University of Massachusetts Amherst

From the Selected Works of Peter A. Monson

January, 2008

Mean field kinetic theory for a lattice gas model of fluids confined in porous materials

Peter A Monson, *University of Massachusetts - Amherst*

Available at: https://works.bepress.com/peter_monson/5/

Mean field kinetic theory for a lattice gas model of fluids confined in porous materials

Peter A. Monson

Citation: *J. Chem. Phys.* **128**, 084701 (2008); doi: 10.1063/1.2837287

View online: <http://dx.doi.org/10.1063/1.2837287>

View Table of Contents: <http://jcp.aip.org/resource/1/JCPSA6/v128/i8>

Published by the [American Institute of Physics](#).

Additional information on J. Chem. Phys.

Journal Homepage: <http://jcp.aip.org/>

Journal Information: http://jcp.aip.org/about/about_the_journal

Top downloads: http://jcp.aip.org/features/most_downloaded

Information for Authors: <http://jcp.aip.org/authors>

ADVERTISEMENT

AFM-RAMAN **BRUKER**

LEADING PERFORMANCE
WIDEST PRODUCT RANGE

www.bruker-axs.com

[CLICK TO REQUEST INFO](#)

Mean field kinetic theory for a lattice gas model of fluids confined in porous materials

Peter A. Monson^{a)}

Department of Chemical Engineering, University of Massachusetts, Amherst, Massachusetts 01003, USA

(Received 27 September 2007; accepted 3 January 2008; published online 25 February 2008; publisher error corrected 26 February 2008)

We consider the mean field kinetic equations describing the relaxation dynamics of a lattice model of a fluid confined in a porous material. The dynamical theory embodied in these equations can be viewed as a mean field approximation to a Kawasaki dynamics Monte Carlo simulation of the system, as a theory of diffusion, or as a dynamical density functional theory. The solutions of the kinetic equations for long times coincide with the solutions of the static mean field equations for the inhomogeneous lattice gas. The approach is applied to a lattice gas model of a fluid confined in a finite length slit pore open at both ends and is in contact with the bulk fluid at a temperature where capillary condensation and hysteresis occur. The states emerging dynamically during irreversible changes in the chemical potential are compared with those obtained from the static mean field equations for states associated with a quasistatic progression up and down the adsorption/desorption isotherm. In the capillary transition region, the dynamics involves the appearance of undulates (adsorption) and liquid bridges (adsorption and desorption) which are unstable in the static mean field theory in the grand ensemble for the open pore but which are stable in the static mean field theory in the canonical ensemble for an infinite pore. © 2008 American Institute of Physics.

[DOI: [10.1063/1.2837287](https://doi.org/10.1063/1.2837287)]

I. INTRODUCTION

For some time there has been significant interest in using lattice models to describe confined fluids.^{1–14} This is because the simplicity of the models makes them computationally efficient for studying the thermodynamics of inhomogeneous systems, whether through Monte Carlo simulations or theories. Applications range from the study of wetting transitions^{2,6} to the effect of confinement on phase transitions for simple^{5,7,8} and complex pore structures.^{13–15} Confined lattice gas models studied in mean field theory (MFT) have been especially effective in elucidating the nature of adsorption/desorption hysteresis for fluids confined in porous materials with complex interconnected void spaces, such as porous glasses.^{13–15}

It has also been possible to study the dynamical behavior for such models through the use of dynamic Monte Carlo simulations with Kawasaki dynamics, which models dynamics generated by nearest neighbor hopping processes. Examples include phase separation dynamics for confined liquid mixtures,^{10,11} the kinetics of nonwetting liquids in pores,^{16,17} and the relaxation dynamics during gas adsorption in porous glasses.^{15,18} These approaches are an efficient alternative to very time consuming nonequilibrium molecular dynamics calculations.^{19,20} However, even with the lattice model simplifications, Kawasaki dynamics simulations can be computationally intensive, especially if one wants to consider many trajectories of the dynamics to determine an ensemble average. Thus, it is worthwhile to investigate theoret-

ical approximations that might lead to more computational efficiency while at least offering a qualitatively accurate description of the dynamics.

A recent and comprehensive review by Gouyet *et al.*²¹ describes a mean field approach to Kawasaki dynamics, referred to as mean field kinetic theory (MFKT), with an emphasis on the phase separation in solid state metal alloys. The approach originates from the works of Martin²² and Penrose.²³ The treatment begins by expressing the flux at any site in terms of probabilities for hopping transitions between that site and the neighboring sites. These transition probabilities are determined within a mean field approximation. Conservation of mass leads to a differential equation for the density at each site, which has the form of a generalized diffusion equation similar to that emerging in the Cahn–Hilliard type theories^{24–26} and related dynamic density functional theories (DDFT's).^{27–31} As emphasized by Gouyet *et al.*, however, MFKT incorporates the dependence of the mobility on the local density.²¹ For long times, the theory yields thermodynamic behavior identical to that of the lattice model in mean field theory (e.g., the Bragg–Williams approximation for the case of a binary alloy). The theory provides an approximation to the dynamics obtained by averaging over an ensemble of trajectories generated by Kawasaki dynamics.

In this paper, we describe the application of the MFKT to a lattice gas model of a fluid being adsorbed/desorbed from a porous material, with an emphasis on the dynamics associated with capillary condensation and accompanying hysteresis. For this purpose, we adapt the analysis presented by Gouyet *et al.*²¹ to the case of a fluid confined in a pore, but it is important to note that the equations we derive are

^{a)}Electronic mail: monson@ecs.umass.edu.

equivalent to those presented recently by Aranovich and co-workers³²⁻³⁴ in their work on diffusion in porous materials. The dynamical theory embodied in these equations can be viewed as a mean field approximation to a dynamic Monte Carlo simulation of the system, as a theory of diffusion, or as a DDFT. To illustrate the approach, we have considered the case of a lattice gas model of a fluid confined in an open slit pore in contact with the bulk fluid through the pore openings. To begin with, we compute the density distributions, adsorption/desorption isotherms, and phase transitions for this system using static MFT. We then consider the evolution of the density distribution during relaxation processes as calculated from MFKT for finite changes in the chemical potential. We consider large scale quenches, which take the system from dilute gas to dense liquidlike states and vice versa, as well as small scale quenches between closely spaced states bounding an adsorption or desorption transition. The calculations demonstrate the utility of this approach in understanding the relaxation processes of fluids confined in porous materials.

