Nanofluidics: Fundamentals and Applications in Energy Conversion

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ABSTRACT

As a nonwetting liquid is forced to invade the cavities of nanoporous materials, the liquid-solid interfacial tension and the internal friction over the ultra-large specific surface area (usually billions of times larger than that of bulk materials) can lead to a nanoporous energy absorption system (or, composite) of unprecedented performance. Meanwhile, while functional liquids, e.g. electrolytes, are confined inside the nanopores, impressive mechanical-to-electrical and thermal-to-electrical effects have been demonstrated, thus making the nanoporous composite a promising candidate for harvesting/scavenging energy from various environmental energy sources, including low grade heat, vibrations, and human motion. Moreover, by taking advantage of the inverse process of the energy absorption/harvesting, thermally/electrically controllable actuators can be designed with simultaneous volume memory characteristics and large mechanical energy output. In light of all these attractive functionalities, the nanoporous composite becomes a very promising building block for developing the next-generation multifunctional (self-powered, protective and adaptive) structures and systems, with wide potential consumer, military, and national security applications.

In essence, all the functionalities of the proposed nanofluidic energy conversion system are governed by nanofluidics, namely, the behavior of liquid molecules and ions when confined in ultra-small nanopores. Nanofluidics is an emerging research frontier where solid mechanics and fluid mechanics meet at the nanoscale. The complex interactions between liquid molecules/ions and solid atoms at the nanointerface, as well as the unique structural, thermal and electrical characteristics of fluids confined in nanocavities collectively represent an outstanding challenge in physical science. A thorough understanding of the science of nanofluids, in particular the detailed molecular mechanisms as well as the roles of various material and system parameters, does not only underpin the development and optimization of the aforementioned nanofluidic energy conversion system, but it also have broad impact on a number of other areas including environmental engineering, chemical engineering, bioengineering, and energy engineering, etc.

This dissertation carries out a systematic computational study to explore the fundamental nanofluidic infiltration and transport mechanisms, as well as the thermal and electrical characteristics of the solid-liquid interface. New physical models describing the unique nanofluidic phenomena will be established, where critical parameters, such as the surface tension, contact angle, and viscosity, will be reinvestigated at the nanoscale. The effects of various material and system parameters, such as the solid phase, liquid phase, pore size and pore geometry, as well as the external thermal, electrical and mechanical loads, etc., will be systematically investigated and bridged with the nanofluidic energy conversion processes. The energy conversion efficiencies under various conditions will be evaluated via a synergy between simulation and experiment. Reverse analysis based on the revealed
principles can guide the optimization of the various material and system parameters, which potentially may contribute to the design of highly efficient and sustainable nanofluidic energy conversion devices. Besides the direct impact on the nanofluidic energy conversion, the study is also directly relevant to biological conduction and environmental sustainability, in both of which infiltration and transport play important roles.
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Dedicated to my family!
Chapter 1. Overview and Motivation

1.1. Grand Challenges of Materials for Enhancing Efficiency of Energy Conversion and Sustainability

As an indication of the capacity of a physical system to perform work, energy exists in a variety of forms, including mechanical energy, thermal energy, electrical energy, chemical energy, biological energy, etc. Energy conversion among these various forms is a process ubiquitous throughout the vast cosmos.

The past decades have witnessed some greatest accomplishments of engineering in utilizing and enhancing energy conversion. For example, (1) electricity generated from fossil fuels, fusion and fission, and manifold renewable sources (hydropower, biomass, wind, geothermal, solar, ocean energy, etc.) is being widely distributed and consumed at a stunning rate of approximately 12TW.[1] (2) Protection modules, such as bumpers and damping units, are integrated in myriad consumer products as well as industrial and military structures to isolate and alleviate impacts and shockwaves (by converting excessive mechanical energy to thermal and/or other forms of energy) so as to protect user safety and critical/delicate components. (3) Field-responsive smart materials, such as piezoelectric materials and shape memory alloys, are utilized in a variety of engineering structures to actively control and manipulate the structural morphologies (by converting electrical energy and/or thermal energy to mechanical energy).

Despite these advances, the decades ahead pose many significant challenges. First, most material systems that are currently adopted for energy conversion are specifically designed for one purpose alone (e.g. energy generation, energy absorption, or actuation). There is no unified solution available for an “all-in-one” multifunctional material system which can integrate all the energy conversion functionalities mentioned above and be self-powered, self-actuated, and self-protective. The implementation of such a material system, though, may dramatically simplify the system design and enhance the system integrity.

Another and a more pressing issue is to increase “energy efficiency”. In view of the ever growing demand for sustainability, enhancing the efficiency of energy conversion is urgent and may lead to immediate and enormous economic and societal impacts. This is not only critical to “conventional” energy conversion techniques, but
also crucial for new and alternative energy approaches where the energy conversion efficiency is still a bottleneck. Take electricity generation as an example. In the conventional approach burning fossil fuels to rotate turbines, the overall efficiency is about 35%-50%;[1] on the alternative energy side, even using today’s best photovoltaic materials, the efficiency is only around 20% for solar cells based on thin film technologies.[2] The issue of low “efficiency” also exists for protection and smart materials. For instance, the energy density of typical metal foams is about 1-20 J/g, and that of Ti-Ni alloys is only 0.05 J/g.[3]

Given these facts, increasing the efficiency of energy conversion can contribute tremendously (and arguably more rapidly compared with other approaches, e.g. finding alternative energies[4]) to the global sustainability. For instance, if 10% of the waste heat (an estimation based on the Carnot limit for relevant low-grade heat) can be recovered from the conventional fossil fuel-based electricity generation process, that would account for Terawatts of power, and thus equivalently less fuel consumption and carbon emission. If 10% of otherwise wasted solar thermal energy can be harvested, that would account for about 30-40% increase of the current potential of solar power. If one can effectively scavenge the abundant thermal gradients and mechanical motions throughout buildings and landscapes and convert that into useful electricity, that will enable wirelessly powered sensor networks for smart infrastructures and energy efficient buildings, as well as a wide variety of “place and forget” intelligence, surveillance, and reconnaissance systems. For protection and smart materials, the benefit of increasing efficiency is also obvious: high efficiency (or more specifically, high energy density) cuts the weight of the structure carrying protection/actuation modules, thereby minimizing the demand on batteries/fuels or supportive materials (especially when these functions are integrated with energy harvesting and an all-in-one multifunctional material system is used).

Although promising, immense challenges have to be surmounted before these goals can be achieved. First, as most of traditional techniques have reached their limits, further increase of energy conversion efficiency requires fundamental understanding and scientific breakthroughs in innovative energy technologies and advanced new materials. Moreover, as almost all materials currently adopted for energy conversion are specifically designed for one purpose alone, novel multifunctional materials need to be sought so as to realize manifold energy conversion functionalities within the same platform.

Among the current research endeavors towards this direction, nanostructured and nanofunctional materials have shown a promise of new opportunities. For example, with tunable band gap and designable arrangements of semiconducting

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* For energy absorption and smart materials, “energy efficiency” is usually characterized by the term “energy density”, which indicates the amount of energy that could be absorbed or released by unit mass of materials.
nanocrystals, the third generation quantum dot solar cells can boost its efficiency beyond the Shockley and Queisser limit of 32% for silicon-based solar cells.[5] Using superlattices containing alternate ultra-thin layers of Bi$_2$Te$_3$ and Sb$_2$Te$_3$, an unprecedented figure of merit (ZT) of 2.5 has been achieved for thermoelectric energy conversion.[6] With ZnO nanowires, an efficiency of 6.8% has been achieved in the harvesting of wasted mechanical energy (such as body-movement, light wind, and vibration of acoustic waves).[7] Using nanopillar-shaped Cu-Al-Ni alloys, the figure of merit of energy absorption has reached an unprecedented value of 0.9, much larger than those of conventional shape memory alloys.[8]

Despite the encouraging energy efficiencies, the aforementioned materials have a limitation in common, namely, the lack of multifunctionality. As noted above, multifunctional materials can offer the dual benefits of drastically simplifying the system design as well as reducing the system weight/cost. The realization of the multifunctionality, though, requires a versatile and powerful material platform that can efficiently accommodate the manifold energy conversion functionalities, which is, however, not present in those materials mentioned above. In addition, the aforementioned materials all have some other inherent deficiencies. For example, in solar cells, most of the solar energy is still being wasted as heat; for thermoelectric materials based on the Seebeck effect, the efficiency is still low at relatively low temperature gradients (e.g. the low-grade heat with temperature difference <100 °C, which represents the main market); in the thermal-to-electrical energy conversion, ZnO nanowires are somewhat too brittle to harvest significant loadings.

In view of these challenges, in this dissertation, we propose a novel form of nanocomposite that combines nanoporous materials and functional liquids. As illustrated in Figure 1, this conceptually new material can offer superior efficiencies of energy absorption, actuation and energy harvesting, and all these functionalities are readily integrated within one platform, elaborated on below.

1.2. A New Form of Nanocomposite Combining Nanoporous Materials and Functional Liquids

Nanoporous materials are solids containing large volume fractions of nano-sized pores. Owing to its low cost and ultra-large specific surface area (100-2000 m$^2$/g, compared to ~0.001 m$^2$/g for bulk materials), nanoporous materials constitute an ideal yet relatively less explored platform for accepting or actuating liquids. In order to take advantage of the vast platform of energy conversion nestled in nanoporous materials of small mass/volume, we propose a new form of nanocomposite that combines nanoporous materials with functional liquids. As a consequence of the complex interactions between the solid and the liquid taking place
at their interface, the novel nanocomposite has been demonstrated to have manifold energy conversion capabilities including energy absorption, actuation, and energy harvesting (Figure 1). In this section, we will first review the manifold functionalities of the proposed nanoporous composite; these functionalities will be rationally understood in Section 1.2.2; and in Section 1.2.3, the central role of nanofluidics will be introduced.

