Modeling the Thermodynamics and Dynamics of Fluids Confined in Three-Dimensionally Ordered Mesoporous (3DOm) Carbon Materials

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Modeling the Thermodynamics and Dynamics of Fluids Confined in Three-Dimensionally Ordered Mesoporous (3DOm) Carbon Materials

A Thesis Presented

by

ANISH DESOUZA

Submitted to the Graduate School of the University of Massachusetts Amherst in partial fulfillment of the requirements for the degree of

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Department of Chemical Engineering
Modeling the Thermodynamics and Dynamics of Fluids Confined in Three-Dimensionally Ordered Mesoporous (3DOM) Carbon Materials

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ABSTRACT

MODELING THE THERMODYNAMICS AND DYNAMICS OF FLUIDS CONFINED IN THREE-DIMENSIONALLY ORDERED MESOPOROUS (3DOM) CARBON MATERIALS

MAY 2016

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Porous materials have application in adsorption based processes due to their high internal surface area and tailorable pore size. They find uses in fields such as catalysis, separation, biotechnology, and microelectronics. Fluids confined in such materials exhibit interesting behavior in regards to the condensation and evaporation mechanisms. Understanding study the behavior of fluids confined in these porous materials is necessary for the efficient design of these materials. The adsorption/desorption isotherm provides valuable information about the effect of network features like pore connectivity and pore size distribution on fluid behavior during pore condensation and evaporation. Such insight can be useful in the characterization of these porous materials.

Three dimensionally ordered mesoporous (3DOM) carbon is a porous material that has recently emerged and is of interest. These porous structures are obtained from templating colloidal crystals formed from lysine-silica nanoparticles. The resulting
structure consist of spherical pores connected to each other by windows. Due to the use of silica nanoparticles a range of tunable pore sizes can be obtained. These structures have high degree of order. They find applications in the synthesis of zeolites due to their highly controllable pore size. Hence a study of the adsorption properties of these structures is of importance.

Molecular modeling has proved effective in the study of porous materials. The development of the density functional theory (DFT) and the dynamic mean field theory (DMFT) has led to great advances in the study of the behavior of confined fluids. The DFT enables the study of the adsorption desorption hysteresis phenomena of confined fluids. The DMFT describes the density profile versus time for a step change in relative pressure on the isotherm. These theories have been applied in the past to two dimensional model pore networks to investigate the mechanisms of adsorption and desorption. In this research project we aim to apply the same to various model 3DOm carbon pore networks. Studying the density distributions in these networks can help understand the thermodynamics of fluid adsorption and desorption in these structures. The results could be useful in understanding the effect of pore structure features like pore size and windows on adsorption and desorption. Also the effect of disorder in the pore network as well as effect of variation in pore size on fluid behavior can be studied. Study of the dynamics of adsorption gives an insight into the nucleation mechanisms that govern the condensation of fluid in the pore. These results could prove useful in the characterization of these porous structures.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>ABSTRACT</td>
<td>iii</td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
<td>vii</td>
</tr>
</tbody>
</table>

## CHAPTER

### 1. INTRODUCTION

1.1. Background .................................................................1
1.2. 3DOm Carbon: Introduction .................................................4
1.3. Illustrative example .........................................................5
1.4. Thesis Outline ..............................................................9

### 2. MODELS AND METHODS

2.1. Static Behavior ..........................................................13
2.1.1. Density Functional Theory (DFT) ..................................13
2.2. Dynamic behavior ........................................................14
2.2.1. Dynamic Mean Field Theory (DMFT) ..........................15
2.2.2. Dynamic Mean Field Theory: Implementation .............17

### 3. DFT: AN APPLICATION TO 3DOm CARBON

3.1. Lattice gas model of 3DOm carbon .................................19
3.2. Results ..........................................................................22
3.2.1. Static behavior: Ordered network of 3DOm carbon ...........22
3.2.2. Study of fluid behavior in a single isolated sphere ..........28
3.2.3. Static behavior: 3DOm carbon network with disordered arrangement of pores ......................................................................30
3.2.4. Static behavior: 3DOm carbon network with variation in pore size .................................................................35
3.3. Comparison with experimental results ..................................44
3.4. Summary .........................................................................46

### 4. DMFT: AN APPLICATION TO 3DOm CARBON

4.1. Results ...........................................................................48
4.1.1. Dynamic behavior: Ordered network of 3DOm carbon
4.1.2. Dynamic behavior: 3DOm carbon network with variation in pore size
4.2. Summary

5. CONCLUSIONS AND SUGGESTION FOR FUTURE WORK

BIBLIOGRAPHY
LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1. Adsorption/desorption isotherms of (a) type IV and (b) type V from the IUPAC classification of 1985 showing hysteresis loops of type H1 and H2 respectively [6]</td>
<td>2</td>
</tr>
<tr>
<td>1.2. a) Isotherms of the density (average fractional occupancy), $\rho$, and grand potential, $\Omega$, versus relative activity, $\lambda/\lambda_0$ for a slit pore with $H = 6$ kept in contact with the bulk fluid. The curve above the zero line is the density isotherm and the curve below the zero line is the grand potential isotherm. b) Density versus time for $L = 40$ during a quench of the relative activity from $\lambda/\lambda_0 = 0.00674$ 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 half way between the ends of the pore. [33]</td>
<td>7</td>
</tr>
<tr>
<td>1.3. Visualizations of the density distribution for a three-dimensional slit pore with $L=40$ and $H = 6$ during a change of the relative activity $\lambda/\lambda_0 = 0.00674$ to $\lambda/\lambda_0 = 0.951$. Each panel shows, at the top, a visualization from a two-dimensional slice into the distribution half-way across the pore in the $x-z$ plane, and, below, the density in an $x-y$ plane halfway between the pore walls. Darker shading means higher density: (a) $\omega_0 t = 2000$, (b) $\omega_0 t = 5000$, (c) $\omega_0 t = 6000$, (d) $\omega_0 t = 8000$, (e) $\omega_0 t = 8100$, (f) $\omega_0 t = 9000$. [33]</td>
<td>8</td>
</tr>
<tr>
<td>3.1. Formation of 3DOm carbon template (right) from silica nanoparticles [55]</td>
<td>19</td>
</tr>
<tr>
<td>3.2. Lattice model of a 3DOm carbon established from coarse graining of hard spheres</td>
<td>21</td>
</tr>
<tr>
<td>3.3. Adsorption/desorption isotherms for 3DOm pore network with interconnected pores (full line) and for independent pores (dashed line)</td>
<td>23</td>
</tr>
<tr>
<td>3.4. Visualizations of the density distributions for states along the isotherm for adsorption in the model 3DOm pore network with isolated pores. The states on the left are for adsorption and those on the right for desorption. The values of $P/P_o$ for each state are as follows: (a) 0.002, (b) 0.1, (c) 0.877, (d) 0.879, (e) 0.99, (f) 0.99, (g) 0.8, (h) 0.612, (i) 0.610, (j) 0.1</td>
<td>26</td>
</tr>
<tr>
<td>3.5. Visualizations of the density distributions for states along the isotherm for adsorption in the model 3DOm pore network with interconnected pores. The states on the left are for adsorption and those on the right for desorption. The values of $P/P_o$ for each state are as follows: (a) 0.002, (b) 0.1, (c) 0.877, (d) 0.879, (e) 0.99, (f) 0.99, (g) 0.675, (h) 0.673, (i) 0.671, (j) 0.1</td>
<td>27</td>
</tr>
<tr>
<td>3.6. Condensation, vapor-liquid equilibrium and evaporation points versus inverse pore size for spherical pores</td>
<td>29</td>
</tr>
</tbody>
</table>
3.7. Cross section of a model 3DOm carbon system with disordered arrangement of pores. The grey sites represent the spherical voids. White areas represent the surrounding solid. .................................................................32

3.8. Adsorption/desorption isotherms for 3DOm pore network for system with disordered arrangement of spheres (full line) and for ordered system (dashed line) .........................................................................................33

3.9. Visualizations of the density distributions for states along the isotherm for adsorption in the model 3DOm pore network with disordered arrangement of spheres. The states on the left are for adsorption and those on the right for desorption. The values of P/P_o for each state are as follows: (a) 0.02, (b) 0.877, (c) 0.879, (d) 0.99, (e) 0.99, (f) 0.653, (g) 0.651, (h) 0.649 .............................................34

3.10. Theoretical pore size distribution (continuous line) from which sampling of hard spheres is taken and pore size distribution (points) obtained from coarse graining of hard spheres. (a) System size of 108 spheres. (b) System size of 256 spheres ............37

3.11. Cross section of a model 3DOm carbon system with variation in pore size. The grey sites represent the spherical voids. White areas represent the surrounding solid. (a) System size of 108 spheres. (b) System size of 256 spheres .............................38

