APPLICATION OF NANOPOROUS MATERIALS IN MECHANICAL SYSTEMS

A Dissertation

Presented to

The Graduate Faculty of the University of Akron

In Partial Fulfillment

of the Requirements for the Degree

Doctor of Philosophy

Xinguo Kong

August, 2006
ABSTRACT

The rapid progress in processing techniques has greatly promoted the use of nanoporous materials in chemical engineering and biosciences fields for catalysis, selective absorption, purification, etc. The most attractive property of these materials is their high specific area which is typically in the range of 100-1000 m²/g. However, the application of them in mechanical systems was seldom reported.

In the current study, we perform first-order analyses and proof-of-concept experiments for a novel application of nanoporous materials in developing high-performance nanoporous energy absorption systems (NEAS) and thermally/electrically controllable active nanoporous systems (ANS). When nanoporous particles are immersed in a nonwetting liquid, due to the capillary effect the infiltration will not occur unless the applied pressure reaches the critical value \( p_{\text{in}} \). In a NEAS, as the pressure is reduced the confined liquid remains in the energetically unfavorable nanopores. Thus, the large increase in interface energy is “absorbed”. The energy absorption efficiency is higher by orders of magnitude than that of composites or shape memory alloys that are used in protection devices such as car bumpers and soldier armors.

For ANS, on the other hand, if temperature or electrical potential is changed, due to the variation in interface energy caused by the thermocapillary or electrocapillary effect, the confined liquid can “flow” into or out of the nanopores, resulting in a significant system volume change. Since this process is reversible, it leads to a “volume memory”
characteristic. The energy density and displacement of such a system are much higher than that of conventional intelligent materials such as piezoelectrics and magnetostrictives.

In addition to the experimental study, a framework has been established to analyze the aggregate response of nanoporous materials in context of effective phase transformation. The forced infiltration is characterized by the evolution of the number density of nanopore clusters. This model provides a scientific basis for the design of experiments for future study and the first-order system optimization.
ACKNOWLEDGMENTS

My deepest sense of gratitude is to my advisor, Dr. Yu Qiao, whose guidance, encouragement and patience have been so important to my work. Also, I wish to express my sincere thanks to my committee members: Dr. Wieslaw K. Binienda, Dr. Ping Wang, Dr. Michelle S. Hoo Fatt, Dr. Ernian Pan and Dr. Alper Buldum.

I also give my thanks to Falgun B. Surani, Dr. Aijie Han and Venkata K. Punyamurtula for their help with the experiments and the useful discussions.

I would also like to heartily thank my family for all of the support that they have given me over the years.
TABLE OF CONTENTS

LIST OF TABLES........................................................................................................viii
LIST OF FIGURES.....................................................................................................ix

CHAPTER
I  INTRODUCTION...........................................................................................................1

II STATUS OF DEVELOPMENT OF NANPOROUS MATERIALS..............................4
   2.1 General Definition of Nanoporous Materials................................................. 4
   2.2 Microporous Materials.....................................................................................6
   2.3 Mesoporous Materials.................................................................................... 8
   2.4 Macroporous Materials.................................................................................. 9

III PASSIVE NANPOROUS SYSTEMS....................................................................16
   3.1 Consideration of Fundamental Mechanism...................................................16
   3.2 Direct Observation of Liquid Infiltration........................................................17
   3.3 Thermal Effects on the Infiltration.................................................................19
      3.3.1 Experimental.........................................................................................19
      3.3.2 Results and Discussion.........................................................................21
      3.3.3 Resting Time Effects.............................................................................24
   3.4 NEAS Subjected to Dynamic Loadings...........................................................26

IV ACTIVE NANOPOROUS SYSTEMS.................................................................38


LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1 Comparison of characteristics of smart materials/systems</td>
<td>2</td>
</tr>
<tr>
<td>3.1 The defiltration pressure as a function of temperature</td>
<td>21</td>
</tr>
<tr>
<td>3.2 The system recoverability, $R_s = E_2^<em>/E_1^</em>$, as a function of the thermal treatment temperature, $T$, where $E_i^*$ is the absorbed energy in the $i$th loading-unloading cycle ($i = 1, 2$)</td>
<td>24</td>
</tr>
<tr>
<td>3.3 The postponed system recoverability, $R_p$, as a function of the resting time, $t_r$</td>
<td>25</td>
</tr>
</tbody>
</table>
LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1 Schematic representation of the synthesis of a nanoporous material by removing the template</td>
<td>11</td>
</tr>
<tr>
<td>2.2 A schematic diagram of zeolite molecular framework</td>
<td>11</td>
</tr>
<tr>
<td>2.3 Scanning electron micrographs (SEM) of (a) the top view of in situ b-oriented pure silica zeolite (PSZ) MFI films on stainless steel, (b) the cross-sectional view of (a), and (c) the schematic of the pore structure of b-oriented PSZ MFI zeolite film</td>
<td>12</td>
</tr>
<tr>
<td>2.4 HRTEM images taken down the b axis of MFI crystals in which the crystal lattice is visualized</td>
<td>13</td>
</tr>
<tr>
<td>2.5 The needle-like nanopore in the porous carbon with the imperfect packing or bending of graphene layers</td>
<td>14</td>
</tr>
<tr>
<td>2.6 (a) SEM microscopy of the mesoporous silica particles; (b) TEM microscopy of the particle surface; (c) the mesoporous structure (Carlos B, 2003)</td>
<td>14</td>
</tr>
<tr>
<td>2.7 Schematic diagram of the colloidal crystal</td>
<td>15</td>
</tr>
<tr>
<td>3.1 Wetting of different fluids. “A” shows a fluid with very high surface tension (and thus non-wetting), while “C” shows a fluid with very low surface tension</td>
<td>31</td>
</tr>
<tr>
<td>3.2 Schematic representation of the infiltration of a NEAS by external pressure</td>
<td>31</td>
</tr>
<tr>
<td>3.3 Pore volume histogram</td>
<td>32</td>
</tr>
<tr>
<td>3.4 The energy sorption isotherm: (a) the first loading-unloading cycle; (b) the second, third, and fourth loading-unloading cycles without thermal treatment; (c) after the immediate thermal treatment; and (d) after the postponed thermal treatment</td>
<td>32</td>
</tr>
<tr>
<td>3.5 Sorption isotherm varies at different temperatures: (a) the first infiltration cycle; (b) the second infiltration cycle</td>
<td>33</td>
</tr>
<tr>
<td>3.6 The thermal effect on the infiltration pressure</td>
<td>34</td>
</tr>
<tr>
<td>3.7 The system recoverability at different temperatures</td>
<td>34</td>
</tr>
</tbody>
</table>
3.8 Schematic diagram of the temperature dependence of $\Delta \gamma$ ........................................35

3.9 A schematic diagram of the experimental setup.........................................................35

3.10 The transmitted pulses measured in the output piston for a system consisting of 0.3g of nanoporous silica particles. The reference curve is the transmitted pulse of distilled water. The curves have been moved along the time axis......................36

3.11 The incident and reflected pulses in the input piston.............................................37

4.1 A schematic diagram of a liquid-solid interface......................................................49

4.2 Schematic diagrams of the wetting-nonwetting transition at different pressures ($p_2 > p_1$): (a) $|\partial \gamma_s^*/\partial T| > |\partial \gamma_{ls}/\partial T|$; (b) $|\partial \gamma_s^*/\partial T| < |\partial \gamma_{ls}/\partial T|$..................................................49

4.3 The experimental set-up for the thermally controllable active nanoporous smart system..................................................................................................................50

4.4 The infiltration curve for water-zeolite system at different temperatures..............50

4.5 (a) Close-up of the multichannel structure. (b) Sketch of the device geometry (side view) (M. W. J. Prins, 2001)........................................................................................................51

4.6 A schematic diagram of the nanoporous intelligent system ...............................51

4.7 The pressure variation, $\delta p$, and the change in interfacial energy difference, $\delta \gamma$, as functions of the applied potential difference......................................................52

4.8 A schematic diagram of the liquid interface in a nanopore.................................52

5.1 A schematic diagram of the effective phase transformation in a nanoporous particle.................................................................61

5.2 The distribution of the SPC number density integrated over $c$.............................61

5.3 The influences of the pressure difference and the pore size on the absorption time...62

5.4 The influence of $\dot{p}$ and $\beta$ on the absorption time. The characteristic time $t_1 = 1ms$ ..............................................................................................................62

6.1 Schematic diagram of the confined liquid in nanopore......................................72

6.2 Schematic diagram of a microporous particle.......................................................72

6.3 Evolution of the number density of EPCs............................................................73
6.4 Evolution of the average size and the total volume fraction of EPCs................73
6.5 Dewetting time as a function of $\dot{r}/\gamma$ and $\beta$.................................74

7.1 The mesoporous structure........................................................................84
7.2 The nonwetting flow confined in a mesopore under the external pressure, $p$....85
7.3 Schematic diagram of the growth of filled mesopore clusters......................86
7.4 Evolution of $n_c(\varphi,t)$, where $\varphi_0 = 2r/R$ is the characteristic angle......87
7.5 The saturation time as function of $p\mu^2/\rho\gamma^2$ and $R/\tilde{r}$.....................88
7.6 The saturation time as function of $t^* \dot{\rho} \mu^2/\rho \gamma^2$ and $\beta$...............89
CHAPTER I

INTRODUCTION

While the application of nanoporous material such as charcoal can be tracked back to the ancient Egypt era, the modern studies of nanoporous materials became active at the beginning of the 20th century. Nearly all the early research of that period was concentrated on the advanced sorption properties of natural nanoporous materials, e.g. zeolites and activated carbon as well as their applications in the protection masks and purification procedures. Since the post World-War II years, a large number of synthetic nanoporous materials including porous carbons, porous silica, and colloidal crystals have been developed and applied for the catalysis, separation of mixtures, and purification of water, sewages, air and soils, etc. However, although the importance of these materials has been well appreciated, currently their applications are limited in catalysis, selective absorption, and purification processes (A. Dabrowski et al, 2001; R. Kimmich et al, 2002). The studies of using nanoporous materials in mechanical devices are rare.

The smart materials, also known as shape memory materials, can be classified into (a) shape memory alloys (SMA) such as Ti-Ni/copper/iron based alloys and intermetallic compounds; (b) shape memory ceramics (SMC) such as mica/β-spodumene glass-ceramics and martensitic/ferroelectric ceramics; and (c) shape memory polymers (SMP) consisting of fixed and reversible phases, often with polyurethane as chain extenders. As temperature varies, the SMA and SMC can undergo diffusionless martensitic
transformation while the dominant process in SMP is glass transition. The critical temperature usually depends upon composition, processing condition, and thermal/mechanical treatment procedures. These phase transformations, which can also be induced by external pressure and magnetic/electric fields, result in significant thermalelastic or electroelastic deformation and, as a result, the material exhibit shape memory characteristics.

Table 1.1 Comparison of characteristics of smart materials/systems

<table>
<thead>
<tr>
<th>Properties</th>
<th>Nanoporous smart system</th>
<th>Ti-Ni Shape-memory alloy</th>
<th>Piezoelectric</th>
<th>Magnetostrictive</th>
</tr>
</thead>
<tbody>
<tr>
<td>Energy density (J/g)</td>
<td>3-30</td>
<td>0.3-2.0</td>
<td>0.05</td>
<td>0.1</td>
</tr>
<tr>
<td>Maximum strain</td>
<td>60%</td>
<td>10%</td>
<td>&lt;0.5%</td>
<td>1%</td>
</tr>
</tbody>
</table>

One of the technical challenges for the conventional SMA is the long response time due to the slow heat exchange processes required for the phase transformation. If SMA are deposited in the form of thin films the working frequency can be as high as 50 Hz, yet this demands sophisticated micro-processing and currently the cost-performance balance is still far from satisfactory. The complicated processes that govern the phase transformation are still quite inadequately understood, and thus predicting material behaviors, controlling microstructures, and tailoring key parameters such as the critical temperature cannot be performed accurately. For SMC and SMP, the major problems include the low energy density and the poor deformability, as shown in table 1.1. To meet the functional requirements of the industrial world, new smart materials/systems that are of high output energy density and can provide large, high frequency displacements or strokes must be developed.

The area in particular need of further study is the application of nanotechnologies in developing smart systems. Recently, the application of nanoporous materials in
developing advanced energy absorption systems has drawn increasing attention (V. Eroshenko et al, 2001; T. Martin et al, 2002; X. Kong et al, 2005; Y. Qiao et al, 2005). Since the specific areas of the nanoporous materials are usually in the range of $100–1000m^2/g$, the capacity for energy exchange of such systems can very high.
CHAPTER II

STATUS OF DEVELOPMENT OF NANOPOROUS MATERIALS

2.1 General Definitions of Nanoporous Materials

Nanoporous materials can be considered as nanovoid-surrounding networks usually covalently cross-linked together, with the gas-solid interfaces as the most dominant characteristic (Polartz and Smarsly, 2002). This microstructure is metastable since when the temperature is high the material start to fuse or break down. There are a variety of nanoporous organic-inorganic hybrids in nature, e.g. diatoms, radiolarii, and abalone shell, exhibiting synergistic properties. Other examples include the nanoporous foams in lungs permitting the exchange of oxygen between air and the blood, and various photonic materials such as butterfly wings (Dabrowsk, 2001; Pandey and Chauhan, 2001; Polartz and Smarsly, 2002). Porous materials are abundant in nature and the type and nature of porosity in natural materials depend on their formation (for instance rocks can be of igneous, sedimentary or metamorphic origin). Porosity strongly determines many important physical properties of materials such as durability, mechanical strength, permeability, adsorption properties, etc. The knowledge of pore structure is an important step in characterizing these materials and predicting their behaviors. There are two basic types of pores: closed and open pores. Closed pores are completely isolated from the external surface, not allowing the access of external fluids in neither liquid nor gaseous phase. Closed pores influence parameters such as density, mechanical and thermal
properties. Open pores are connected to the external surface and are therefore accessible to fluids, depending on the pore nature/size and the nature of fluid. Open pores can be further divided in dead-end or interconnected pores. Further classification is related to the pore shape, whenever is possible to determine it.