1.2.1. Nanoporous Composite: An Overview

Amplified by the ultra-large interface zone attainable in nanoporous materials and assisted by the unique interaction between nanoconfined liquid molecules/ions and solid atoms, the performance of energy conversion can be extremely high using the new nanoporous composite.

In terms of energy absorption (Figure 1b), the energy density of the proposed nanocomposite (e.g. using hydrophobic nanoporous silica and water) is typically on the order of 100 J/g under quasi-static loading conditions, which is much higher than conventional cellular materials (Table 1).[9-11] Under dynamic loading conditions, the energy density can be even more significant, measured to be about 50-300 J/g, which is several times higher than that in the quasi-static cases.[10,12]

On the other hand, the deformation of the nanocomposite system is controllable via thermal and electric fields (Figure 1c). This makes the nanocomposite an “intelligent” material exhibiting volume memory characteristics.[13,14] For example, as the temperature is varied by 80 °C in a system of Zeolyst ZSM-5 zeolite and water, the output energy is measured about 5 J/g, two orders of magnitude higher than that of conventional shape-memory alloys, e.g. Ti-Ni alloys (Table 2).[15]

The nanoporous system can also output electricity as the liquid-solid interface is disturbed by externally applied thermal or mechanical load. For example, as illustrated in Figure 1d, two nanoporous carbon disks (weighting about 0.1g) are bathed in NaCl solutions with different temperatures. An output voltage of 3.8 mV/°C is measured as the temperature difference between the two nanoporous electrodes increases continuously from 0 to 30 °C, which is larger than that of conventional thermoelectrics based on the Seebeck effect by 1-2 orders of magnitude.[16,17] The peak output power is more than 1 mW† (compared with 1-5 μW of complex oxides, superlattices, and nanowires or nanotubes). The energy conversion efficiency (percentage of electrical energy generated with respect to the consumed thermal energy) is about 8-9%, close to the Carnot cycle limit and much higher than that of

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† Such a power harvesting system is ideal for biodevices and microcontrollers. For instance, the power requirement is 10 μW for a cardiac pacemaker, 1 mW for a passive sensor, and 10-100 mW for a microchip. With the high conversion efficiency, if multiple energy conversion systems form a network, a much higher power can be provided.
conventional thermoelectric materials (less than 2% for the same 30 °C temperature difference). Similarly, illustrated in Figure 1e, a voltage of about 12mV is measured by forcing an electrolyte to flow through a nanoporous electrode at a rate of 10 mm min⁻¹.

Figure 1. (a) Energy conversion with the proposed nanoporous composite. (b-e) Schematics of the validation experiments.

Table 1. Comparison of energy absorption materials

<table>
<thead>
<tr>
<th>Energy Absorbing Materials</th>
<th>Weight Density (g/cm³)</th>
<th>Energy Absorption per Unit Mass (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polymer foams</td>
<td>0.03-0.3</td>
<td>0.1-2</td>
</tr>
<tr>
<td>Metal foams</td>
<td>0.1-0.3</td>
<td>1-20</td>
</tr>
<tr>
<td>Cellular textile composites</td>
<td>0.1</td>
<td>1-10</td>
</tr>
<tr>
<td>Shape memory alloys</td>
<td>5-7</td>
<td>&lt; 1</td>
</tr>
<tr>
<td>Nanoporous composites</td>
<td>0.8-1.2</td>
<td>30-300</td>
</tr>
</tbody>
</table>
Table 2. Comparison of smart materials and systems

<table>
<thead>
<tr>
<th>Properties</th>
<th>Piezoelectrics</th>
<th>Magnetostrictives</th>
<th>Ti-Ni alloy</th>
<th>TCNC**</th>
<th>ECNC**</th>
</tr>
</thead>
<tbody>
<tr>
<td>Energy density* (mJ/g)</td>
<td>~0.5</td>
<td>~3</td>
<td>~50</td>
<td>1000-30000</td>
<td></td>
</tr>
<tr>
<td>Maximum strain</td>
<td>&lt; 0.5%</td>
<td>~1%</td>
<td>&lt;10%</td>
<td>60%</td>
<td></td>
</tr>
<tr>
<td>Response time (sec.)</td>
<td>10^-6</td>
<td>10^-5</td>
<td>10^-2</td>
<td>10^-2</td>
<td>10^-7-10^-6***</td>
</tr>
<tr>
<td>Thermal controllability</td>
<td>——</td>
<td>——</td>
<td>Good</td>
<td>Good</td>
<td>——</td>
</tr>
<tr>
<td>Electrical controllability</td>
<td>Good</td>
<td>Good</td>
<td>——</td>
<td>——</td>
<td>Good</td>
</tr>
</tbody>
</table>

* The data of piezoelectrics, magnetostrictives, and Ti-Ni alloy are drawn from Wei et al.[3]
** TC: thermally controllable; EC: electrically controllable; NC: nanoporous composites
*** The assessment is based on the wetting/dewetting time for a nanoporous particle with the size of 1 μm.

In addition to the appealing performance, the new nanocomposite also shows a distinction of combining all those exciting functionalities mentioned above, leading to a promising building block for the next-generation multifunctional structures and systems (Figure 1a). In order for this promise to be fulfilled, though, the manifold functionalities and the superior performance that has been demonstrated in experiment must be rationally understood and optimized. In Section 1.2.2, the involved energy conversion processes will be understood from theoretical perspectives.

1.2.2. Understanding the Energy Conversion Functionalities

1.2.2.1. Energy Absorption

The nanocomposite system for energy absorption is prepared by dispersing fine hydrophobic nanoporous particles (usually 1-30 μm in diameter) in a nonwetting liquid (Figure 2a-c)[18]. The solid phase could be zeolites, silica, or other nanoporous materials, and the liquid phase is typically pure water or salt solutions. To measure the mechanical performance (Figure 2d), the mixture is first sealed in a stainless steel pressure cylinder, which is then firmly mounted onto a steel base and wired with a data acquisition system. The piston in the pressure cylinder is driven downwards and upwards by a servo motor to load and unload the cylindrical cell, during which the applied pressure and the displacement of the piston are continuously recorded and output.
Figure 2. System setup and experimental measurement of the Nanoporous Particle Suspended Liquid (NPSL) for energy absorption: (a) a stainless steel pressure cylinder enclosing the NPSL sample; (b) the solid particles are zeolites, silica, or other nanoporous materials, and the liquid phase is typically pure water or salt solutions; (c) the typical appearance of NPSL; (d) in mechanical testing, the pressure cylinder is firmly mounted on a steel base and wired with a data acquisition system; the piston is driven downwards and upwards by a servo motor to load and unload the cylindrical cell, during which pressure and displacement are constantly recorded and output.\(^{[19]}\)

![Figure 2](image1.png)

Figure 3. Three representative \(P-\Delta V\) curves: (a) in a non-reusable system (Fluka 100 \(C_8\) reversed phase mesoporous silica and pure water), liquid is stuck in the nanoporous materials after the first loading cycle;\(^{[11]}\) (b) in a reusable system (Fluka 100 \(C_8\) reversed phase mesoporous silica and 23.1% aqueous solution of NaCl), the liquid defilters after the system is fully unloaded;\(^{[11]}\) (c) the effect of surface treatment: different surface treatment time, \(t\), leads to varied performance of energy absorption.\(^{[20]}\)

![Figure 3](image2.png)
Figure 3 plots three groups of representative $P$-$\Delta V$ curves. Apparently, these $P$-$\Delta V$ curves share many characteristics in common despite a few quantitative differences. Take Figure 3a as an example. Initially (from point “O” to “A”), the absorption isotherm is almost linear, showing an effective bulk modulus close to that of pure water. As the pressure $P$ exceeds the critical pressure, $P_{cr} \approx 17$ MPa, the liquid starts to enter and transport inside the nanopores, forming a plateau from point “A” to “B” in the $P$-$\Delta V$ curve. As most of the nanopores are filled up, another linear regime (“B” to “C”) is observed, which corresponds to the compression of the liquid mixed with filled nanoporous particles. Finally, as the system is unloaded (“C” to “D”), the pressure is reduced back to the atmospheric pressure. Apparently, from “O” to “D”, a pronounced hysteresis is formed in this absorption isotherm. The enclosed area indicates the amount of energy absorbed during this loading-unloading cycle. For the illustrated case, the energy absorption is around 10 J/g, which is very competitive compared with other protective materials (Table 1).

It is noted that the plateau shown in Figure 3a is inclined rather than being parallel with the horizontal axis. This slope can be attributed to two reasons. First, most nanoporous materials (except those well crystallized, e.g. zeolites) have a distribution of pore size; namely, the nanopores are not uniformly sized. As will be elaborated on in Chapter 2, liquid intrusion into different-sized nanopores requires different pressures: the larger pore size, the smaller infiltration pressure. Thus, as the pressure increases, relatively large nanopores will be first penetrated, followed by relatively small nanopores, which partially contributes to the formation of the slope shown in Figure 3a. The other reason lies in the viscous transport of the liquid phase inside the nanopores. Basically, confined liquid phase is always subjected to a resistance against its motion relative to the nanopore. Hence, in order to sustain the liquid infiltration, an external force must be input to counter the resistance; reflected in the $P$-$\Delta V$ curve, $P$ must increase as $\Delta V$ increases.

Another phenomenon that deserves mention is that in the case shown in Figure 3a, $\Delta V$ does not return to zero as $P$ is reduced to zero, implying that a large amount of liquid is stuck inside the nanoporous particles even after the system is fully unloaded. Hence, nanopores remain occupied after the first cycle and the absorption ability is lost. When a second loading-unloading cycle is performed, the energy absorption is much lower compared with that in the first cycle. By contrast, the system shown in Figure 3b exhibits nearly full recoverability; most confined liquid comes out of the nanopores after unloading. From a practical point of view, the system shown in Figure 3a has no reusability and the system shown in Figure 3b is reusable. In practice, the reusability can be achieved by appropriately selecting the liquid and solid materials (or, adding chemical admixtures).\textsuperscript{[11,21]} Given the practical importance of the reusability, the molecular mechanism of defiltration will be discussed in Section 3.5.
Figure 4. The two effects governing the nanofluidic infiltration/defiltration and transport: (a) capillary effect and (b) viscosity effect. During infiltration, both effects impede the liquid motion. In (c) defiltration, the viscosity effect continues to resist the liquid flow while the capillary effect starts to offer assistance. The mechanical mechanisms of both effects are illustrated in (d) and (e), respectively.