The remainder of our paper is organized as follows. In the next section, we present the lattice gas model and its treatment in static MFT and in MFKT. Next, in Sec. III, we consider the application to the slit pore model. Finally, in Sec. IV, we give a summary of our results and conclusions.

II. THEORY

A. Lattice gas Hamiltonian and thermodynamics in mean field

We consider a nearest neighbor lattice gas in an external field with a configurational energy given by^{1,2,13,15}

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

where ϵ is the nearest neighbor interaction strength, $n_{\mathbf{i}}$ is the occupancy (0 or 1) at site $\mathbf{i}$, $\phi_{\mathbf{i}}$ is the external field at site $\mathbf{i}$, with $\mathbf{i}$ denoting a set of lattice coordinates, and $\mathbf{a}$ denotes the vector to a nearest neighbor site for any site on the lattice.²¹ In the mean field approximation, the Helmholtz energy for this system is given by

$$F = kT \sum_{\mathbf{i}} [\rho_{\mathbf{i}} \ln \rho_{\mathbf{i}} + (1 - \rho_{\mathbf{i}}) \ln(1 - \rho_{\mathbf{i}})] - \frac{\epsilon}{2} \sum_{\mathbf{i}} \sum_{\mathbf{a}} \rho_{\mathbf{i}} \rho_{\mathbf{i}+\mathbf{a}} + \sum_{\mathbf{i}} \rho_{\mathbf{i}} \phi_{\mathbf{i}}, \quad (2)$$

where $\rho_{\mathbf{i}}$ is the mean density at site $\mathbf{i}$. The density distribution at equilibrium, subject to the constraint of fixed overall density ($\sum_{\mathbf{i}} \rho_{\mathbf{i}} = N$, where N is the total number of molecules), is determined from

$$\frac{\partial F}{\partial \rho_{\mathbf{i}}} - \mu = 0 \quad \forall \mathbf{i}, \quad (3)$$

where μ is the chemical potential, emerging as a Lagrange multiplier for the constraint of fixed overall density. Using Eq. (3) with Eq. (2), we obtain

$$kT \ln \left[\frac{\rho_{\mathbf{i}}}{1 - \rho_{\mathbf{i}}} \right] - \epsilon \sum_{\mathbf{a}} \rho_{\mathbf{i}+\mathbf{a}} + \phi_{\mathbf{i}} - \mu = 0 \quad \forall \mathbf{i}. \quad (4)$$

This set of equations together with the constraint equation can be expressed as

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

and

$$\sum_{\mathbf{i}} \frac{\lambda c_{\mathbf{i}}}{1 + \lambda c_{\mathbf{i}}} - N = 0, \quad (6)$$

where $\lambda = \exp(\mu/kT)$ is the activity and $c_{\mathbf{i}} = \exp[-(\phi_{\mathbf{i}} - \epsilon \sum_{\mathbf{a}} \rho_{\mathbf{i}+\mathbf{a}})/kT]$. Equations (5) and (6) are solved simultaneously to yield the equilibrium density distribution and the chemical potential. The solutions give the behavior of the system in the canonical ensemble (fixed N, V, T). The mean field theory may also be solved in the grand ensemble (fixed μ, V, T) by solving Eq. (5) without the constant density constraint, Eq. (6).

Notice that Eq. (4) gives us an expression for the chemical potential at site $\mathbf{i}$

$$\mu_{\mathbf{i}} = kT \ln \left[\frac{\rho_{\mathbf{i}}}{1 - \rho_{\mathbf{i}}} \right] - \epsilon \sum_{\mathbf{a}} \rho_{\mathbf{i}+\mathbf{a}} + \phi_{\mathbf{i}}. \quad (7)$$

Solutions of the static MFT equations must lead to the $\mu_{\mathbf{i}}$ being uniform throughout the system. In the treatment of the dynamics, we will use this expression to establish the behavior of the system in the long time (steady state) limit.

B. Mean field kinetic equations

Our presentation of MFKT follows closely that of Gouyet *et al.*²¹ We begin by writing the ensemble average density for site $\mathbf{i}$ at time t $\rho_{\mathbf{i}}(t)$ as

$$\rho_{\mathbf{i}}(t) = \langle n_{\mathbf{i}} \rangle_t = \sum_{\{n\}} n_{\mathbf{i}} P(\{n\}, t), \quad (8)$$

where $n_{\mathbf{i}}$ is an occupation number and $P(\{n\}, t)$ is the probability of observing a given occupancy configuration $\{n\}$ at time t . The evolution equation for the local density can be written as

$$\frac{\partial \rho_{\mathbf{i}}}{\partial t} = - \sum_{\mathbf{j}} J_{\mathbf{ij}}(t), \quad (9)$$

where the summation is taken over all (nearest) neighbor sites and the transport is restricted to hopping between the nearest neighbor sites. $J_{\mathbf{ij}}(t)$ is the net flux from site $\mathbf{i}$ to site $\mathbf{j}$, and is given by

$$J_{\mathbf{ij}}(t) = \langle J_{\mathbf{ij}}(\{n\}) \rangle_t = \langle w_{\mathbf{ij}}(\{n\}) n_{\mathbf{i}} (1 - n_{\mathbf{j}}) - w_{\mathbf{ji}}(\{n\}) n_{\mathbf{j}} (1 - n_{\mathbf{i}}) \rangle_t, \quad (10)$$

where $w_{\mathbf{ij}}(\{n\})$ is the transition probability for transitions from site $\mathbf{i}$ to site $\mathbf{j}$ for a configuration $\{n\}$.