Since the last century a number of synthetic nanoporous materials have been developed, especially in the past two decades. The small pore size and the large pore volume fraction in the nanoporous materials lead to the very high area/mass ratio in the range of 10-1000 m²/g, which together with the excellent cost-performance balance, makes them attractive for the sorption and catalysis applications (Kruk and Jaroniec, 2001). The most commonly used synthesis method is the templating technique, in which the network surrounding the template is produced first through phase separation or nanocasting, and then the template is removed by etching or heating, as depicted in Figure 2.1. The interface energy between the network material and the template should be relatively small such that the rearrangement does not occur spontaneously. During this process, the template must be compatible with all the solvents (Polartz and Smarsly, 2002).

The nanoporous materials can be classified into three categories (1) microporous materials with the pore size below 2 nm, (2) mesoporous materials with the pore size in the range of 2 nm-50 nm, and (3) macroporous materials with the pores large than 50 nm but small than 1000 nm (Sebastian et al, 2002). The synthetic nanoporous materials are often of ordered microstructure with nearly uniform pore size and pore shape distribution, resulting in somewhat homogeneous properties. However, due to the grain packing or additional microporosity, the porosity can vary in a broad range. Most of these materials
are inorganic, including oxide-type materials such as silica and titania, carbon materials, binary compounds such as sulfides and nitrides, and porous materials (Polartz and Smarsly, 2002). The organic nanoporous materials include polyurethane and polypyrrole.

The material properties of nanoporous material such as pore size distribution and pore volume can be characterized by a variety of available techniques, e.g. gas adsorption, electron microscopy, x-ray diffraction scanning, positron annihilation, and mercury porosimetry, as well as the molecular dynamics simulation.

2.2 Microporous Materials

The two most important types of microporous materials are zeolites and porous carbons. Zeolites are inorganic crystalline solids with small pores (0.1-2 nm diameter) running throughout the solids. In the zeolites, the metal atoms (silicon or aluminum) are surrounded by four oxygen anions forming an approximate tetrahedron consisting of a metal cation at the center and oxygen anions at the four apexes. The tetrahedral metals are called T-atoms and these tetrahedra then stack in beautiful, regular arrays called channels (see Figure 2.2). The possible ways for the stacking to occur is limitless, and hundreds of unique structures are known so far (http://www.galleries.com/minerals).

The zeolitic channels (or pores) are microscopically small, and in fact, have molecular size dimensions such that they are often termed “molecular sieves”. The size and shape of the channels have extraordinary effects on the properties of these materials for adsorption processes. Zeolites have been widely used in separation processes. Molecules can be separated via shape and size effects related to their possible orientation.
in the pore, or by differences in strength of adsorption. Since silicon typically exits in a 4+ oxidation state, the silicon-oxygen tetrahedra are electrically neutral. However, in zeolites, aluminum typically exists in the 3+ oxidation state so that aluminum-oxygen tetrahedra form centers that are electrically deficient one electron. Thus, zeolite frameworks are typically anionic, and charge compensating cations populate the pores to maintain electrical neutrality. These cations can participate in ion-exchange processes, and this yields some important properties for zeolites. Zeolites are also commonly used in catalytic operations and catalysis with zeolites is often called "shape-selective catalysis". Figure 2.3 shows the micro-structure of the situ $b$-oriented pure silica zeolite (PSZ) MFI films on stainless steel, which can be well described in the context of coordination sequences (Shuang and Zijian, 2004). Figure 2.4 shows HRTEM images taken down the $b$ axis of MFI crystals in which the crystal lattice is visualized (Shuang and Zijian, 2004).

Most of the porous carbons, including carbon blacks, carbon fibers, glassy carbons and activated carbons, can be produced through the appropriate carbonization and activation treatments of a number of organic materials such as coal, phenolic resin, and furfuryl alcohol. They can be applied as electrodes, filters, catalysts, molds, substrates, etc. The basic structural unit is the small plane of carbon atoms (graphene). As depicted in Figure 2.5, needle-like nanopores can be formed through the imperfect packing and bending of the graphene layers. Usually the nanopores form a three-dimensional interpenetrating structure throughout the whole particle, except in the glassy carbon where most of the nanovoids are inaccessible. Another important nanoporous carbon is
carbon nanotube. However, due to the high cost, currently its applicability in mechanical systems is quite limited.

For a variety of liquids including water, polymer melts or solutions, and liquid metal, the liquid-zeolite and liquid-carbon interfaces can be either wetting or non-wetting. The interfacial tension,

2.3 Mesoporous materials

One of the most suitable network materials to the mesoporous structure is silica. In the past decade, processing techniques have been well established to synthesize nanoporous silica with various pore size from 2 nm to 80 nm, pore shapes (regular or irregular), pore volume fractions, pore distributions (ordered or disordered), and surface properties (Evans and Wennerstrom, 1999). They have been applied in sensing, catalysis, dielectric coating, molecular sieve applications, etc. The mesoporous structure can be obtained through the synergistic co-assembly method, in which the silica network and the template are formed at the same time, or through the precision imprinting based on nanocasting mechanism (Yang and Chao, 2002). In order to produce the porous structure, the template needs to be removed by liquid-liquid extraction, and the solvent can be evacuated through sub-critical or super-critical drying.

The nanoporous silica can be either in powder form with the particle size in the range of 0.1-100 µm or in monolith form as large as 100 mm. As shown in Figure 2.6, in ordered porous system the nanopores are of similar size and shape, and there exist a strong three-dimensional correlation among them. In a disordered system, which is
usually formed above the percolation threshold of the template, the pore size and shape vary in large ranges (Polarz and Antonietti, 2002). The interfacial tension of hydrophobic silica-water interface is usually around 0.02, depending on the processing techniques, template, and impurities in water.

In addition to silica, transition metal oxides such as TiO$_2$, metal sulfides such as CdS and ZnS, aluminum phosphates, silicon nitride, and aluminum can also be used to synthesize mesoporous materials (e.g. Caro, et al., 1998). However, because these materials crystallize easily and are relatively reactive, the processing and reliability are difficult to control.

2.4 Macroporous Materials

If the size distribution of colloidal particles such as silica spheres, latex spheres, and gold or silicon crystals is nearly uniform, they can form close-packed colloidal crystals through sintering or annealing (see Figure 2.7), which often are of the quasi-face centered cubic (FCC) symmetric macroporous structure (Lozinsky, et al., 2001). These “opal type” materials can be used as templates to obtain the “inversed opal” type macroporous silica, silicon, gold, etc. This technique has important relevance to the catalysis, selective sorption, insulation, and photonic processes.

The behavior of the liquid in the macroporous material is somewhat similar to that of macroscopic flow confined in porous media that has been discussed intensively in permeability and mass/heat transfer studies. In addition, a number of numerical simulations have been performed for the wave propagation in saturated or unsaturated
porous media (Bradford, et al., 2003). Usually, the confined liquid can flow out from the
nanopores spontaneously as the external pressure decreases. However, little attention has
been given to the effects of the interface zone and the high pore volume fraction that must
been considered when the pore size approaches the nanometer level. Furthermore, in
these researches usually the liquid is wetting and the solid media is continuous, which is
quite different from the nanoporous systems that will be discussed in the following
chapters.
Figure 2.1 Schematic representation of the synthesis of a nanoporous material by removing the template.

Figure 2.2 A schematic diagram of zeolite molecular framework (http://www.zeoponix.com/zeolite.htm).
Figure 2.3 Scanning electron micrographs (SEM) of (a) the top view of in situ $b$-oriented pure silica zeolite (PSZ) MFI films on stainless steel, (b) the cross-sectional view of (a), and (c) the schematic of the pore structure of $b$-oriented PSZ MFI zeolite film (Shuang and Zijian, 2004).
Figure 2.4 HRTEM images taken down the $b$ axis of MFI crystals in which the crystal lattice is visualized. The interfaces of the crystals are inclined slightly with respect to the \{100\} and \{101\} planes. The interfaces of the crystal in (a) are subparallel to \{101\}, whereas in (b) the interfaces are subparallel to \{100\} and \{101\}. The structure of the interface has stepwise character. Usually the steps are parallel to low index crystallographic directions. The interfaces are coherent and no distortion of the atomic planes has been observed. As an inset in (a) is shown an $8 \times 8$ unit cell segment of a simulated HRTEM image down \{010\}. The white spots can be attributed to the positions of the open channels parallel to $b$ (Shuang and Zijian, 2004).
Figure 2.5 The needle-like nanopore in the porous carbon with the imperfect packing or bending of graphene layers

Figure 2.6 (a) SEM microscopy of the mesoporous silica particles; (b) TEM microscopy of the particle surface; (c) the mesoporous structure (Carlos B, 2003).
Figure 2.7 Schematic diagram of the colloidal crystal
CHAPTER III

PASSIVE NANOPOROUS SYSTEMS

3.1 Consideration of Fundamental Mechanism

When a drop of liquid is placed on the surface of another matter, unless it dissolves, it has two choices. It can spread to cover the surface, like oil on water, or it can remain in a drop, like water on wax. The first behavior is called "wetting" and the second called "non-wetting". Intermolecular forces play a significant role here. If liquid molecules are more strongly attracted to substrate molecules than to each other, the drop wets otherwise non-wets. As depicted in Figure 3.1, when a liquid has a high surface tension (strong internal bonds), it will form a droplet, whereas a liquid with low surface tension will spread out over a greater area (bonding to the surface).

When hydrophobic nanoporous particles are immersed in water, water is non-wetting to the particles and at the atmosphere pressure, \( p_{at} \), due to the capillary effect, soaking does not occur spontaneously. As the pressure increases to a critical value, \( p_{in} \), and the water can be forced into the nanopores, as depicted in Figure 3.2.

When the pressure is reduced back to \( p_{at} \), however, the water molecules may or may not come out of the nanoenvironment, depending on the factors that will be discussed shortly. According to the limited data currently available in open literature (V. Eroshenko et al, 2001; T. Martin et al, 2002), the “nonoutflow” is likely to occur when the pore size is in the mesoporous range (2-50 nm), and the “outflow” is relatively easy as the pore
size is smaller than about 1-2 nm. This process is also affected by the temperature, the pore shape, as well as the surface groups.

In order to model the pressure induced infiltration, a few assumptions such as the flow-direction dependence of contact angle (V. D. Borman et al, 2000), the phase transformation with constant system volume and zero gas-phase nucleation barrier (B. Lefevr et al, 2004), and the evolution of filled pore clusters (Y. Qiao et al, 2005), have been proposed. However, currently, since the experimental set-ups are usually sophisticated and the direct observation of infiltration processes is difficult, there are few experimental evidences that can support these analyses. For instance, at the nm scale, the basis of continuum fluid mechanics involved in the flow direction theory and the pore cluster model may no longer be valid, and ignoring the system volume change and the energy exchange between gas/liquid phases can lead to large errors. It is still not clear, what is the role of the entrapped gas in the nanopores, whether the mass and energy exchanges between gas and liquid phases are important at the nm scale, and at what level the confinement effect of pore walls affects the system performance.

3.2 Direct Observation of Liquid Infiltration

In the current study, we designed a simple, transparent poly (methyl methacrylate) (PMMA) system so as to directly observe the infiltration behavior of nanoporous particles. The material under investigation was end-capped Fluka 100 C8 reversed phase mesoporous silica with the average pore size $\bar{r} = 7.8$ nm and the standard deviation $\delta r = 2.4$ nm (see Figure 3.3). The specific pore volume was 560 mm$^3$/g, and the specific area
was 287 m$^2$/g. The Barrett-Joyner-Halenda (BJH) adsorption characterization measurement was performed at the Quantachrome Instruments. The surface coverage was 10-12\% ($\pm$ 4 $\mu$mol/m$^2$), which led to a high degree of hydrophobicity. The particle size was in the range of 15-35 $\mu$m. Prior to the infiltration tests, the silica particles were calcinated in air at 150$^\circ$C for 12 hours.

The aqueous suspension of 0.5 g of the mesoporous silica particles was sealed in a PMMA cylinder by a stainless steel piston with reinforced gaskets. Initially, no air bubble could be observed. The infiltration experiment was performed using an Instron 5569 machine. The piston was first compressed into the container at a constant rate of 1.0 mm/min. Once the pressure exceeded about 50 MPa, the crosshead was moved back at the same speed. The loading-unloading cycle was repeated until the absorption isotherm curves converged to the steady-state, as shown by curves (a, b) in Figure 3.4, where the specific volume variation is defined as $\Delta V_0/W$, with $\Delta V_0$ being the volume change of the system and $W$ the weight of the silica particles. The system was then thermally treated in a temperature bath at elevated temperatures in the range of 30-80$^\circ$C for 0.5 hour either (1) immediately or (2) after resting at room temperature for 6-24 hours, followed by another loading-unloading test. The measurement results are shown by curves (c, d) in Figure 3.4, respectively. Altogether four samples were tested, and the difference between their absorption isotherms was less than 0.5\%, close to the uncertainty of the testing machine. Curve (a) in Figure 3.4 shows that, following the initial linear stage, as the pressure reached the infiltration pressure, $p_{\text{in}} \approx 17$ MPa, the water was forced into the nanopores, causing the large increase in system compressibility. If the pore size were perfectly uniform, the plateau should be flat. In the current system, due to the pore size distribution,
the slope of the absorption isotherm was finite. Eventually, at about 30 MPa, most of the pores were filled and the system compressibility decreased rapidly. The volume variation associated with the plateau region was about 0.55 cm$^3$/g, which is close to the BJH result of the specific pore volume. As the pressure was reduced, the confined water remained in the nanopores, and thus the unloading curves were quite linear.

During the loading-unloading process, there was no significant change in system appearance, except for the variation in volume, indicating that the gas entrapped in the nanopores dissolved in the liquid phase. Since there was no air bubble could be observed even when the pressure was reduced back to the atmosphere pressure, the gas content in the liquid phase outside the nanoporous particles must be quite constant, that is, the dissolved gas molecules remained in the nanopores. Because of the “nonoutflow”, the extent of infiltration was negligible in the following loading-unloading cycles (see curve b in Figure 3.4).

3.3 Thermal Effects on the Infiltration

3.3.1 Experimental

The NEAS studied in the current research was based on Fluka 100 C8 reversed-phase mesoporous silica. According to the gas absorption measurement performed at Quantachrome Instruments, the specific area is $287 \text{m}^2$/g. The average pore size is 7.8 nm, with a standard deviation of 2.4 nm. The material is in powder form, and the particle size is in the range of 15–35 nm. The surface coverage, which is defined as the percentage of the surface area covered by functional groups, is 10–12%, leading to a high degree of
hydrophobicity. Such nanoporous materials have been widely applied in chromatography. The testing sample consisted of 0.5 g of the mesoporous silica particles immersed in deionized water, which was sealed in a compressible container. In a type 5569 Instron machine under displacement control mode, the system was compressed at a constant rate of 1 mm/min, and the pressure, $p$, increased continuously. Initially, under atmospheric pressure the water could not enter the nanopores. When the pressure reached about 17 MPa, infiltration started to occur in the relatively large pores, leading to an abrupt decrease in the slope of absorption isotherm, as shown in fig.3.5a. As $p$ exceeded about 24 MPa, most of the porous space was filled, and the slope of sorption isotherm increased rapidly. The effective infiltration pressure, $p_{in}$, was taken as the pressure at the middle point of the plateau region. When the pressure exceeded about 50 MPa, the applied load was reduced back to 0. The loading–unloading cycle was repeated for four times.