In order to understand the fundamental mechanisms of infiltration and transport, we start from a single nanopore and a nonwetting liquid (Figure 4). Initially, due to the well-known capillary effect, the liquid phase stays outside the nanopore (Figure 4a). Only when a sufficiently large pressure (the critical infiltration pressure, $P_{cr}$) is attained can the liquid phase enter the nanopore. This infiltration process is energetically unfavorable because two changes occur simultaneously as a water molecule enters a nanopore: (1) the water molecule tends to lose part of hydrogen bonding (black dotted line in Figure 4d) and (2) it directly interacts with solid atoms (red dashed line in Figure 4d). Both changes are associated with energy variations. Denoting the surface tension (energy per unit surface area) of the liquid as $\gamma$ and the liquid-solid interaction energy (per unit surface area) as $\gamma_{LS}$, the total energy consumption of creating a unit liquid surface inside the nanopore can be written as

$$\gamma_{LS} = \gamma + \gamma_{LS}$$

(1)

where $\gamma_{LS}$ denotes the liquid-solid interfacial energy. If the liquid is nonwetting, $\gamma_{LS}$ is positive so energy input is required to initiate the infiltration. During this process, mechanical energy is absorbed and stored as the liquid-solid interfacial energy inside the nanoporous materials. The total stored interfacial energy can be estimated as $\gamma_{LS} \cdot A$ where $A$ denotes the total area of the solid surface accessed by the liquid.
phase. We note that $\gamma_{ls}$ is a term that can be affected by a number of factors, including the surface treatment (Figure 3c), liquid phase, ion concentration, solid phase, pore size, etc. Hence, the performance of the nanoporous composite can be fine-tuned to suit a wide range of target applications.

When the pressure exceeds $P_{cr}$, presumably the energy barrier caused by the capillary effect should be overcome and thus liquid molecules can continuously enter the nanopore. Nevertheless, this may not be the case because there exists another mechanism that dominates nanofluidics – the so-called viscosity effect or lattice frictional effect. As shown in Figure 4e, during the transport, liquid molecules have to overcome an energy barrier caused by their interactions with the solid atoms (e.g. lattice friction). An additional input of energy (or force) is therefore required to sustain the liquid flow inside a nanopore. During this process, considerable energy is dissipated as heat by transferring the momentum/kinetic energy of the liquid molecules to the solid surface atoms. This phenomenon is rather similar to the Poiseuille flow in macroscopic capillaries/tubes (both need driving force), but due to the confining effect of the nanopores, nanofluidic transport is subjected to novel physical mechanisms and new formulation (which will be elaborated on in Sections 3.3-3.4).

During infiltration, both capillary effect and frictional effect contribute to resisting the liquid to flow towards the interior of the nanopore. When the liquid attempts to defiltrate, however, the flow direction is reversed so the frictional force is also reversed, but the direction of the capillary force is unchanged. Hence, while infiltration is a process in which the capillary effect works together with the frictional effect to resist the liquid intrusion, in defiltration the two effects compete. If the capillary effect wins, the liquid should fully defiltrate; if the frictional effect turns out to be more dominant, the liquid would be stuck inside the nanopore.

Now we consider the energy conversion during the loading-unloading cycle. During pressure-assisted infiltration, the input mechanical energy is stored in part as interfacial energy inside nanoporous materials (due to the capillary effect) and in part dissipated as heat (due to the frictional effect). Note that the first part is reversible (through defiltration) while the second is not. As for defiltration, there should be two possibilities as discussed above, full-defiltration and non-outflow. If the liquid is stuck inside the nanopore (the confined liquid remains stationary throughout the defiltration process), defiltration would not contribute to the overall energy absorption, since no interfacial energy would be released and no additional heat would be generated. Hence, the overall energy absorption should equal to the interfacial energy stored during infiltration plus the energy dissipated during infiltration. On the other hand, if the liquid fully defiltrates, all the stored interfacial energy would be released (as no interface exists) while an additional part of energy would be dissipated as heat (as the liquid slides against the solid phase during defiltration). Thus, the overall energy absorption in this case should be fully
contributed by the energy dissipation caused by the surface friction (during both infiltration and defiltration).

Very importantly, no matter whether the liquid defiltrates or not, the overall energy absorption/dissipation must be proportional to the interface area between the solid and liquid phases (since both the capillary effect and the frictional effect are linearly correlated with the interface area). Hence, in the proposed nanoporous composite, the ultra-large surface area can largely amplify the two energy absorption/dissipation mechanisms discussed above, leading to superior performance of energy absorption compared with conventional materials (Table 1). A word of caution is that, while the above analyses are valid for the idealized single pore/channel, in real cases where both the pore size and geometry have much complexity, more detailed analyses have to be performed. For example, in the following chapters, some counterintuitive nanofluidic phenomena will be shown, which cannot be fully understood by the above discussions.

![Diagram of an electrically controllable nanoporous intelligent system](image)

**Figure 5.** (a) Schematic of an electrically controllable nanoporous intelligent system.\textsuperscript{[22]} (b) Variation of infiltration pressure as a function of the applied potential.\textsuperscript{[22]} (c) Thermal effect on the infiltration pressure of a silicalite.

### 1.2.2.2. Field-responsive Actuation

An experiment illustrating the electro-actuation capability of the nanoporous composite is performed with a number of nanoporous silica disks (16.5 mg each)
tightly stacked between aluminum layers (Figure 5a). A 15\% aqueous solution of KCl is sealed in the container. The counter electrode and the nanoporous silica disks are separated by an 80 \( \mu \)m thick porous membrane separator. A voltage, \( \Delta \phi \), is applied between the lower piston and the counter electrode. \( P_c \) is found strongly dependent on the applied electric field. When \( \Delta \phi = 400 \) V, for instance, the infiltration pressure can be varied by 10\% (Figure 5b). If the pistons are subjected to a constant external loading, the pressure variation would result in a displacement, which is more than two orders of magnitude higher than that of piezoelectrics of the same size.\(^{[14]} \) Similarly, thermal field can also make a control. Using a silicate with the specific surface area \((A)\) of 370 m\(^2\)/g and the pore radius \((R)\) of 0.8 nm, the specific output energy is measured about 5 J/g when the temperature is varied by \( \pm\)25 °C.

The mechanism of the field-responsive actuation capability of the nanoporous composite is straightforward: as temperature or the applied electric potential difference is changed, the liquid-solid interfacial energy can vary considerably and the equilibrium condition at interface would be disturbed (i.e. the system can become relatively more hydrophobic or more hydrophilic); thus, the infiltration pressure is varied to a large extent, which grants the confined liquid an inclination to flow out of or into the nanopores.\(^{[14]} \) While this phenomenon has long been known as the thermocapillary\(^{[23]} \) or electrocapillary effect,\(^{[24]} \) only by using nanoporous materials can the total liquid-solid interface be large enough such that a significant output energy density can be achieved.

1.2.2.3. Thermal-to-Electrical Energy Harvesting

In an experiment illustrated in Figure 6, two nanoporous electrodes are immersed in the 26 wt\% NaCl solution in two separate cells (Figure 6a).\(^{[17]} \) The nanoporous electrodes are prepared by uniformly mixing surface treated nanoporous carbon particles (nanopore size = 1-10 nm; specific surface area = 800 m\(^2\)/g), acetylene, and vinyldene chemicals. Both electrodes are sandwiched with copper counter electrodes and porous insulation membranes. The two counter electrodes are directly connected via a copper wire, and the two nanoporous carbon electrodes are connected through a 10 k\( \Omega \) resistor. Container “A” is maintained at room temperature and container “B” is heated at a rate lower than 0.5 °C/min. The output voltage across the resistor is measured and shown in Figure 6b as a function of the temperature difference between the two cells. The temperature sensitivity of the output voltage of a 60 mg nanoporous electrode is around 7.2 mV/°C, which is larger than that of thermocouples by two orders of magnitude.

From an electrochemical point of view, as a conductive solid and an electrolyte solution contact each other, near the interface ions and liquid molecules are subjected to different forces from the solid atoms and from the bulk liquid phase, which tends to form an electrical double layer of high ion densities. Due to the fluctuating distribution of net charge, a net potential difference is generated across the
liquid-solid interface, which has been well appreciated for cathode protection and electro-coating, among others.[23] Due to thermal motion, ions randomly diffuse toward and away from the solid surface, and the steady-state ion density in the double layer is thermally dependent. Thus, as two identical liquid-solid systems of different temperatures are connected, charges would move from the system of the higher interfacial potential difference to the one of lower potential, thereby generating thermoelectricity. This mechanism of converting thermal energy to electrical energy is, again, based on the liquid-solid interface, so it can also be greatly amplified by the ultra-large surface area of nanoporous materials. A similar application would be to use nanoporous composites as supercapacitor to store electrical energy.[25]

![Diagram of thermal-to-electrical energy harvesting system](image)

Figure 6. (a) Schematic of an thermal-to-electrical energy harvesting system.[17] (b) The variation of the potential difference as a function of the temperature difference between the two cells (m denotes the mass of each of the nanoporous electrodes).