In a mean field approximation, we can express Eq. (10) as

$$J_{ij}(t) = w_{ij}\rho_i(1 - \rho_j) - w_{ji}\rho_j(1 - \rho_i). \quad (11)$$

We can then write Eq. (9) in the form

$$\frac{\partial \rho_i}{\partial t} = - \sum_a [w_{i,i+a}\rho_i(1 - \rho_{i+a}) - w_{i+a,i}\rho_{i+a}(1 - \rho_i)]. \quad (12)$$

We will consider Kawasaki dynamics with Metropolis transition probabilities so that in the mean field approximation³³

$$w_{ij} = w_0 \exp(-E_{ij}/kT), \quad (13)$$

where

$$E_{ij} = \begin{cases} 0 & E_j < E_i \\ E_j - E_i, & E_j > E_i \end{cases} \quad (14)$$

and

$$E_i = -\epsilon \sum_a \rho_{i+a} + \phi_i \quad (15)$$

w_0 is the jump rate in the absence of interactions and sets the time scale. Equation (12) can be solved to obtain $\{\rho_i\}$ as a function of t . It is equivalent to that given by Matuszak *et al.*³³

C. The approach to steady state

The steady state ($\partial \rho_i / \partial t = 0$) solution of Eq. (12) is generated when

$$\frac{w_{ji}}{w_{ij}} = \frac{\rho_i(1 - \rho_j)}{\rho_j(1 - \rho_i)}. \quad (16)$$

Using the Eqs. (7) and (13), we can write

$$\frac{w_{ji}}{w_{ij}} = \exp[(E_j - E_i)/kT], \quad (17)$$

$$= \exp[(\mu_j - \mu_i)/kT] \frac{\rho_i(1 - \rho_j)}{\rho_j(1 - \rho_i)}, \quad (18)$$

so that Eq. (11) can be written as

$$J_{ij}(t) = w_{ij}\rho_i(1 - \rho_j)[1 - \exp[(\mu_j - \mu_i)/kT]] \quad (19)$$

or

$$J_{ij}(t) = w_{ij}\rho_i(1 - \rho_j)[1 - \lambda_j/\lambda_i]. \quad (20)$$

From this, we see that the steady state condition coincides with uniformity of the mean field chemical potential defined by Eq. (7), i.e., the static mean field density distribution is a steady state solution of Eq. (19) encountered in the long time limit. We also note that close to equilibrium, Eq. (19) can be written as

$$J_{ij}(t) = -\frac{1}{kT} w_{ij}\rho_i(1 - \rho_j)[\mu_j - \mu_i], \quad (21)$$

where the flux is in the form of a mobility multiplying a chemical potential gradient.

Following Martin,²² we can use Polkowicz's identity

$$A - B = \sqrt{AB}(\sqrt{A/B} - \sqrt{B/A}) \quad (22)$$

to rewrite Eq. (11) as

$$J_{ij}(t) = \sqrt{w_{ij}\rho_i(1 - \rho_j)w_{ji}\rho_j(1 - \rho_i)} \left(\sqrt{\frac{w_{ij}\rho_i(1 - \rho_j)}{w_{ji}\rho_j(1 - \rho_i)}} - \sqrt{\frac{w_{ji}\rho_j(1 - \rho_i)}{w_{ij}\rho_i(1 - \rho_j)}} \right), \quad (23)$$

$$= \sqrt{w_{ij}\rho_i(1 - \rho_j)w_{ji}\rho_j(1 - \rho_i)} \{ \exp[(\mu_i - \mu_j)/2kT] - \exp[(\mu_j - \mu_i)/2kT] \}. \quad (24)$$

Close to equilibrium, this expression becomes

$$J_{ij}(t) = -\frac{1}{kT} \sqrt{w_{ij}\rho_i(1 - \rho_j)w_{ji}\rho_j(1 - \rho_i)} (\mu_j - \mu_i). \quad (25)$$

Using Eq. (16), it can be seen that Eqs. (25) and (21) are identical.

It is perhaps useful to clarify our use of the terms static, steady state, and equilibrium. We use the term static to describe the nondynamical version of the MFT presented in Sec. II A. Using the term static rather than equilibrium allows us to take account of the fact that in the neighborhood of phase transitions, the static mean field equations will typically have multiple solutions, associated with stable (equilibrium), metastable, and unstable states of the system. Stable states are those that yield the global minimum Helmholtz energy (constant density) or global minimum grand potential (constant chemical potential). Metastable states are associated with local free energy or grand potential minima. Both stable and metastable states are of interest in modeling fluids in porous materials. Metastable states can be realized experimentally when adsorption/desorption hysteresis is encountered. By steady state we mean the condition of the system when $\partial \rho_i / \partial t = 0$. In the MFKT, the system can encounter either thermodynamically stable or metastable states in the long time (steady state) limit.

D. Relationship with Cahn–Hilliard and dynamic density functional theories

We begin by expressing the flux in the form of a mobility multiplying the gradient of the chemical potential via²²

$$\mathbf{J} = -\mathbf{M} \nabla \mu. \quad (26)$$

The discrete version of this is

$$J_{ij} = -M_{ij}(\mu_j - \mu_i). \quad (27)$$

We can easily achieve this form by writing

$$M_{ij} = -\frac{J_{ij}}{(\mu_j - \mu_i)}. \quad (28)$$

We note that Eq. (24) shows that M_{ij} is symmetric with respect to interchange of i and j . This mobility is a local function but it is associated with a pair of sites rather than a single site. We could similarly write the flux in the form of Fick's first law via

$$J_{ij} = -D_{ij}(\rho_j - \rho_i), \quad (29)$$

where

$$D_{ij} = -\frac{J_{ij}}{(\rho_j - \rho_i)}. \quad (30)$$

Again, the local diffusivity is symmetric and is associated with a pair of sites.

