University of Massachusetts Amherst

From the Selected Works of Peter A. Monson

2009

Modeling relaxation processes for fluids in porous materials using dynamic mean field theory: an application to partial wetting

Peter A Monson, *University of Massachusetts - Amherst*
John R Edison

Available at: https://works.bepress.com/peter_monson/7/

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

John R. Edison · Peter A. Monson

Received: 11 May 2009 / Accepted: 28 June 2009 / Published online: 25 July 2009
© Springer Science+Business Media, LLC 2009

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.

J.R. Edison · P.A. Monson (✉)
Department of Chemical Engineering, University of Massachusetts, Amherst, MA 01003, USA
e-mail: monson@ecs.umass.edu

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

Fig. 1 The slit pore geometry considered in this work. The pore is infinite in the y -direction. Periodic boundaries are used in the x -direction with the pore in contact with the bulk fluid

are applying it. It has its origin in the dynamic mean field theories of the Ising [43] and binary alloy [30] models first developed almost 20 years ago and reviewed by Gouyet et al. [21]. It has also been used to model diffusion in membranes and bulk fluids by Matuszak et al. [31–33].

In previous work we have applied the DMFT to model pores where the solid-fluid interaction was sufficiently strong to give rise to complete wetting [37, 38] (in referring to wetting states here we have in mind the behavior of the free solid-fluid interface for the same solid-fluid interaction as we have for the fluid in the pore). This is the typical situation encountered in nitrogen adsorption experiments. In the present work we investigate a case where the solid-fluid interaction is weaker and there is partial wetting, employing the slit pore geometry shown in Fig. 1. This type of behavior is encountered for water in graphitic carbon adsorbents and carbon nanotubes. In a recent paper one of us discussed the link between wetting, pore condensation and hysteresis for a lattice gas model of fluid in slit a pore [36]. A key effect here is that in adsorption from a vapor at sub-critical temperatures, low density states may persist up to and beyond the bulk saturation pressure, as has been seen in experiments on water adsorbed in graphitized carbon black [15], even though the equilibrium vapor-liquid transition lies below bulk saturation. Our calculations reveal the nature of the processes involved during pore filling for a partial wetting system.

In Sect. 2 we describe the lattice model and theoretical methods used, including both the static and dynamic mean field theory. Section 3 presents our results, first for the static behavior and dynamics. A summary of our results and conclusions is given in Sect. 4.

2 Models and Methods

2.1 Lattice Model and Static Mean Field Approximation

For a nearest neighbor lattice gas in an external field the Hamiltonian can be written [14, 16, 22, 37, 48]

$$H = -\frac{\epsilon_{ff}}{2} \sum_{\mathbf{i}} \sum_{\mathbf{a}} n_{\mathbf{i}} n_{\mathbf{i}+\mathbf{a}} + \sum_{\mathbf{i}} n_{\mathbf{i}} \phi_{\mathbf{i}} \quad (1)$$

where n_i is the occupancy (0 or 1) at site $\mathbf{i}$, $\mathbf{a}$ is the vector to a nearest neighbor site for any site on the lattice [21] and ϵ_{ff} is the nearest neighbor interaction strength. The second term in the Hamiltonian describes the solid-fluid interactions, where ϕ_i denotes the strength of the wall-fluid interaction (wettability). In this work we use a simple cubic lattice and a wettability of strength $-\epsilon_{sf}$ for sites adjacent to the solid wall. The mean field (MFT) grand free energy is given by

$$\Omega = kT \sum_i [\rho_i \ln \rho_i + (1 - \rho_i) \ln(1 - \rho_i)] - \frac{\epsilon_{ff}}{2} \sum_i \sum_{\mathbf{a}} \rho_i \rho_{i+\mathbf{a}} + \sum_i \rho_i (\phi_i - \mu) \quad (2)$$

where μ is the chemical potential and ρ_i is the mean density at site $\mathbf{i}$. Similarly for the Helmholtz energy we have

$$F = kT \sum_i [\rho_i \ln \rho_i + (1 - \rho_i) \ln(1 - \rho_i)] - \frac{\epsilon_{ff}}{2} \sum_i \sum_{\mathbf{a}} \rho_i \rho_{i+\mathbf{a}} + \sum_i \rho_i \phi_i \quad (3)$$

By minimizing Ω at fixed chemical potential or F at fixed overall density we can obtain solutions of the mean field equations for the grand canonical and canonical ensembles, respectively. We make use of both of these types of calculations in this work.