1.2.2.4. Mechanical-to-Electrical Energy Harvesting

As illustrated in Figure 7, a nanoporous metal rod is tightly inserted in a polypropylene pipe. An aqueous solution of electrolyte is driven by a syringe pump to flow across it. The nanoporous electrode is connected to a copper counter electrode through a 1 MΩ resistor. The output voltage is shown in Figure 7b to be about 70 mV, as the flow velocity linearly increases with time.[26]

The underlying mechanism is similar to that of the thermal-to-electrical energy conversion discussed in Section 1.2.2.3: as a liquid flows across a nanopore, it can spontaneously disturb the double layer structure from equilibrium, thereby affecting the potential difference across the liquid-solid interface. Then by connecting two electrodes, one disturbed by the liquid flow and the other kept in equilibrium, a potential difference would be generated, which harvests the mechanical energy into the electrical energy.
Figure 7. (a) Schematic of a mechanical-to-electrical energy harvesting system.\cite{26,27} (b) The variation of the output potential as a function of the flow velocity.

Figure 8. Role of nanofluidics in nanofluidic energy conversion: via the specific nanofluidic mechanisms, the various material and system parameters (on the left) are bridged with the multiple indices (on the right) that determine the performance of the nanoporous composite in various applications.

1.2.3. Role of Nanofluidics

According to the analyses in Section 1.2.2, all the exciting functionalities of the proposed nanoporous composite are attributable to the physical processes taking place at the liquid-solid interface. For example, energy absorption and dissipation is based on the capillary effect and the effect of surface friction; field-responsive actuation results from the thermal and electrical dependence of the infiltration
pressure; thermoelectric/mechanolectric energy harvesting is a consequence of the thermal/flow rate dependencies of the double layer structure and the potential difference across the liquid-solid interface. All these physical processes are governed by the behavior of fluids when confined in solid nanochannels, or, simply put, nanofluidics.

Nanofluidics does not only induce the manifold functionalities, but it also plays a central role in determining the performance of the nanoporous composite. As shown in Figure 8, nanofluidics is a critical link between the system performance and the various materials parameters (e.g. pore size and geometry, liquid phase, solid phase, and surface treatment) and system parameters (e.g. temperature, electric field, and mechanical load). By adjusting these system and material parameters, the performance of the nanoporous composite can be fine-tuned in a wide range. This grants the proposed nanoporous composite a high degree of “customizability”, so it can be applied in a variety of target applications. For example, in some applications where the external load is relatively low (e.g. damping or vibration proof), $P_\alpha$ can be designed low enough such that the energy absorption mechanisms can be activated; in some other applications where the peak load is extremely high (e.g. body armor or car bumper), both the infiltration pressure and the shearing stress can be designed as high as possible such that considerable mechanical energy can be absorbed and dissipated.

Despite its importance, nanofluidics is still a much under-studied and a wide open field. The lack of knowledge in this emerging area has significantly hindered the development and optimization of the proposed nanoporous composite. For example, considering the various system and material parameters as inputs and those performance-related variables (such as the infiltration pressure, surface friction, interfacial potential difference, and the energy conversion density) as outputs, quantitative relations between the inputs and outputs have not been well established. Conventional wisdom provides some useful hints, but most classical theories of fluidics have not been sufficiently validated at the nanoscale (with the characteristic length ranging from 10 nm to 1 nm and even below). In view of the needs and obstacles, this dissertation is dedicated to exploring the broad area of nanofluidics. Basic mechanisms of nanofluidic infiltration, transport, and structural reorganization will be intensively investigated with direct implications for the nanofluidic energy absorption, actuation, and energy harvesting.
Chapter 2.
An Introduction to Nanofluidics

The fundamental behavior of liquid molecules and ions in confined nanoenvironment is highly relevant to a number of critical challenges in energy, biology, and environmental sustainability.\textsuperscript{[28-32]} An important and ever expanding one is to provide alternative solutions to energy conversion. In addition to the nanoporous composite proposed in this dissertation (which can be used for energy absorption, actuation, and energy harvesting; see Section 1.2 for details),\textsuperscript{[13,28,33-40]} electricity can also be generated by driving a flow through nanoporous materials, which may be attributed to the motion of free charge carrier\textsuperscript{[36]} and the quantum-induced charge effect.\textsuperscript{[35]} Moreover, nanofluidics can also contribute to the storage of electric power and the fuels for electricity generation. For instance, an unprecedented capacitance has been achieved in an electrical double-layer capacitor where the solid pore size is reduced below 1 nm.\textsuperscript{[39,41-44]} Also, nanoporous materials have shown a superior hydrogen uptake of more than 7 wt\%\textsuperscript{[34]}

From a fundamental perspective, due to the stringent nanoconfinement and the complex liquid-solid interactions, most liquid molecules and ions confined in nanocavities belong to the “boundary layer”, and they interact with the solid (surface) atoms in unconventional (and sometimes counterintuitive) manners. Hence, many aspects of nanofluid behavior are radically different from their macroscopic counterparts; as such, classical theories usually break down. The emerging subject of nanofluidics aims to elucidate the intrinsic structural, mechanical, thermal, and electrical characteristics of nanofluids, in particular, the liquid intrusion and transport through nanochannels, the structural reorganization at the interface, as well as the phase separation characteristics. Indeed, while the size effect in solid materials has been extensively studied, the relevant size effect and other coupled intrinsic and extrinsic effects of nanofluidics, remain relatively unexplored and represent an outstanding challenge in materials and surface engineering.\textsuperscript{[45-47]}

In this chapter, we first compare nanofluidics and its macroscopic counterpart in four aspects (namely, infiltration, transport, phase separation and the interface structure), all of which account for important nanofluidic energy conversion mechanisms. In the second part, a short review of nanofluidic energy conversion mechanisms will highlight some of the most important contributions to the field in recent years.
2.1. Conventional Fluids vs. Nanofluids

2.1.1. Conventional Treatment of Capillary Infiltration and Transport

The current understanding of quasi-static capillary liquids is primarily based on the classical work of Laplace, Young, and Poiseuille. Due to the liquid-solid interfacial energy, an external pressure is required to infiltrate a non-wetting liquid into a cylindrical capillary. Such a phenomenon can be well characterized by the equation named after Laplace and Young, i.e.

\[ P_{cr} = \frac{4\gamma_{LS}}{D} \]

with \( P_{cr} \) being the pressure, \( \gamma_{LS} \) the liquid-solid interfacial energy, and \( D \) the diameter of the capillary. After infiltration, the fluidics is then governed by the Navier-Stokes equation. For a Newtonian fluid that undergoes laminar and incompressible flow, the velocity profile is proved to be parabolic. By assuming the non-slip boundary, the flow rate is correlated with the pressure drop and viscosity in the form of

\[ Q = (\frac{dP}{dz}) \frac{\pi D^4}{128\eta} \]

where \( Q \) denotes the flow rate, \( \frac{dP}{dz} \) the pressure drop in the axial direction, and \( \eta \) the viscosity.

2.1.2. Conventional Treatment of Electrical Double Layer

As a liquid phase meets a solid surface (e.g. metal and semiconductor), charges and dipoles, if present, are subjected to forces of considerable anisotropy, leading to substantial molecular redistribution and reorientation at the solid-liquid interface zone. The Helmholtz-Perrin parallel-plate model assumes that the charge on the solid, if any, would draw out all excess charges in the liquid to form a counter-layer close to the solid surface. This model takes a very simple form, giving a prediction of constant differential capacities. Nevertheless, such a simple treatment is too rigid to explain some important characteristics of the electrical double layer, e.g. the dependence of capacity upon potential. About half a century later, Louis Gouy and David Chapman took some counter-charges away from the condensed row and had them randomly swim in the solution. This leads to the well-known Gouy-Chapman diffuse-charge model, which predicts inverted parabolas for the differential capacities. An obvious deficiency of this model lies in the consideration of ions as point-charges, which eliminates the interactions between ions in the condensed row.
In order to resolve this problem, Stern proposed a combination of the Helmholtz-Perrin and Gouy-Chapman models, dividing the liquid phase into a compact layer (Helmholtz region) part and a diffuse layer (Gouy-Chapman region) part. Then, the overall interfacial capacity conforms to the follow relation:

\[
\frac{1}{C} = \frac{1}{C_c} + \frac{1}{C_d}
\]  

(4)

where \( C \) is the total capacity of the interface, \( C_c \) the compact layer capacity, and \( C_d \) the diffuse layer capacity. This idea has been extensively used, and various models have been proposed leading to different forms of \( C_c \) and \( C_d \). In general, one can estimate

\[
C_c = \frac{\varepsilon_0 \varepsilon^*}{d}
\]  

(5)

where \( d \) denotes the closest approach of ions to the solid surface, \( \varepsilon^* \) is an effective dielectric constant of the compact layer, and \( \varepsilon_0 \) the vacuum permittivity. Following the Gouy-Chapman theory in the diffuse layer, one can get

\[
C_d = \left[ \frac{2\varepsilon_0 \varepsilon Z^2 e^2 c}{kT} \right]^{1/2} \cosh\left( \frac{ZeU}{2kT} \right)
\]  

(6)

where \( Z \) is the valence of the ion, \( e \) the charge on the electron, \( \varepsilon \) dielectric constant, \( c \) salt concentration in the bulk solution, \( k \) Boltzmann constant, \( T \) temperature, \( U \) the total potential drop across the double layer.

### 2.1.3. Uniqueness of Nanofluids

When the length scale is reduced to the nanometer range, several physical
properties of fluids are radically changed, which can significantly influence fluid behavior in the nanoenvironment. First, nanofluids usually exhibit much stronger inhomogeneity than their macroscopic counterparts. Within the nanoconfinement, multi-phase liquids such as electrolytes are no longer “continuum” and each component of the liquid, e.g. solvent molecule or solute ions, may have unique interactions with the solid phase and surrounding liquid particles. The complex solid-liquid interactions are further coupled with ambient electrical or magnetic fields, rendering highly diverse nanofluid behavior. Even for single-phase fluids, such as water, inhomogeneity is still dominant, which is highlighted by the fluctuating radial distribution of water molecules inside hydrophobic nanotubes and a depletion layer right inside the outermost peak of the highest concentration. Furthermore, when the size of the nanopore is sufficiently small, the gap between the solid and liquid phase formed due to the van der Waals (vdW) repulsion becomes non-negligible, which calls for a redefinition of the capillary size. In addition to the nonuniform spatial distribution of the confined liquid molecules, the velocity profile of nanofluids is usually plug-like, featuring a constant velocity across the cross-section.