The infiltration tests were performed at different temperatures. The sorption isotherm curves for the first two infiltration cycles are shown in Figure 3.5. The thermal effects on $p_{in}$ are shown in Figure 3.6. Figure 3.7 shows the temperature dependence of energy absorption effectiveness, $E^*$, which is calculated as the area enclosed by the hysteresis loop of sorption isotherm. Note that $E^*$ indicates the energy absorbed by 1 g of nanoporous silica particles. The outflow pressure, which is defined as the pressure at the point in the unloading section of the first infiltration cycle where the slope of the sorption isotherm is reduced by 50%, is shown in table 3.1 as a function of temperature.
Table 3.1 The defiltration pressure as a function of temperature.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>20</th>
<th>35</th>
<th>50</th>
<th>65</th>
<th>80</th>
</tr>
</thead>
<tbody>
<tr>
<td>Outflow pressure (MPa)</td>
<td>2.2</td>
<td>2.6</td>
<td>3.4</td>
<td>3.9</td>
<td>5.1</td>
</tr>
</tbody>
</table>

3.3.2 Results and Discussion

According to fig.3.5a, for the first loading–unloading cycle, the widths of the plateau regions at different temperatures are about the same, indicating that the accessible specific volume is not sensitive to the temperature, $T$. However, the infiltration pressure, $P_{in}$, decreases consistently with temperature (see fig.3.6). When $T$ rises from $20^\circ$C to $80^\circ$C, $P_{in}$ is lowered by about 0.7MPa. Based on classic surface theory, as a first-order approximation, the infiltration pressure required to overcome the capillary effect can be estimated as (J.A. Fay, 1997).

\[ P_{in} = \frac{2\Delta\gamma}{r} \]  

(3.1)

Where $r$ is the pore radius and $\Delta\gamma = \gamma_{SL} - \gamma_{SG}$ is the difference between the solid–liquid interfacial energy, $\gamma_{SL}$, and the surface energy of the solid, $\gamma_{SG}$. Note that since the nanoporous particles are hydrophobic, $\Delta\gamma > 0$. Both $\gamma_{SG}$ and $\gamma_{SL}$ are dependent of temperature. The $\gamma_{SG} - T$ relation can be described by a power-law function (J.M. Howe, 1997)

\[ \gamma_{SG} = C_1G_m + C_2(T_m - T)^m \]  

(3.2)
Where $C_1$ and $C_2$ are material constants in the ranges of 0.5–3 and 0.2–0.6, respectively; $G_m$ is the free energy of melting; $T_m$ is the melting point; and $m$ is a material constant in the range of 1–1.2. Usually, especially when the temperature range under consideration is much lower than $T_m$, a linear simplification can be used (S.K. Milonjic, 1999; D.D. Do, 1994)

$$
\gamma_{SG} = \gamma_0 - \alpha T
$$

(3.3)

Where $\gamma_0$ is the reference surface energy and $\alpha$ is the temperature sensitivity.

The $\gamma_{SL} - T$ relation, on the other hand, is usually highly nonlinear. Through the Clapeyron equation (D.D. Do, 2002)

$$
q_{st} = RT^2 \left( \frac{\partial \ln p}{\partial T} \right)_\Gamma
$$

(3.4)

Where $q_{st}$ is the isosteric heat, $\Gamma = H_p p, H_p = \frac{1}{k_B T} \int_0^\infty \left[ \exp(-\varphi(z)/k_B T) - 1 \right] dz$

is the Henry constant, $k_B$ is the Boltzmann constant, and $\varphi(z)$ is the potential energy along the normal of the interface, $z$. At zero loading we have (D.D. Do, 2002)

$$
\frac{q_{st}^0}{k_B T} = f \left( \frac{\gamma_{SL}}{k_B T}, \sigma_{sf} \right)
$$

(3.5)

where $\sigma_{sf}$ is the collision diameter and $f$ is a nonlinear function determined by the $p - T$ relation. As depicted in fig.3.8, since $\partial \gamma_{SL} / \partial T$ and $\partial \gamma_{SG} / \partial T$ are different, there exists a critical temperature, $T_{cr}$, at which $\partial \gamma_{SL} / \partial T = \partial \gamma_{SG} / \partial T$. At $T_{cr}$, $\Delta \gamma$ is minimized. When $T < T_{cr}$, as temperature increases $\Delta \gamma$ decreases; and when $T > T_{cr}$, $\Delta \gamma$ increases with $T$. The experimental data of $p_{in}$ indicate that in the temperature range under
For the second and the following infiltration cycles, the thermal effect is much more pronounced, as shown in fig. 3.5b. At 20°C, the infiltration pressure associated with the second loop is much higher than that in the first loop. As T rises, \( p_{in} \) decreases rapidly and when \( T > 50°C \), the difference of \( p_{in} \) in different loading–unloading cycles is negligible. A more significant effect is that the system recoverability increases considerably with temperature. When the temperature is relatively low, owing to the phenomenon of non-outflow, the porous space remains being occupied after unloading, and therefore the energy absorption effectiveness after the first infiltration cycle is nearly zero (see fig. 3.7). When \( T > 50°C \), \( E^* \) decreases only slightly after unloading, that is, under this condition the system is nearly fully recoverable. If the infiltration tests are performed at room temperature, but in between the loading–unloading cycles the system is thermally treated at different temperatures, the sorption isotherm curves are about the same, i.e. the sequence of the thermal treatment and the infiltration test does not affect \( E^* \). This phenomenon has great potential in reactivating nanoporous protection devices.

The thermal effect on \( E^* \) (see Table 3.2) should be attributed to the temperature dependence of the outflow pressure, \( p_{out} \). At relatively low temperatures, even under \( p_{at} \), the confined liquid cannot come out of the nanopores. At an elevated temperature, especially when \( T > 50°C \), \( p_{out} \) is much higher and as a result most of the confined liquid can be released. As discussed above, the desorption process is insensitive to the pressure.
Table 3.2 The system recoverability, \( R_s = E^*_2/E^*_1 \), as a function of the thermal treatment temperature, \( T \), where \( E^*_{i} \) is the absorbed energy in the \( i \)th loading-unloading cycle (\( i = 1,2 \)).

<table>
<thead>
<tr>
<th>( T (^\circ C) )</th>
<th>21</th>
<th>30</th>
<th>40</th>
<th>50</th>
<th>70</th>
<th>80</th>
</tr>
</thead>
<tbody>
<tr>
<td>( R_s (%) )</td>
<td>11.3</td>
<td>24.4</td>
<td>45.0</td>
<td>94.3</td>
<td>97.4</td>
<td>97.0</td>
</tr>
</tbody>
</table>

3.3.3 Resting Time effects

If, on the other hand, after the first infiltration cycle, the specimen was rested at room temperature under \( p_{at} \), the system appearance could change significantly. After 6 hours, a large number of air bubbles with the sizes in the range of 0.05 mm to 0.5 mm were formed and therefore the sample was no longer transparent. After 24 hours, the total volume of the air bubbles was estimated as 0.25cm\(^3\)/g, while the energy absorption capacity was still close to zero, indicating that the nanopores were filled by liquid. Thermal treating such a system would cause a partial recovery, as shown by curve (d) in Figure 3.4 as well as Table 3.3, where the system recoverability, \( R_p \), is defined as \( E^*_{t}/E^*_1 \), with \( E^*_{t} \) being the absorbed energy in the loading-unloading cycle subsequent to the postponed thermal treatment; the treatment temperature was set to 70\(^\circ\)C, and \( t_r \) is the room-temperature resting time. Clearly, during the resting period, a certain amount of gas molecules diffused out of the nanopores, and the decrease in system recoverability should be attributed to the reduced excess gas content in the nanoenvironment.
Table 3.3 The postponed system recoverability, $R_p$, as a function of the resting time, $t_r$.

<table>
<thead>
<tr>
<th>$t_r$ (hr)</th>
<th>0</th>
<th>6</th>
<th>12</th>
<th>18</th>
<th>24</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_p$ (%)</td>
<td>97.4</td>
<td>86.2</td>
<td>73.8</td>
<td>65.7</td>
<td>58.5</td>
</tr>
</tbody>
</table>

Based on a FTIR measurement, it was confirmed that, at liquid-solid interfaces, there exist a large number of nm-scale gas phase nuclei (J. D. Miller et al, 1999). At a higher temperature, the fraction of bigger nuclei increases, which explains when $T > 50^\circ$C the gas phase nucleation and growth could occur. After the room-temperature resting, however, due to the significant decrease in gas content in the nanopores, the average size of gas phase nuclei is smaller, and therefore the same thermal treatment can cause only a reduced system recovery.

Thermal effects on the performance of a NEAS consisting of hydrophobic mesoporous silica particles have been investigated experimentally. Through the loading–unloading tests at different temperatures, the sorption isotherm curves are characterized by $p_{in}$ and $E^*$. While the influence of temperature variation on $p_{in}$ is only secondary, the outflow of the confined liquid is strongly dependent of thermal treatment, indicating that the mechanisms of the pressure induced absorption and desorption are different. The following conclusions are drawn:

(1) As temperature increases, the infiltration pressure decreases slightly.

(2) Temperature has little influence on the accessible specific pore volume.

(3) The efficiency of energy absorption associated with the first infiltration cycle is quite insensitive to the temperature.
(4) The system recoverability increases rapidly with temperature. When the temperature exceeds about $50^\circ\text{C}$, the system becomes almost fully reusable.

(5) The outflow is a thermally aided process and insensitive to pressure.

(6) In the nanoenvironment, the geometrical aspect of the porous structure as well as the mass/energy exchange between the gas and the liquid phases must be taken into consideration.

(7) Due to the energy barrier of gas-phase nucleation, the mechanisms of pressure induced absorption and desorption of nanoporous materials are quite different. The desorption behavior is affected by pore size, pressure, and surface and interfacial properties. There exists a critical pore size above which the “outflow” is impossible.

3.4 NEAS Subjected to Dynamic Loadings

Most of current studies in NEAS are focused on quasi-static responses, and shed little light on the actual system performance under dynamic loadings. For instance, one important yet still unanswered question is whether the characteristic time of infiltration, $t_i$, is smaller than that of wave propagation, $t_{wp}$. If $t_i < t_{wp}$, the nanopores can be infiltrated as the impact wave bypasses a nanoporous particle, and the energy absorption capacity of NEAS can be fully utilized; otherwise, the utility factor would be smaller than 1.0. Both $t_i$ and $t_{wp}$ are dependent on a variety of factors, such as the pressure of incident pulse, the size and the microstructure of nanoporous particles, among others. In this work, by using a Hopkinson bar testing system, we investigate the high strain rate performance of a mesoporous silica, for which the quasi-static behaviors have been documented above.
The nanoporous material under investigation was a Fluka 100 C₈ reversed phase
nanoporous silica, with the average pore size of 7.8 nm, the standard deviation of 2.4 nm,
and the surface coverage of 10–12%. The particle size is 10–30 µm. Both the pressure-
induced infiltration experiment and the Berrett–Joyner–Halenda measurement have
shown that the specific pore volume is 0.5 cm³/g. The material has a relatively simple
end-capped porous structure. Under quasi-static loadings, the energy absorption
efficiency is about 15 J/g in distilled water, indicating that Δγ is 92 mJ/m². Note that in
the nanoenvironment, there is no well-defined interface zone. The effective interface
energy contains the contributions from the solid-liquid interaction and the chemical
potential difference of gas and liquid phases (Y. Qiao et al, 2005).

The testing sample was produced by sealing 0.3–0.8 g of nanoporous silica particles
and 7 g of distilled water in a stainless-steel cylinder, as depicted in Figure 3.9. The inner
diameter of the cylinder is 19.05 mm, and the outer diameter is 38.1 mm. Under
atmosphere pressure, because the silica particles are hydrophobic, the solid and liquid
phases were separate. By using a Type 5569 Instron machine, the piston was compressed
into the cylinder at a constant rate of 2 mm/min. Once the pressure reached about 17 MPa,
the pressure induced infiltration began in relatively large pores. As the pressure increased
to about 20 MPa, the infiltration was completed and the porous space was filled. The
unloading curve was quite linear, indicating that the confined liquid remained in the
nominally energetically unfavorable nanoenvironment. The sample was then annealed in
a controlled temperature bath at 80°C for 30 min, which led to the thermally aided
defiltration and thus the energy absorption capacity was fully recovered (X. Kong and
Y. Qiao, 2005). After the thermal treatment, the silica particles were uniformly dispersed in the liquid phase.

The dynamic response of the thermally recovered nanoporous system was characterized in a Hopkinson bar arrangement. The striker, with the length of $L_s=76.2$ mm and the cross-sectional diameter of $d=19.05$ mm, impacted the input piston at about 11 m/s, through which two compressive wave fronts were generated and propagated along opposite directions. The front in the striker would be reflected by the free end, forming a compressive incident pulse (K. Graff, 1991). As the incident pulse reached the steel-liquid interface, part of it would be reflected and the rest of it would enter the nanoporous system, propagate across it, and partly transmit into the output piston. The incident pulse, the reflected pulse in the input piston, and the transmitted pulse in the output piston were measured by the strain gauges.

Due to the large impedance difference of the steel and the liquid phase, it was prohibitively difficult to obtain the effective stress-strain relation through the standard Hopkinson bar analysis. In the current study, the transmitted pulse of a system consisting of only distilled water is used as the reference curve. Since there is no nanoporous particle, the energy absorption of this system is negligible. Therefore, the variation in shapes of transmitted pulses of PNSS reflects the effect of pressure-induced infiltration, as shown in Figure 3.10. Altogether three groups of samples were investigated, with the silica particle contents of 0.3g, 0.5g, and 0.8g, respectively. Each sample was impacted repeatedly until the transmitted pulse converged to the reference curve. The time interval between the impact tests was less than 5 min. As shown in Figure 3.11, for all the samples, the measured incident pulses and the reflected pulses were quite similar,
indicating that the addition of silica particles did not cause significant changes in impedance of liquid phase.