3.12. Average adsorption/desorption isotherms for 3DOm pore networks with pore size variation for a system with 108 spheres .................................................................................................39

3.13. Visualizations of the density distributions for states along the isotherm for adsorption in the model 3DOm pore network with pore size variation for a system with 108 spheres. The states on the left are for adsorption and those on the right for desorption. The values of P/P_o for each state are as follows: (a) 0.002, (b) 0.891, (c) 0.909, (d) 0.914, (e) 0.99, (f) 0.99, (g) 0.760, (h) 0.758, (i) 0.738, (j) 0.678 ..............40

3.14. Average adsorption/desorption isotherms for 3DOm pore networks with pore size variation for a system with 108 spheres (straight line) and for a system with 108 spheres (dashed line) .................................................................................................42

3.15. Visualizations of the density distributions for states along the isotherm for adsorption in the model 3DOm pore network with pore size variation for a system with 108 spheres. The states on the left are for adsorption and those on the right for desorption. The values of P/P_o for each state are as follows: (a) 0.02, (b) 0.881, (c) 0.895, (d) 0.900, (e) 0.917, (f) 0.99, (g) 0.99, (h) 0.760, (i) 0.745, (j) 0.727, (k) 0.680, (l) 0.612 .................................................................................43

3.16. Normalized adsorption/desorption isotherms for model 3DOm pore networks (straight line). Nitrogen adsorption isotherm at 77K for 20 nm 3DOm carbon (▲) and for 30 nm 3DOm carbon (●) .............................................................................................................45

4.1. Density versus time for a model 3DOm carbon network during a quench of the relative activity from λ/λ_o=0.00674 to λ/λ_o =0.951. The dashed line gives the
average density throughout the pore network and the full line gives the average
density in the middle of the pore network..............................................................50

4.2. Visualizations of the density distribution for a model 3DOm carbon network during
a quench of the relative activity from $\lambda / \lambda_o = 0.00674$ to $\lambda / \lambda_o = 0.951$: (a) $\omega_b t = 5000$, (b) $\omega_b t = 8000$, (c) $\omega_b t = 27500$, (d) $\omega_b t = 42500$, (e) $\omega_b t = 62500$, (f) $\omega_b t = 75000$ .........51

4.3. Density versus time for a model 3DOm carbon network during a quench of the
relative activity from $\lambda / \lambda_o = 0.951$ to $\lambda / \lambda_o = 0.00674$. The dashed line gives the
average density throughout the pore network and the full line gives the average
density in the middle of the pore network..............................................................53

4.4. Visualizations of the density distribution for a model 3DOm carbon network during
a quench of the relative activity from $\lambda / \lambda_o = 0.951$ to $\lambda / \lambda_o = 0.00674$: (a) $\omega_b t = 500$, (b) $\omega_b t = 1500$, (c) $\omega_b t = 2000$, (d) $\omega_b t = 3500$, (e) $\omega_b t = 5000$, (f) $\omega_b t = 6000$ .................54

4.5. Density versus time for a model 3DOm carbon network with variation in pore size
during a quench of the relative activity from $\lambda / \lambda_o = 0.00674$ to $\lambda / \lambda_o = 0.951$. The
dashed line gives the average density throughout the pore network and the full line
gives the average density in the middle of the pore network ...............................57

4.6. Visualizations of the density distribution for a model 3DOm carbon network with
variation in pore size during a quench of the relative activity from $\lambda / \lambda_o = 0.00674$ to
$\lambda / \lambda_o = 0.951$: (a) $\omega_b t = 5000$, (b) $\omega_b t = 8000$, (c) $\omega_b t = 27500$, (d) $\omega_b t = 42500$, (e) $\omega_b t = 62500$, (f) $\omega_b t = 75000$ .................................................................58

4.7. Density versus time for a model 3DOm carbon network with variation in pore size
during a quench of the relative activity from $\lambda / \lambda_o = 0.951$ to $\lambda / \lambda_o = 0.00674$. The
dashed line gives the average density throughout the pore network and the full line
gives the average density in the middle of the pore network ...............................60

4.6. Visualizations of the density distribution for a model 3DOm carbon network with
variation in pore size during a quench of the relative activity from $\lambda / \lambda_o = 0.951$ to $\lambda / \lambda_o = 0.00674$: (a) $\omega_b t = 500$, (b) $\omega_b t = 1800$, (c) $\omega_b t = 3000$, (d) $\omega_b t = 5000$, (e) $\omega_b t = 6500$, (f) $\omega_b t = 9000$ .................................................................61
CHAPTER 1
INTRODUCTION

1.1. Background

Porous materials are of scientific and technological interest because of their ability to interact with atoms, ions and molecules not only at their surfaces, but throughout the bulk of the material [1]. They find applications in catalysis, adsorption and membrane separations, microelectronics and biotechnology [2]. Some examples of porous materials are MCM-41, MCM-48, Vycor glass and silica gel [3-5]. Most of the applications of porous materials involve the adsorption and desorption of fluid within the pores. The distribution of sizes, shapes and volumes of the void spaces in porous materials affect the behavior of the adsorbed fluid and hence directly relates to their ability to perform desired functions in particular applications. It is imperative to characterize porous materials based on pore network geometry and pore size distribution. A study of the behavior of the confined fluids in these materials will reveal information about the features of the porous material; such as network geometry and pore size distribution and aid in the characterization of the material. Hence the study of adsorption thermodynamics and dynamics of fluids in these materials is of interest.

Hysteresis loops are a feature of adsorption in porous solids. They are advantageous to understanding the thermodynamics of adsorption of fluids in porous materials. Figure 1.1 shows typical adsorption isotherms with hysteresis loops of the H1 and H2 type [6]. The H1 loop is typically found in independent pore networks such as MCM-41 and is associated with the metastability of liquid and vapor states in the pores.
The rounding of the loops suggests a variation in the size of the pores. [7, 8] The H2 loop is typical of more complex systems such as porous glass and silica gels. [9].

Apart from the thermodynamics, a study of the kinetics of adsorption/desorption helps understand pore morphology and can serve as another characterization tool. The dynamics of adsorption/desorption of fluids in pores can describe the nucleation mechanisms for pore condensation and evaporation as well as more complex mechanisms of pore blocking and cavitation.

Figure 1.1. Adsorption/desorption isotherms of (a) type IV and (b) type V from the IUPAC classification of 1985 showing hysteresis loops of type H1 and H2 respectively [6]

The Density Functional Theory (DFT) has been employed for the study in this research project. DFT has previously been used to facilitate the understanding of the
thermodynamics of confined fluids and for pore structure characterization [10, 11]. It also provides accurate estimates of pore size distribution [12, 13]. A key feature of DFT is that it describes the thermodynamics of fluids confined in pore networks ranging from simple to complex geometries. DFT can describe the density profile of the confined fluid in one dimension fairly easily but becomes computationally expensive for two dimensional and three dimensional pore geometries. In such cases the lattice gas models with a coarse grained approach [14-16] is useful. In the present study the lattice gas model was used to describe the pore structures and study the density distributions in three dimensions.

The Mean Field Kinetic Theory (MFKT) which is a mean field approach to Kawasaki dynamics has been developed by Gouyet et al. [17] and is used to study the relaxation dynamics of adsorption and desorption. Matuszak and co-workers [18-22] developed the MFKT during their work on diffusion in porous materials. This was further built on by Monson and Edison [7, 22-25] and developed into the Dynamic Mean Field Theory (DMFT). DMFT is capable of investigating the response of a model porous material in contact with a bulk fluid to a step change of chemical potential or pressure in the bulk state. The system evolves to a final state in which the density distribution is also a solution of the mean field DFT for the system [17, 26, 27] showing that the theory of dynamics is fully consistent with the DFT for thermodynamics. DMFT reveals the nature of nucleation processes for confined fluids which otherwise would have to be assumed in the DFT thermodynamic studies.

DFT and DMFT have been used by Monson and co-workers to study the fluid confinement in two -dimensional pore networks of various geometries [7, 22-25, 28-30].
The aim of this research project is to apply DFT and DMFT to study the fluid confinement in three dimensionally ordered mesoporous (3DOm) carbon materials.

1.2. 3DOm Carbon: Introduction

Three dimensionally ordered mesoporous (3DOm) carbons are formed by templating colloidal crystals that are formed from silica nanoparticles [31]. The use of colloidal crystals with various primary particle sizes (e.g., 10, 20, 30, 40 nm) as templates leads to the formation of 3DOm carbons with a wide range of pore sizes. The resulting material consists of spherical pores interconnected by windows due to sintering in the silica sphere assembly. There have been experimental adsorption studies on 3DOm carbon carried out by Cychosz et al., who measured nitrogen and argon adsorption/desorption isotherms for 3DOm carbon templates using 10, 20, 30, and 40 nm nanoparticles [32]. The measured adsorption/desorption hysteresis loop for the 3DOm carbons revealed important information about pore size effects and were useful in classifying the pore. In this project DFT and DMFT have been applied to study the fluid behavior in various model 3DOm carbon structures.