Another unique feature of nanofluids is the size effect. Various fluidic characteristics (e.g. concentration distribution, ionic hydration, and hydrogen bonding) can be drastically varied as the size of the nanoconfinement is changed. For instance, when the nanopore dimension is at the molecular-level (<1nm), confined water molecules tend to form a quasi-one dimensional chain and transport as a single file as the pressure is sufficiently high, some more complex structures may emerge such as the n-gonal ring and the double helical chain. By contrast, inside larger nanopores, a multilayered structure is often formed near the tube surface due to the less restrictive confinement, water molecules are usually bonded by more hydrogen bonds, which tends to cause more diverse dipole orientation. For electrolytes, ionic hydration is often severely suppressed as the liquid enters a nanopore, and thus the coordination number is considerably reduced. Similarly, other nanofluidic characteristics, such as the contact angle, infiltration pressure, and the apparent viscosity all have certain size effects. In particular, given the inhomogeneous molecular distribution in small confinement, the variation of electrical potential is expected to be much more complicated than that predicted by various mean-field theories (e.g. the Gouy-Chapman model). Moreover, when the confinement is extremely small (close to molecular size), the electrical double layer may be so tightly squeezed that in some cases, the diffuse layer can vanish, leaving the compact layer alone.

Given all these fluidic characteristics that are unique to the nanoscale (e.g. the inhomogeneous molecular distribution, slippery boundary, non-parabolic velocity profile, size-dependent surface tension, and the squeezed electrical double layer), conventional fluidic/electrochemical theory usually breaks down at the nanoscale.
2.2. Previous Nanofluidic Studies and their Limitations

Previous studies of nanofluidics fall into three major categories identified by the type of the nanoconfinement, namely, nanoporous materials, nanotubes, and biological channels. Although the three nanocavities share several characteristics in common, e.g. ultra-high surface-to-volume ratio (~$10^2$-10$^3$ m$^2$/g) and ultra-small size (~0.6-10 nm), they do bear some distinct physical and chemical features that can substantially influence fluid behavior. Nanotubes, such as carbon nanotubes (CNT) and boron nitride nanotubes, are perhaps the most regular among the three in terms of the molecular structure (long and straight cylindrical shell with simple crystalline arrangement of atoms). Advanced fabrication techniques have enabled many different varieties of such materials (e.g. Y-junction nanotubes, kinked nanotubes, helical nanotubes, functionalized nanotubes, and nanotube-based membranes and composites), which have greatly expanded the applications. In nanoporous materials, such as zeolites and nanoporous carbons, nanochannels (which are seldom straight but usually have rough surface profiles) are interconnected, forming complicated networks of nanochannels; numerous vacant cages are scattered in the solid, providing additional accommodation for liquid molecules. Last but not least, biological channels, such as AQP1 and ASIC1, feature complex surface morphologies and various functional residues; owing to the structural and chemical complexities, biological channels are usually multifunctional.

2.2.1. Fluidics in Nanoporous Materials

Many existing applications of nanoporous materials result from their intrinsic sorption and separation capabilities, which usually require the assistance of an external pressure, especially when the solid-gas/liquid interaction is weaker than the intermolecular interaction in the gas/liquid. Under these circumstances, the infiltration of gas/liquid phases usually remains slow until the pressure attains a critical value, after which the fluidic uptake becomes spontaneous, either in a gradual manner or in a sudden manner. This critical infiltration pressure varies significantly among materials. For activated carbons, the critical infiltration pressure has been shown to be extremely low, even below the bulk saturation pressure of vapor. According to the Dubinin-Serinsky model, adsorbed water molecules tend to condense and form clusters around defective sites, leading to the ultra-low infiltration pressure. By contrast, for zeolites in which cages and channels are periodically arranged and few defects are present (Figure 10a), very high intrusion pressure has been measured, e.g. 100 MPa for the silicalite-1 and 55MPa for the beta zeolite at room temperature. These scattered results suggest that the value of intrusion pressure is highly sensitive to the solid composition and pore geometry.

An important application of nanoporous materials is for phase separation at the sub-nanometer level, which is typically based on two major mechanisms:
molecular sieving\cite{91,92} and preferential permeability.\cite{93,94} While the screening performance intimately depends on the solid composition and pore geometry, defects may provide alternative pathway for molecular diffusion, thus significantly influencing the filtering results.\cite{95} If crystalline materials such as zeolites are used, the performance of separation also strongly depends on the lattice orientation.\cite{96-98} Interestingly, based on the reverse-selective separation mechanism, zeolite composites are not limited by the permeability/selectivity tradeoff inherent in polymeric films.\cite{99,100} In addition to phase separation, zeolite films have also been found promising in various other applications related to fluids, including ion-exchange electrodes\cite{101} and chemical sensors.\cite{102}

![Figure 10](image)

Figure 10. Highlights of previous nanofluidics research: (a) ion diffusion in a zeolite membrane;\cite{103} (b) structure of a hydrogen-bonded water chain inside a carbon nanotube (CNT);\cite{63} (c) TEM micrograph of a water strand confined in a carbon nanotube with the diameter of 2 nm;\cite{45} and (d) an MD simulation showing a single file of water molecules inside the pore of GlpF.\cite{104}

2.2.2. Fluidics in Nanotubes

Previous nanofluidic research with nanotubes is mainly focused on the fluid transport driven by pressure,\cite{105} thermal,\cite{106} or electric difference.\cite{107} Water transport through CNT has been shown to be ultra-fast,\cite{38,40,108,109} with a rate comparable to that in biological channels such as aquaporins.\cite{110} This fascinating property is attributed in part to the inherent smoothness of the nanotube (Figure 10b-c)\cite{111} and low friction at the surface,\cite{112} and in part to the thermodynamically driven low-density depletion
For electrolytes confined in nanotubes, ionic solubility\textsuperscript{113} and hydration\textsuperscript{114,115} are both reduced, which strongly affects ionic diffusion\textsuperscript{68} and makes the fluid behavior very sensitive to the type of ions and the solvent.\textsuperscript{47} In addition, nanofluid behavior is also affected by the chemical/physical properties of the solid phase.\textsuperscript{56,116} By anchoring functional groups to nanotube surface, both the structure of confined fluids and the flow behavior can be modified significantly.\textsuperscript{117-119} With appropriate design of the attached functional groups, modified carbon nanotubes may be provided a capability to pump water at a significantly high rate,\textsuperscript{120} or even filter unwanted phases from a fluid mixture.\textsuperscript{121} We note that most previous theoretical studies neglect quantum effects.\textsuperscript{122} The incorporation of quantum effects in the study of water transport through CNTs has shown the occurrence of the L-defect,\textsuperscript{123,124} which contributes to the enhancement of the diffusion rate.

Carbon nanotube as a fast transporter has also drawn increasing attention in its applications as molecular separators.\textsuperscript{125-129} Some of these applications are based on the diffusion/transport rate mechanism,\textsuperscript{125-127} while some others perform the screening directly based on the molecular size.\textsuperscript{77,128,129} The latter designs introduce constriction\textsuperscript{77,128} or kink\textsuperscript{129} to the CNT such that only smaller molecules can pass the artificially formed valve and larger ones are effectively screened. In addition to separating a gas mixture, nanotubes have also been found promising in desalinating water via reverse-osmosis and ion rejection.\textsuperscript{32,130}

2.2.3. Fluidics in Biological Channels

Biofluidics is crucial to a wide variety of biological processes, e.g. the selective conduction of water, glycerol, ions and gases (O\textsubscript{2}, CO\textsubscript{2}, and NO) through cell membrane. The working mechanisms of the selectivity are diverse, depending on the type of channels, the location of active sites, and the species of screened/permeated substances (Figure 10d).\textsuperscript{81-84,131-133} For example, cation conduction is hampered in nAchR mainly because of the hydrophobic barrier and the interaction of ions with the charged residues near nanopore openings.\textsuperscript{131} In aquaporins, protons are excluded from the NPA region by a dipole-induced electrostatic barrier based on the desolvation effect;\textsuperscript{82-84} and the ar/R region features a strong constriction in size, effectively filtering phases that exceed the size threshold.\textsuperscript{81} By comparing a highly selective K\textsuperscript{+} channel, KcsA, and a non-selective cation channel, NaK, the loss of the selectivity in NaK is primarily attributed to the flexibility of the filter;\textsuperscript{132} interestingly, in the presence of K\textsuperscript{+}, the filter of NaK would adopt a conformation similar to that of the filter in KcsA\textsubscript{2};\textsuperscript{132} and moreover, if the filter undergoes conformational change, potassium channels such as KcsA would be inactivated.\textsuperscript{133}

2.2.4. Remaining Issues

Despite the progress, many fundamental questions remain. First, at the
nanoscale, can we simply follow the macroscopic definitions of various fluidic quantities? In particular, some of them, such as the “hydrophobicity”\textsuperscript{[85,134-136]} and “viscosity"\textsuperscript{[137-141]} have already raised controversy. On the other hand, as nanofluids have shown a variety of unconventional properties, can we continue to use classical theories to describe their behavior? In addition, as the “specific ion effect” has been shown to play a critical role at the two-phase nanofluidic interface,\textsuperscript{[142-147]} does it also affect the liquid-solid interaction at the nanoscale? Moreover, with regard to the multifunctional nanoporous energy system introduced in Section 1.2, how do the various system parameters (e.g. mechanical loading rate, thermal variation, and electric field) and material parameters (e.g. ion concentration and pore size) influence the physical/chemical processes (e.g. infiltration, transport, and electrification) that determine the system performance? How can we optimize the nanoporous composite for desired performance of energy conversion among mechanical energy, thermal energy, and electrical energy?