We can now rewrite Eq. (12) as

$$\frac{\partial \rho_i}{\partial t} = \sum_a M_{i,i+a}(\mu_{i+a} - \mu_i). \quad (31)$$

For a lattice with a center of symmetry for each term $M_{i,i+a}(\mu_{i+a} - \mu_i)$ in the sum, there is a corresponding term for $-a$ given by $M_{i,i-a}(\mu_{i-a} - \mu_i)$. Equation (31) can then be written as

$$\frac{\partial \rho_i}{\partial t} = \frac{1}{2} \sum_a M_{i,i+a}(\mu_{i+a} - \mu_i) + M_{i,i-a}(\mu_{i-a} - \mu_i). \quad (32)$$

Using forward and backward difference operators, $\mathcal{D}_a$ and $\mathcal{D}_{-a}$, defined by $\mathcal{D}_a f_i = f_{i+a} - f_i$ and $\mathcal{D}_{-a} f_i = f_i - f_{i-a}$, respectively, this equation can be expressed as

$$\frac{\partial \rho_i}{\partial t} = \frac{1}{2} \sum_a \mathcal{D}_{-a} M_{i,i+a} \mathcal{D}_a \mu_i = \frac{1}{2} \sum_a \mathcal{D}_{-a} M_{i,i+a} \mathcal{D}_a \left(\frac{\partial F}{\partial \rho_i} \right). \quad (33)$$

Equation (33) has the appearance of a finite difference version of the typical Cahn-Hilliard type or DDFT expression

$$\frac{\partial \rho(\mathbf{r})}{\partial t} = \nabla \cdot \left(M \nabla \frac{\delta F}{\delta \rho(\mathbf{r})} \right). \quad (34)$$

A significant difference is that this lattice based theory yields an explicit expression for the mobility in terms of the local densities²¹ based on the dynamics used to describe the flux between sites—Metropolis transition probabilities in this case.

The question of whether to incorporate stochastic noise into DDFT's as a means of modeling fluctuations has been discussed in the literature.^{31,35} The present theory, as formulated²¹ and implemented here, gives a deterministic dynamics for the evolution of ensemble average density distribution in the system. In principle, one can incorporate a stochastic noise term into the present approach and the results would then have more of the character of individual Kawasaki dynamics trajectories. Of course, this would be at the cost of losing the ensemble average information that emerges from the original deterministic equation.

III. APPLICATION TO ADSORPTION AND DESORPTION IN A SLIT PORE

We consider a simple cubic lattice gas confined in a slit pore open at both ends in the x direction, infinite in the y direction, and in contact with a bulk lattice gas. The geometry is illustrated in Fig. 1. The density is independent of the y direction in this system and this can be included in both the static and dynamic calculations to render the problem two dimensional. The total length of the bulk region was set at 20 lattice constants, more than sufficient to achieve bulk lattice gas behavior away from the pore ends. Periodic boundary conditions are applied in the x direction and in the z direction

FIG. 1. Schematic representation of the open slit pore geometry considered in this work.

(except between the pore walls). We first discuss the results for this system from the static mean field theory and then we consider the dynamics. For the static mean field theory, we also have considered the slit pore of infinite length without contact with the bulk, where the density only varies in the z direction. We achieve this by placing a pore of a given finite length directly in periodic boundaries in the x direction without the intervening bulk region. All the illustrative calculations here are for nearest neighbor walls with $\epsilon_{sf}/\epsilon_{ff}=3.0$, a pore width, $H=6$ lattice constants, and a temperature, $T^*=kT/\epsilon_{ff}=1.0$.

A. Static behavior in mean field theory

We begin by considering the results obtained from static MFT for fixed μ, V, T . Figure 2 shows isotherms of the density in a slit pore with $L=40$ lattice constants and an overall system length of 60 lattice constants. The relative activity is the activity divided by the activity of the bulk saturated vapor and is, except for the (small) effect of gas imperfection, essentially equivalent to relative pressure. The solutions on adsorption (desorption) were obtained by starting from a low (high) relative activity and increasing (decreasing) the relative activity in a series of steps, with the solution at each state forming the initial guess for the solution at the next state. The density plotted is averaged over a plane halfway between the two ends of the pore where pore, end effects have minimal influence. In this way, the results are essen-

FIG. 2. Isotherms of the density (average fractional occupancy) ρ and grand potential Ω vs relative activity λ/λ_0 for slit pores with $H=6$. The curves above the zero line are the density isotherms for the open pore ($L=40$), full line, and the infinite length pore, dashed line. The adsorption and desorption isotherms for the infinite length pore and finite length pore are indistinguishable except for the desorption branch within the hysteresis region. The curve below the zero line gives the grand potential isotherm for the infinite length pore. The point where the adsorption and desorption branches cross denotes the equilibrium vapor-liquid transition. Note that this is close to the desorption transition for the finite length pore.

FIG. 3. Visualizations of the density distribution for adsorption states on the isotherm shown in Fig. 2: (a) $\lambda/\lambda_0=0.1$, (b) $\lambda/\lambda_0=0.2$, (c) $\lambda/\lambda_0=0.791$, (d) $\lambda/\lambda_0=0.909$, and (e) $\lambda/\lambda_0=0.914$.

tially independent of the pore length. Also shown are the density and grand potential for the infinite length pore without contact with the bulk. The density isotherms for the two systems are essentially identical except for the desorption branch for the infinite pore which extends to a lower relative activity, a point we discuss in more detail below. The grand potential isotherm for the infinite pore indicates two phase transitions. The transition at lower activity is associated with monolayer formation, or two-dimensional condensation within the layer of sites adjacent to each of the pore walls. The lack of hysteresis in the isotherm in this region suggests proximity to the critical temperature for the transition. Indeed, the critical temperature for this transition should be close to that of the two-dimensional lattice gas with the nearest neighbor interactions in mean field, which is precisely $T^*=1.0$.

Our primary interest is in the behavior at higher activity where hysteresis is seen, associated with a vapor-liquid transition for the confined lattice fluid. We see that the hysteresis is narrower for the finite length pore. This is due to the fact that desorption occurs with direct contact between the pore liquid and vapor starting at the pore ends at a state very close to the relative activity associated with vapor-liquid coexistence in the infinite pore, an observation first made for a model of this type by Marconi and van Swol.^{7,8} There is a very slight extension of the desorption branch beyond the equilibrium transition, associated with the formation of menisci near the pore ends. In contrast, the desorption branch for the infinite pore extends to the limit of mechanical stability of the pore fluid. The identification of desorption with an equilibrium phase transition for open ended independent ideal pores (where there are no network or surface roughness effects) is frequently made in the literature^{36,37} and the present calculations and those of Marconi and van Swol^{7,8} provide support for such an identification.