The aim of this study was to answer the following interesting questions:

- What are the phase transitions associated with pore filling and pore emptying?
  Phase transitions are associated with the formation of nuclei which are separated from the existing phase by an interface. This nucleation mechanism is related to a free energy barrier associated with the thermodynamics of the system.

- How does pore connectivity and structural effects play a role in confined fluid phase transitions? Structural irregularities in the pore network often cause the
confined fluid to redistribute itself between different regions of the pore to facilitate the evolution to an equilibrium state.

- What are the various resistances that the fluid encounters during filling and emptying of the pore? Mass transfer resistances might be present in a system, or might emerge as it approaches equilibrium. These can give rise to mechanisms like pore blocking during the emptying of the pore.

The following example shows the utility of DFT and DMFT in understanding the fluid behavior in a porous structure.

1.3. **Illustrative example**

Casselman et al, [33] applied the DFT and DMFT to study the fluid behavior in a three dimensional (3D) slit pore. The system is a slit pore geometry which consists of two solid plates kept parallel to each other. The walls of this system strongly attract the fluid under study. The equilibrium behavior of fluid in a pore is given by its adsorption isotherm and it gives the pore fluid density at a fixed relative activity. The adsorption isotherm of a slit pore of height $H = 6$ lattice sites; together with its grand potential is shown in Figure 1.2(a). The step in the isotherm at lower activity is associated with the formation of a monolayer, and the step closer to the bulk saturation is associated with a capillary condensation transition. The grand potential isotherm shows two branches, the intersection of which denotes the equilibrium vapor liquid transition. The dynamics associated with pore filling were also studied. The slit pore is initialized at an initial state corresponding to a dilute vapor phase in the pore. The activity of the bulk fluid is then changed to a state where fluid is present in a condensed state in the pore. Figure 1.2(b)
shows the two plots for the density averaged throughout the slit and for the density averaged on a line of sites spanning the two walls at the center of the slit.

The pore-averaged density shows three regimes of behavior and can be studied by observing the visualizations of the density distributions shown in Figure 1.3. The short-time behavior is associated with the formation of a monolayer at the pore wall followed by multilayer adsorption (Figure 1.3(a)). Next liquid bridges appear in the four corners of the slit where there is the highest flux of fluid from the bulk and these grow in size and spread. The final regime begins where the liquid bridges merge (Figure 1.3(d)). This leads to the final stage of pore filling, where there is a bubble of vapor at the center of the slit which gradually narrows and disappears. Another feature that is noticeable is the decrease in the average density at the center of the slit at lower time lengths. During bridge formation fluid is pulled away from other regions of the system to contribute to the local density increases in the neighborhood of the nucleation events.
Figure 1.2. a) Isotherms of the density (average fractional occupancy), $\rho$, and grand potential, $\Omega$, versus relative activity, $\lambda/\lambda_0$ for a slit pore with $H = 6$ kept in contact with the bulk fluid. The curve above the zero line is the density isotherm and the curve below the zero line is the grand potential isotherm. b) Density versus time for $L = 40$ during a quench of the relative activity from $\lambda/\lambda_0 = 0.00674$ 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 half way between the ends of the pore. [33]
Figure 1.3. Visualizations of the density distribution for a three-dimensional slit pore with L=40 and H = 6 during a change of the relative activity $\lambda/\lambda_0 = 0.00674$ to $\lambda/\lambda_0 = 0.951$. Each panel shows, at the top, a visualization from a two-dimensional slice into the distribution half-way across the pore in the $x$–$z$ plane, and, below, the density in an $x$–$y$ plane halfway between the pore walls. Darker shading means higher density: (a) $\omega t = 2000$, (b) $\omega t = 5000$, (c) $\omega t = 6000$, (d) $\omega t = 8000$, (e) $\omega t = 8100$, (f) $\omega t = 9000$. [33]
The example illustrates the level of information provided by DFT and DMFT. DFT provides important information about the thermodynamics occurring during condensation and evaporation of liquid from the pore. The nucleation mechanisms in phase transitions of confined fluids are emergent features of the DMFT calculations. These theories can be applied to almost any pore geometry.

1.4. Thesis outline

The organization of the thesis after the introduction chapter is as follows-

In chapter 2 the lattice gas mean model of fluids is presented. The static Density Functional theory (DFT) of lattice gas models and the implementation details to study the equilibrium behavior of fluids in pores is discussed. The lattice gas model for the 3DOm carbon structure has been set up in three dimensions and the fluid density distribution is calculated in the three dimensions. The equations of DFT are set up in order to attain the density distribution at the lattice sites for a range of chemical potentials. This gives the adsorption/desorption hysteresis loop which is of interest in studying the confined fluid behavior. The Dynamic Mean Field theory (DMFT) and its implementation to study the dynamics of fluids in pores is then described. The mean field kinetic equations are set up to describe the relaxation dynamics of the confined fluid. These equations give the time dependency of the density distribution. The solution of these equations gives the evolution of the system with time when the system is made to go from an initial state to a final state on the adsorption/desorption isotherm. The implementation of the DMFT is such that it is consistent with the DFT. The solutions for the DMFT equations at long time correspond to the state of the DFT at the final value of chemical potential. By
studying the time evolution of the density distribution it is possible to understand the nucleation barriers associated with mechanisms of adsorption and desorption.

In chapter 3 the DFT is implemented to study model 3DOm carbon networks. The DFT has been used to understand the adsorption/desorption hysteresis phenomena of fluid confined in 3DOm carbon structures. Lattice gas models of the 3DOm carbon structure have been set up and the density distribution of the fluid has been calculated in all three dimensions. A three dimensional study of the density distribution gives us a new insight into the behavior of confined fluids in 3DOm carbon. Various models of the 3DOm carbon were studied to determine the effect of pore structure and pore size on fluid behavior. At first the simplest structure consisting of an ordered arrangement of spherical pores was considered. Two variations of this system, one with isolated pores and one with pores connected with windows were studied to investigate the effect of windows on fluid behavior. The phenomena of cavitation and pore blocking during desorption were observed. These were related to the presence of windows. Systems with disorder in arrangement of spherical pores were then studied and finally the effect of variation of pore size within the system was investigated. Disordered systems gave rise to regions of localized condensation during the adsorption step as well as more prominent pore blocking phenomena during the desorption step. The difference in the size of the pores leads to sequential condensation and the difference in size of windows leads to pore blocking in desorption.

In chapter 4 the dynamics of adsorption and evaporation have been studied using DMFT. The systems under consideration here are similar to those described above. The DMFT solutions predict the nucleation processes that affect the mechanisms of
adsorption and desorption. The uptake dynamics were studied by making the system to evolve from a dilute vapor state to a completely filled liquid state and the desorption dynamics during the emptying of the pore was calculated by evolving the system from a completely filled liquid phase to a dilute vapor phase. The study of the dynamics of adsorption in the ordered system of the 3DOm carbon shows the filling of the pore through the formation of liquid bridges at the pore windows. The desorption dynamics show the formation of menisci which retract into the pores. Further studies of the dynamics of fluids in disordered systems with variation in pore size lead to the understanding of the effect of variation in pore size on the nucleation processes in adsorption and desorption.