The necessary condition for a Helmholtz energy minimum, at fixed temperature and overall density is

$$\frac{\partial F}{\partial \rho_i} - \mu = 0 \quad \forall \mathbf{i} \quad (4)$$

where the chemical potential, appears as a Lagrange multiplier associated with the constraint of fixed overall density. Using (4) with (3) it is readily shown that

$$\rho_i = \frac{\lambda c_i}{1 + \lambda c_i} \quad \forall \mathbf{i} \quad (5)$$

where $\lambda = \exp(\mu/kT)$ is the activity and $c_i = \exp[-(\phi_i - \epsilon_{ff} \sum_{\mathbf{a}} \rho_{i+\mathbf{a}})/kT]$. This set of equations can be solved together with the density constraint expressed as

$$\sum_i \frac{\lambda c_i}{1 + \lambda c_i} - N = 0 \quad (6)$$

to give the equilibrium density distribution and the chemical potential. We iterate through (5) and (6) by writing

$$\rho_i^{(n+1)} = \frac{\lambda^{(n)} c_i^{(n)}}{1 + \lambda^{(n)} c_i^{(n)}} \quad \forall \mathbf{i} \quad (7)$$

and

$$\lambda^{(n+1)} = \lambda^{(n)} N \left(\sum_i \frac{\lambda^{(n)} c_i^{(n)}}{1 + \lambda^{(n)} c_i^{(n)}} \right)^{-1} \quad (8)$$

The results for the grand ensemble (fixed μ, V, T) are obtained by solving (5) without the density constraint, (6).

Equation (5) can be rearranged to give an expression for the chemical potential at site $\mathbf{i}$

$$\mu_{\mathbf{i}} = kT \ln \left[\frac{\rho_{\mathbf{i}}}{1 - \rho_{\mathbf{i}}} \right] - \epsilon_{ff} \sum_{\mathbf{a}} \rho_{\mathbf{i}+\mathbf{a}} + \phi_{\mathbf{i}} \quad (9)$$

Solutions of the static MFT equations lead to the $\mu_{\mathbf{i}}$ being uniform throughout the system. This equation also helps establish the limiting behavior of the dynamic mean field theory for long times.

2.2 Dynamic Mean Field Theory

Our presentation of DMFT follows closely that of Monson [37], which is in turn based on that of Gouyet et al. [21]. The theory gives an approximation to the time evolution of the density distribution averaged over an ensemble of many kinetic Monte Carlo simulations of the lattice gas model. The particular focus here is on Kawasaki dynamics, which we have used extensively to make kinetic Monte Carlo simulations of adsorption/desorption dynamics for fluids in porous materials [47, 48, 50, 51]. We begin by writing the ensemble average density for site $\mathbf{i}$ at time t , $\rho_{\mathbf{i}}(t)$, as

$$\rho_{\mathbf{i}}(t) = \langle n_{\mathbf{i}} \rangle_t = \sum_{\{n\}} n_{\mathbf{i}} P(\{n\}, t) \quad (10)$$

where $P(\{n\}, t)$ is the probability of observing an occupancy configuration $\{n\}$, at time t . The transport is restricted to hopping between nearest neighbor sites as in Kawasaki dynamics and the evolution equation for the local density can then be written as

$$\frac{\partial \rho_{\mathbf{i}}}{\partial t} = - \sum_{\mathbf{a}} J_{\mathbf{i}, \mathbf{i}+\mathbf{a}}(t) \quad (11)$$

where $J_{\mathbf{i}, \mathbf{i}+\mathbf{a}}(t)$ is the net flux from site $\mathbf{i}$ to site $\mathbf{i} + \mathbf{a}$. Equation (11) can be written as

$$\frac{\partial \rho_{\mathbf{i}}}{\partial t} = - \sum_{\mathbf{a}} \langle w_{\mathbf{i}, \mathbf{i}+\mathbf{a}}(\{n\}) n_{\mathbf{i}} (1 - n_{\mathbf{i}+\mathbf{a}}) - w_{\mathbf{i}+\mathbf{a}, \mathbf{i}}(\{n\}) n_{\mathbf{i}+\mathbf{a}} (1 - n_{\mathbf{i}}) \rangle_t \quad (12)$$

where $w_{\mathbf{i}, \mathbf{i}+\mathbf{a}}(\{n\})$ is the transition probability for transitions from site $\mathbf{i}$ to site $\mathbf{i} + \mathbf{a}$ for a configuration $\{n\}$. The factors $n_{\mathbf{i}}(1 - n_{\mathbf{i}+\mathbf{a}})$ and $n_{\mathbf{i}+\mathbf{a}}(1 - n_{\mathbf{i}})$ impose the requirement that in a hopping move from site $\mathbf{i}$ to site $\mathbf{j}$, site $\mathbf{i}$ must be occupied and site $\mathbf{j}$ unoccupied, and vice versa.