Figures 3 and 4 show visualizations of the density distributions for the finite length pore for representative states along the adsorption and desorption branches of the isotherm and are similar to those seen in an earlier application of the static MFT to this system.³⁸ They are also very similar to

FIG. 4. Visualizations of the density distribution for desorption states on the isotherm shown in Fig. 2: (a) $\lambda/\lambda_0=0.914$, (b) $\lambda/\lambda_0=0.852$, (c) $\lambda/\lambda_0=0.795$, (d) $\lambda/\lambda_0=0.791$, and (e) $\lambda/\lambda_0=0.1$.

those obtained via grand canonical molecular dynamics and Monte Carlo simulations for an off-lattice model of an open slit pore.²⁰ Figure 3 shows that adsorption proceeds first through the formation of a monolayer on the pore walls followed by a pore filling condensation leading to a liquid state in the pore with menisci at the pore entrances. Desorption, illustrated in Fig. 4, involves a series of states in which the vapor-liquid interface retracts into the pore until a state where a quite sharp evaporation transition occurs and the system goes from the state visualized in Fig. 4(c) to that visualized in Fig. 4(d). Notice that the density of the liquid at the center of the pore just before evaporation [see Fig. 4(c)] is substantially lower than for the higher activity states on desorption [see Figs. 4(a) and 4(b)]. The evaporation transition occurs close to the equilibrium vapor-liquid transition for the infinite length pore, as discussed above.

For comparison with the results from the MFKT, it is also of interest to look at the solutions of the static MFT for the case of an infinite pore for fixed N , V , T . The solution space of the MFT in the canonical ensemble for the infinite slit pore can be very complex, as demonstrated by Maier and Stadtherr.³⁹ We have made two sequences of solutions of the canonical ensemble MFT equations. In the first case, we consider a series of increasing densities starting at very low density, with the solution at each state forming the initial guess for the solution at the next state. We are interested primarily in solutions corresponding to vapor-liquid coexistence in the pore. To do this, we modify the initial guess solution for each state by setting the local densities to high values for two sites in the second layer on each side of the pore equidistant from the pore ends. This makes no difference for states away from the capillary transition region. Within that region, however, it allows the iteration scheme to find solutions associated with undulates and liquid bridges. In the second case, we consider a series of decreasing densities starting at very high density. In this case, we set the initial guess densities to very low values for two sites at each end of the pore halfway between the pore walls. This allows the iteration algorithm to find solutions associated with vapor bubbles (due to the periodic boundaries, the vapor bubble and liquid bridge morphologies

FIG. 5. Isotherms of the density (average fractional occupancy) ρ and grand potential Ω vs relative activity λ/λ_0 for an infinite slit pore (pore with $L=40$, periodic boundaries in the x direction and no bulk region) with $H=6$ determined at fixed N, V, T . The curves above the zero line are the density isotherms from the two solutions sequences: low density to high density—full line; high density to low density—dashed line. The curve below the zero line gives the grand potential isotherm.

are equivalent). The resulting isotherms are shown in Fig. 5, with visualizations for several states shown in Figs. 6 and 7.

The behavior underlying in Fig. 5 is as follows. Starting at low average density, the sequence of states follows that in Fig. 3 until the end of the adsorption branch within the capillary transition region, which is close to a stability limit of the pore vapor in MFT. For all these states, the density along the pore axis is uniform for any value of z . After that, there is a jump associated with local multilayer adsorption (undulate formation⁴⁰) on each side of the pore [see Figs. 6(a) and 6(b)]. There is then a small range of densities where the undulates are stable. After that, there is another sharp transition associated with the appearance of a liquid bridge at a chemical potential close to that for vapor-liquid equilibrium in the pore [see Figs. 6(b) and 6(c)]. The chemical potential is then essentially unchanged until the pore is almost filled with liquid. At this point, there is a jump to a state in the neighborhood of the stability limit of the pore liquid where

FIG. 6. Visualizations of density distributions for states on the isotherm shown in Fig. 5 for the low density to high density sequence: (a) $\rho=0.47$, (b) $\rho=0.51$, (c) $\rho=0.52$, (d) $\rho=0.70$, (e) $\rho=0.89$, and (f) $\rho=0.90$. Note that because of the periodic boundaries, the liquid bridge and vapor bubble states are equivalent.

FIG. 7. Visualizations of density distributions for states on the isotherm shown in Fig. 5 for high density to low density sequence: (a) $\rho=0.90$, (b) $\rho=0.89$, (c) $\rho=0.70$, (d) $\rho=0.52$, (e) $\rho=0.48$, and (f) $\rho=0.47$. Note that because of the periodic boundaries, the liquid bridge and vapor bubble states are equivalent.

the density along the pore axis is again uniform for any value of z [see Figs. 6(e) and 6(f)]. After this, the high density branch of the isotherm is identical to that in Fig. 3. The small oscillations in the isotherm in the transition region are a consequence of a stepwise progression of the menisci along the pore axis as the average density changes and are likely a consequence of the mean field approximation. The solution sequence starting at high density tracks the states obtained at in the sequence starting at low density except that the liquid bridge persists down to lower density and the undulate states are not seen [see Figs. 7(e) and 7(f)]. The overall picture is similar to that envisaged in the classical thermodynamic analysis of Everett and Haynes⁴⁰ and recent Monte Carlo simulation studies for fluids in cylindrical pores for fixed N, V, T .⁴¹

B. Dynamic behavior

We now consider the dynamics of the system during irreversible changes in the chemical potential, which we accomplish by solving Eq. (31). In doing, so we make one small change to the system illustrated in Fig. 1 by adding one additional layer of sites in the bulk phase at one end of the system. The density in this layer is fixed at the value obtained from MFT for the bulk phase at the given chemical potential or activity. This layer acts as a source or sink for fluid entering or leaving the system. The configuration of the boundaries is similar to that used in Kawasaki dynamics simulations of lattice models of gas adsorption in porous materials.¹⁵ To integrate Eq. (31), we have used Euler's method so that

$$\rho_i(t + \Delta t) = \rho_i(t) + \Delta t \sum_a M_{i,i+a}(t) [\mu_{i+a}(t) - \mu_i(t)]. \quad (35)$$