A summary of the work and possible future directions are presented in chapter 5.
CHAPTER 2
MODELS AND METHODS

Fluids confined in porous materials exhibit interesting behavior. Due to the length and time scales the use of models that define the domain as a continuous structure are computationally expensive. Coarse grained models are an attractive alternative to describe the system. Lattice gas models fall into this class and they have been widely used to study confined fluids [16, 34-38]. The model used in the present study to describe the system is a single occupancy lattice gas, with nearest neighbor interactions, in the presence of an external field whose Hamiltonian is given as

\[ H = -\frac{\varepsilon}{2} \sum_i \sum_a n_in_{i+a} + \sum_i n_i\phi_i \]  

(2.1)

where \( \varepsilon \) is the nearest neighbor interaction strength, \( n_i \) is the occupancy of site \( i \) (0 or 1) and \( a \) is the vector that denotes the set of nearest neighbors. The field imposed on site \( i \) by the confining solid is given by \( \phi_i \). A simple cubic lattice has been used in all of the calculations and the interaction with the walls occurs via a nearest neighbor interaction with strength \( -\alpha\varepsilon \).
2.1. Static Behavior

2.1.1. Density Functional Theory (DFT)

The lattice density functional theories that are used to study the equilibrium behavior of confined fluids is described in this subsection. The mean field Helmholtz energy is given by

$$ F = kT \sum_i \left[ \rho_i \ln \rho_i + (1 - \rho_i) \ln (1 - \rho_i) \right] - \frac{\varepsilon}{2} \sum_i \sum_a \rho_i \rho_{i+a} + \sum_i \rho_i \phi_i $$

where $\rho_i$ is the mean density at site $i$. Similarly the grand free energy is given by

$$ \Omega = kT \sum_i \left[ \rho_i \ln \rho_i + (1 - \rho_i) \ln (1 - \rho_i) \right] - \frac{\varepsilon}{2} \sum_i \sum_a \rho_i \rho_{i+a} + \sum_i \rho_i (\phi_i - \mu_i) $$

where $\mu$ is the chemical potential. By minimizing $\Omega$ at fixed chemical potential; the solutions of the mean field equations for the grand canonical can be obtained. These yield the free energy and density distributions in these ensembles. The necessary condition for equilibrium leads to the following equations relating the chemical potential to the local density at site $i$. The necessary condition for minimizing the Gibb’s free energy at fixed temperature and overall density is

$$ \left( \frac{\partial \Omega}{\partial \rho_i} \right)_{\mu,\{\phi\},T} = 0 \quad \forall \ i \quad (2.4) $$

Imposing the condition in equation 2.4 on equation 2.3 yields the following expression for chemical potential at site $i$

$$ kT \ln \left[ \frac{\rho_i}{1 - \rho_i} \right] - \varepsilon \sum_a \rho_{i+a} + \phi_i - \mu = 0 $$

$$ \quad (2.5) $$
Solutions of the static MFT equations lead to the $\mu_i$ being uniform throughout the system. The following equation also helps establish the limiting behavior of the dynamic mean field theory for long times.

$$kT \ln \left[ \frac{\rho_i}{1 - \rho_i} \right] - \varepsilon \sum_a \rho_{i+a} + \phi_i - \mu = 0 \quad \forall \ i$$

In the grand ensemble these equations are solved iteratively for the density distribution, $\{\rho_i\}$, at fixed uniform $\{\mu_i = \mu\}$, T and $\{\phi_i\}$.

In the DFT calculations presented in this study the bulk vapor state relative to the saturated vapor state is discussed. The chemical potential for saturated vapor is given by $\mu_0 = -3\varepsilon$ for a simple cubic lattice gas in the DFT. The temperature is taken relative to the bulk critical temperature. In the DFT the bulk critical temperature is given by $kT_c/\varepsilon=1.5$. The reduced temperature $T^*$ is given by $T/T_c$. The adsorption isotherms are calculated at a reduced temperature $T^* = 1$ which is two thirds of the bulk critical temperature [28].

### 2.2. Dynamic behavior

The density functional theories described in section 2.1 allow us to calculate the free energy and density distribution for fluids inside porous materials for equilibrium states of the system. In formulating theories to describe relaxation dynamics under confinement, it is advantageous to focus on approaches that have an inbuilt description of the thermodynamics from DFT. A similar approach was developed by Cahn [39] who incorporated the Cahn-Hilliard square gradient free energy functional [40] into a diffusion equation and used the resulting equation to describe the early stages of spinodal
decomposition. Following this approach Monson [7] developed the dynamic mean field theory (DMFT). DMFT [7, 17, 18] gives an approximation of the time evolution of the density distribution averaged over an ensemble of kinetic Monte Carlo simulations of the lattice gas model using Kawasaki dynamics. It provides a theory of the dynamics of the system consistent with the thermodynamics in mean field theory [7] as described in section 2.1.1. The DMFT approach of Monson closely follows the work of Gouyet and coworkers [17] which in turn is based on the seminal contributions of Martin [26] and Penrose [27], and yields equations identical to those of Matuszak et al [18].

2.2.1. Dynamic Mean Field Theory (DMFT)

In DMFT the evolution of the ensemble average density at site $i$ can be expressed exactly in terms of the net fluxes from site $i$ to its nearest neighbor sites $i + a$ as follows

$$\frac{\partial \rho_i(t)}{\partial t} = -\sum_a \omega_{i,i+a}(\{n\}) n_i(1-n_{i+a}) - \omega_{i+a,i}(\{n\}) n_{i+a}(1-n_i)$$

(2.7)

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

Applying the mean field approximation we obtain

$$\frac{\partial \rho_i}{\partial t} = -\sum_a [\omega_{i,i+a}(\{\rho\}) \rho_i(1-\rho_{i+a}) - \omega_{i+a,i}(\{\rho\}) \rho_{i+a}(1-\rho_i)]$$

(2.8)
Using the expressions for the transition probabilities, equation 2.8 can be solved to obtain \( \{ \phi_i \} \) as a function of \( t \). The mean field approximation for the Metropolis transition probabilities in Kawasaki dynamics are given by Matuszak et al [18] as follows

\[
\omega_{ij}(\{\rho\}) = \omega_{ij} \exp\left(-E_{ij} / kT\right)
\]  \hspace{1cm} (2.9)

where

\[
E = \begin{cases} 
0 & E_j < E_i \\
E_j - E_i & E_j > E_i 
\end{cases}
\]  \hspace{1cm} (2.10)

and

\[
E_i = -\varepsilon \sum_a \rho_{i+a} + \phi_i
\]  \hspace{1cm} (2.11)

Using equations 2.8 and 2.9 we obtain

\[
\frac{\partial \rho_i}{\partial t} = -\sum_a \omega_{i,j+a}(\{\rho\}) \rho_i (1 - \rho_{j+a}) [1 - \exp\{ (\mu_i - \mu_{i+a}) / kT \}]
\]  \hspace{1cm} (2.12)

This expression shows that the long time limit of the DMFT equations, where flux approaches zero, is associated with uniform chemical potential throughout the system. \( \omega_0 \) is the jump rate in the absence of interactions in the system and can be used to define a dimensionless time and will be discussed in detail in the next subsection.

The above description of the DMFT has taken into account two different stages of mean field type approximations. In equation 2.7 the occupancies have been replaced by their averages. This results in the solution of the mean field kinetic equations coinciding with the DFT solution in the long time limit. In equation 2.8 the occupancy factors have been written as the fluid density. This results in eliminating the vacancy correlations in this model. These approximations lead to the solution of the mean field kinetic equations coinciding with the DFT solution in the long time limit.
2.2.2. Dynamic Mean Field Theory: Implementation

DMFT is implemented as follows. For a given pore geometry the DFT equations are solved at an initial value of the activity (chemical potential) to give the initial density distribution in the system. A layer of sites at the perimeter of the system is added where the density is fixed at the value associated with the activity of the state to which the system has to be evolved. The fixed density layer acts as a source/sink of fluid during the dynamics. The system is then evolved by numerically solving equation 2.12. Euler’s method has been used to numerically solve equation 2.12 in this study. For Euler’s method to be of acceptable accuracy for time; steps less than about $\omega_0 t = 0.1$ have been used. All calculations in this work are for nearest neighbor walls with a wettability of $\alpha=3.0$ and at a reduced temperature $T^*=kT/\epsilon=1.0$ as described in section 2.1.
CHAPTER 3
DFT: AN APPLICATION TO 3DOM CARBON

The void spaces in many porous materials consist of networks of interconnected pores. Fluids confined in such spaces exhibit interesting behavior in relation to condensation and evaporation. In the past such materials have been viewed as a network of independent pores with variation in pore size. Gas adsorption measurements have been used to study and characterize these materials [6, 41]. However the ability to model the thermodynamics of fluids confined in model network structures with classical density functional theory gives a better understanding of these systems as shown in a number of recent studies [10, 16, 42-51]. The use of lattice gas models also makes the density calculations in 2D and 3D systems more feasible.

DFT has been used by Monson and co-workers to study simple pore geometries like slit pores [22] and duct pores [28]. More complex pore networks such as a network of slit pores with variation in pore sizes and a network of ink-bottle pores have been studied using DFT [29]. Disordered pore networks such as Vycor glass [52] have also been successfully studied using DFT [28,38,51,53]. In addition to providing results in excellent agreement with experimental data, DFT serves as a tool to better understand the thermodynamics of adsorption and the effect of pore structure on fluid behavior. DFT will thus be important in the study of the fluid behavior in 3D0m carbon with regards to the effect of pore connectivity, windows and pore size distribution which have been studied in detail.
3.1. Lattice gas model of 3DOm carbon

As stated in chapter 2 the use of lattice gas models is an attractive option due to the resulting decrease in computational time as compared to off-lattice models. An understanding of the experimental synthesis of 3DOm carbon would be useful in the setting up of the model.

