unified approach to understanding thermodynamics, relaxation dynamics and self-diffusivity for confined fluids.

We describe several applications of DMFT. We begin with an application to a slit pore in contact with the bulk gas and show how the theory can describe the evolution of the density distribution during capillary condensation or evaporation. Figure 1 shows visualizations of the density distribution in a slit pore during capillary condensation where nucleation via formation of an undulate and then a liquid bridge is seen to occur. A remarkable feature of DMFT is that the nucleation mechanisms in phase transitions of confined fluids are emergent features of the calculations. We also present applications to model pore networks. Several phenomena are explored, including mass transfer resistances to equilibration and the dynamics of cavitation in inkbottle pores. Finally we show how DMFT can be applied to the calculation of self-diffusivity by using the color

field concept. Predictions from this approach agree well with the results from NMR measurements for fluids in Vycor porous glass [4,5].

References

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