This dissertation aims to answer all these questions through a systematic study of the fundamental nanofluidics via a synergy of experiment, simulation, and theoretical analysis. The validity of classical theories will be reassessed and critically examined at the nanoscale. New physical models describing the unique nanofluidic phenomena will be established, where critical parameters, such as the surface tension, contact angle, and viscosity, will be reinvestigated at the nanoscale. The effects of various material and system parameters, such as the solid phase, liquid phase, pore size and pore geometry, as well as the external thermal, electrical and mechanical loads, etc., will be systematically investigated and bridged with the nanofluidic energy conversion processes. The energy conversion efficiencies under various conditions will be evaluated via a synergy between simulation and experiment.

2.3. Modeling of Nanofluids

In this dissertation, we use Molecular Dynamics (MD)\textsuperscript{[148]} to investigate nanofluidics which has been shown to play a central role in the nanoscale energy conversion (Section 1.2.3). MD is a simulation technique based on statistical mechanics. Although not entirely accurate, it can provide valuable insight into the behavior of molecules and ions at a length scale that challenges present experimental techniques. Hence, MD has been extensively applied in the study of proteins and biomolecules, as well as in materials science. A nice introduction to this simulation technique can be found in a book written by Frenkel and Smit.\textsuperscript{[149]}

This section is intended to elucidate the following issues regarding the
modeling of nanofluids in MD simulation:

(1) Since MD is very expensive computationally, with the present computational capability it is difficult to simulate the entire nanofluidic systems as considered in experiments (e.g. Figure 5a which contains several grams of nanoporous materials and liquids and that accounts for at east $10^{20}$ atoms/molecules). Hence, simplified models must be conceived and adopted in the simulation. The question is how to design the computational models so they can be simple enough yet represent the main features of real nanofluidic systems?

(2) Since MD is based on the assumption of empirical force fields, the computational results critically depend on the adoption of empirical parameters. Here arises another issue, how to choose the empirical parameters so the computation can well approximate the behavior of real nanofluidic systems?

(3) In essence, MD treats atoms and ions as individual particles, and studies their interactions and motion over a period of time. However, the motion of individual ions and atoms is just one focus of nanofluidics. Another, and perhaps a more important one, is to consider the discrete ions and atoms as a whole and investigate the associated nanofluidic characteristics, such as the infiltration pressure, shearing stress, interfacial potential difference, and the contact angle. It therefore becomes very important to interpret MD simulation output to those physical quantities mentioned above.

All of these issues will be elucidated in this section, which may help the discussions in the following chapters.

### 2.3.1. Empirical Parameters Used in MD Simulation

MD models molecules and ions via empirical potentials, or force fields. Most force fields are empirical, consisting of a summation of bonded forces (namely, bonds, bond angles, and bond dihedrals) and non-bonded forces (namely, van der Waals forces and electrostatic forces).

There are many models available for these force terms. For example, the equation that governs bond stretching can take a harmonic form, a quartic form, a Morse form, or a polynomial form, among others. All of these empirical models can only represent quantum-mechanical effects in a limited way, so none of them is entirely accurate. However, depending on the chemical properties of involved atoms, there is always a choice that can better approximate real interactions. For example, the C-C bond in a carbon nanotube is usually modeled by the Morse equation, and the H-O bond in a water molecule is usually modeled by the harmonic equation. All of these empirical models contain free parameters, such as the atomic charge, van der

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‡ The simulation time usually scales with $O(n^2)$ or $O(n \log(n))$ depending on the adopted algorithm, where $n$ denotes the total number of particles in the system.
Waals (vdW) parameters that reflect an estimate of atomic radius, the equilibrium bond length, angle and dihedral, among others. Typically, these parameters are obtained by fitting against detailed quantum chemical calculations or experimental physical properties such as elastic constants, lattice parameters and spectroscopic measurements.

The empirical models and parameters used in this dissertation are all taken from the literature. The interatomic van der Waals interaction is modeled by the Lennard-Jones (LJ) equation,

$$U_{\text{vdW}}(r) = 4\alpha[(\sigma/r)^12 - (\sigma/r)^{6}]$$

where \( r \) denotes the distance between atoms, \( \alpha \) and \( \sigma \) are energy and length parameters, respectively. The electrostatic interaction is modeled by the Coulombic equation,

$$U_{\text{Elec}}(r) = \frac{k_q q_i q_j}{\varepsilon r}$$

where \( q_i \) and \( q_j \) are the charges on the two atoms, \( k_e \) is a energy conversion constant, and \( \varepsilon \) is the dielectric constant. The flexibility of water molecules is modeled by a harmonic bond and a harmonic angle.\cite{150} The flexibility of CNT is addressed by a Morse bond, a harmonic cosine angle and a 2-fold torsion potential.\cite{151} The harmonic bond takes the form of

$$U_{\text{Bond-Harmonic}}(r_B) = k_{B-H}(r_B - r_{B,0})^2$$

and the Morse bond takes the form of

$$U_{\text{Bond-Morse}}(r_B) = k_{B-M}(1 - e^{-\alpha(r_B - r_{B,0})})^2$$

where \( \alpha \), \( k_{B-H} \) and \( k_{B-M} \) are constants, \( r_B \) the bond length, and \( r_{B,0} \) the equilibrium bond length. The harmonic bond angle takes the form of

$$U_{\text{Angle-Harmonic}}(\theta) = k_{A-H}(\theta - \theta_0)^2$$

and the harmonic cosine angle takes the form of

$$U_{\text{Angle-Cosine}}(\theta) = k_{A-C}(1 + \cos \theta)$$

where \( k_{A-H} \) and \( k_{A-C} \) are constants, \( \theta \) the bond angle, and \( \theta_0 \) the equilibrium bond angle. The 2-fold torsion takes the form of

$$U_{\text{Torsion}}(\vartheta) = k_\vartheta(1 + \cos 2\vartheta)$$

where \( k_\vartheta \) is a constant and \( \vartheta \) denotes the dihedral.

If not otherwise indicated, the parameters for water molecules used in this dissertation are taken from the extended simple point charge potential SPC/E.\cite{150} The carbon nanotube is parameterized following the Amber96 LJ force field\cite{152} and the model described above.\cite{151} The parameters for ions are taken from free energy perturbation simulations.\cite{153} The carbon-oxygen LJ parameters are extracted from the experimental low-coverage isotherm data of oxygen adsorption on graphite.\cite{154} By using these models and parameters, the graphene as the raw material for building CNTs and CNCs is ensured to be physically hydrophobic.\cite{70} All the other interatomic
parameters are evaluated by the Lorentz combining rule. It deserves mention that the adoption of force fields and empirical parameters will inevitably affect the magnitude of the computational results, e.g. pressure and contact angle. However, the general molecular mechanisms and trends discovered in simulation should not change. For example, in Section 3.2 we will introduce an intriguing ion couple structure formed when an electrolyte solution is forced to enter a molecular-sized nanopore. The simulation in that section is performed using COMPASS force field. In fact, we have also performed another set of simulations, in which a different set of parameters is used. According to our analysis, the ion couple structure forms in both sets of simulations, implying that the unveiled nanofluidic behavior is not sensitive to the adoption of force fields. After all, all the force fields were delicately developed by chemists; they should not radically differ from each other.

2.3.2. Computational Models and Derivation of Nanofluidic Quantities

This section gives an overview of the computational models that have been used by us in the investigation of nanofluidics. Also, this section reviews the derivation of the various nanofluidic quantities directly from MD output. For clarity, we divide this section into several subsections in terms of the quantity of interest. In each subsection, the computational model and simulation procedure will be described in details, followed by the derivation of the quantity of interest.

2.3.2.1. Infiltration Pressure

Figure 11a illustrates the computational model for the simulation of nanofluidic infiltration. As an example, a carbon nanotube (CNT) is adopted as a model nanochannel. One of its openings is immersed in a reservoir which is filled with water molecules. The top and bottom surfaces of the reservoir are bounded by two rigid planes. The upper one is fixed and the lower one is movable to mimic a piston. Periodic boundary conditions are imposed on the four lateral planes of the computational cell. At the temperature of $T$, a specific number of water molecules are placed in the reservoir such that the initial pressure is close to the ambient (zero) after equilibrium. Next, the water phase is pressurized by moving the piston upwards. There are two choices in loading the system - quasi-static and dynamic.

(1) In the quasi-static case, we carefully load the system in a stepwise and quasi-static manner so as to rule out possible dynamical effects. In each step, we move the piston by 0.05 Å, after which the position of the piston is temporarily fixed and the system is allowed a sufficiently long time to reach new equilibrium (where the temperature distribution is close to uniform). Note that the equilibrium time varies throughout the simulation, on the order of 1ns after water intrusion and shorter before.

(2) In the dynamic case, the system is also loaded in a stepwise manner, but
the simulation time following the movement of the piston is set to be a constant which reflects the loading rate. For example, supposing in each loading step the piston is moved by 0.05 Å and the system is simulated for 1 ps afterwards, the loading rate should be 5 m/s. Dynamic infiltration is not included in this dissertation, but we have carried out a systematic study on this topic.[156]

At every step of the simulation, pressure is evaluated from the immediate density of the liquid inside the reservoir. For water, if not otherwise indicated, the pressure-density relationship is deduced from the data published by IAPWS,[157]

\[ P = \rho \delta(T + T_0) - P_0 \]  \hspace{1cm} (14)

where \( \rho \) is the density of water (in the unit of g/cm\(^3\)), \( T \) denotes the ambient temperature, \( P_0 \) equals to 378 MPa, and \( T_0 \) equals to 85 K, respectively. Based on the calculated pressure in the reservoir, we can plot a curve of pressure versus infiltration volume (Figure 11b). Based on this plot, infiltration pressure can be identified as the pressure at the beginning of the infiltration plateau (where the liquid overcomes capillary effect and starts to enter and transport inside the nanopore).