An appropriate dimensionless time for these calculations is $w_0 t$ and we have found that time steps $w_0 \Delta t$ less than about 0.2–0.3 give stable solutions. To initialize the density distri-

FIG. 8. Density vs time for $L=20$ during a quench of the relative activity from $\lambda/\lambda_0=0.006\,74$ to $\lambda/\lambda_0=0.951$. The full line gives the average density throughout the pore and the dashed line gives the average density in a plane halfway between the ends of the pore.

bution in the system, we have used the static MFT density distribution computed at the initial chemical potential. We have checked the results from Eq. (35) by comparing the density distributions for long times with the solutions of the static mean field equations and by examining the effect on the trajectory of varying the time step.

Figure 8 shows the uptake dynamics for a slit pore with $L=20$ during a quench from a chemical potential at a dilute gas bulk state to one close to bulk saturation. We plot both the averaged density throughout the pore and the density averaged over a plane halfway between the pore ends. The pore averaged density curve shows two regimes separated by a cusp in the uptake curve. The regime at shorter times is associated with the formation of adsorbed layers on the pore walls. The regime at longer times is associated with condensation and pore filling. The difference between the curve for the density at the middle of the pore and that for the density averaged over the pore reflects the local changes in density in the middle of the pore where pore condensation is initiated. Visualizations of the density distribution at various stages of the dynamics are shown in Fig. 9. The pore filling process is initiated in the middle of the pore through undulate formation, followed by the appearance of a liquid bridge, and proceeds via the increase in length of the liquid bridge. The cusp in the uptake curve for the pore averaged density coincides with the sharp increase in the density at the center of the pore and is due to transition from the undulate to bridge state [see Figs. 9(d) and 9(e)]. As we have seen in our static MFT calculations, these kinds of states are not thermodynamically stable in the static MFT at fixed μ , V , T . However, they appear in the static MFT at fixed N , V , T (see Fig. 6).

Figure 10 shows the corresponding uptake dynamics for a pore with $L=40$. The qualitative behavior of the average density is similar to that seen in Fig. 8 with the time scale stretched primarily by the additional length of the pore. The curve for the density at the center of the pore is very different due to the fact that pore condensation is initiated near the ends of the pore rather than in the middle. This is illustrated in the visualizations of the density distributions shown in Fig. 11. It appears that for longer pores there is not sufficient time for the fluid to accumulate at the pore center before pore condensation begins near the pore ends. An interesting feature of Fig. 10 is that the density at the pore center is not

FIG. 9. Visualizations of the density distribution for $L=20$ during a quench of the relative activity from $\lambda/\lambda_0=0.006\,74$ to $\lambda/\lambda_0=0.951$: (a) $w_0t=200$, (b) $w_0t=1000$, (c) $w_0t=4000$, (d) $w_0t=8000$, (e) $w_0t=8200$, (f) $w_0t=9000$, (g) $w_0t=10\,000$, and (h) $w_0t=12\,000$.

monotonically increasing with time as the density builds up near the pore ends, as shown in Fig. 11. During this period, there is a net flux from the center of the pore toward the region where pore condensation is occurring. Figure 12 shows the uptake dynamics for a pore with $L=60$. The uptake dynamics is qualitatively similar to that seen in Fig. 10 and the visualizations of the density distributions, shown in Fig. 13, are similar to those seen in Fig. 11. It seems likely that the multiple bridge states seen here could emerge in solutions of the static MFT at fixed N , V , T for longer pores, although we have not investigated this yet.

We have also studied the uptake dynamics when the chemical potential is quenched between states close to those visualized in Figs. 3(d) and 3(e). The dynamic uptake is shown in Fig. 14. The behavior is now similar to that seen in Fig. 8 with the pore condensation initiated at the center of the pore rather than near the pore entrances. Visualizations of states encountered in the dynamics are shown in Fig. 15. In this case, the small difference in chemical potential between

FIG. 10. Density vs time for $L=40$ during a quench of the relative activity from $\lambda/\lambda_0=0.006\,74$ to $\lambda/\lambda_0=0.951$. The full line gives the average density throughout the pore and the dashed line gives the average density in a plane halfway between the ends of the pore.

FIG. 11. Visualizations of the density distribution for $L=40$ during a quench of the relative activity from $\lambda/\lambda_0=0.006\,74$ to $\lambda/\lambda_0=0.951$: (a) $w_0t=6000$, (b) $w_0t=16\,000$, (c) $w_0t=16\,400$, (d) $w_0t=18\,400$, (e) $w_0t=24\,000$, (f) $w_0t=28\,000$, (g) $w_0t=28\,400$, and (h) $w_0t=30\,000$.

the initial and final states provides a relatively small driving force for mass transfer and a lower flux of fluid into the system leading to a slower relaxation than that seen in Fig. 8.

Finally, we consider the desorption dynamics during a quench from a chemical potential at a state close to bulk saturation to one in a dilute gas bulk state. The density versus time is shown in Fig. 16, again averaged both over the entire pore and in the middle of the pore, and visualizations are shown in Fig. 17. Desorption proceeds via the evaporation of the liquid and the retraction of the menisci into the pore until a narrow liquid bridge spans the adsorbed layers on the two pore walls. This bridge then breaks leaving adsorbed layers on each pore wall. The adsorbed layers desorb by evaporation into the vapor at the center of the pore and by mass transfer within the layer toward to the pore entrances. We

FIG. 12. Density vs time for $L=60$ during a quench of the relative activity from $\lambda/\lambda_0=0.006\,74$ to $\lambda/\lambda_0=0.951$. The full line gives the average density throughout the pore and the dashed line gives the average density in a plane halfway between the ends of the pore.