The energy carried by a stress pulse can be obtained as

\[ U = U_s + U_K = \xi \int_0^T \sigma^2(t) dt \]  

(3.6)

Where \( U_s \) and \( U_K \) are strain energy and kinetic energy, respectively, \( t \) is time, \( T \) is the pulse length, \( \sigma \) is the measured stress, and \( \xi = cA/(2E) + \rho A c^3/(2E^2) \), with \( c \) being the sound speed, \( E \) the Young’s modulus, \( A \) the cross-sectional area, and \( \rho \) the weight density. For the steel sample, \( A = 285 \text{ mm}^2 \), \( c = 5.92 \times 10^3 \text{ m/s} \), \( E = 2.11 \times 10^{11} \text{ Pa} \), \( \rho = 7.8 \times 10^3 \text{ kg/m}^3 \), and thus \( \xi = 9.2 \times 10^{-12} \text{ m/Ns} \). According to Eq.(3.6), the energies of the incident, the reflected, and the transmitted pulses of the reference system are, respectively, \( U_{ir} = 10.8 \text{ J} \), \( U_{rr} = 4.9 \text{ J} \), and \( U_{tr} = 3.4 \text{ J} \). Note that \( U_{ir} \) is close to the kinetic energy of the striker, as it should be. The fraction of energy carried by the transmitted pulse across the interface between the liquid phase and the output piston can be calculated as \( \alpha = U_{tr}/(U_{ir} - U_{rr}) = 0.57 \).

Figure 3.10 shows the output pulses of a system consisting of 0.3 g of nanoporous silica particles. The energies carried by the output pulses in the first three impact tests were 0.8 J, 0.9 J, and 1.5 J, respectively. From the fourth impact test, the energy was stabilized at about 3.4 J, the same as that of distilled water, indicating that the system could not be recovered by itself. The total energy that the 0.3 g of nanoporous particles absorbed can be estimated as \( \Delta U/\alpha = 12.3 \text{ J} \), with \( \Delta U \) being the accumulated energy difference of the transmitted pulses. Thus, the energy absorption efficiency of this system is 41.0 \( \text{J/g} \), which is about three times higher than the quasi-static value. Similarly, the energies absorbed by the systems consisting of 0.5 g and 0.8 g of nanoporous particles
can be calculated as 19.5 \( J \) and 30.0 \( J \), respectively. It can be seen that the energy absorption capacity is quite linear to the amount of nanoporous particles, suggesting that the interaction among the particles is negligible. The increase in energy absorption efficiency with the loading rate can be related to the internal friction. For instance, it has been reported that, in shear thickening systems formed by dispersing nm-sized particles in liquids, the damping ratio can increase considerably as the strain rate exceeds a certain value (Y. S. Lee et al, 2003). The energy dissipation associated with the “flow” in nanopores can also be pronounced as a liquid penetrates into a porous material (J. C. M. Li, 2000). Note that, in Figure 3.11, the shapes of the transmitted pulses in the first two impact tests are quite similar. Similar phenomena were observed for all the nanoporous systems, which demonstrate that the pressure-induced infiltration took place simultaneously in nanopores of different sizes; otherwise, the pressure of the next pulse must be higher than the previous one since the larger pores were filled. This can be attributed to that, at the wave front, the local pressure increases to the peak value in a short period of time and therefore the priority of infiltration in larger pores is suppressed. However, this effect must be further evaluated by testing nanoporous materials of similar pore size distributions but different particle sizes.

In summary, through the impact experiment, it has been validated that the PNSS can be used for energy absorption applications under dynamic loadings. Compared with the quasi-static case, under a dynamic loading the energy absorption efficiency of the PNSS was much higher. The interaction among the nanoporous particles was negligible. No detectable priority of infiltration in larger pores over smaller ones was observed in the current study.
Figure 3.1 Wetting of different fluids. “A” shows a fluid with very high surface tension (and thus non-wetting), while “C” shows a fluid with very low surface tension.

Figure 3.2 Schematic representation of the infiltration of a NEAS by external pressure.
Figure 3.3 Pore volume histogram.

Figure 3.4 The energy sorption isotherm: (a) the first loading-unloading cycle; (b) the second, third, and fourth loading-unloading cycles without thermal treatment; (c) after the immediate thermal treatment; and (d) after the postponed thermal treatment.
Figure 3.5 Sorption isotherm varies at different temperatures: (a) the first infiltration cycle; (b) the second infiltration cycle.
Figure 3.6 The thermal effect on the infiltration pressure.

Figure 3.7 System recoverability at different temperatures.
Figure 3.8 Schematic diagram of the temperature dependence of $\Delta \gamma$.

Figure 3.9 A schematic diagram of the experimental setup.
Figure 3.10 The transmitted pulses measured in the output piston for a system consisting of 0.3g of nanoporous silica particles. The reference curve is the transmitted pulse of distilled water. The curves have been moved along the time axis.
Figure 3.11 The incident and reflected pulses in the input piston.
CHAPTER IV

ACTIVE NANOPOROUS SYSTEMS

4.1 Thermally Controllable Systems

4.1.1 Basic Concepts

The temperature dependence of surface and interfacial properties has been well noticed since the beginning of the development of classic physics. For example, increasing or decreasing temperature can cause the shrinkage or expansion of a thin soap film spanned in a deformable frame, which has been used as a good demonstration in high-school physics education. However, not until recently with the process in the processing of nanoporous material does it become feasible to utilize the thermocapillary concepts in design of smart systems of high energy density and large deformability, for which the technical importance can be recognized by the industry world.

When a liquid contacts a solid, the thermodynamics equilibrium condition can be stated as (Howe, 1997)

$$ dG = -SdT + Vdp + \Delta\gamma_0 dA = 0 $$

(4.1)

where $G$ is the Gibbs free energy, $S$ is entropy, $T$ is temperature, $V$ is volume, $p$ is pressure difference across the liquid-gas interface, $A$ is the area of liquid-solid interface, and $\Delta\gamma_0$ is the “driving force” of liquid-solid separation, which can be stated as (Fay, 1994)

$$ \Delta\gamma_0 = \gamma_{ls} - \gamma_s = -\gamma_l \cos \theta $$

(4.2)
where \( \gamma_{ls}, \gamma_l, \) and \( \gamma_s \) are the liquid-solid interfacial tension, the surface tension of the liquid, and the surface energy of the solid, respectively; and \( \theta \) is the contact angle (see Figure 4.1). If we assume that, for porous particles, the inflow/outflow is dominated by the processes at the pore walls, \( V = Ar/2 \), with \( r \) being the pore radius. Thus, at a constant temperature the effective “driving force” of liquid-solid separation can be written as

\[
\Delta \gamma = \gamma_{ls} - \gamma_s^*
\]

(4.3)

where \( \gamma_s^* = \gamma_s + pr/2 \). If \( \gamma_{ls} < \gamma_s^* \), \( \Delta \gamma \) is negative and the liquid-solid separation does not occur; otherwise the liquid will flow out of the pores (nonwetting).

The effective surface free energy (Howe, 1997)

\[
\gamma_i = H_i - TS_i
\]

(4.4)

Where \( i = 1 \) denotes “LS” (liquid-solid interface) and \( i = 2 \) denotes “SG” (solid-gas interface); and \( H \) is enthalpy. Differentiating Eq. (4.4) leads to

\[
\left( \frac{\partial \gamma_i}{\partial T} \right)_p = -S_i
\]

(4.5)

i.e. both \( \gamma_s \) and \( \gamma_{ls} \) are lowered as the temperature rises. This can be attributed to the change in the positive excess entropy associated with the high degree of freedom and vacancies at surface/interface.

The \( \gamma_{SG} - T \) relation can be described by a power-law function (J.M. Howe, 1997)

\[
\gamma_{SG} = C_1 G_m + C_2 (T_m - T)^m
\]

(4.6)

where \( C_1 \) and \( C_2 \) are material constants in the ranges of 0.5–3 and 0.2–0.6, respectively; \( G_m \) is the free energy of melting; \( T_m \) is the melting point; and \( m \) is a material constant in
the range of 1–1.2. Usually, especially when the temperature range under consideration is much lower than \( T_m \), a linear simplification can be used (S.K. Milonjic, 1999; D.D. Do, 1994)

\[
\gamma_{SG} = \gamma_0 - \alpha T
\]  

(4.7)

Where \( \gamma_0 \) is the reference surface energy and \( \alpha \) is the temperature sensitivity.

The \( \gamma_{SG} - T \) relation, on the other hand, is usually highly nonlinear. Through the Clapeyron equation (D.D. Do, 2002)

\[
q_s = RT^2 \left( \frac{\partial \ln \rho}{\partial T} \right)_\Gamma
\]  

(4.8)

Where \( q_s \) is the isosteric heat, \( \Gamma = H_p - H = 1/k_B T \int_0^\infty \left[ \exp(-\phi(z)/k_B T) - 1 \right] dz \)

is the Henry constant, \( k_B \) is the Boltzmann constant, and \( \phi(z) \) is the potential energy along the normal of the interface, \( z \). At zero loading we have (D.D. Do, 2002)

\[
\frac{q_s^0}{k_B T} = f \left( \frac{\gamma_{SG}}{k_B T}, \sigma_{sf} \right)
\]  

(4.9)

where \( \sigma_{sf} \) is the collision diameter and \( f \) is a nonlinear function determined by the \( p - T \) relation.

Figure 4.2 depicts the pressure-aided wetting-nonwetting-transition (WNT) of at liquid-solid interfaces. In the first case (a), \( \frac{\partial \gamma_s^*}{\partial T} > \frac{\partial \gamma_{ls}}{\partial T} \). As temperature rises, the surface energy of the solid decreases more rapidly than the liquid-solid interfacial tension. At \( T_{cr}, \gamma_s^* = \gamma_{ls} \) and the system is neutral-stable. When the temperature is below \( T_{cr}, \gamma_s^* > \gamma_{ls} \), i.e. the interface is effectively wetting. In a system consisting of
nanoporous particles suspended in a liquid, the liquid will flow into the particles and eventually the saturation status will be reached. If the temperature is increased to above \( T_{cr} \cdot \gamma_s^* < \gamma_{ls} \) and, consequently, the liquid will flow out, leading the significant increase in system volume. Since with the increasing of the applied pressure, \( T_{cr} \) rises, at a constant temperature, the system volume can also be controlled through the external pressure, as shown in Figure 4.2b. This phenomenon was observed in water-hexatriacontane system (Newmann and Spelt, 1996). As temperature increases from 20\(^{0}\)C to 50\(^{0}\)C, at atmosphere pressure the contact angle changes from 104.6\(^{0}\) to 107.6\(^{0}\), indicating that \( \Delta \gamma \) is raised from 18.2\(mJ/m^2\) to 20.5\(mJ/m^2\). For such a system, through Figure 4.2 it can be estimated that at \( T_{cr} \approx -200^{0}C \), \( \Delta \gamma \) tends to zero. Clearly, far before this condition can be reached the water will be frozen and, therefore, the interface will always be nonwetting. Increasing the external pressure, however, can increase \( T_{cr} \) considerably.

In the second case (b) where \( |\partial \gamma_s^*/\partial T| < |\partial \gamma_{ls}/\partial T| \), it can be seen that as temperature rises to above \( T_{cr} \), the system changes from nonwetting to wetting, and \( T_{cr} \) decreases as \( p \) increases. This type of behavior has been observed in a water-cholesteryl acetate system (Newmann and Spelt, 1996), in which, as temperature is raised from about 40\(^{0}\)C to 70\(^{0}\)C, the contact angle is reduced from 103.2\(^{0}\) to 101.9\(^{0}\) and, correspondingly, \( \Delta \gamma \) is lowered by 2.6\(mJ/m^2\) to 13.3\(mJ/m^2\). If we assume that the \( \Delta \gamma - T \) relation is linear, at \( T_{cr} \approx 223^{0}C \) the nonwetting-wetting-transition will occur, which is obviously beyond the temperature range of liquid phase for water. A sufficient external pressure \( p \) must be applied in order to reduce \( T_{cr} \) to below 100\(^{0}\)C.
4.1.2 Experimental

The UOP HISIV 3000 zeolite particles (from UOP LLC www.uop.com) were dispersed in distilled water and then sealed in a hydraulic device. The system was then thermally controlled in a temperature bath at elevated temperatures in the range of 4-98°C (see Figure 4.3). By measuring the piston displacement, the volume variation of the energy absorption system was obtained as a function of the pressure. The compressive force was applied by a type-5569 Instron machine in displacement control mode. The crosshead speed was set to 1 mm/min. As the crosshead moved downwards, the force \( F \) was measured by an Instron 50KN loadcell and the system pressure \( P \) was calculated as \( F / A \), where \( A = 286.5 \text{ mm}^2 \) is the cross-sectional area of the container. Once \( P \) exceeded 140 MPa, the crosshead was moved back to its initial position at the same speed of 1 mm/min. At each temperature, 3-4 samples were tested.

In this test \( \left| \frac{\partial \gamma_s}{\partial T} \right| < \left| \frac{\partial \gamma_u}{\partial T} \right| \), it can be seen that as temperature rises to above \( T_{cr} \), the system changes from nonwetting to wetting, and \( T_{cr} \) decreases as \( p \) increases. If the pressure is kept as a constant (see Figure 4.4 Path I), the volume change will be increased with temperature raising from \( 4^\circ C \) to \( 98^\circ C \) which means the system will become more wetting. If the volume of the system is kept as a constant (see Figure 4.4 Path II), the pressure will be increased with temperature decreasing from \( 98^\circ C \) to \( 4^\circ C \) which means the system will become more nonwetting.
4.2 Electrically controllable Systems

4.2.1 Basic Concepts

Electro-wetting describes the way that an electrical charge on a material can alter the material’s attraction to a conductive fluid. An electrode is called “ideal polarizable” if no electrode reactions can occur within a fairly wide electrode potential range. Consequently, the electrode behaves like a capacitor and only capacitive current (no faradaic current) is flowing upon a change of potential. Many electrodes can behave as an ideal polarized electrode but only within an electrode potential range called the “double-layer range”. The wetting by liquids can be changed by electrical fields directly on the interface without any current flowing. This effect is referred to as electro-capillarity and allows changes to the contact angle of up to 100° in certain systems. The effect is polarity dependent, and is reversible. Researchers from Philips are using electricity to control fluid in networks of very small channels. The Philips researchers made fluid flow through the 20-millimeter-long channels at a rate of several centimeters per second. The channels are 350 microns wide, or about four times the diameter of a human hair, and there are about 4,000 of them in the researcher’s micro-channel device, (see Figure 4.5). The inside of each channel is coated with a 20-nanometer layer of aluminum, an 11.5 nanometer insulating layer, and a 10 nanometer hydrophobic coating (M. W. J. Prins, 2001).