Three-dimensionally ordered mesoporous (3DOm) carbons are obtained by templating colloidal crystals formed from lysine-silica nanoparticles [31]. These materials have been developed by Tsapatsis and co-workers using the methods described by Yokoi et al. [54]. A solution containing furfuryl alcohol and oxalic acid is impregnated within an arrangement of packed silica nanoparticles. This arrangement is heated to allow polymerization to occur and to carbonize the polymer. The silica particles are removed by dissolving in a KOH solution. The resulting structure consists of spherically shaped pores connected by windows (Figure 3.1).

![Figure 3.1](image_url)  
**Figure 3.1.** Formation of 3DOm carbon template (right) from silica nanoparticles [55]

The setting up of the lattice model for this study has been done in a manner similar to the above experimental method. The model 3DOm carbon structure has been set up by coarse graining of hard spheres. The centers of the hard spheres are placed at
the sites of a FCC lattice to replicate the arrangement of the silica nanoparticles. In this study system sizes of 108 and 256 spheres have been chosen. This is done to create a system that closely resembles the experimentally synthesized structure and also the system size is suitable enough so that the computations are not expensive. The spheres are then allowed to expand till the radii of the spheres reach the desired value. The overall size of the lattice depends on the size of the pores. For example, for a system with 108 spherical pores each of size 18 lattice sites in diameter the overall lattice dimension turns out to be 90 lattice sites in all three directions. To introduce windows in the system the radii of the spheres were adjusted to allow for a degree of overlapping. Figure 3.2 illustrates the coarse grained model of the 3DOm carbon. In the illustration the grey sites are the solid structures that surround the spherical voids. The next step in the project was to study the fluid behavior in a disordered system. For the setting up of a model 3DOm carbon network with a disordered arrangement of pores, the hard spheres were reduced in size and were first allowed to attain a random arrangement through a Monte Carlo simulation. The spheres were allowed to attain a new configuration in a manner in which the center of mass of the system was conserved. The spheres were then allowed to expand to incorporate windows in the system. Another variant of the system was to introduce pore size distribution. This was done by sampling hard spheres of different sizes from a normal distribution of differently sized hard spheres. These methods are discussed in more detail in the coming sections.
Figure 3.2. Lattice model of a 3DOm carbon established from coarse graining of hard spheres
3.2. Results

3.2.1. Static behavior: Ordered network of 3DOm carbon

Two versions of the 3DOm geometry have been considered in this study. The first version has the spherical pores connected by windows and in the second version the pores are independent of each other. The entire system is in contact with a bulk lattice gas. 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. For both the systems the pore diameter was set at 18 lattice constants and for the system with windows, the width of the windows were 8 lattice constants.

The results obtained from static DFT in the grand canonical ensemble are represented in Figure 3.3 which shows the two adsorption isotherms and the free energy isotherms for the two geometries under study. The solutions on the adsorption/desorption isotherm were obtained by starting from a low/high relative pressure $P/P_o$ and increasing/decreasing the relative pressure in a series of steps, with the solution at each state forming the initial guess for the solution at the next state. $P_o$ is the pressure of the bulk saturated vapor. The density plotted is averaged over a cube in the middle of the pore structure. This is done to reduce the effect of the boundaries.
Figure 3.3. Adsorption/desorption isotherms for 3DOm pore network with interconnected pores (full line) and for independent pores (dashed line)

The isotherms show two increases in density. The increase at lower pressure corresponds to the monolayer formation, 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. 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. The adsorption in both the systems proceeds through capillary condensation. The condensation occurs through the formation of a liquid nucleus which then propagates and fills the pore. This is associated with a nucleation barrier which is related to the vapor stability limit. From the isotherm it is apparent that the adsorption in
both the systems takes place at the same pressure. This suggests that the presence or absence of windows does not affect the process of adsorption. The difference, however, lies in the desorption step. Specifically, two observations are notable from Figure 3.3. First, in both the cases desorption occurs at a point well below the vapor-liquid equilibrium point. Second, the desorption for the system with independent pores occurs at a pressure lower than that of the system with windows. The desorption in these pore networks proceeds through either the pore blocking percolation or cavitation. For the pore system with the pores connected by windows the pores empty through the pore blocking mechanism. The fluid in the larger pores persists until the fluid in the windows has emptied. For the system with independent pores; the pores empty through cavitation. As the relative pressure is decreased the liquid in the pores is stretched until it reaches its stability limit and then cavitates. The cavitation mechanism is associated with a nucleation barrier associated with the formation of a liquid droplet. Contrary to this, the pore blocking mechanism is associated with the crossing of the free energy barrier associated with the evaporation of the liquid from the windows. As a result cavitation occurs at a pressure lower than the pressure at which pore blocking occurs. This is due to the size of the windows being much smaller as compared to the size of the pores. This confirms the second observation from Figure 3.3. The free energy isotherms in Figure 3.3 have two branches. The two branches are associated with the liquid and vapor states of the fluid confined in the pore. The point at which these two branches intersect is the point of vapor liquid equilibrium. The states to the right of this point are associated with the metastable pore vapor states and to the left of the vapor liquid equilibrium point are associated with the metastable pore liquid states. There is a greater metastability
associated with the liquid states than with the vapor states which results in desorption occurring at a pressure much lower than the vapor liquid equilibrium point.

Figure 3.4 shows visualizations of the density distributions for the system with isolated pores for representative states along the adsorption and desorption branches of the isotherm. These visualizations are the cross sections of the pore structure taken at a point halfway along the length of the structure. Figure 3.4 shows that adsorption proceeds first through the formation of a monolayer on the pore walls (Figure 3.4(b)) followed by a pore filling condensation leading to a liquid state in the pore (Figures 3.4(d) and 3.4(e)). Desorption shown in figure 3.4 displays how the inner pores empty by cavitation. The pores that are closest to the bulk are the first to empty (Figure 3.4(g)). This is followed by the simultaneous emptying of the remaining pores (Figure 3.4(i)).

The visualizations of the density distributions for the system with interconnected pores are shown in Figure 3.5. Adsorption proceeds in a manner similar to the above case. Desorption however follows a series of steps. The pores that are closest to the bulk are the first to empty (Figure 3.5(g)). This is followed by the emptying of the inner pores in a step wise manner (Figure 3.5(h) and Figure 3.5(i)). The inner pores cannot empty unless the fluid in the surrounding pores has been emptied. This confirms the pore blocking mechanism.
Figure 3.4. Visualizations of the density distributions for states along the isotherm for adsorption in the model 3DOm pore network with isolated pores. The states on the left are for adsorption and those on the right for desorption. The values of $P/P_o$ for each state are as follows: (a) 0.002, (b) 0.1, (c) 0.877, (d) 0.879, (e) 0.99, (f) 0.99, (g) 0.8, (h) 0.612, (i) 0.610, (j) 0.1
Figure 3.5. Visualizations of the density distributions for states along the isotherm for adsorption in the model 3DOM pore network with interconnected pores. The states on the left are for adsorption and those on the right for desorption. The values of $P/P_0$ for each state are as follows: (a) 0.002, (b) 0.1, (c) 0.877, (d) 0.879, (e) 0.99, (f) 0.99, (g) 0.675, (h) 0.673, (i) 0.671, (j) 0.1
3.2.2. Study of fluid behavior in a single isolated sphere

To get a better understanding of the fluid behavior in a spherical pore DFT was applied to study the fluid behavior in a single isolated sphere. The effect of increasing the size of the pore on the condensation step was investigated. The size of the sphere was varied from a width of 6 lattice sites to 50 lattice sites. Figure 3.6 shows the condensation and desorption points for varying pore sizes. It was observed that as the size of the pore increased the point at which condensation occurred moved closer to the vapor saturation pressure. However the condensation would occur below the vapor saturation pressure for all the pore sizes. This shows that the vapor stability limit always is below the saturation pressure for a spherical pore. As the pore size increases the desorption points approach the bulk spinodal for the liquid phase. For the large pores the liquid inside the pore approaches the conditions of the bulk liquid and cavitation of the liquid occurs near the bulk liquid spinodal. These findings are in line with the work by Rasmussen et al. [56]. Similar work has been done by Neimark and coworkers who studied the adsorption in spherical cavities [57]. They compared the results with the Derjaguin-Broekhoff-de Boer (DBdB) theory [58] for capillary condensation in ink-bottle spherical cavities. It was observed that for pores with sufficiently small neck diameters the desorption step occurs via spontaneous cavitation and at a pressure limited by the liquid spinodal pressure. The DBdb theory predicts condensation to occur through the filling of the necks of the pores followed by a development of an instability of the adsorbed film on the pore walls. These results closely resemble the results predicted by our model as shown in Figure 3.6.
Figure 3.6. Condensation, vapor-liquid equilibrium and evaporation points versus inverse pore size for spherical pores
The systems discussed above are for a highly ideal case. It is not possible to synthesize experimentally such an ordered arrangement of hard spheres with uniform pore size [31]. The disorder can result from random arrangement of hard spheres and variation in pore sizes. These various cases of disorder are discussed in the coming subsections.