FIG. 13. Visualizations of the density distribution for $L=60$ during a quench of the relative activity from $\lambda/\lambda_0=0.006\,74$ to $\lambda/\lambda_0=0.951$: (a) $w_0t=8000$, (b) $w_0t=19\,200$, (c) $w_0t=20\,000$, (d) $w_0t=22\,400$, (e) $w_0t=40\,000$, (f) $w_0t=47\,200$, (g) $w_0t=48\,000$, and (h) $w_0t=52\,000$.

have also studied the desorption when the chemical potential is quenched between the states visualized in Figs. 4(c) and 4(d). The behavior is qualitatively similar to that shown in Figs. 16 and 17 but with the dynamics slowed by the smaller driving force for mass transfer. An interesting feature of the dynamics of desorption is that the density distributions encountered are similar to those obtained in the high density to low density solution sequence of the static MFT at fixed N , V , T (see Fig. 7) and the undulate states are not seen.

IV. SUMMARY AND CONCLUSIONS

We have discussed the application of the mean field kinetic equations for a lattice gas to the case of confinement in

FIG. 14. Density vs time for $L=40$ during a quench of the relative activity from $\lambda/\lambda_0=0.909$ to $\lambda/\lambda_0=0.914$. The full line gives the average density throughout the pore and the dashed line gives the average density in a plane halfway between the ends of the pore.

FIG. 15. Visualizations of the density distribution for $L=40$ during a quench of the relative activity from $\lambda/\lambda_0=0.909$ to $\lambda/\lambda_0=0.914$: (a) $w_0t=800$, (b) $w_0t=40\,000$, (c) $w_0t=48\,000$, (d) $w_0t=58\,400$, (e) $w_0t=59\,200$, (f) $w_0t=64\,000$, (g) $w_0t=68\,000$, and (h) $w_0t=76\,800$.

a porous material. The theory embodied in these equations can be regarded in three ways: (i) as an approximation to a kinetic Monte Carlo simulation; (ii) as a theory of diffusion in porous materials; and (iii) as a dynamical density functional theory. The results allow us to investigate the density distribution in the system during adsorption and desorption processes and to discover the mechanisms underlying the relaxation dynamics in the system.

An implementation to the case of adsorption in a open ended slit pore has been used to illustrate the utility of this approach. We have compared the density distribution encountered in large irreversible quenches of the chemical potential from low density to high density states and vice versa with those obtained from the static MFT for sequences of states along the adsorption/desorption isotherm representative of quasistatic processes. Quenches between closely

FIG. 16. Density vs time for $L=40$ during a quench of the relative activity from $\lambda/\lambda_0=0.951$ to $\lambda/\lambda_0=0.006\,74$. The full line gives the average density throughout the pore and the dashed line gives the average density in a plane halfway between the ends of the pore.

FIG. 17. Visualizations of the density distribution for $L=40$ during a quench of the relative activity from $\lambda/\lambda_0=0.951$ to $\lambda/\lambda_0=0.006\,74$: (a) $w_0t=200$, (b) $w_0t=1000$, (c) $w_0t=2000$, (d) $w_0t=3000$, (e) $w_0t=3400$, (f) $w_0t=3600$, (g) $w_0t=4000$, and (h) $w_0t=8000$.

neighboring states bounding condensation or evaporation transitions have also been considered. The density distributions in the dynamics are sensitive to the magnitude of the chemical potential quench, which determines the overall flux of fluid into or out of the pore, especially for longer pores.

We find that the density distributions encountered in the capillary transition during dynamic uptake resemble those obtained from the static MFT for an infinite slit pore at fixed N , V , T (in the low density to high density solution sequence), featuring the formation of undulates and liquid bridges. Similarly, we find that the density distributions encountered during the desorption dynamics resemble those obtained from the static MFT at fixed N , V , T (in the high density to low density solution sequence), with no undulates appearing. These observations reflect the fact that, in the present implementation of the theory, fixed N , V , T (conserved order parameter) dynamics¹⁵ makes a significant contribution to the time evolution of the system. The mechanism of capillary condensation envisaged by Everett and Haynes⁴⁰ is qualitatively realized in the dynamics seen in these calculations but not in the equilibrium or metastable equilibrium states obtained for long times, which coincide with the static MFT results at fixed μ , V , T .

The MFKT has potentially much wider applicability than to just the slit pore system considered here. Dynamic Monte Carlo simulation, especially Kawasaki dynamics, has been used to study the dynamical behavior of several lattice models of confined fluids, including applications to fluids in complex pore structures such as Vycor glass,¹⁵ and MFKT can similarly be applied to such systems. An important point of

comparison is that a single MFKT trajectory provides information approximating results obtained after averaging over many dynamic Monte Carlo trajectories. This can lead to a more precise picture of the system behavior during the dynamics for a much lower investment of computer time. The results from the present calculation may at first appear puzzling to readers familiar with the studies of single trajectories from molecular dynamics or dynamic Monte Carlo simulations for individual pores. Consideration of how our calculations relate to experiments may help in this regard. As an example, consider the case of adsorption/desorption of a fluid into a sample of MCM-41,⁴² a mesoporous silica believed to consist of arrays of independent cylindrical pores. The dynamics of adsorption or desorption for each pore in the system will have the characteristic of single molecular dynamics or dynamic Monte Carlo trajectories. However, the dynamics of the system as a whole will be an average over these single pore trajectories, thus having the character of the theory presented here.

The lack of explicit treatment of fluctuations in the underlying thermodynamics means that the MFKT treatment has the same limitations as the static MFT with respect to the observation of phase transitions and in the critical region. Of particular to note is the question of the role of fluctuations in the nucleation of condensation and evaporation transitions. Since desorption in this ideal open pore system happens very close to the equilibrium transition, it seems likely that the heterogeneous nucleation of desorption via meniscus formation at the pore ends is correctly described by the theory. Fluctuations can act to shorten the adsorption branch of the hysteresis loop.⁴³ However, a significant component of nucleation is again heterogeneous involving undulate formation and liquid bridging,^{40,41} which are the mechanisms seen in our calculations. While, as discussed in Sec. II D, there is also the possibility of incorporating stochastic noise into the calculations, this would not affect the underlying thermodynamics which would still be that from MFT.