This setup, together with liquid in the micro-channel, is effectively a capacitor, with the aluminum acting as one electrode and the liquid as a second electrode. A capacitor is a device that stores electric charge. When the capacitor is charged, the tension between the fluid and wall decreases, which draws the fluid into the channel. In a device with
many channels, this pushes the liquid along at a rate that is useful. "We wanted to achieve fast control of liquids in a device with thousands of micro-scale channels," said Menno Prins, a senior scientist at Philips Research. The technique could be used to quickly transport fluids that conduct electricity, like water or saltwater, in microelectromechanical systems (MEMS) without having to use external pumps. The technique also allows for dynamic control of fluid in MEMS because the researchers can shift the pressure in a channel at will. Since potential difference will cause contact angle change, wetting/non-wetting transition can be achieved by applying voltage between nano-porous material and conducting liquid.

4.2.2 Experimental

In the current study, we investigate a nanoporous monel rod produced by sintering monel nanoparticles at near-melting-point temperature. The average pore size \( r = 480 \text{ nm} \) and the specific surface area is about \( 1.3 \text{ m}^2/\text{g} \). The diameter of the rod is \( 9.5 \text{ mm} \) and the length is \( 19.1 \text{ mm} \). The monel rod was tightly inserted in a metal cylinder, as depicted in Figure 4.6 The metal cylinder was connected to two polymethyl methacrylate (PMMA) cylinders, forming a container. A 15wt.% aqueous solution of calcium chloride was added in the container from end “B” and sealed by a metal piston with gasket. From the other end (“A”), a Sigma M2047 methyl salicylate oil was added and sealed. Then, piston “A” was compressed into the container so that the oil-water interface was within the nanoporous monel rod and close to the end toward “B”. By using a Proteck 6030 DC power supply, a voltage was applied between the monel electrode and piston “B”. With
the piston position being fixed, the pressure variation in the oil phase, $\delta p$, was measured by an embedded Honeywell model-s pressure sensor, and the results are shown in Figure 4.7.

4.2.3 Results and Discussion

It can be seen clearly that the pressure increases monotonically with the magnitude of potential difference, which can be attributed to the difference in voltage dependence of wettability of the oil and the aqueous solution (see Figure 4.8). When a potential difference presents across the solid-liquid interface, both sides are electrified (Parsons, R. 1997). The electrified layer in the liquid phase is often referred to as the outer Helmholtz plane (OHP). Beyond the OHP the charge diffusion is dependent on the thermal motion. This structure is sometimes simplified as an electrical double layer with the thickness $d_1 \approx 1$-5 nm. Due to the small thickness, even a low potential difference can cause a large electric field (Bard, A. J. & Faulkner, 2000). As the voltage, $\Delta \phi$, varies, the charge density at the interface, $\sigma_M$, changes accordingly, which in turn affects the interfacial energy. The total potential difference can be decomposed as $\Delta \phi = ^M \Delta^S \psi + ^M \Delta^S \chi$, where $^M \Delta^S \psi = \psi_M - \psi_S$ is the Volta potential, with $\psi_M$ and $\psi_S$ being the potentials of isolated solid and liquid phases, respectively; and $^M \Delta^S \chi$ is the Chi potential accounting for the dipole contribution. At constant temperature and pressure, the thermodynamic equilibrium condition is reduced to the Lippmann equation, $\partial \gamma_{ls} / \partial \Delta \phi = -\sigma_M$ (Habib, M. A. & Bockris, 1985).
Note that $\frac{\partial \sigma_M}{\partial \Delta \phi} = C_e$, with $C_e$ being the capacity. If $C_e$ is constant, $\gamma_{ls}$ follows the Helmholtz-Perrin theory

$$\gamma_{ls} = \gamma_{\text{max}} - \varepsilon_0 \Delta \phi^2 / 2 \epsilon_0$$  \hspace{1cm} (4.10)

with $\gamma_{\text{max}}$ being the maximum interfacial energy, $\varepsilon$ the dielectric constant, and $\varepsilon_0$ the permittivity of free space. If the $\Delta \phi$ dependence of $C_e$ must be taken into account, the effect of the “charge cloud” should be considered (Lund, H. & Hammerich, 2000).

The measured $\delta p-\Delta \phi$ curve shown in Figure 4.7 fits well with the parabolic $\gamma_{ls}-\Delta \phi$ relation (4.10). As $\Delta \phi = 0$, the equilibrium condition at the water-oil interface can be stated as

$$\Delta \gamma = \gamma_0 \cos \theta = \frac{\Delta p \cdot r}{2}$$  \hspace{1cm} (4.11)

where $\Delta \gamma$ is the difference in solid-liquid interfacial energies of the oil and the aqueous solution, $\gamma_0$ is the liquid-liquid interfacial energy, $\theta$ is the effective contact angle, and $\Delta p$ is the pressure difference across the oil-water interface. Since the oil-solid and the water-solid interfacial energies change with $\Delta \phi$ at different rates, the contact angle is a function of $\Delta \phi$. In the system under investigation, the water-monel interfacial energy decreases with $\Delta \phi$ slower than the oil-monel interfacial energy, and thus the aqueous solution becomes effectively more wetting to the solid under the applied pressure, which must be balanced by the pressure change, $\delta p$. Similar to Eq.(4.11), we have

$$\delta \gamma = \frac{\delta p \cdot r}{2}$$  \hspace{1cm} (4.12)
where $\delta \gamma$ is the variation in $\Delta \gamma$ caused by $\Delta \phi$, which is also shown in Figure 4.7. The result is in consistent with the literature data that, with a 0.5 V potential difference, the interfacial energy can vary by 10-30% (Bard, A. J. & Faulkner, 2000).

If the pistons are subjected to constant external loadings, the pressure variation would result in a large displacement $d = V_0/A_0$ of 7.8 mm, equivalent to a strain of nearly 40%, with $V_0 = 2.8 \times 10^3$ mm$^3$ being the volume of the pores initially filled by the oil and $A_0 = 283$ mm$^2$ the cross-sectional area of the container. This effective strain is larger than that of conventional shape memory ceramics and magnetostrictives by orders of magnitude. The output energy can be calculated as $\delta p \cdot A_0 \cdot d = 92$ mJ. The mass of the functional components of the intelligent system, including the nanoporous electrode and the liquid, is 20.5 g. Thus, the output energy density is 4.6 mJ/g, much higher than that of piezoelectrics.

The concept discussed above can be extended to a large number of liquids and nanoporous solids. In fact, one of the liquid phases can be air, which would further simplify the system structure. Note that since the compressability of air is much larger than that of liquids, the working pressure of an air-based system can be relatively low. For a multiple-liquid system, a key factor affecting the system performance is the stability of the liquid-liquid interface in nanopores. Depending on the porous structure, as the liquid-liquid contact line moves, a creaming interface layer can be formed. While this phenomenon should not affect the pressure variation since $\delta p$ is determined by the net interfacial tension, deemulsification is preferred so as to avoid additional complexity. This technique has important relevance to programmable actuators, smart structures, intelligent platforms, among others, which, when incorporated with electrohydraulic
devices or microelectromechanical systems, will provide simple yet powerful actuation mechanisms.
Figure 4.1 A schematic diagram of a liquid-solid interface.

Figure 4.2 Schematic diagrams of the wetting-nonwetting transition at different pressures ($p_2 > p_1$): (a) $|\frac{\partial \gamma_s^*}{\partial T}| > |\frac{\partial \gamma_{ls}}{\partial T}|$; (b) $|\frac{\partial \gamma_s^*}{\partial T}| < |\frac{\partial \gamma_{ls}}{\partial T}|$. 
Nanoporous particles immersed in a near-WNT liquid

Figure 4.3 The experimental set-up for the thermally controllable active nanoporous smart system.

Figure 4.4 The infiltration curve for water-zeolite system at different temperatures.
Figure 4.5 (a) Close-up of the multichannel structure. (b) Sketch of the device geometry (side view) (M. W. J. Prins, 2001).

Figure 4.6 A schematic diagram of the nanoporous intelligent system.
Figure 4.7 The pressure variation, $\delta p$, and the change in interfacial energy difference, $\delta \gamma$, as functions of the applied potential difference.

Figure 4.8 A schematic diagram of the liquid interface in a nanopore.
CHAPTER V

AN ANALYSIS OF AGGREGATE RESPONSE OF CONFINED LIQUIDS IN NANOENVIRONMENT

5.1 Basic Concepts

At the nm scale, the behavior of the liquid confined in nanopores is quite different from that observed at the macroscopic level. According to the nuclear magnetic resonance (NMR) analysis, depending on the nature of the atom-atom interaction, the mobility of the molecules near the solid-liquid interface can be either higher (superdiffusive) or lower (subdiffusive) than that in the interior (R. Kimmich, 2002; C. Cramer, 1997; J. Yi, 1996). Consequently, the average diffusion distance can be stated as a two-power-law function (V. Crupi, 2000). Usually, the thickness of the interface zone is in the range of 1-5nm. In a nanopore with the pore size comparable with this value, there exists a significant size effect, i.e. the confined flow is affected by the pore radius. Due to the influence of molecular mobility, the distribution profile of a specific component can also be dependent of the particle size or membrane thickness (V. D. Borman, 2000).

While a variety of experimental data of confined liquid behavior can be found in open literature (e.g., R. Kimmich, 2002; C. Cramer, 1997; J. Yi, 1996; V. D. Borman, 2000), since the measurement results are quite sensitive to the processing and testing conditions, very often the data from different research team do not agree with each other quantitatively. Furthermore, even if the confined liquid in a single nanopore were fully
understood, there is still no satisfactory model that can relate the molecular behaviors to the micro-mechanical analysis of the system response.

A nanoporous particle or membrane can be considered as a three-dimensional, interpenetrating nanovoid-surrounding network, with the characteristic length ranging from 1 to 1000µm. Due to the high specific area around 100-1000 m²/g, the ordinary percolation theories cannot capture the nonlinear and size dependent nature. In view of the above considerations, in order to provide a scientific basis for developing the next generation intelligent catalysts with the adjustable surface/interface properties, we will establish a multiscale model to study the aggregate system performance. We study the wetting process in a nanoporous particle immersed in a liquid subjected to an increasing pressure. The system response is characterized by the absorption time, \( t_a \), which is essential to the assessment of design variables of precision reaction control. Since the particle size is much larger than the pore size, the particle is assumed to be homogeneous and isotropic.

5.2 Effective Phase Transformation

In a nonwetting liquid, initially the solid and liquid phases are separate. As the pressure increases to the critical value, the energetically favorable inflow starts. Due to the large pore volume fraction and the high connection density, this process can be considered as an effective phase transformation from empty pore clusters (EPCs) to saturated pore clusters (SPCs) (V. D. Borman, 2000; J. van Brakel, 1981; P. S. Grinchuk, 2002), as depicted in Figure 5.1. If the pressure is sufficient high and the pore size
distribution is narrow, the capillary effect can be overcome fully and the factor of the
pore radius comes in by affecting the inflow rate instead of determining whether or not
the inflow can occur. The boundary of a SPC can be fractal yet the interior is filled, and
thus in the following discussion we consider only the average behavior.

Under the relatively high pressure, the liquid penetrate into the particle surface at a
number of points, which are referred as the nucleation sites of SPCs. As the liquid flows
into the adjacent pores, the SPC expands along both radial and circumferential directions,
and at meanwhile new SPCs are nucleated continuously. While it is clear that wetting is
easier in large pores and these places are more likely to serve as nucleation sites, other
factors such as the precursor film formation and the dependence of the contact angle on
flow direction, even thermal fluctuations, can be important in nm level. Thus, in the
current research, the SPC nucleation will be collectively considered as a random process.

The concept of number density can be employed to describe the SPC population. In
this framework, each SPC is characterized by its radial depth, $c$, and opening angle, $\phi$
(see Figure 5.1). The evolution of the SPC number density is governed by
\[
\frac{\partial n(c, \phi, t)}{\partial t} + \frac{\partial [C(c, \phi, t)n(c, \phi, t)]}{\partial c} + \frac{\partial [\psi(c, \phi, t)n(c, \phi, t)]}{\partial \phi} = n_N(c, \phi, t) + n_c(c, \phi, t) \tag{5.1}
\]
where $n(c, \phi, t)$ is the number density of SPC of size $\{c, \phi\}$ at time $t$ per unit volume, and
$n_N$ and $n_c$ are the average SPC nucleation and coalescence rates, respectively. The last two
terms at LHS reflect the influence of SPC growth, with $C$ being the radial growth rate
and $\psi$ being the circumferential growth rate.

The average growth rate should be proportional to the flow rate in nanopore, $v$,
which is a function of pressure $p$, liquid density $\rho$, wetting driving force $\Delta \gamma$, and, as
discussed above, pore radius \( r \). The driving force of wetting can be taken as the difference between the interfacial tension and the surface energy of the network material. Note that for a system where \( r \approx 10 - 100 \text{nm} \), \( v \approx 100\text{m/s} \), and the viscosity coefficient \( \nu \approx 10^{-7} \text{m}^2/\text{s} \), the Reynold’s number \( Re \gg 1 \). Hence, following the classic two-power-law relation, through the dimensional analysis we have

\[
v = \alpha' \sqrt{\frac{p}{\rho}} (pr/\gamma)^{\beta'} + \alpha'' \sqrt{\frac{p}{\rho}} (pr/\gamma)^{\beta''},
\]

where \( \alpha', \beta' \) are system parameters associated with the normal flow, and \( \alpha'', \beta'' \) are related to the interface flow, respectively. When \( r \to \infty \), the second term should vanish and the first term should converge to the result of the Bernoulli’s equation, \( v \propto p^{1/2} \). Therefore, \( \beta' \) is set to 0 and \( \alpha'' \) can be taken as \( \sqrt{2(1-d/r)^2} \), where \( d \) is the effective thickness of interface zone. Similarly, \( \alpha' \) can be considered as \( \alpha\left[1 - (r - d)^2/r^2\right] \), with \( \alpha \) being a material constant. The average SPC growth rates in a porous particle with the pore size distribution function of \( P(r) \) can then be stated as

\[
C = \int_0^\infty P(r) \left\{ (1 - \frac{d}{r})^2 \sqrt{\frac{2p}{\rho}} + \alpha \left[ 1 - \left( \frac{r - d}{r} \right)^2 \right] \sqrt{\frac{p}{\rho}} \left( \frac{pr}{\gamma} \right)^{\beta''} \right\} dr \quad (5.2)
\]

and

\[
\psi = 2C/(R - c/2).
\]

The average SPC nucleation rate, \( n_N \), is proportional to the number of available nucleation sites,

\[
n_N(c, \varphi, t) = \eta_0 \mathcal{P}(c) P(R \varphi) \left[ 1 - \frac{1}{4\pi R^2} \iint n(c, \varphi, t) \cdot \zeta \varphi^2 R^2 dc d\varphi \right] \quad (5.3)
\]
where \( R \) is the particle radius; \( \zeta \) is a geometry factor, which equals \( \pi \) for regular shaped SPCs; \( \eta_0 = \eta_1 \int_0^\infty P(r)dr \), with \( r_{cr} = 2\Delta \gamma / p \) being the critical pore size and \( \eta_1 \) a parameter dependent of time resolution.