In a mean field approximation we can express (12) as

$$\frac{\partial \rho_{\mathbf{i}}}{\partial t} = - \sum_{\mathbf{a}} [w_{\mathbf{i}, \mathbf{i}+\mathbf{a}}(\{\rho\}) \rho_{\mathbf{i}} (1 - \rho_{\mathbf{i}+\mathbf{a}}) - w_{\mathbf{i}+\mathbf{a}, \mathbf{i}}(\{\rho\}) \rho_{\mathbf{i}+\mathbf{a}} (1 - \rho_{\mathbf{i}})] \quad (13)$$

Given expressions for the transition probabilities, (13) can be solved to obtain $\{\rho_{\mathbf{i}}\}$ as a function of t . It is equivalent to that given by Matuszak et al. [31]. For Kawasaki

dynamics with Metropolis transition probabilities we can express the transition probabilities in the mean field approximation [31]

$$w_{ij}(\{\rho\}) = w_o \exp(-E_{ij}/kT) \quad (14)$$

where

$$E_{ij} = \begin{cases} 0 & E_j < E_i \\ E_j - E_i & E_j > E_i \end{cases} \quad (15)$$

and

$$E_i = -\epsilon_{ff} \sum_{\mathbf{a}} \rho_{i+\mathbf{a}} + \phi_i \quad (16)$$

w_0 is the jump rate in the absence of interactions and can be used to define the timescale. One way of obtaining a physically relevant value for w_0 is by comparing between estimated and experimental self-diffusion coefficients. The self-diffusion coefficient obtained via a Kawasaki Dynamics Lattice Monte Carlo simulation is normalized i.e. $\hat{D} = D_s/(a^2 w_0)$, where a is the lattice spacing. Fixing the lattice spacing, an estimate of w_0 can be obtained. We plan to explore this in future work. The transition probability stated above, depends only on the site energy difference, with the influence of the solid wall entering through the term ϕ_i . Simple as it may be, this phenomenology captures the essential physics of mass transfer in mesoporous materials.

Our primary interest is in the application to the slit pore geometry shown in Fig. 1. We will be focusing on the relaxation processes when the chemical potential external to the system is changed to some new value, with the system initially in an equilibrium (or metastable) state obtained by solving the static MFT. We achieve this by adding a layer of sites at the end of the system, while maintaining periodic boundary conditions, with the density in this layer of sites fixed at the value associated with the given chemical potential as determined by MFT. We can change the state of the system by changing the properties in this layer of sites. Due to the form of the transition probabilities it is readily shown [37] that after the change in the chemical potential the system will move towards a new state where $\partial \rho_i / \partial t = 0$ for all i and the chemical potential given by (9) will be everywhere uniform at the new specified value. It is also possible to configure a different type of steady state where we remove the periodic boundaries in the x -direction and place a control layer at each end of the system. If the control layers have different chemical potentials then the system can describe steady state mass transfer of fluid through the pore, as has been done by Matuszak et al. [32].

3 Results

The calculations presented here are for a pore of width 6 sites with a wettability of strength $\epsilon_{sf} = 0.75\epsilon_{ff}$. The temperature is fixed at $T^* = kT/\epsilon_{ff} = 0.9$. This represents a fraction of the bulk critical temperature $T_c^* = 1.5$ for a simple cubic lattice gas in mean field comparable to that encountered in a nitrogen adsorption experiment near the normal boiling point, $T = 77$ K. For a planar surface the above

Fig. 2 Isotherms of (a) density and (b) grand free energy for the lattice model of a fluid in a slit pore from static MFT in the grand ensemble. *Full line*—finite length pore in contact with the bulk; *dashed line*—infinite length pore

stated value for wettability, gives rise to partial wetting with a contact angle of about 60° [36].

3.1 Static Behavior

We have calculated the static behavior using MFT in both the grand canonical and canonical ensembles. The grand canonical ensemble results give us the behavior encountered by the DMFT in the long time limit and correspond to the results obtained in adsorption experiments. On the other hand the canonical ensemble results give some insight into the nature of the density distributions encountered during the dynamics.