In future work, we plan to apply the approach presented here to a wider range of systems. We will also assess the accuracy of the approximations built into the theory. Direct comparison with Kawasaki dynamics simulations can be used to assess the impact of the mean field theory on the diffusional dynamics. The dynamics described by this approach includes only transport generated by diffusionlike mechanisms. The importance of momentum transport, especially for processes with large changes in the density distribution over short times, will need to be investigated in the first instance through comparison with off-lattice molecular dynamics simulations.

ACKNOWLEDGMENTS

This work was supported by the National Science Foundation (Grant No. CBET-0649552). The author is grateful to Professor Jon Machta and Professor David Ford for helpful discussions and comments on the manuscript.

- ¹M. J. DeOliveira and R. B. Griffiths, *Surf. Sci.* **71**, 687 (1978).
- ²C. Ebner, *Phys. Rev. A* **23**, 1925 (1981).
- ³R. Pandit, M. Schick, and M. Wortis, *Phys. Rev. B* **26**, 5112 (1982).
- ⁴H. Nakanishi and M. E. Fisher, *J. Chem. Phys.* **78**, 3279 (1983).
- ⁵E. Bruno, U. B. M. Marconi, and R. Evans, *Physica A* **141**, 187 (1987).
- ⁶D. Nicolaides and R. Evans, *Phys. Rev. B* **39**, 9336 (1989).
- ⁷U. M. B. Marconi and F. van Swol, *Europhys. Lett.* **8**, 531 (1989).
- ⁸U. M. B. Marconi and F. van Swol, *Phys. Rev. A* **39**, 4109 (1989).
- ⁹R. Evans, *J. Phys.: Condens. Matter* **2**, 8989 (1990).
- ¹⁰L. Monette, A. J. Liu, and G. S. Grest, *Phys. Rev. A* **46**, 7664 (1992).
- ¹¹A. Chakrabarti, *Phys. Rev. Lett.* **69**, 1548 (1992).
- ¹²G. Aranovich and M. Donohue, *J. Colloid Interface Sci.* **200**, 273 (1998).
- ¹³E. Kierlik, P. A. Monson, M. L. Rosinberg, L. Sarkisov, and G. Tarjus, *Phys. Rev. Lett.* **8705**, 055701 (2001).
- ¹⁴H. J. Woo, L. Sarkisov, and P. A. Monson, *Langmuir* **17**, 7472 (2001).
- ¹⁵H. J. Woo and P. A. Monson, *Phys. Rev. E* **67**, 041207 (2003).
- ¹⁶A. Luzar and K. Leung, *J. Chem. Phys.* **113**, 5836 (2000).
- ¹⁷F. Porcheron and P. A. Monson, *Langmuir* **21**, 3179 (2005).
- ¹⁸R. Valiullin, S. Naumov, P. Galvosas, J. Karger, H. J. Woo, F. Porcheron, and P. A. Monson, *Nature (London)* **443**, 965 (2006).
- ¹⁹L. Sarkisov and P. A. Monson, *Langmuir* **16**, 9857 (2000).
- ²⁰L. Sarkisov and P. A. Monson, *Langmuir* **17**, 7600 (2001).
- ²¹J. F. Gouyet, M. Plapp, W. Dieterich, and P. Maass, *Adv. Phys.* **52**, 523 (2003).
- ²²G. Martin, *Phys. Rev. B* **41**, 2279 (1990).
- ²³O. Penrose, *J. Stat. Phys.* **63**, 975 (1991).
- ²⁴J. W. Cahn, *J. Chem. Phys.* **42**, 93 (1965).
- ²⁵J. W. Cahn and J. E. Hilliard, *J. Chem. Phys.* **28**, 258 (1958).
- ²⁶S. Puri, *Mod. Phys. Lett. B* **19**, 919 (2005).
- ²⁷A. J. Archer, *J. Phys.: Condens. Matter* **18**, 5617 (2006).
- ²⁸A. J. Archer and R. Evans, *J. Chem. Phys.* **121**, 4246 (2004).
- ²⁹J. Fraaije, *J. Chem. Phys.* **99**, 9202 (1993).
- ³⁰K. Fuchizaki and K. Kawasaki, *Physica A* **266**, 400 (1999).
- ³¹U. M. B. Marconi and P. Tarazona, *J. Chem. Phys.* **110**, 8032 (1999).
- ³²G. L. Aranovich and M. D. Donohue, *J. Phys. Chem. B* **109**, 16062 (2005).
- ³³D. Matuszak, G. L. Aranovich, and M. D. Donohue, *J. Chem. Phys.* **121**, 426 (2004).
- ³⁴D. Matuszak, G. L. Aranovich, and M. D. Donohue, *Phys. Chem. Chem. Phys.* **8**, 1663 (2006).
- ³⁵A. J. Archer and M. Rauscher, *J. Phys. A* **37**, 9325 (2004).
- ³⁶P. C. Ball and R. Evans, *Langmuir* **5**, 714 (1989).
- ³⁷P. C. Ball and R. Evans, *Europhys. Lett.* **4**, 715 (1987).
- ³⁸B. Libby and P. A. Monson, *Langmuir* **20**, 4289 (2004).
- ³⁹R. W. Maier and M. A. Stadtherr, *Langmuir* **47**, 1874 (2001).
- ⁴⁰D. H. Everett and J. M. Haynes, *J. Colloid Interface Sci.* **38**, 125 (1972).
- ⁴¹A. Vishnyakov and A. V. Neimark, *J. Chem. Phys.* **119**, 9755 (2003).
- ⁴²J. S. Beck, J. C. Vartuli, W. J. Roth, M. E. Leonowicz, C. T. Kresge, K. D. Schmitt, C. T. W. Chu, D. H. Olson, E. W. Sheppard, S. B. McCullen, J. B. Higgins, and J. L. Schlenker, *J. Am. Chem. Soc.* **114**, 10834 (1992).
- ⁴³L. D. Gelb, *Mol. Phys.* **100**, 2049 (2002).