Figure 11. (a) The computational model. One end of a long carbon nanotube (CNT) is immersed in a reservoir which is filled with water molecules. The upper rigid plane is fixed while the lower one is moved to adjust the pressure inside the reservoir. Periodic boundary conditions (PBCs) are applied on the four lateral planes of the computational cell. (b) A representative relationship between the applied pressure and the number of infiltrated water molecules.
Table 3. Use of the computational model of nanofluidic infiltration (Figure 11a) in this dissertation

<table>
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<tr>
<th>Section</th>
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<td>4.3</td>
<td>Water</td>
<td>“Functionalized” CNT</td>
<td>300 K</td>
<td>Rigid</td>
</tr>
</tbody>
</table>

Figure 12. Critical pressure that infiltrates water into (a) rigid carbon nanotubes and (b) flexible carbon nanotubes at four representative temperatures. The pore diameter, $D$, is 13.56 Å, 17.63 Å, 20.34 Å, and 27.12 Å, respectively, from top to bottom.

The computational model shown in Figure 11a is extensively employed in this dissertation to study the infiltration of different liquids into different nanopores, as tabulated in Table 3. We note that only in Section 4.1 is the flexibility of nanopore considered in the simulation; in the other sections, rigid nanopore is always assumed to save computational time. Section 4.1 considers the flexibility of nanopore because this section is aimed to study the effect of temperature on nanofluidic infiltration. Presumably, temperature can not only affect the bonding energy between water molecules, but it can also affect the vibration of the solid atoms. According to the previous analysis, nanofluidic infiltration is governed by the solid-liquid interaction at the nanoscale, so both solid and liquid phases should contribute to the infiltration behavior. Hence, the flexibility of nanopore should be considered in the analysis of the thermal effect on nanofluidic infiltration. In all the other sections, however, temperature is fixed at 300 K. It is therefore not necessary to involve the flexibility of
nanopore in the simulation, because the effect of nanopore flexibility on the infiltration pressure is marginal. In Figure 12, comparing flexible and rigid systems, the difference in $P_c$ is found to be less than 10%. More importantly, the general size effect and thermal effect are not affected by the flexibility of nanopore; both sets of simulations show $P_c$ decreasing with temperature and diameter.

2.3.2.2. Static Contact Angle

TEM micrograph has confirmed that even inside an ultra-small nanopore, an interface can form between two different phases (Figure 13a). Such nanointerfaces can also be studied via MD simulation. Figure 13b-c shows an example of water-vacuum interface inside a flexible (20,20) CNT with $D=27.12$ Å and $L=220$ Å. The computational model contains 1220 water molecules, which are placed inside the nanotube to form a discrete water drop. Periodic boundary condition (PBC) is applied along the axial direction. The system is simulated for 10 ns at a fixed temperature without any external load. Molecular trajectories are output every 0.1 ps for statistical purposes. Shown in Figure 13d is the map of water density at $T=300$ K. It is readily seen that a convex meniscus is formed on top of the liquid drop due to the hydrophobic nature of the nanotube. In order to characterize the water front, the spatial positions of boundary water molecules are averaged over all recorded time frames (100000 frames in total), leading to the squared symbols in Figure 13d. The squared symbols are further fitted by a circular arc, leading to an average water front (the black curve in Figure 13d). Based on this average water front, a contact angle ($\alpha$) can be measured as the angle between the tangent of the water front and the solid surface. As will be shown in Section 4.1, this contact angle has a strong thermal dependency, which contributes to the thermal dependency of the infiltration pressure. Regarding the definition and measurement of contact angle at the nanoscale, we have a few remarks:

1. The measured contact angle is valid only in statistical sense. Indeed, the water front is fluctuating throughout the simulation; the positions of boundary water molecules change from frame to frame. However, after averaging over time, a clear meniscus is derived, which agrees well with the hydrophobicity of the solid surface.

2. In addition to the case shown above, the water-vacuum interface is also studied in smaller CNTs following the same procedure. It is found that the (20,20) ($D=27.12$ Å) is among the smallest nanopores in which a clear meniscus can be identified. When the pore size is further reduced, the shape of the interface becomes rather irregular and highly dependent on the pore size.

3. The contact angle is measured while the water drop stays stationary in the CNT. Hence, the measurement yields only the static contact angle, which corresponds to the quasi-static infiltration investigated in this dissertation. In the dynamic case, advance and retreat of the liquid may lead to distinct contact angles, both different from the measured static contact angle.
2.3.2.3. Shearing Stress

Figure 14 illustrates the computational model for the simulation of nanofluidic transport. The system consists of a single-walled CNT filled up with water molecules (Figure 14a). The length of the CNT is 300 Å and periodic boundary condition is applied along the axial direction.\textsuperscript{5} A specific number ($N$) of water molecules are placed inside the nanotube such that the initial water density is 0.998 g/cm\textsuperscript{3} inside the occupied volume. After relaxation, a constant acceleration is applied to each atom of water molecules to mimic a pressure drop. Initially, the applied force is larger than the resistance against the liquid flow, so the water molecules are accelerated. After a sufficiently long time of simulation, the flow resistance grows to the same magnitude as the applied force. This leads to a steady flow of water molecules inside the CNT, where the flow velocity is almost a constant. Subsequently, the system is concentrically sliced, and the average velocity of water molecules in all the slices is calculated over a sufficiently long simulation time. This leads to the so-called radial velocity profile (RVP). Figure 14b shows an example of RVP for water molecules flowing at $\bar{v} = 165$ m/s inside a (60,60) CNT.

\textsuperscript{5} We have verified that the computational results are insensitive to the variation of the size of the cell.
For nanofluids, the aforementioned flow resistance mostly comes from the “boundary layer”, i.e. the interface zone that separates the solid and liquid phases; in other words, as the liquid flows inside the nanopore, solid atoms tend to exert a resistance against the liquid motion. Such a interface-induced “resistance” can be accounted for by a very intuitive physical term, i.e. the shearing stress, $\tau$. Due to the direct “contact” between the solid surface and the liquid column, this shearing stress is expected to dominate nanofluidic transport. A deceleration test can be carried out to quantify the shearing stress. In a water flow that has reached the steady state (flowing at a constant velocity of $\bar{v}$), we first remove the acceleration force that drives the flow, and then monitor the variation of the flow velocity in the next several picoseconds. The flow velocity ($\bar{v}$) is calculated at every time step by averaging the axial speed of all water molecules. From the results it is found that $\bar{v}$ decreases almost linearly with time. It is therefore possible to extract a deceleration ($a$) acting on the water flow, with which the effective shearing stress can be calculated as $\tau = Nma/(2\pi RL)$, where $m$ is the mass of a water molecule and $L$ is the tube length.

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**" The time period of the deceleration test varies case by case. In general, we want the variation of the flow velocity to be controlled below 3% throughout the deceleration test, such that the flow rate effect would not kick in, and the measured deceleration and the calculated shearing stress can be regarded as that for the starting velocity (because the shearing stress is dependent on the flow velocity)."**
It deserves mention that the flexibility of nanopore may play an important role in nanofluidic transport. In general, using rigid nanopore in simulation may underestimate the shearing stress to some extent. However, in a study that will be shown in Section 3.3, the assumption of rigid nanopore is still adopted. The reason is that in Section 3.3, we are only concerned about the effects of pore size and flow rate on the shearing stress. It is expected that, similar to the observations in Figure 12, the assumption of rigid nanopore should only affect the magnitude of the shearing stress, while the general size and rate effects should not be influenced. Nanofluidic transport using flexible nanopore will be a subject of future study.

2.3.2.4. Interfacial Potential Difference

As introduced in Sections 1.2.2.3-1.2.2.4, if the solid-liquid potential difference has a prominent dependence on temperature or flow velocity, a voltage would be generated by connecting two cells operated at different temperatures or different flow velocities. It is therefore of much fundamental value and practical interest to study the effects of temperature ($T$) and flow velocity ($v$) on the structural and electrical characteristics of electrolytes confined in nanopores (see Chapter 5 for details). There are three quantities involved in our analysis, namely, the net charge density ($\rho_c$), the electrical potential ($\phi$), and the solid-liquid potential difference ($\phi$). When an electrolyte solution is confined in a nanopore (Figure 15a), ions and atoms usually form layered structures; the dipoles in solvent molecules also tend to adopt new orientations. As a consequence, the density profiles of ions and atoms usually exhibit large fluctuations at the interface region (Figure 15b), leading to a prominent net charge distribution (Figure 15c). According to the Poisson’s equation (eqn (a) in Figure 15, where $\varepsilon_0$ and $\varepsilon$ are the vacuum permittivity and the dielectric constant of the medium, respectively), the distribution of net charge density, $\rho_c$, must induce a distribution of the electrical potential, $\phi$, inside the nanopore (Figure 15c). A solid-liquid interfacial potential difference, $\phi$, is then generated, which conforms to eqn (b) in Figure 15, where $R$ is the radius of the circular nanopore, $\phi|_{r=R}$ and $\phi|_{r=0}$ represent the electrical potentials at the solid surface and the center of the confined liquid, respectively.
It is readily seen that the net charge density, electrical potential, and the solid-liquid potential difference all stem from the fluctuating distribution of liquid particles inside the nanoconfinement. As long as the particle distribution is obtained, the other quantities can be evaluated via eqns (a) and (b) in Figure 15. In this dissertation, MD is employed to derive the distribution of liquid particles. In the computational model (Figure 15a), a nanopore (e.g. CNT) is filled with a specific number of water molecules and ions to meet the prescribed ion concentration. Periodic boundary condition is applied along the axial direction to ensure the continuity of the computational model. The nanopore is assumed to be flexible because thermal effect is one of the focuses of Chapter 5. The system is first relaxed for 100 ps, and then simulated for another 5 ns, during which the atomic positions are output every 50 fs for the statistics of number density (100000 frames in total). Note that, for each nanopore, 50 initial configurations of the confined electrolyte are sampled and independently simulated. Any of the MD results shown in Chapter 5 is in fact an average among all these sampled systems.