Figure 2 shows isotherms of the density and grand free energy for the slit pore system we have studied that were obtained in the grand ensemble. The average density at the center of the pore is shown versus the relative activity, λ/λ_0 with the bulk saturation associated with $\lambda/\lambda_0 = 1$. Results for adsorption and desorption are shown for the open slit pore as well as for an infinite pore with no bulk contact, modeled by a pore of finite length with periodic boundaries in the x -direction. We see that there is a hysteresis loop with the adsorption branch continuing beyond bulk saturation. Usually such states are not accessible in experiments because bulk condensation occurs without any metastability. A notable exception is work by Easton and Machin [15] for water in graphitized carbon black where special precautions were taken to delay water condensation in the sample cell. In our system the bulk region is comparable in size to the pore space and bulk condensation is nucleated as soon as the pore is filled with liquid. Presumably this did not happen in the Easton and Machin [15] experiment because of the small size of the porous material sample relative to the bulk region of the sample cell. In studying desorption we switched the bulk over to vapor once the bulk saturation state is reached. Otherwise the desorption would be delayed by the extended metastability of the bulk liquid treated in mean field.

The grand free energy isotherm in Fig. 2 shows a phase transition between vapor and liquid states in the pore. Notice that this transition is close to the desorption step in the isotherm for the open pore system. This is a key feature of desorption

Fig. 3 (Color online) Visualizations of the density distributions for states on adsorption for the finite length pore from the isotherm in Fig. 2. The values of activity λ/λ_0 are (a) 1.1101, (b) 1.1999, (c) 1.2405, (d) 1.2474

Fig. 4 (Color online) Visualizations of the density distributions for states on desorption for the finite length pore from the isotherm in Fig. 2. The values of activity λ/λ_0 are (a) 1.0440, (b) 0.9988, (c) 0.8839, (d) 0.8791

from simple pores that are in contact with the bulk vapor and has been discussed in detail elsewhere [28, 29, 36, 37]. The fact that desorption occurs for λ/λ_0 slightly lower than the equilibrium vapor to liquid transition is related to the formation of the meniscus at the pore ends during desorption for the open pore. For the infinite pore we see no change in the adsorption branch but the desorption branch extends to lower pressure relative to that for the finite length pore, with the desorption step occurring at the stability limit of the pore liquid [28, 29, 36, 37].

The density distributions associated with points on the isotherms in Fig. 2 are shown in Figs. 3 and 4. We see that adsorption proceeds by the formation of relatively low density layers on the pore surfaces followed by filling of the pore in a single sharp step. Desorption occurs first with the appearance of a meniscus at the pore entrance which retreats into the pore until the equilibrium value of λ/λ_0 associated with the vapor-liquid transition is reached when desorption occurs in a single step leaving medium to low density adsorbed layers on the pore walls.

Figure 5 shows the density and grand free energy isotherms obtained from static MFT in the canonical ensemble, with visualizations of the density distributions obtained shown in Fig. 6. For this case we consider the pore of infinite length as described above. The solution space of the MFT in the canonical ensemble is much more complex as was demonstrated by Maier and Stadherr [24]. We have found that for this partial wetting case the complexity is greater than that encountered for a complete wetting case in our earlier work [37] and solutions obtained sensitive to the initialization procedure. For instance, for average densities of about 0.5 we have encountered solutions where the density on one side of the pore is vapor-like and on the other side liquid-like with a vapor-liquid interface in the x -direction, as well as solutions corresponding to a liquid bridge between the two pore walls. This extra

Fig. 5 Isotherms of (a) density and (b) grand free energy (b) for the lattice model of a fluid in a slit pore from static MFT in the canonical ensemble. The results are for the infinite length pore

Fig. 6 (Color online) Visualizations of the density distributions for states on pore filling for the infinite length pore from the isotherm in Fig. 5. The values of density ρ are (a) 0.070, (b) 0.128, (c) 0.162, (d) 0.221, (e) 0.222, (f) 0.775

complexity occurs because for partial wetting situations low density adsorbed layers on the pore walls have comparable stability to high density adsorbed layers.

We present results for two solution sequences chosen because of their interest in relation to the dynamics and generated in the following way. One sequence starts with an empty pore and gradually increases the average density. At each step we initialize the density a high value for pairs of sites in four layers on one side and at the center of the pore, equidistant from the pore ends. This procedure allows us to search for undulate and bridge states, which we have found in previous work [37] feature prominently in the dynamics. The other sequence starts with a filled pore and gradually decreases the density. In this case at each step we set the density to a very low value for a layer of sites at each end of the system. This allows us to search for bubble states on desorption. As noted in our previous work the bubble and bridge states are indistinguishable due to the periodic boundaries in the x -direction.