### 3.2.3. Static behavior: 3DOm carbon network with disordered arrangement of pores

One of the structural irregularities in a 3DOm pore network is the disorder that arises due to the silica nanoparticles not being able to attain a fully ordered arrangement during the synthesis of a 3DOm carbon structure. In this subsection the effect of the disordered arrangement of pores on static behavior of fluid is discussed.

To study the effect of disorder in arrangement of the pores on fluid behavior in a 3DOm system, several replicates of a disordered system of a 3DOm carbon structure obtained by a Monte Carlo random arrangement of hard spheres was generated and the adsorption isotherm was averaged over all these replicates. A cross section of one such disordered structure is shown in Figure 3.7. The grey sites are the spherical voids and the white area is the surrounding solid structure. It can be seen how the spheres are not aligned as compared to the ordered system and the different position of the spheres gives rise to windows of different sizes. Figure 3.8 shows the averaged isotherm for the disordered 3DOm system along with the isotherm for the ordered system. It is clear that the disorder in the arrangement of the pores does not have an effect on the condensation step. The pores fill at a pressure equal to the condensation pressure for the ordered
system. The desorption for disordered system does not occur at a fixed pressure suggesting that the pores do not empty all at once but there is selective emptying occurring. This could be due to the difference in the size of the windows which is brought about by the disordered arrangement of the pores. As the size of the windows affects the desorption as explained in the previous subsection this behavior is to be expected. This is evident on observing the visualizations of the fluid density in the system. Figure 3.9 shows visualizations of the density distributions for a disordered system. The adsorption proceeds in a manner similar to that for the ordered system with the pores filling up simultaneously when the nucleation barrier is reached. The desorption however takes place in a step wise fashion as seen in Figure 3.9(h) and Figure 3.9(i). The pores empty selectively with the pores with smaller windows emptying the last. This gives rise to a gradual desorption step and not a constant desorption pressure like in the ordered system.
Figure 3.7. Cross section of a model 3DOm carbon system with disordered arrangement of pores. The grey sites represent the spherical voids. White areas represent the surrounding solid.
Figure 3.8. Adsorption/desorption isotherms for 3DOm pore network for system with disordered arrangement of spheres (full line) and for ordered system (dashed line)
Figure 3.9. Visualizations of the density distributions for states along the isotherm for adsorption in the model 3DOm pore network with disordered arrangement of spheres. The states on the left are for adsorption and those on the right for desorption. The values of $P/P_o$ for each state are as follows: (a) 0.02, (b) 0.877, (c) 0.879, (d) 0.99, (e) 0.99, (f) 0.653, (g) 0.651, (h) 0.649
3.2.4. Static behavior: 3DOm carbon network with variation in pore size

Experimental adsorption studies on a 3DOm carbon system have shown that there exists a pore size distribution that resembles a normal distribution [32]. An experimentally synthesized 3DOm carbon structure can have spherical pores with different pore sizes. This could be due to the silica nanoparticles that are used to template the 3DOm carbon having variation in particle size. In order to introduce such a variation in pore size in our model a sampling of hard spheres of different sizes was done from a Gaussian distribution as shown in Figure 3.10. The mean value of the distribution is equal to the diameter of the pore in the absence of any variation in pore size. The spread of the distribution is suitably chosen such that all the spheres will remain connected to each other. The spheres are then placed on the sites of a FCC lattice and are allowed to expand to account for windows in the system. The resulting variation in pore size results in the spheres have different size windows. The resulting discrete pore size distribution is also plotted in Figure 3.11. Due to the coarse grained nature of the model the resulting pore size distribution will be slightly different from the initial normal distribution from where the samples were drawn. For the case with the system of 256 spheres it is seen that there is a wider range of resulting pore sizes as compared to the case for 108 spheres. Figure 3.12 shows a cross section of a model 3DOm carbon network with variation in pore sizes for a system size of 108 and 256 spheres. The grey areas show the spherical pores and the white areas are the surrounding solid. The variation in pore size can be seen in both the cases. Also due to the variation in pore size there is a difference in the window sizes as well.
The results for the system size of 108 spheres are discussed first. The adsorption isotherm is averaged over 100 replicates that have been generated as described above and is shown in Figure 3.12. The resulting isotherm resembles a type H1 isotherm with rounded edges indicating variation in pore size in the system [7, 8]. The condensation in this case occurs gradually and not at a fixed pressure indicating possibilities of localized condensation. The pores that are smaller in size will have a smaller nucleation barrier and hence will fill at a pressure lower than that at which the larger pores fill up. The desorption proceeds sequentially as well. The variation in pore size as well as resulting variation in window size gives rise to increased pore blocking effects with the emptying of one pore depending on the state of its neighbors. The visualizations of the density distribution for a disordered system is shown in Figure 3.13. The sequential condensation of pores becomes apparent from Figure 3.13(b) and Figure 3.13(c). The pores that are smaller in size fill at a lower pressure than the pores of a larger size. The pores also empty sequentially as shown in Figure 3.13(h) and Figure 3.13(i). The pores have windows of different sizes due to the variation in pore size and this leads to a sequential emptying of the pores.
Figure 3.10. Theoretical pore size distribution (continuous line) from which sampling of hard spheres is taken and pore size distribution (points) obtained from coarse graining of hard spheres. (a) System size of 108 spheres. (b) System size of 256 spheres
Figure 3.11. Cross section of a model 3DOm carbon system with variation in pore size. The grey sites represent the spherical voids. White areas represent the surrounding solid. (a) System size of 108 spheres. (b) System size of 256 spheres
Figure 3.12. Average adsorption/desorption isotherms for 3DOm pore networks with pore size variation for a system with 108 spheres.
Figure 3.13. Visualizations of the density distributions for states along the isotherm for adsorption in the model 3DOm pore network with pore size variation for a system with 108 spheres. The states on the left are for adsorption and those on the right for desorption. The values of P/P₀ for each state are as follows: (a) 0.002, (b) 0.891, (c) 0.909, (d) 0.914, (e) 0.99, (f) 0.99, (g) 0.760, (h) 0.758, (i) 0.738, (j) 0.678
In order to study the effect of pore size variation in more detail, a system with increased number of spheres was considered. The increase in number of spheres gave an opportunity to study the system with more number of spheres of different sizes. This resulted to a greater pore size variation which would have an interesting effect on fluid behavior. The structure studied had a system size of 256 spheres as shown in Figure 3.11. The adsorption isotherm was calculated over a 100 replicates of the model 3DOm carbon structures. The resulting average isotherm is plotted in Figure 3.14 along with the isotherm for the system with 108 spheres. It can be seen that both the isotherms are similar. For the system with 256 spheres the desorption branch show step decreases in density as opposed to a smooth transition which was observed in the system with 108 spheres. This could be due to the pore blocking effect due to the greater variation in pore size which results in different window sizes causing the pores to empty in a step like manner. It could also be due to the fact that the number of replicates chosen is too small to average the isotherm over. Further studies could include calculating the isotherm over a greater number of replicates.

Figure 3.15 shows the visualizations for the density distributions at various points on the isotherm. Due to an increased variation in pore size because of larger system size there is a more sequential condensation of fluid in pores with more localized regions of condensation (Figure 3.15(b) and Figure 3.15(c)). The desorption step shows a more sequential emptying of pores (Figure 3.15(i) and Figure 3.15(j)).
Figure 3.14. Average adsorption/desorption isotherms for 3DOm pore networks with pore size variation for a system with 256 spheres (straight line) and for a system with 108 spheres (dashed line)
Figure 3.15. Visualizations of the density distributions for states along the isotherm for adsorption in the model 3DOm pore network with pore size variation for a system with 256 spheres. The states on the left are for adsorption and those on the right for desorption. The values of $P/P_o$ for each state are as follows: (a) 0.02, (b) 0.881, (c) 0.895, (d) 0.900, (e) 0.917, (f) 0.99, (g) 0.99, (h) 0.760, (i) 0.745, (j) 0.727, (k) 0.680, (l) 0.612
3.3. Comparison with experimental results