The average SPC coalescence rate, \( n_c \), on the other hand, is determined by the probability that the summation of the sizes of two adjacent SPCs equals the distance between them, i.e.

\[
n_c(c, \varphi, t) = N(t)\left[ \tilde{n}_c(\varphi, t) - 2\hat{n}_c(\varphi, t) \right] \frac{c}{\varphi}
\]  

(5.4)

where \( N(t) = \int \int n(c, \varphi, t)dc \varphi \) is the total SPC number, \( \tilde{n}_c \) is the probability of forming a large SPC, and \( \hat{n}_c \) is the probability of the disappearance of a small SPC. According to the principal of conditional probability,

\[
\tilde{n}_c(\varphi, t) = \frac{2}{N} \int_0^\varphi g(x/\pi R) \left\{ \int_0^{\varphi - x} n_0(\varphi, t) \left[ 1 - \left(1/N\right) \int_0^{\varphi - x} n_0(\varphi, t) d\varphi \right] d\varphi \right\} dx
\]  

(5.5)

\[
\hat{n}_c(\varphi, t) = \frac{1}{2} \int_0^\varphi \tilde{n}_c(\varphi, t) \left[ n_0(\varphi, t) + n_0(\varphi - \varphi, t) \right] \left[ \int_0^{\varphi} n_0(\varphi, t) d\varphi \right] d\varphi
\]  

(5.6)

where \( n_0(\varphi, t) = \int_0^\varphi n(c, \varphi, t)dc \), and \( g(\hat{x}, t) = \xi \sqrt{N(1 - \hat{x})^{N-1}} \) is the probability that two adjacent nucleation sites are \( \hat{x} = x/\pi R \) apart, with \( \xi \) being the normalization coefficient.

Equations (5.1)-(5.6), together with the initial condition of \( n(c, \varphi, t) = 0 \) and the boundary condition of \( n(0,0,t) = 0 \), provide a convenient framework for analyzing the effective phase transformation in the porous particle or membrane. When the total SPC volume increases to the particle/membrane volume, the saturation is reached and the absorption time, \( t_a \), can be calculated accordingly.
5.3 Results and Discussion

Figure 5.2 shows the numerical results of $n_0(\varphi,t)$. The pore size distribution is described by a lognormal function with the mean value $\bar{r} = 100nm$. The pressure difference is assumed to be $10^4 MPa$, and $\Delta\gamma = 10 mJ/m^2$. The values of $d$ is taken as 10nm, which is compatible to the NMR data (C. Cramer, 1997). The characteristic angle $\varphi_0 = r/R$. The nucleation coefficient $\eta_1$ is set to 0.001 to obtain a sufficiently fine time resolution. It can be seen that at the early stage when $t/t_a << 1$ the $n_0$ distribution is dominated by the SPC nucleation term $n_N$ and of a quasi-parabolic form, with the peak around $\bar{r}$. As the SPCs grow continuously, the coalescence is increasingly pronounced and the distribution curve becomes somewhat irregular. A most important phenomenon in this stage is the rapid decrease in $n_0$ in the low $\varphi$ region and gradual formation of a plateau in the high-$\varphi$ region. Eventually the $n_0$ curve consists of two plateaus separated by a narrow “pulse” with the height keeping decreasing. In the late stage of the wetting process, due to the large average SPC size, the system performance is dominated by the SPC coalescence. The low-$\varphi$ plateau vanishes quickly and finally the high-$\varphi$ plateau is reduced to a unit delta function at $R$, indicating the eventual saturation. The evolution process is highly nonlinear. When $t/t_a$ is about 0.4 the largest SPC angle is only around 0.1 at $t/t_a \approx 0.8$, the SPC angle tends to $2\pi$, i.e. a complete, saturated shell has been formed between the EPC and the liquid phase. The shell expands inward with a rate of $C$ at $t/t_a = 1.0$ arrives at the center of the particle.
The influence of the average pore size $\bar{r}$ and the particle size $R$ on the saturate time $t_a$ is shown in Figure 5.3. The characteristic time $t_0$ is $1\mu s$. As expected, as the pressure difference or the pore size decreases the flow rate in the nanopore, $v$, is lowered, and as a result $t_a$ becomes larger. The factor of $\bar{r}$ comes in also by affecting the SPC nucleation and coalescence. With a smaller $\bar{r}$ the starting point of SPC growth moves to the low-$\phi$ end, which in turn suppresses the coalescence. Increasing $R$ has a similar effect. The magnitude of $\partial t_a/\partial \bar{r}$ is quite high when $\bar{r}$ is relatively small, while when $p\bar{r}/\Delta \gamma$ exceeds about 0.05 the influences of $p$ and $\bar{r}$ are relatively small. Over the ranges of expected variation of these factors, the ratio of $t_a/t_0$ is around 1-10, which indicates that the assumption of flow rate discussed above is self-compatible.

In dynamic working environment the characteristic time of pressure variation can be comparable with or even smaller than the absorption time. Under this condition, the increasing rate of the pressure, $\dot{p}$, must be taken into account. Figure 5.4 shows that $t_a$ increases with the decreasing of $\dot{p}$ and $\beta$, as it should. The factor of $\dot{p}$ comes in through two mechanisms. Firstly, at a given time, a higher $\dot{p}$ leads to a larger pressure difference, which increases the flow rate. Secondly, as $\dot{p}$ rises, more pores will be involved in the SPC growth and coalescence, i.e. $r_{cr}$ increases. Both of the two mechanisms promote the forced infiltration. However, since the effect of $\dot{p}$ is accumulated over the wetting process, the degree of nonlinearity of the $t_a - \dot{p}$ relation is relatively low compared with that of $t_a - p$ relation (see Figure 5.3).

To summarize, a framework has been established to study the aggregate response of nanoporous materials by the analysis of effective phase transformation. The forced
infiltration is characterized by the evolution of the number density of SPCs. This model provide a scientific basis for the design of experiments for future study and the first-order system optimization. Clearly, for the final validation of the above discussion the theoretical results must be tested against the experimental data of the degree of saturation. The following conclusions are drawn:

(1) The evolution of the number density of pore clusters is highly nonlinear due to the complicated nucleation, growth, and coalescence behaviors. At the early stage the $n_0 - c$ relation is quasi-parabolic, which then turns into a two-plateau curve and eventually converges to a unit delta function.

(2) Prior to the final saturation, a saturated shell is formed surrounding the core area of the particle, after which the system behavior resembles that of a spherically symmetric percolation process.

(3) The absorption time rises as the average pore size or the pressure difference decreases, or as the particle size increases.
Figure 5.1 A schematic diagram of the effective phase transformation in a nanoporous particle.

Figure 5.2 The distribution of the SPC number density integrated over $c$. 
Figure 5.3 The influences of the pressure difference and the pore size on the absorption time.

Figure 5.4 The influence of $\dot{p}$ and $\beta$ on the absorption time. The characteristic time $t_r = 1ms$. 
6.1 Basic concepts

As the pressure decreases, in a mesopore, the separation of the liquid and the solid can be difficult; that is, there are significant hysteresis loops in sorption isotherm curves, probably due to the difficulty in gas phase formation or the difference between contact angles of intruding and extruding liquids (Borman, V. D., 2000; Martin, T., 2002; Grinchuk, P.S., 2002). In microporous particles, on the other hand, the energetically favorable “outflow” will lead to a complete dewetting at the liquid-solid interface in the nanoenvironment. However, currently, most of the experimental and theoretical investigations in this area are focused on the molecular behaviors in a single nanopore. The studies on the aggregate response of the nanoporous particle are scarce. In view of the above considerations, in this chapter we will develop a pore-cluster model to relate the system performance, such as the dewetting time, to the important global design variables, such as the pore-size distribution. Since the particle size is much larger than the pore size and the orientation distribution of the nanopores is usually random, in the following discussion the confined flow is assumed to be isotropic.
6.2 Governing Equations

As the external pressure decreases to below the critical value $p_0$, the liquid confined in the nanopores in a microporous particle becomes unstable and the dewetting starts randomly at a number of points. Note that the critical pressure can be assessed as $p_0 = 2\gamma/r$, where $\gamma = \gamma_{ls} - \gamma_s$, with $\gamma_{ls}$ being the solid-liquid interfacial energy and $\gamma_s$ the effective surface energy of the network material. As the liquid flows out of the porous space surrounding the initiation site, an empty pore cluster (EPC) is formed and it grows along both radial and circumferential directions. Hence, the dewetting process can be considered as an effective phase transformation from filled pore clusters (FPCs) to EPCs. In the early stage, the number and average size of EPCs keep increasing as new EPCs are nucleated. As the number of EPCs reaches the peak value, it is envisioned that the EPC coalescence would become dominant.

According to the nuclear magnetic resonance (NMR) measurements as well as the atomistic simulations (Yi, J., 1996; Cramer, C., 1997), there is an interface zone of the thickness of a few nanometers in a nanopore, as depicted in Figure 6.1. For mesoporous or macroporous materials, the pore size is larger than the characteristic interface-zone thickness. In order to analyze the average flow rate of confined liquid $\bar{v}$, both the contributions of the interface flow and the normal flow in the interior must be taken into consideration (Qiao, Y., 2005). For a microporous material, however, the pore size can be smaller than the thickness of interface zone and, therefore, the normal flow is negligible. Under this condition, the effective flow rate is dependent on the applied pressure $p$, the effective kinematics viscosity of confined liquid $\chi$, the pore size $r$, as
well as $\gamma$. Note that the molecular density in the interface zone is a function of $\gamma$ (Bockris, J. O., 1998). According to the $\Pi$ theorem, by assuming that the $\bar{v} - p$ relationship can be described by a power-law equation, the average flow rate can be stated as

$$\frac{\bar{v}}{\gamma} = \alpha \left( \frac{Pr}{\gamma} \right)^\beta$$

(6.1)

where $\alpha$ and $\beta$ are system parameters. The form of Eq.(6.1) is compatible with the experimental observation that the average diffusion rates of confined liquids in nanoporous materials follow power-law functions. For normal flow, $\beta = 1$; for subdiffusive flow, $\beta < 1$; and if $\beta > 1$, the flow is of a superdiffusive characteristic.

An EPC consists of a number of empty pores connected together and can be characterized by its radial depth $c$ and the circumferential width $l$, as shown in Figure 6.2. The collective EPCs can be characterized by the number density $n(c,l,t)$, which is defined as the number of EPCs of size $\{c,l\}$ at time $t$. Following the classic number density equilibrium equation, the evolution of $n(c,l,t)$ is governed by

$$\frac{\partial n(c,l,t)}{\partial t} + \frac{\partial [C(c,l,t)n(c,l,t)]}{\partial c} + \frac{\partial [L(c,l,t)n(c,l,t)]}{\partial l} = n_n(c,l,t)$$

(6.2)

where $C$ and $L$ are the EPC growth rates along the radial and circumferential directions, respectively; and $n_n$ is the nucleation/coalescence rate. Equation (6.2) describes the mass transportation between the EPCs to the saturated area.

As a first-order approximation, $C$ and $L$ can be taken as the average growth rate of the EPC-FPC boundary

$$C = L = \tilde{\alpha} \int_0^\infty P(r)\bar{v}dr$$

(6.3)
where $P(r)$ is the pore size distribution, which can be considered as a lognormal function with the mean value of $\bar{r}$ and the standard deviation of $\sigma_r$; and $\tilde{\alpha}$ is a parameter accounting for the orientational correlation of the micropores. For isotropic porous structure, the directions of confined flows in nanopores are random, and therefore $\tilde{\alpha} = 2/3$. The term of $n_N$ consists of two components

$$n_N(c,l,t) = \tilde{n}_N(c,l,t) + n_C(c,l,t) \quad (6.4)$$

where $\tilde{n}_N$ is caused by EPC nucleation and $n_C$ is the component associated with EPC coalescence. The nucleation rate can be stated as

$$\tilde{n}_N(c,l,t) = \eta_0 P(c \leq r_0) \left[ 1 - \frac{V(t)}{\left(\frac{4}{3}\pi R^3\right)} \right] \quad (6.5)$$

where $r_0 = 2\gamma/p$, $R$ is the particle radius,

$$V(t) = \int_0^\infty \int_0^{2\pi} n(c,l,t) l^2 dc dl$$

is the total volume of EPCs, and $\eta_0 = \eta_1 \int_0^\infty P(r) dr$, with $\zeta$ being a geometry factor and $\eta_1$ a parameter determined by the time resolution.

For regular-shaped EPCs, $\zeta = 1$. The term in the brackets in Eq.(6.5) is the volume fraction of FPCs.

If the distribution of the EPC nucleation sites is random, the EPC coalescence can be analyzed in the framework of conditional probability

$$p_d R/d = \sqrt{N_d} (R/d - d)^{1/N_d - 1} \quad (6.7)$$
where $p_d$ is the probability for two adjacent EPCs to be $d$ apart and $N_d$ is the total number of the EPCs in the area under consideration. When the sum of the radial depths of two EPCs equals the distance between them, the radial coalescence occurs and the associated probability is

$$f_r(d,t) = \eta p_d(R/d) \int_0^{d} n_c(c,t) \int_0^{e-c} n_c(\tilde{c},t) d\tilde{c} dt$$  \hspace{1cm} (6.8)$$

where $n_c(c,t) = \int_0^{e} n(c,l,t) dl$, $\eta \propto 1/N^2$ is a normalization constant, and $N_d$ can be expressed as $N(V/N)^{1/3} R^{4/3} \pi R^3$, with $N = \iint n(c,l,t) dcdl$ being the total EPC number.