The behavior we see here is somewhat different to that described in our work for a complete wetting situation [37]. In that case pore filling proceeded via the formation of undulates on both walls followed by the formation of a liquid bridge (this terminology follows that used by Everett and Haynes [18]). Instead we found that pore filling occurred via the formation of a droplet on one wall followed by bridge formation as see in Fig. 6—we will see something like this in the dynamics as well. The distinction we make between undulate and droplet is that an undulate is associated with complete wetting (zero contact angle) while droplet is associated with partial wetting (finite

Fig. 7 (Color online) Visualizations of the density distributions for states on pore emptying for the infinite length pore from the isotherm in Fig. 5. The values of density ρ are (a) 0.959, (b) 0.840, (c) 0.660, (d) 0.460, (e) 0.129, (f) 0.128

contact angle). We did not find solutions with droplets on both walls even with a variety of different initialization procedures. The non zero vapor-liquid-solid contact angle is evident in the droplet and bridge states. Pore emptying proceeds via the appearance of a bubble in the system and the progressive narrowing of the liquid bridge which eventually becomes unstable (see Fig. 7). No droplet state is seen on pore emptying, which parallels the behavior seen for the complete wetting system where no undulate state was encountered in the pore emptying sequence. The density isotherm is similar to that seen in Fig. 2 for the high and low density branches. For intermediate densities the differences reflect the states which are accessible in the canonical ensemble. There are a set of states where the isotherms follow a step-like progression within a narrow range of activities around the value associated with vapor-liquid coexistence in the pore. These are the states associated with the growth/contraction of the liquid bridge. The fact that the liquid bridge grows/contracts in steps is a combined effect of the lattice model and the mean field approximation.

3.2 Dynamics of Pore Filling

To integrate (13) we have used Euler's method. We use $w_0 t$ as a dimensionless time for the calculation and we have used a time step $w_0 \Delta t = 0.001$ but substantially larger step sizes can be used as was shown for a complete wetting case [37]. We have studied the dynamics of pore filling for two pore lengths, $L = 20$ sites and $L = 40$ sites. We have focused our attention on small quenches in chemical potential or activity that take the system from one side of the pore filling transition in Fig. 2 to the other. There is a very slight dependence of the location of the pore filling step upon pore length so the initial and final activities are slightly different for the two pore lengths.

Figure 8 shows results for the density versus dimensionless time for the $L = 20$ case. There are two curves in the figure. One shows the average density throughout the pore while the other shows the density at the center of the pore. Differences between these two curves reflect the evolution of the density distribution in the system. The strongly varying part of the pore averaged density shows two regimes, one associated with the droplet formation and growth, and the other associated with the liquid bridge formation and growth, as can be seen by matching the density distributions visualized in Fig. 9 with points on the isotherm in Fig. 8. The visualizations reveal that the density distribution is initially symmetric about the center of the pore but as time

Fig. 8 Density versus time for $L = 20$ during a quench from $\lambda/\lambda_0 = 1.2475$ for $\lambda/\lambda_0 = 1.2490$. *Full line*—average density throughout the pore; *dashed line*—average density in a plane equidistant from the pore ends

Fig. 9 (Color online) Visualizations of the density distribution during pore filling for $L = 20$ during a quench from $\lambda/\lambda_0 = 1.2475$ for $\lambda/\lambda_0 = 1.2490$. The values of time w_0t are (a) 400, (b) 10800, (c) 11200, (d) 12400, (e) 12800, (f) 15200, (g) 16000, (h) 18000, (i) 18400, (j) 19600, (k) 22400, (l) 24400

progresses the density builds up on one wall. This symmetry breaking is quite striking and we believe that it is a consequence of the partial wetting nature of the solid fluid interaction in this case, where as mentioned earlier, low density adsorbed layers on the pore walls have comparable stability to high density adsorbed layers. Once a droplet forms on one wall it grows and spreads towards the ends of the pore. After this a quite sharp transition occurs where a liquid bridge forms in the system. The density distribution now regains symmetry, and pore filling is completed by the growth of the liquid bridge. Notice that there is some resemblance between the density distributions encountered in the dynamics in Fig. 9 and those seen in our canonical MFT calculations in Fig. 6, especially between the short time states in Fig. 9 and the low density states in Fig. 6.