The model that has been developed of the 3DOm carbon has incorporated most of the structural characteristics of the experimentally synthesized 3DOm carbon. The model has introduced disorder in the arrangement of hard spheres. The effect of variation in pore size has also been studied. The model can be validated by comparing the results with the adsorption isotherms that have been obtained experimentally. Cychosz et al., has conducted the nitrogen adsorption on 3DOm carbon structures with pore sizes 10nm, 20 nm, 30 nm and 40 nm at 77K [32]. The average isotherm for the system with variation in pore size is compared to the experimental isotherms. Figure 3.16 shows the normalized isotherm obtained from DFT calculations along with the experimental normalized isotherms for the 20 nm and 30 nm 3DOm carbon. It can be seen that the isotherm of the model shows a close agreement with the isotherm of the 30 nm 3DOm carbon. The average pore size for the model 3DOm carbon is 18 lattice sites. Hence for this model one lattice site is equivalent to 1.66 nm. This can be used as a basis for future calculations.
Figure 3.16. Normalized adsorption/desorption isotherms for model 3DOm pore networks (straight line) and nitrogen adsorption isotherms at 77K for 20 nm 3DOm carbon (▲) and for 30 nm 3DOm carbon (●)
3.4. Summary

DFT has been useful in understanding the mechanisms governing the fluid behavior in 3DOm carbon porous networks. The effect of windows on desorption is a key finding and is useful in the classification of these materials. The presence of windows does not have an effect on the condensation pressure. Condensation proceeds via the bridging of the windows and the formation of a liquid film on the pore surface. The liquid then fills the pore when there is a development of instability of the film on the pore walls as predicted by the DBdB theory. For the pore network with isolated pores; desorption takes place via cavitation and for the system with interconnected pores, desorption occurs via pore blocking. Also the effect of spatial disorder as well as pore size variation was studied. The selective desorption that arises from disorder in the system due to spatial disorder as well as from pore size variation was studied. The DFT provides a better understanding of the nucleation barriers that are associated with adsorption. A comparison with experimental studies also revealed reasonable agreement of experimental results with the DFT calculations. A more detailed understanding of the mechanisms of nucleation is possible by studying the dynamics of adsorption which will be discussed in the next chapter.
CHAPTER 4
DMFT: AN APPLICATION TO 3DOm CARBON

The results in the previous chapter have shown how the classical density functional theory (DFT) has provided a better understanding of the thermodynamics of fluids confined in 3DOm carbon networks. The effect of pore structure, windows and variation in pore size on fluid behavior could be studied. In this chapter the study is taken a step further by considering the dynamic behavior of adsorption and desorption in 3DOm carbon network systems. A study of the adsorption dynamics can help understand the mass transfer resistances associated with fluid uptake and also explain how the pore structure affects the nucleation mechanisms during condensation and evaporation. In the past there has been an interest in studying the dynamics of adsorption in pore networks using of lattice models [37]. Such studies were helpful in understanding nucleation mechanisms such as cavitation [36-37]. DMFT has been used by Monson and co-workers to study fluid adsorption dynamics in complex pore networks like ink bottle pore networks [29]. Casselman et al., applied the DMFT to a three dimensional slit pore lattice gas model [33]. This was an extension of the dynamic studies on a 2D slit pore by Monson [7]. Hence a pathway has been paved for application of DMFT to study the dynamics in a complex 3D pore network like 3DOm carbon.

For the implementation of DMFT in a model 3DOm carbon; lattice sites were added on all sides of the structure. The thickness of the region was kept at 10 lattice sites. This was done in order to replicate the conditions of a bulk gas surrounding the porous structure. The DMFT was implemented by allowing the system to evolve with time from
an initial state to a final state on the adsorption isotherm. An additional layer of sites was then added on the periphery of the system. The density in this layer was maintained corresponding to the chemical potential of the final state of the system. This acted as a source for the fluid during dynamics. The density distribution of the system was taken as the DFT solution for the chemical potential of the initial state of the system. The DMFT equations were then solved with Euler’s method with a step size of $\omega_0 t = 0.1$ and a reduced temperature of $kT/\varepsilon = 1$. These parameters were sufficient to observe the phenomena occurring during pore condensation in the system.

4.1. Results

4.1.1. Dynamic behavior: Ordered network of 3DOm carbon

Figure 4.1 shows the uptake dynamics for the interconnected pore system during a quench from a relative pressure at a dilute gas bulk state to one close to bulk saturation. Both the averaged density throughout the pore structure and the density averaged over an inner cube are plotted. The two curves show the evolution of the density at different regions in the porous structure during the dynamics. The pore averaged density shows different regimes of behavior. The regimes can be better understood by observing the visualizations of the density distribution at various stages of the dynamics as shown in Figure 4.2. The short time behavior is associated with the filling of the windows at the corners of the system (Figure 4.2(a)). This liquid then propagates to fill the surrounding pore (Figure 4.2(b) and Figure 4.2(c)). The windows at the corners are the first to fill as these regions have the highest amount of fluid flux from the bulk phase. At higher time scales the behavior is associated with the merging of the propagating liquid at the center
of the pore (Figure 4.2(e)). From Figure 4.1 we see that the density at the center of the pore is always less than the pore averaged density throughout the dynamics indicating the absence of any fluid at the center of the pore structure at the short time scales. The density at the center of the pore also shows a steady increase indicating that once pores are filled with liquid, it is not pulled away when other nucleation events are occurring within the pore structure. The source of the fluid that contributes to the density increase in the neighborhood nucleation events; is from the bulk phase.
Figure 4.1. Density versus time for a model 3DOm carbon network during a quench of the relative activity from $\lambda/\lambda_o=0.00674$ to $\lambda/\lambda_o=0.951$. The dashed line gives the average density throughout the pore network and the full line gives the average density in the middle of the pore network.
Figure 4.2. Visualizations of the density distribution for a model 3DOm carbon network during a quench of the relative activity from $\lambda/\lambda_o=0.00674$ to $\lambda/\lambda_o=0.951$: (a) $\omega_b t=5000$, (b) $\omega_b t=8000$, (c) $\omega_b t=27500$, (d) $\omega_b t=42500$, (e) $\omega_b t=62500$, (f) $\omega_b t=75000$
The desorption dynamics during a quench from a relative pressure at a state close to bulk saturation to one in a dilute gas bulk state has also been considered. The plot of density versus time is shown in Figure 4.3, again averaged both over the entire pore structure and in the middle of the pore structure. The density distribution visualizations are shown in Figure 4.4. Since there is a direct contact with the bulk gas there is no nucleation barrier to be overcome for desorption to take place. Desorption proceeds through the emptying of the liquid into the bulk phase at the vapor liquid interface (Figure 4.4(a)). The resulting vapor liquid menisci retract through the pore (Figure 4.4(c)) with the pores in the center of the structure emptying the last (Figure 4.4 (e)). We see a formation of a bridge like structure in Figure 4.2(b) which then breaks leaving behind an adsorbed layer of liquid on the pore surface. This liquid can desorb by emptying into the vapor at the center or the pore and also by mass transfer into the bulk through the windows of the pore. Figure 4.3 shows a gradual decrease in density for the pore averaged density. The density at the center of the pore is greater than the pore averaged density indicating the inner pores empty at higher time scales.
Figure 4.3. Density versus time for a model 3DOm carbon network during a quench of the relative activity from $\lambda/\lambda_o=0.951$ to $\lambda/\lambda_o=0.00674$. The dashed line gives the average density throughout the pore network and the full line gives the average density in the middle of the pore network.
Figure 4.4. Visualizations of the density distribution for a model 3DOm carbon network during a quench of the relative activity from $\lambda/\lambda_o=0.951$ to $\lambda/\lambda_o=0.00674$: (a) $\omega_o t=500$, (b) $\omega_o t=1500$, (c) $\omega_o t=2000$, (d) $\omega_o t=3500$, (e) $\omega_o t=5000$, (f) $\omega_o t=6000$. 
4.1.2. Dynamic behavior: 3DOm carbon network with variation in pore size

As discussed earlier in the previous chapter, imperfections exist in the porous structure and their effect on the dynamics of adsorption has to be studied. The method employed here is similar to the one described in section 3.2.4. The variation in pore is introduced into the model by sampling 108 hard spheres from a normal distribution. These hard spheres are then placed on an FCC lattice and are then allowed to expand to introduce windows. 20 such replicates of model 3DOm carbon structures were generated with variations in pore size. The density profile with time was averaged over these replicates.