The lateral coalescence, on the other hand, is dependent on the distance of the EPCs to the center of the particle $r$. The probability of the coalescence along the circumferential direction of two EPCs that are initially $d$ apart is

$$f_l(r,d,t) = \eta' \cdot \eta p_d(2\pi r/d) \int_0^{d} n_L(l,t) \int_0^{d-l} n_L(\tilde{l},t) d\tilde{l} dl$$  \hspace{1cm} (6.9)$$

where $n_L(l,t) = \int_0^{e} n(c,l,t) dc$ and $\eta' \propto 1/N^2$ is a normalization constant. In Eq.(6.9) the effective EPC number $N_d$ should be taken as $3N r^2 (V/N)^{1/3} / R^3$.

Consequently, the contribution of EPC coalescence is

$$n_c(c,l,t) = n_{cr}(c,l,t) + n_{cl}(c,l,t)$$  \hspace{1cm} (6.10)$$

The two terms at right-hand side of Eq.(6.10) capture the effects of radial and lateral coalescences, respectively, and

$$n_{cr}(c,l,t) = N(t) [\rho_i(c,l,t) - 2 \tilde{p}_i(c,l,t)]$$  \hspace{1cm} (6.11)$$
where $\tilde{p}_i$ reflects the contribution of EPC formation, $\tilde{p}_i$ reflects the contribution of EPC disappearance, and the subscript $i = R$ or $L$ denotes the radial or lateral direction, respectively. These components can be stated as

$$\tilde{p}_R(c, l, t) = n_L(l, t) \int_0^R f_R(d, t) \int_0^{R-d} n_c(\tilde{c}, t) d\tilde{c} d\tilde{d} dc dt$$  \hspace{1cm} (6.12a)

$$\tilde{p}_L(c, l, t) = n_L(c, t) \int_0^R \int_0^{2\pi} n_L(\tilde{l}, t) d\tilde{l} d\tilde{d} dc dt \int_0^{\pi} \int_0^{2\pi} n_L(\tilde{l}, t) d\tilde{l} d\tilde{d} dt$$  \hspace{1cm} (6.12b)

$$\tilde{p}_R(c, l, t) = n_L(l, t) \int_0^R f_R(d, t) \int_0^{R-d} n_c(\tilde{c}, t) dc \int_0^{n_c(c \leq R)} d\tilde{d}$$  \hspace{1cm} (6.12c)

$$\tilde{p}_L(c, l, t) = n_L(c, t) \int_0^R \int_0^{2\pi} n_L(\tilde{l}, t) d\tilde{l} \int_0^{n_L(\tilde{l}, t) \leq \pi} d\tilde{d}$$  \hspace{1cm} (6.12d)

Finally, the model is completed by setting the initial condition as $n(c, l, t) = 0$, that is, initially the particle is fully saturated; and setting the boundary condition as $n(0,0,t) = 0$.

6.3 Results and Discussion

Figure 6.3 shows the numerical results of Eqs. (3)-(12), where the average pore size $\bar{r} = 1\text{nm}$, $\sigma_r = 0.3\text{nm}$, $\gamma$ is taken as 20 mJ/m2, $p = 2.0 \times 10^4 Pa$, and $\beta \approx 1.3$. The value of $\nu$ is set to $3.2 \times 10^{-6} \text{m}^2/\text{s}$. It can be seen clearly that the $n_c(c, t)$ distribution consists of two regions separated by an abrupt drop in $n_c$. A similar characteristic can also be observed in the $n_L(l, t)$ distribution curves. The boundary of the two regions is close to $\int_0^t C dt$, which would be the upper limit of the EPC size at time $t$ if the EPC coalescence did not occur. The lower $c$ region is dependent on the EPC nucleation, growth, and coalescence, while the higher $c$ region is mostly determined by the coalescence behavior,
particularly, the term of $\tilde{p}_i$ in Eq. (11). The coalescence leads to the tendency of decrease in $n_c$ in the lower $c$ region and the increase in the higher $c$ region. As the average size and volume fraction of EPCs increase, the coalescence becomes increasingly important and the higher $c$ region dominates the system behavior. The height of the abrupt drop between the two regions keeps decreasing and eventually vanishes. When the effective dewetting process is completed, $n_c$ in the lower $c$ region is reduced to zero and there is only one EPC left in the higher $c$ region with the size of $R$.

The evolution of the average EPC size $\bar{c}$ is highly nonlinear, as shown in Figure 6.4. In the early stage of dewetting, before the EPC coalescence becomes pronounced, the increase in $\bar{c}$ is mostly caused by the EPC growth, which is quite slow. As $t/t_{dw}$ reaches 0.5, $\bar{c}$ is only about 1% of $R$, with $t_{dw}$ being the dewetting time. After that, with the increasing EPC volume fraction the coalescence leads to the rapid increase in $\bar{c}$ as small EPCs merge together. Compared to that of $\bar{c}$, the extent of nonlinearity of the evolution of EPC volume fraction is much lower, since EPC coalescence cannot be reflected in the $V - t$ relation. As $V$ rises, because of the reduction in the number of available nucleation sites, the nucleation rate is lowered, which reduces $dV/dt$. Furthermore, the coalescence causes a decrease in the specific area of the EPC-FPC interface, which retards the EPC growth. As a result, $V(t)$ increases with a descending rate.

In a number of engineering applications, the nanoporous materials work under dynamic environments with the pressure differences varying in broad ranges. The rate of pressure change $\dot{p}$ affects $t_{dw}$ by influencing $\dot{V}$ see Figure 6.5. The characteristic time $t_0$ is taken as the dewetting time if the pressure were fixed at the initial value. As
increases, with everything else the same, $\bar{\nu}$ is higher and thus is $t_{dw}$ lowered. Note that increasing the average pore size $\bar{r}$ and decreasing the dewetting “driving force” $\gamma$ have similar effects. The dewetting time is also a function of $\beta$. When $\beta = 1$, the flow rate in the nanoenvironment is proportional to $r$, and Eq.(6.2) is reduced to that of normal flow. If $\beta < 1$, subdiffusive process dominates and the dewetting takes a longer time, and vice versa. It is clear that with a constant $\bar{r}$, the broader the pore size distribution, the more large pores are involved in the EPC growth. Because $\bar{\nu}$ increases with $r$, although as $\sigma_r$ rises the fraction of small pores becomes higher, the overall effect of raising $r$ is beneficial to reducing $t_{dw}$. However, since changing $r$ does not directly affect the EPC coalescence, and the influence of EPC growth is important only in the early stage, the $r$ dependence of $t_{dw}$ is relatively weak.

A pore-cluster model is developed so as to provide an appropriate framework for the study on the aggregate behaviors of nanoporous systems. Although the details of the solid-liquid interaction and the EPC geometry are not taken into consideration and currently it is difficult to directly compare the theoretical results to experimental data, the system response (e.g., the dewetting time) can be related to the control parameters quite conveniently by the EPC number density analysis. The numerical results indicate that there exist two abruptly separated regions in the EPC number density distribution, with the lower $c$ region formed by the EPC nucleation and the higher $c$ region dominated by the EPC coalescence. At the early stage of dewetting, the EPC nucleation is the most important factor affecting $n$, whereas at the late stage the EPC coalescence results in the eventual disappearance of the lower $c$ region and the rapid increase in average EPC size.
The dewetting time decreases as the mean value or the standard deviation of pore-size distribution increases.
Figure 6.1 Schematic diagram of the confined liquid in nanopore.

Figure 6.2 Schematic diagram of a microporous particle.
Figure 6.3 Evolution of the number density of EPCs.

Figure 6.4 Evolution of the average size and the total volume fraction of EPCs.
Fig. 6.5 Dewetting time as a function of $\dot{p}\bar{r}/\gamma$ and $\beta$. 
CHAPTER VII

MODELLING OF NONWETTING LIQUID IN MESOPORES

7.1 Basic concepts

Through the well established synergistic co-assembly method, in which the silica network and the template are first formed simultaneously and then the template is removed by liquid-liquid extraction (Yang, 2002; Raman, N. K., 1996), nearly homogeneous and isotropic mesoporous silica particles with various surface properties can be obtained (Evans, D. F., 1999). The pore size is usually in the range of 2–80 nm, leading to the high specific area around 200–2000 m$^2$/g, which is the most dominant characteristic. In the interior of the particle the three-dimensional interpenetrating porous structure can be considered as a nanovoid-surrounding network covalently crosslinked together, as depicted in Fig. 7.1 (Terasaki, O. T., 2001). Usually, the particle size ranges from 1 micron to 1 mm.

In applications of catalysis or selective absorption, as well as characterization procedures such as mercury porosimetry, the mesoporous particles are often immersed in non-wetting liquids such as polymer melts/solutions and, if the particles are hydrophobic, water. The external pressure, $p$, can vary in a large range. If $p$ is smaller than the critical value, $p_{cr}$, the solid phase and the liquid phase are separate due to the capillary effect, while if $p > p_{cr}$ the nonwetting liquid can be forced into the mesopores (see Fig. 7.2). The behaviors of the confined inflow, particularly the inflow rate $v$ and the saturation time $t_s$, 
are critical to the precision control and accurate measurement of the reaction processes. In large pores, such flow is often described by invasion percolation models that are essentially hydrodynamic (Dommermuch, D. G., 1987; Blunt, M. J., 2001). For mesopores, due to the small pore size and the short \( t_s \), which is at the \( p_s-u_s \) level, the capillary effect and the probabilistic characteristic in the filling process are important (Dabrowski, A., 2001; Pandey, P., 2001).

Over years, a number of studies have been carried out on the diffusion of liquid molecules in the nanoenvironment. Through nuclear magnetic resonance (NMR) analysis, it has been confirmed that there exists an interface layer near the solid-liquid interface, where surface diffusion is dominant (Cramer, C., 1997; Yi, J., 1996). The average molecular diffusion distance can be described by

\[
\langle x^2 \rangle = \alpha \cdot t + \beta \cdot t^\kappa
\]  

(7.1)

where \( t \) is time and \( \alpha, \beta \) and \( \kappa \) are system parameters (Metzler, R., 2000). The first term in the RHS captures the single-file diffusion in the interior (normal flow) and the second term reflects the surface diffusion (subdiffusive or superdiffusive flow). However, currently the studies on the confined inflow subjected to a dynamic pressure are rare. In order to relate the liquid behavior in the nanoporous particle to the processing parameters, we will develop a model based on the equilibrium of cluster number density. The phenomenological probability functions will be used to capture the randomness of the pore cluster nucleation in the nanoenvironment and the flow rate will be assessed by a dimensional analysis.
7.2 Confined Non-Wetting Inflow in a Single Mesoporous Particle

Borman et al. (Borman, V. D., 2001; Borman, V. D., 2000) modeled the flow in porous media as a process consisting of nucleation and growth of clusters of filled pores. Under a relatively low pressure the solid and the liquid are separate, while as the pressure increases to above $p_{cr}$, the filled status becomes energetically favorable. Thus, starting from the particle surface, the liquid is forced to penetrate into the porous structure at a number of points and flow in adjacent pores, forming filled pore clusters and eventually resulting in saturation. Note that in the following discussion the pressure difference is assumed to be sufficiently high such that the factor of the pore size comes in by affecting the inflow rate instead of determining whether or not the capillary effect can be overcome.

To describe this phenomenon quantitatively, the concept of the number density of filled mesopore clusters (FMC), $n(c, \phi, t)$, can be employed. $n(c, \phi, t)$ is defined as the number of FMC with depth $c$ and angle $\phi$ at time $t$. Once $p > p_{cr}$ and the inflow occurs, the liquid randomly penetrates into the particle surface. The filled clusters expand along both radial and tangential directions. In this framework, the average behavior of the inflow can be considered as a continuous process of nucleation of new FMCS on the particle surface and the growth and coalescence of existing FMCS in the interior (see Fig. 7.3).

Consider the phase space of $n$ spanned by $c$ and $\phi$. In a small time increment $\Delta t$, the change of the number of FMCS in the area of $c$ to $c + \Delta c$ and $\phi$ to $\phi + \Delta \phi$ can be stated as

$$\Delta n = \Delta t \left[ n_N + \left[ \bar{C}(c)n(c) - \bar{C}(c + \Delta c)n(c + \Delta c) \right] + \left[ \bar{\Psi}(\phi)n(\phi) - \bar{\Psi}(\phi + \Delta \phi)n(\phi + \Delta \phi) \right] \right]$$  (7.2)

where $n_N$ is the nucleation rate, $\bar{C}$ is the average radial growth rate, $\bar{\Psi}$ is the average
tangential growth rate, and $\bar{n}$ is the average number density. If we neglect the high-order terms, as $\Delta t, \Delta c$ and $\Delta \phi \to 0$, Eq. (3.2) can be rewritten as

$$\frac{\partial n(c, \phi, t)}{\partial t} + \frac{\partial [C(c, t)n(c, \phi, t)]}{\partial c} + \frac{\partial [\Psi(\phi, t)n(c, \phi, t)]}{\partial \phi} = n_N(c, \phi, t)$$  \hspace{1cm} (7.3)$$

where $C$ and $\Psi$ are the radial growth rate and the tangential growth rates of FMC, respectively. Equation (7.3) describes the equilibrium of FMC number density. The second and third terms at LHS capture the effect of FMC growth, and the RHS reflects the nucleation and coalescence. When the total FMC volume equals the particle volume, i.e.

$$\int\int n(c, \phi, t_i) \cdot \lambda \cdot (1 - \cos(\frac{\phi}{2})) \times (3R^2 + c^2 - 3cR) \, dc \, d\phi = \frac{4}{3} \pi R^4$$  \hspace{1cm} (7.4)$$

where $R$ is the particle radius and $\lambda$ is a geometry factor, the particle is saturated. For isotropic FMC growth, $\lambda = \frac{2}{3} \pi$.