The uptake curve for the center of the pore indicates that there are stepwise changes in the local density and these appear to be associated with changes in the morphology of the droplet. The large step is associated with the transition from the

Fig. 10 Density versus time for $L = 40$ during a quench from $\lambda/\lambda_0 = 1.2455$ to $\lambda/\lambda_0 = 1.2470$. *Full line*—average density throughout the pore; *dashed line*—average density in a plane equidistant from the pore ends

droplet to bridge morphology. Notice from Fig. 9 that once the pore is filled with liquid the liquid-vapor interface moves out into the bulk region. What is happening here is that since we are in a metastable state of the bulk vapor, the pore liquid is nucleating condensation of the bulk liquid as we discussed in relation to the MFT results in the grand ensemble in Sect. 3.1. This is a consequence of the pore and bulk regions being comparable in size in our system geometry.

The behavior observed for $L = 40$ is substantially different. First of all the timescale for pore filling is longer than for $L = 20$ but that is simply a consequence of the pore length. On the other hand, the uptake curve for the pore center indicates a more complex process. For short times the behavior is similar to the $L = 20$ case with the formation of a droplet that then spreads along the length of the pore. However, instead of a single bridge we see two bridges form with a large transfer of fluid from the center of the pore as is seen in the uptake curve for the center of the pore in Fig. 10. In our study of a complete wetting case we did see two bridges form for pore filling when there was a large quench in the chemical potential, but not for the small quench we are using here. In that case it was felt that the formation of the two bridges was consequence of the large flux of fluid into the pore but that is not what is happening here. Another interesting feature here is that after the double bridge formation the pore filling is not complete until there has been significant condensation in the bulk region. If we use a larger bulk region this does not happen.

4 Summary and Conclusions

We have given a brief review of the dynamic mean field theory for lattice models of fluids in pores and have described an application to the dynamics of pore filling in a slit pore where there is partial wetting of the pore walls. This situation is relevant to systems such as water in graphitized carbon black or carbon nanotubes. In our previous work we had considered complete wetting cases. For partial wetting the adsorption branch of the isotherm extends beyond the bulk-vapor liquid transition even though the equilibrium transition lies below this transition. In experiments studying adsorption from supersaturated states requires that special steps be taken to prevent condensation of the bulk liquid. In our system geometry the bulk region is actually comparable in size to the pore so that bulk condensation is nucleated by the pore being filled with liquid.

Fig. 11 (Color online)

Visualizations of the density distribution during pore filling for $L = 40$ during a quench from $\lambda/\lambda_0 = 1.2455$ to $\lambda/\lambda_0 = 1.2470$. The values of time $w_0 t$ are (a) 25900, (b) 28000, (c) 30800, (d) 31500, (e) 42000, (f) 44100, (g) 44800, (h) 45500, (i) 47600, (j) 53200, (k) 56700, (l) 58800

The most striking feature of the results is the asymmetry of the density distributions that appear during the dynamics. In particular we note the formation of droplet on one of the walls. While we do not fully understand why this symmetry breaking occurs it is related to the special nature of the solid-fluid interface when there is partial wetting. With partial wetting both low density vapor-like states and dense liquid-like states can be stable near the pore wall. This makes it possible to have asymmetric density distributions, with low density states on one pore wall and high density states on the other. Such states do not appear in the static MFT in the grand ensemble but are readily found in the canonical ensemble MFT. Moreover such asymmetry has also been observed in the literature [34, 45, 46].

Together with our previous applications of the dynamic mean field theory the present work shows the utility of the approach in helping us to understand the nature of the processes involved during phase transitions of confined fluids. The method is not limited to the simple pore geometry considered here and we anticipate significant insights emerging from applications to more complex pore geometries such as models of Vycor glass [48, 49].

Acknowledgement This work was supported by the National Science Foundation (Grant No. CBET-0649552).

References

1. G. Aranovich, M. Donohue, Analysis of adsorption isotherms: Lattice theory predictions, classification of isotherms for gas-solid equilibria, and similarities in gas and liquid adsorption behavior. *J. Colloid Interface Sci.* **200**(2), 273–290 (1998)
2. A.J. Archer, Dynamical density functional theory: phase separation in a cavity and the influence of symmetry. *J. Phys., Condens. Matter* **17**(45), S3253–S3258 (2005)
3. A.J. Archer, Dynamical density functional theory for dense atomic liquids. *J. Phys., Condens. Matter* **18**(24), 5617–5628 (2006)
4. A.J. Archer, R. Evans, Dynamical density functional theory and its application to spinodal decomposition. *J. Chem. Phys.* **121**(9), 4246–4254 (2004)