The plot of density vs time shown in Figure 4.5 is averaged both over the entire pore structure and in the middle of the pore structure. The nature of this curve is similar qualitatively and quantitatively to the plot in Figure 4.3 suggesting that the variation in pore size does not affect the overall mechanism of adsorption. Visualizations of the density distribution at various stages of the dynamics are shown in Figure 4.6. It can be seen from the visualizations that there exist parts in the porous structure where localized condensation occurs. The entire pore structure fills in an asymmetric manner. This is due to the variation in size of the windows. Figure 4.6(a) shows the filling of smaller windows while larger windows still remain empty. The liquid in these windows then propagate to fill the surrounding pores (Figure 4.6(b)). Larger windows remain empty at the start as sufficient time has not elapsed in order for nucleation to occur. Pores that are smaller in size also fill first at shorter times as compared to the larger pores (Figure 4.6(c)). At larger time scales the larger windows fill with liquid (Figure 4.6(e)). The liquid propagates to meet at the center of the pore (Figure 4.6(f)). The effect of localized
condensation is not evident from Figure 4.5. The plot of the pore averaged density does not show a step like behavior. Since the density profile has been averaged over a number of replicates the plot of density shows a gradual increase.
Figure 4.5. Density versus time for a model 3DOm carbon network with variation in pore size during a quench of the relative activity from $\lambda/\lambda_o=0.00674$ to $\lambda/\lambda_o =0.951$. The dashed line gives the average density throughout the pore network and the full line gives the average density in the middle of the pore network.
Figure 4.6. Visualizations of the density distribution for a model 3DOm carbon network with variation in pore size during a quench of the relative activity from $\lambda/\lambda_o = 0.00674$ to $\lambda/\lambda_o = 0.951$: (a) $\omega_o t = 5000$, (b) $\omega_o t = 8000$, (c) $\omega_o t = 27500$, (d) $\omega_o t = 42500$, (e) $\omega_o t = 62500$, (f) $\omega_o t = 75000$
The desorption dynamics for a model 3DOm carbon structure with variation in pore size has been considered. The replicates with variations in pore size had been set up in a similar manner to the one described above and the density profile has been averaged over these replicates. The desorption dynamics is calculated by allowing the system to evolve from a state where the structure is filled with liquid to a dilute gas phase. The plot of density vs time in Figure 4.7 is similar to the density profile for the case of the ordered system. The pore averaged density shows a gradual decrease with time. Visualizations of the density distributions also show no regions of localized evaporation. Since the pore structure is in contact with the bulk on all sides there is no nucleation barrier to be overcome. The variation in pore size does not have a significant effect on the manner in which the pore empties. There is some amount of asymmetry in the emptying of the pores closer to the bulk (Figure 4.8(b)) but this effect is less predominant as the vapor liquid interface moves to the center of the pore (Figure 4.8(e)).
Figure 4.7. Density versus time for a model 3DOm carbon network with variation in pore size during a quench of the relative activity from $\lambda/\lambda_o=0.951$ to $\lambda/\lambda_o=0.00674$. The dashed line gives the average density throughout the pore network and the full line gives the average density in the middle of the pore network.
Figure 4.6. Visualizations of the density distribution for a model 3DOm carbon network with variation in pore size during a quench of the relative activity from $\lambda/\lambda_o=0.951$ to $\lambda/\lambda_o=0.00674$: (a) $\omega_b t=500$, (b) $\omega_b t=1800$, (c) $\omega_b t=3000$, (d) $\omega_b t=5000$, (e) $\omega_b t=6500$, (f) $\omega_b t=9000$
4.2. Summary

In this chapter we have discussed the application of DMFT to the dynamics of capillary condensation and evaporation in model pore networks. The results show the benefits of having a theory of the dynamics that is consistent with a realistic description of the thermodynamics via DFT. The nucleation mechanisms for adsorption were studied for an ordered pore system. Adsorption takes place via the formation of a liquid bridge at the windows of the pore which then propagates to fill the pore. The regions of the pore closest to the bulk experience most flux of fluid and are the first to fill resulting in asymmetric filling of the pores. The desorption takes place via the formation of vapor liquid menisci that retract into the pore emptying it. The effect of pore size variation on adsorption dynamics has been investigated as well. Variation in pore size results in localized condensation within the pore structure with the liquid first filling at the smaller windows at shorter time scales. This results in the smaller pores filling with liquid while larger pores remain empty. This effect is not significant in desorption with the variation in pore size having little effect on the emptying of the pores.
CHAPTER 5

CONCLUSIONS AND SUGGESTIONS FOR FUTURE WORK

The aim of this research project was to study the thermodynamics of fluid adsorption and dynamics associated with the nucleation mechanisms of fluids in 3DOm carbon structures. The theories employed for this were the Density Functional theory (DFT) and the Dynamic Mean Field theory (DMFT) as developed by Monson [7]. Both of these theories have been discussed in Chapter 2 and their implementations for this study have been elaborated.

Chapter 3 discusses the application of DFT to variants of a model 3DOm carbon structure. In the ordered structure the effect of windows on fluid behavior was studied. The presence of windows while not having an effect on adsorption gave rise to a pore blocking effect during desorption. Adsorption depends on the size of the pore being associated with the vapor stability limit of the fluid in the pore. For the system with windows present desorption occurs via a pore blocking mechanism in which the windows are the first to empty followed by the inner pores. The study was then extended to investigate the effect of spatial disorder on fluid behavior. Replicates of systems with disorder in the arrangement of hard spheres were generated and an average adsorption isotherm was calculated over all these replicates. It was observed that the spatial disorder does not have an effect on the adsorption pressure as the pores are all of the same size. However due to the disordered arrangement of the windows there is a difference in the windows; which gives rise to selective desorption with the smaller windows emptying first followed by the larger windows. Finally the last structural effect studied was the
effect of variation in pore size. Variation in pore size had an effect on both adsorption and desorption. During adsorption the pores that were smaller in size filled first followed by the larger pores giving rise to areas of selective condensation. Desorption proceeds selectively again due to variation in window size.

In chapter 4 the dynamics of adsorption and evaporation have been described using DMFT. The study was carried out in a manner similar to the DFT studies in chapter 3; starting with an ordered system and moving on to systems with variation in pore size. The uptake dynamics for the ordered system revealed the formation of liquid bridges across the windows at shorter time regimes. These bridges propagate through the system filling the pores. Pore filling occurs asymmetrically with the areas of the pore closer to the bulk phase filling first due to less resistance to mass transfer. The desorption dynamics has also been discussed. Desorption takes place through the formation of menisci at the windows closest to the bulk which then propagate through the system emptying the pore. The effect of variation in pore size on the dynamics of adsorption was investigated. The uptake dynamics progressed through the selective formation of liquid bridges across the smaller windows first. Asymmetry due to selective formation of liquid bridges as well as asymmetry due to mass transfer resistances in filling of the pore was observed.

In the systems considered in this study, a conservative system size of 108 spherical pores was used in order to decrease the time required for calculations. However for future studies, it would be worthwhile to consider higher system sizes. An increase in system size would further the understanding of the structural effects especially in the investigation of pore size variation. Due to the coarse grained approach that was
employed in this study the pore size distribution that got generated in the model was of a small range. Increasing the system size can result in a wider range of pore size that can be used to better investigate the effect of pore size variation.

This study has only considered systems with completely wetting pore walls. It might be interesting to look at systems with partial wetting pore walls and study the nucleation mechanisms in them. Systems where different regions of the network have different wettability can also be investigated. Such a situation could be encountered in the study of adsorption of a liquid in the 3DOm carbon. The use of furfuryl alcohol as a monomer leads to the presence of aldehyde and ketone functional groups in the final structure. This would lead to regions of hydrophobicity and hydrophilicity in the structure resulting in complex mechanisms during dewetting processes of a fluid from such a structure. The effect of partial wetting surfaces has been studied by Edison and Monson who described the dewetting processes between various pore structures with hydrophobic surfaces [23].

Another interesting aspect could be the study of the effect of fluctuation events for individual molecular dynamics trajectories. The DMFT is implemented by averaging over an ensemble of trajectories. For this reason the nucleation processes studied here are limited to those where the final state lies beyond the stability limit of the confined liquid. Fluctuations can be added to the DMFT evolution equation in a manner described by Restango et al., and this might be useful for studying nucleation from metastable states closer to the equilibrium transition [59].

The coarse grained nature of the model does impart an amount of surface heterogeneity into the system. There has been work reported on the use of similar
heterogeneous models to describe fluid behavior in a slit pore. Schmidt and coworkers have put forward a DFT to describe quenched annealed mixtures [61-62]. Bryk et al., have studied the capillary condensation in a rough slit pore using the DFT approach [60]. Azevedo et al., put forward a model that takes into account heterogeneity in the pore geometries [64]. De Oliveira et al., developed the heterogeneous surface mixed model that was used to calculate the pore size distribution of activated carbon [65]. One aspect of future work could be to check the feasibility of the features in these models to describe the fluid behavior in a model 3DOm carbon structure.

While the results of this research project have been extremely useful in the understanding of a very complex pore network, namely 3DOm carbon; the versatility of the theories involved in this study opens the door to immense possibilities.