The flow rate $v$ in a mesopore should be related to the external pressure $p$, the liquid density $\rho$, the viscosity $\mu$, the pore radius $r$, and the interfacial tension $\gamma$. Similar with Eq. (7.1), the inflow rate can be decomposed into two components

$$v = f_1(p, \rho, \gamma, \mu) + f_2(p, \rho, r, \mu)$$  \hspace{1cm} (7.5)$$

where $f_1$ and $f_2$ reflect the interface flow and the normal flow in the interior, respectively. Note that the interface flow is independent of pore size $r$ and the normal flow in the interior is independent of $\gamma$. Based on the $\Pi$ theorem (Szirtes, T., 1997) and following Eq. (7.1), the average inflow rate can be described by a two-power-law function

$$v = \alpha^* \frac{pr}{\mu} \left( \frac{p \rho r^2}{\mu^2} \right)^\beta + \alpha \sqrt{\rho} \left( \frac{p \mu^2}{\rho \gamma^2} \right)^\beta$$  \hspace{1cm} (7.6)$$

78
where $\alpha^\ast$, $\alpha^\dagger$, $\beta$, and $\beta'$ are system parameters. According to the classic circular Poiseuille flow solution, for normal flow $v \propto p$, i.e. $\beta = 0$. The parameters $\alpha^\ast$ and $\alpha^\dagger$ indicate the degree of importance of the interface layer and can be assumed to be proportional to the cross-sectional areas. Hence, $\alpha^\ast \propto (1 - d_0/r)^2$ and $\alpha^\dagger \propto 1 - [(r - d_0)/r]^2$, with $d_0$ being the thickness of the interface layer. Note that when $d_0 \to 0$ or $r \to \infty$ Eq. (7.6) should converge to the result of conventional fluid mechanics. Consequently, the inflow rate can be obtained as

$$v = \left(1 - \frac{d_0}{r}\right)^2 \frac{pr}{8\mu L} + \alpha \left[1 - \left(\frac{r - d_0}{r}\right)^2\right] \left[\frac{p}{\rho \gamma^2} \right]^\beta$$

(7.7)

where $L$ is the effective pore aspect ratio and $\alpha$ is a material constant [Liu, D.,1997]. Since $v$ increases with $p$ and $\gamma$ and decreases with $\rho$ and $\mu$, the value of $\beta$ should be in the range of 0 to 1/2. The average radial growth rate of FMC can then be calculated as

$$C = \int_0^\infty P(r)vdr$$

(7.8)

where $P(r)$ is the pore size distribution. Similarly, the average tangential growth rate is

$$\Psi = \frac{2}{R - c/2} \int_0^\infty P(r)vdr$$

(7.9)

At the small time scale, the invasion of the nonwetting liquid cannot be considered as an equilibrium process (Polartz,2002; Dabrowski,2001; Pandey, P.,2001). At time $t$, the number of pores in the particle surface where the inflow starts can be stated as

$$\tilde{n}_N(c, \varphi, t) = \eta_0 \left(\frac{\varphi R}{2}\right) e^{-\frac{c}{\varphi}} \times \left[1 - \frac{1}{4\pi R^2} \int \int \eta(c, \varphi, t) \cdot \zeta \varphi R^2 dc d\varphi\right]$$

(7.10)
The term in the bracket indicates the fraction of the surface area of empty pores, with \( \zeta \) being a geometry factor, which equals \( \pi \) when the FMCs are small. The parameter \( \eta_0 = \eta_1 \int_0^{r_f} P(r) dr \), with \( \eta_1 \) being a constant, \( r_{fr} = 2\gamma_l \cos \theta / p \) being the lower limit of the size of the filled pores, \( \gamma_l \) being the surface tension of the non-wetting liquid, and \( \theta \) being the contact angle.

The probability for the center-to-center distance between two adjacent FMCs to be \( x \) is (Chen, H., 2005)

\[
f(\tilde{x}) = \sqrt{D_0} (1 - \tilde{x})^{D_0-1}
\]

(7.11)

with \( \tilde{x} = x/2\pi R \) and \( D_0(t) = \int \int n(c, \varphi, t) dcd\varphi \) being the total number of FMC. Hence, the probability of coalescence is

\[
g(x,t) = \eta \cdot f(\tilde{x}) \int_0^\varphi n_c(\varphi, t) \left[ 1 - \int_0^{x/R-\varphi} n_c(\bar{\varphi}, t) d\bar{\varphi} \right] d\varphi
\]

(7.12)

where \( \eta \) is the normalization coefficient and \( n_c(\varphi, t) = (1/D_0) \int n(c, \varphi, t) dc \). Note that the probability nature of the inflow process is related to the pore size distribution as well as the secondary factors affecting the capillary effect such as the precursor film formation and the dependence of the contact angle on flow direction.

The nucleation rate due to the FMC coalescence can then be obtained as

\[
\bar{n}_N(c, \varphi, t) = D_0(t) \left[ \tilde{g}(\varphi, t) - 2 \tilde{g}(\varphi, t) \right] \frac{c}{c_{fr}}
\]

(7.13)

where \( \tilde{g}(\varphi, t) = 2 \int_0^\varphi g(x) \left[ \int_0^{(x-R-x)/2} n_c(\bar{c}, t) \left[ 1 - \int_0^{x-R-x-\bar{c}} n_c(\bar{\bar{c}}, t) d\bar{\bar{c}} \right] d\bar{\bar{c}} \right] dx \) is the distribution of a FMC nucleated from two smaller FMC with the size distribution of
\[
\tilde{g}(\varphi, t) = \int_0^{\sigma^*} g(x) \frac{n_c(\varphi, t)}{\int_0^{n/2} n_c(\varphi, t) d\varphi} dx
\]

Finally, the overall nucleation rate can be obtained as \( n_N = \tilde{n}_N + \tilde{n}_N \), and the boundary condition and initial condition should be \( n(0,0, t)=0 \) and \( n(c, \varphi, 0)=0 \), respectively. The model for the kinetics of confined inflow is now complete.

7.3 Results and Discussion

Figure 7.4 shows the numerical results of the evolution of \( n_c \) under \( p = 0.1 \) MPa in a particle with a radius of 100 \( \mu m \). The surface tension and the contact angle are taken as 72 mJ/m\(^2\) and 120°, respectively. The pore size distribution is described by a lognormal function with a mean value \( \bar{r} \) of 10 nm and a standard deviation \( \sigma \) of 3 nm. The characteristic time \( t^* = 1 \mu s \). Based on the NMR data, the value of \( \beta \) is taken as 1.2 and \( d_0 \) is assumed to be 5 nm (Cramer, C., 1997; Yi, J., 1996). The value of \( \eta \) can be somewhat arbitrarily chosen since it depends on the time resolution and has little influence on the absolute value of \( n_c \). In this paper it is set to \( 10^{-3} \). The viscosity and density of the liquid are taken as \( 10^{-3} \) Pa·s and \( 10^3 \) kg/m, respectively.

It can be seen that at the early stage when \( \tilde{n}_N \) is dominant the peak of \( n_c \) distribution is around \( \bar{r} \). With the growth of FMCs the peak moves toward the higher end and the height starts to decrease due to the size dependence of \( \Psi \). As the number of FMCs becomes larger, the coalescence of adjacent FMCs is increasingly pronounced and the distribution curve consists of two plateau regions caused by the decrease in \( n_c \) in the lower \( \varphi \) range and the rapid increase in the higher \( \varphi \) range, respectively. The two regions are separated by a sharp
drop in $n_c$ associated with the tangential growth. Eventually the plateau at lower $\phi$ range vanishes and when saturation is reached the total FMC number is reduced to 1.

The saturation time, $t_s$, is influenced by a number of factors. The numerical results shown in Fig. 7.5 indicate that $t_s$ decreases with increasing $p$ and $\bar{r}$ or decreasing $R$, as it should. The value of $t_s$ tends to infinity as $p \to 0$, and decreases rapidly until $\sqrt{p/\rho}$ exceeds 1, after which $t_s$ becomes relatively insensitive to the change in $p$. Through Eqs. (7.10) and (7.13), it can be seen that the $t_s - R$ relation is highly nonlinear. As the particle radius increases the probability of FMC coalescence is lowered and thus the filling process is prolonged, which is equivalent to reducing the pore size $\bar{r}$. Therefore, even if the filling rate $\nu$ were independent of $r$ the inflow in the mesoporous particle is still not scalable. This mechanism, together with the size effect of $\nu$, results in the nonlinear $t_s - R$ relationship.

In a dynamic environment, the characteristic time of pressure variation, $p/p'$, is comparable to the saturation time. Under this condition, the pressure $p$ cannot be assumed to be a constant. By replacing $p$ by $\dot{p}t$ in Eqs. (7.3)–(7.15), this effect can be studied numerically and the results are shown in Fig. 7.6. As $\dot{p}$ rises, the acceleration of inflow becomes higher and thus $t_s$ is lowered. The $\dot{p}$ dependence of $t_s$ is somewhat stronger than that of $p$, since, due to the relatively low early pressure, the early stage of FMC evolution where the FMC growth is nearly isolated is prolonged. In Fig. 7.6, we also show the influence of $\beta$. As suggested by Eq. (7.7), increasing $\beta$ has a beneficial effect in increasing the saturation time. The large extent of variation of $t_s$ associated with the change in $\beta$ indicates clearly that the interface layer plays an important role in the absorption process.
To summarize, based on the analysis of FMC number density, a framework has been developed for the kinetics of the non-wetting flow in a mesoporous particle. The process is modeled as the nucleation, growth, and coalescence of filled pore clusters, with the fractal nature of the inflow being neglected.

The following conclusions are drawn: (1) the evolution of $n_c$ can be characterized by the shifting and eventual vanishing of the plateau in the small angle region and the development of the secondary plateau in the large angle region; (2) a number of factors, such as the pore size distribution, the particle size, the external pressure, come in by affecting both the inflow rate and the coalescence processes; and (3) the influence of the interface layer is significant.
Figure 7.1 The mesoporous structure.
Figure 7.2 The nonwetting flow confined in a mesopore under the external pressure, \( p \).
Figure 7.3 Schematic diagram of the growth of filled mesopore clusters.
Figure 7.4 Evolution of $n_c(\varphi, t)$, where $\varphi_0 = 2r/R$ is the characteristic angle
Figure 7.5 The saturation time as function of $\rho \mu^2 / \rho \gamma^2$ and $R/R^*$. 
Figure 7.6 The saturation time as function of $t^* \frac{\dot{\rho}}{\rho} \gamma^2$ and $\beta$. 
CHAPTER VIII

CONCLUSIONS

In a recent study, we have performed first-order analyses and proof-of-concept experiments for a novel application of nanoporous materials in developing high-performance nanoporous energy absorption system (NEAS) and thermally/electrically controllable active nanoporous system (ANS). When nanoporous particles are immersed in a nonwetting liquid, due to the capillary effect the infiltration will not occur unless the applied pressure reaches the critical value, $p_{in}$. In NEAS, depending on factors that are still inadequately understood, as the pressure is reduced the confined liquid remains in the energetically unfavorable nanopores. Thus, the large increase in interface energy is “absorbed”. The energy absorption efficiency is higher by orders of magnitude than that of composites or shape memory alloys that are used in protection devices such as car bumpers and soldier armors.

Thermal effects on the performance of a NEAS consisting of hydrophobic mesoporous silica particles have been investigated experimentally. Through the loading–unloading tests at different temperatures, the sorption isotherm curves are characterized by $p_{in}$ and $E^*$. While the influence of temperature variation on $p_{in}$ is only secondary, the outflow of the confined liquid is strongly dependent of thermal treatment, indicating that the mechanisms of the pressure induced absorption and desorption are different. The following conclusions are drawn:
(1) As temperature increases, the infiltration pressure decreases slightly.

(2) Temperature has little influence on the accessible specific pore volume.

(3) The efficiency of energy absorption associated with the first infiltration cycle is quite insensitive to the temperature.

(4) The system recoverability increases rapidly with temperature. When the temperature exceeds about 50°C, the system becomes almost fully reusable.

(5) The outflow is a thermally aided process and insensitive to pressure.

(6) In the nanoenvironment, the geometrical aspect of the porous structure as well as the mass/energy exchange between the gas and the liquid phases must be taken into consideration.

(7) Due to the energy barrier of gas-phase nucleation, the mechanisms of pressure induced absorption and desorption of nanoporous materials are quite different. The desorption behavior is affected by pore size, pressure, and surface and interfacial properties. There exists a critical pore size above which the “outflow” is impossible.

Through the impact experiment, it has been validated that the NEAS can be used for energy absorption applications under dynamic loadings. Compared with the quasi-static case, under a dynamic loading the energy absorption efficiency of the NEAS was much higher. The interaction among the nanoporous particles was negligible. No detectable priority of infiltration in larger pores over smaller ones was observed in the current study.

For ANS, on the other hand, if temperature or electrical potential is changed, due to the variation in interface energy caused by the thermocapillary or electrocapillary effect, the confined liquid can “flow” out of the nanopores, resulting in a significant system volume change. Since this process is fully reversible, it leads to a “volume memory”
characteristic. The energy density and displacement of such a system are much higher than that of conventional intelligent materials such as piezoelectrics and magnetostrictives.

A framework has been established to study the aggregate response of nanoporous materials by the analysis of effective phase transformation. The forced infiltration is characterized by the evolution of the number density of SPCs. This model provides a scientific basis for the design of experiments for future study and the first-order system optimization. The following conclusions are drawn:

(1) The evolution of the number density of pore clusters is highly nonlinear due to the complicated nucleation, growth, and coalescence behaviors. At the early stage the $n_o - c$ relation is quasi-parabolic, which then turns into a two-plateau curve and eventually converges to a unit delta function.

(2) Prior to the final saturation, a saturated shell is formed surrounding the core area of the particle, after which the system behavior resembles that of a spherically symmetric percolation process.

(3) The absorption time rises as the average pore size or the pressure difference decreases, or as the particle size increases.

A pore-cluster model is developed so as to provide an appropriate framework for the study on the aggregate behaviors of nanoporous systems. Although the details of the solid-liquid interaction and the EPC geometry are not taken into consideration and currently it is difficult to directly compare the theoretical results to experimental data, the system response (e.g., the dewetting time) can be related to the control parameters quite conveniently by the EPC number density analysis. The numerical results indicate that
there exist two abruptly separated regions in the EPC number density distribution, with the lower $c$ region formed by the EPC nucleation and the higher $c$ region dominated by the EPC coalescence. At the early stage of dewetting, the EPC nucleation is the most important factor affecting $n$, whereas at the late stage the EPC coalescence results in the eventual disappearance of the lower $c$ region and the rapid increase in average EPC size. The dewetting time decreases as the mean value or the standard deviation of pore-size distribution increases.
REFERENCES