5. A.J. Archer, M. Rauscher, Dynamical density functional theory for interacting Brownian particles: stochastic or deterministic? *J. Phys. A, Math. Gen.* **37**(40), 9325–9333 (2004)
6. P.C. Ball, R. Evans, On the mechanism for hysteresis of gas-adsorption on mesoporous substrates. *Europhys. Lett.* **4**(6), 715–721 (1987)
7. P.C. Ball, R. Evans, Temperature-dependence of gas-adsorption on a mesoporous solid—capillary criticality and hysteresis. *Langmuir* **5**(3), 714–723 (1989)
8. E. Bruno, U.B.M. Marconi, R. Evans, Phase-transitions in a confined lattice gas—prewetting and capillary condensation. *Physica A* **141**(1), 187–210 (1987)
9. J.W. Cahn, Free energy of a nonuniform system. 2. Thermodynamic basis. *J. Chem. Phys.* **30**(5), 1121–1124 (1959)
10. J.W. Cahn, Phase separation by spinodal decomposition in isotropic systems. *J. Chem. Phys.* **42**(1), 93 (1965)
11. J.W. Cahn, J.E. Hilliard, Free energy of a nonuniform system. 1. Interfacial free energy. *J. Chem. Phys.* **28**(2), 258–267 (1958)
12. J.W. Cahn, J.E. Hilliard, Free energy of a nonuniform system. 3. Nucleation in a 2-component incompressible fluid. *J. Chem. Phys.* **31**(3), 688–699 (1959)
13. A. Chakrabarti, Kinetics of domain growth and wetting in a model porous-medium. *Phys. Rev. Lett.* **69**, 1548–1551 (1992)
14. M.J. DeOliveira, R.B. Griffiths, Lattice-gas model of multiple layer adsorption. *Surf. Sci.* **71**(3), 687–694 (1978)
15. E.B. Easton, W.D. Machin, Adsorption of water vapor on a graphitized carbon black. *J. Colloid Interface Sci.* **231**(1), 204–206 (2000)
16. C. Ebner, Evidence for the roughening and wetting transitions in the lattice-gas model of adsorption from Monte-Carlo simulations. *Phys. Rev. A* **23**(4), 1925–1930 (1981)
17. R. Evans, Fluids adsorbed in narrow pores—phase-equilibria and structure. *J. Phys., Condens. Matter* **2**(46), 8989–9007 (1990)
18. D.H. Everett, J.M. Haynes, Model studies of capillary condensation. 1. Cylindrical pore model with zero contact angle. *J. Colloid Interface Sci.* **38**(1), 125–137 (1972)
19. J. Fraaije, Dynamic density-functional theory for microphase separation kinetics of block-copolymer melts. *J. Chem. Phys.* **99**(11), 9202–9212 (1993)
20. L.D. Gelb, K.E. Gubbins, R. Radhakrishnan, M. Sliwinski-Bartkowiak, Phase separation in confined systems. *Rep. Prog. Phys.* **62**(12), 1573–1659 (1999)
21. J.F. Gouyet, M. Plapp, W. Dieterich, P. Maass, Description of far-from-equilibrium processes by mean-field lattice gas models. *Adv. Phys.* **52**(6), 523–638 (2003)
22. E. Kierlik, P.A. Monson, M.L. Rosinberg, L. Sarkisov, G. Tarjus, Capillary condensation in disordered porous materials: Hysteresis versus equilibrium behavior. *Phys. Rev. Lett.* **87**(5), 055701 (2001)
23. A. Luzar, K. Leung, Dynamics of capillary evaporation. I. Effect of morphology of hydrophobic surfaces. *J. Chem. Phys.* **113**(14), 5836–5844 (2000)
24. R.W. Maier, M.A. Stadtherr, Reliable density-functional-theory calculations of adsorption in nanoscale pores. *AIChE J.* **47**(8), 1874–1884 (2001)
25. U.M.B. Marconi, P. Tarazona, Dynamic density functional theory of fluids. *J. Chem. Phys.* **110**(16), 8032–8044 (1999)
26. U.M.B. Marconi, P. Tarazona, Dynamic density functional theory of fluids. *J. Phys., Condens. Matter* **12**(8A), A413–A418 (2000)
27. U.M.B. Marconi, P. Tarazona, Nonequilibrium inertial dynamics of colloidal systems. *J. Chem. Phys.* **124**(16), 164901 (2006)
28. U.M.B. Marconi, F. van Swol, Microscopic model for hysteresis and phase-equilibria of fluids confined between parallel plates. *Phys. Rev. A* **39**(8), 4109–4116 (1989)
29. U.M.B. Marconi, F. van Swol, A model of hysteresis in narrow pores. *Europhys. Lett.* **8**(6), 531–535 (1989)
30. G. Martin, Atomic mobility in Cahn diffusion-model. *Phys. Rev. B* **41**(4), 2279–2283 (1990)
31. D. Matuszak, G.L. Aranovich, M.D. Donohue, Lattice density functional theory of molecular diffusion. *J. Chem. Phys.* **121**(1), 426–435 (2004)
32. D. Matuszak, G.L. Aranovich, M.D. Donohue, Modeling fluid diffusion using the lattice density functional theory approach: counterdiffusion in an external field. *Phys. Chem. Chem. Phys.* **8**(14), 1663–1674 (2006)
33. D. Matuszak, G.L. Aranovich, M.D. Donohue, Single-component permeation maximum with respect to temperature: A lattice density functional theory study. *Ind. Eng. Chem. Res.* **45**(16), 5501–5511 (2006)

34. R. Mayol, F. Ancilotto, M. Barranco, E.S. Hernandez, M. Pi, Novel aspects of wedge filling by liquid helium. *J. Low Temp. Phys.* **148**(5–6), 851–855 (2007)
35. L. Monette, A.J. Liu, G.S. Grest, Wetting and domain-growth kinetics in confined geometries. *Phys. Rev. A* **46**(12), 7664–7679 (1992)
36. P.A. Monson, Contact angles, pore condensation and hysteresis: Insights from a simple molecular model. *Langmuir* **24**, 12295–12302 (2008)
37. P.A. Monson, Mean field kinetic theory for a lattice gas model of fluids confined in porous materials. *J. Chem. Phys.* **128**, 084701 (2008)
38. P.A. Monson, Dynamic mean field theory for fluids confined in porous materials: Application to an ink bottle pore geometry, in *Characterization of Porous Solids VIII*, ed. by S. Kaskel, P. Llewellyn, F. Rodriguez-Reinoso, N. Seaton (Royal Society of Chemistry Press, Cambridge, 2009), pp. 103–110
39. T. Munakata, A dynamical extension of the density functional theory. *J. Phys. Soc. Jpn.* **58**(7), 2434–2438 (1989)
40. H. Nakanishi, M.E. Fisher, Critical-point shifts in films. *J. Chem. Phys.* **78**(6), 3279–3293 (1983)
41. D. Nicolaides, R. Evans, Monte-Carlo study of phase-transitions in a confined lattice gas. *Phys. Rev. B* **39**(13), 9336–9342 (1989)
42. R. Pandit, M. Schick, M. Wortis, Systematics of multilayer adsorption phenomena on attractive substrates. *Phys. Rev. B* **26**(9), 5112–5140 (1982)
43. O. Penrose, A mean-field equation of motion for the dynamic Ising-model. *J. Stat. Phys.* **63**(5–6), 975–986 (1991)
44. F. Porcheron, P.A. Monson, Dynamic aspects of mercury porosimetry: A lattice model study. *Langmuir* **21**(7), 3179–3186 (2005)
45. A. Saugey, L. Bocquet, J.L. Barrat, Nucleation in hydrophobic cylindrical pores: A lattice model. *J. Phys. Chem. B* **109**(14), 6520–6526 (2005)
46. V. Talanquer, D.W. Oxtoby, Nucleation in a slit pore. *J. Chem. Phys.* **114**(6), 2793–2801 (2001)
47. R. Valiullin, S. Naumov, P. Galvosas, J. Karger, H.J. Woo, F. Porcheron, P.A. Monson, Exploration of molecular dynamics during transient sorption of fluids in mesoporous materials. *Nature* **443**, 965–968 (2006)
48. H.J. Woo, P.A. Monson, Phase behavior and dynamics of fluids in mesoporous glasses. *Phys. Rev. E* **67**(4), 041207 (2003)
49. H.J. Woo, L. Sarkisov, P.A. Monson, Mean-field theory of fluid adsorption in a porous glass. *Langmuir* **17**(24), 7472–7475 (2001)
50. H.J. Woo, L. Sarkisov, P.A. Monson, Understanding adsorption hysteresis in porous glasses and other mesoporous materials, in *Characterization of Porous Solids VI*, vol. 144 (2002), pp. 155–162
51. H.J. Woo, F. Porcheron, P.A. Monson, Modeling desorption of fluids from disordered mesoporous materials. *Langmuir* **20**(11), 4743–4747 (2004)
52. A. Yoshimori, Time dependent density functional methods and their application to chemical physics. *J. Theor. Comput. Chem.* **3**(1), 117–143 (2004)