It deserves mention that, only radial distribution of liquid particles and electrical quantities will be investigated in Chapter 5. Since nanopores usually have very large length-to-diameter ratio, it is expected that radial distribution dominates the structural and electrical properties of the confined liquid and the solid-liquid interface. Length distribution is therefore excluded from the current analysis. However, the contribution from the length distribution is still of much interest, which may be a subject of future study.
Chapter 3.
Nanofluidic Infiltration and Transport –
Fundamentals and Implications for Energy
Absorption and Dissipation

Nanofluidics involves two fundamental physical processes, namely, the infiltration into nanopores and the transport through nanopores. Both of them are governed by the unique molecular interaction between the solid and liquid phases,\(^\text{[70]}\) the structural\(^\text{[63]}\) and energetic\(^\text{[20]}\) differences between the confined liquid and its bulk counterpart, as well as the physical and chemical properties of the solid phase (e.g. pore size, pore geometry, partial charge and surface roughness\(^\text{[56,59,160]}\)) and the liquid phase (e.g. ionization and ion concentration\(^\text{[161]}\)).

In this chapter, nanofluidic infiltration and transport will be systematically investigated in terms of two characteristic quantities: the critical infiltration pressure for infiltration and the shearing stress for transport. The former indicates the external force required for a non-wetting liquid to intrude a nanopore, and the latter is relevant to the resistance that a liquid has to overcome during the transport. As introduced in Section 1.2.2, both processes (infiltration and transport) as well as the two characteristic quantities (critical pressure and viscosity) have important implications for the nanofluidic energy conversion. Hence, the investigation in this section is expected to provide useful guidelines for developing nanoporous composites of superior energy absorption/dissipation performance, which will be elaborated on at the end of this chapter.

3.1. Nanofluidic Infiltration: Critical Infiltration Pressure and General Size and Geometric Effects

In this study, the cone-shaped nanopore\(^\text{[162-165]}\) is employed as a model structure of the solid phase, which is simple yet able to represent a broad set of practical nanopores including those with cylindrical shapes (a cone with infinitely small apex angle is similar to a tube). According to the classical Young’s relation (Section 2.1.1), in order for a non-wetting liquid to intrude a cylindrical capillary, an
external pressure (usually termed as the critical infiltration pressure, $P_{cr}$) is required to help the liquid overcome the intrinsic energy barrier against infiltration; if the liquid is wetting, however, the infiltration can spontaneously occur even without any external assistance ($P_{cr} \leq 0$). When the capillary is no longer cylindrical, but of inclined walls (e.g. conical), the infiltration can be much more complicated. First, the inclination angle of the solid wall must play an important role. Second, as the cross section is varied along the axial direction, the size effects of various nanofluidic quantities (e.g. molecular structure, contact angle, velocity profile, and surface tension) may have influence.

Figure 16. (a) The computational model: a carbon nanocone (CNC) characterized by $\alpha$ and $H$ is fixed in space, with its opening end immersed in a reservoir filled with water molecules. When no external pressure is applied, the water front attains different positions depending on the apex angle, $\alpha$, of the nanocone: (b-c) infiltration is prohibited in the (10,10) CNT as well as the CNC with $\alpha=19.5^\circ$ (and similarly for all the other CNTs and for CNCs with smaller $\alpha$); (d-e) infiltration spontaneously occurs in the two CNCs with $\alpha$ equal to 30° and 41.8°, respectively.

Molecular Dynamics (MD) simulation is used to explore useful insights into the complex liquid intrusion into cone-shaped nanopores. Water is considered as the liquid phase and carbon nanocone (CNC) is adopted as a model structure of the cone-shaped nanopore. As illustrated in Figure 16a, in simulation, the nanocone
(assumed rigid) is fixed in space with its opening end immersed in a reservoir filled with water phase. The top and bottom surfaces of the reservoir are bounded by two rigid planes, with the upper one fixed and the lower one movable to mimic a piston. Periodic boundary conditions are imposed on the four lateral planes of the computational cell. Initially, the opening of the nanocone is covered by a rigid lid, and a specific number of water molecules are placed in the reservoir such that the pressure inside is close to zero (ambient) after equilibrium. Next, the lid is removed, and upon reaching the new equilibrium state, one can explore whether or not the liquid molecules spontaneously infiltrate the nanocone when no external force is applied. Further, as the piston is moved upwards and the reservoir volume is reduced, a relationship is measured between the elevated reservoir pressure and the number of infiltrated water molecules. The loading is carried out in a quasi-static manner, as the piston’s position is held for a sufficiently long time after each loading increment to allow system equilibrium. Pressure is evaluated at all loading steps according to the immediate density of water inside the reservoir.[170]

The carbon nanocones used in simulation are rolled up from cropped graphene sheets. Geometrically, a nanocone can be characterized by two parameters, the half apex angle, $\alpha$, and the height, $H$. Four representative nanocones are adopted ($\alpha=9.6^\circ$, $19.5^\circ$, $30^\circ$ and $41.8^\circ$, respectively) to account for a relatively large variation of the apex angle. CNTs of varying diameters are analyzed to represent the special case with $\alpha=0^\circ$. Furthermore, different values of $H$ are also taken into account. In all these cases, the pore diameter, $D$, is adopted as the characteristic length, which according to Figure 16a is a function of the depth (distance from the pore opening), $h$, as well as $\alpha$ and $H$. The interatomic van der Waals interaction is described by the Lennard-Jones (LJ) empirical forcefield. Water molecules are modeled by the rigid extended simple point charge potential SPC/E,[150] while the carbon-oxygen LJ parameters are extracted from the experimental low-coverage isotherm data of oxygen adsorption on graphite.[154] By using these molecular models and parameters, the graphene as the raw material for building CNTs and CNCs is ensured to be physically hydrophobic.[70]

3.1.1. Spontaneous Infiltration vs. Pressure-Assisted Infiltration

The nanofluidic infiltration into cone-shaped nanopores is found strongly dependent on the apex angle, $\alpha$. We first consider the ambient condition where no external force is applied. Figure 16b-e shows the equilibrium positions of the water front for various $\alpha$ (including a nanotube with $\alpha$ equal to zero). For nanocones with small apex angles, water molecules are expelled outside, suggesting that external assistance is required in these cases to initiate infiltration. For blunt nanocones, nevertheless, spontaneous infiltration occurs despite the hydrophobic nature of
graphene, making the nanocones nominally hydrophilic.†† Very interestingly, spontaneous infiltration in these cases does not wet the entire nanocone; the water front stops at a particular height, which corresponds to a pore diameter of about 19 Å when $\alpha=30^\circ$ and about 11.4 Å when $\alpha=41.8^\circ$, respectively (for all $H$ studied). As will be discussed in Section 3.1.3, this phenomenon cannot be understood by conventional fluidic theories.

Figure 17. Pressure versus the number of infiltrated water molecules. The curve for CNT has a plateau at a critical pressure ($P_{cr}$), while in the curve for CNC, $P$ increases continuously. The first and second indices of the CNC show its $\alpha$ and $H$, respectively.

No matter where the water front is under the ambient condition, water molecules can start to intrude the nanopore or continue to infiltrate if a pressure is externally applied to the system and gradually increased with time (pressure-assisted infiltration). If we plot the applied pressure as a function of the number of infiltrated molecules, the geometric effect becomes rather evident. As shown in Figure 17, for the nanotube, the infiltration behavior follows the classical Young’s relation, i.e. infiltration becomes spontaneous only after the pressure attains a critical level ($P_{cr}$). By contrast, in the nanocone, pressure keeps increasing in a nonlinear fashion, which is attributable to the varying pore size.

3.1.2. General Size and Geometric Effects

†† A nanopore is nominally hydrophilic if water can spontaneously infiltrate the nanopore. When the cross-section of a nanopore is invariant, the hydrophobicity (hydrophobic or hydrophilic) of the nanotube is determined by that of the solid phase. However, such correspondence breaks down for the nanopores with varying cross-sections.
In order to more systematically investigate both the spontaneous and the pressure-assisted infiltration mechanisms, in Figure 18 we plot pressure as a function of the pore diameter reached by the water front, for various values of $\alpha$. It is revealed that both the pore size and the inclination have profound effects on the nanofluidic infiltration (while the variation of $H$ is found not critical). First, for all the nanocones under investigation (including nanotubes), pressure increases as the pore size decreases. Second, enlarging the apex angle always leads to lowered pressure for any given pore size. Third and most interestingly, when the apex angle is large, the $P-D$ curve tends to intersect with the $P=0$ axis, reflecting the unusual mechanism transition between the spontaneous infiltration and the pressure-assisted infiltration observed for blunt nanocones in Figure 16d-e. These phenomena can be explained only by the classical theory enriched with nanoscale characteristics, elaborated below.

![Figure 18. Pressure versus pore size: it depicts the external pressure required to infiltrate water molecules to a certain pore diameter (which is equal to the diameter of the water front). The relationship is shown to be insensitive to the cone height, $H$. Symbols show MD simulation results. Lines show theoretical predictions from the enriched Young’s relation. For nanotubes (square solid symbols), $P_{cr}$ has a one-to-one correspondence with the diameter. For each nanocone, pressure depends on the infiltration depth (or volume, see Figure 17) and therefore the pore size reached by the water front. The critical pore sizes identified in Figure 16d-e, i.e. 11.4Å and 19Å, are marked by the two symbols lying on the axis of $P=0$.](image)

3.1.3. Limitations of Laplace-Young Equation

From the energy point of view, there are two terms competing during the
fluidic infiltration into the cone-shaped nanopore, one associated with the liquid-solid
interface and the other related to the liquid-vacuum interface (inset of Figure 19).
Denoting the liquid-solid interfacial energy as $\gamma_{LS}$ and the liquid-vacuum interfacial
energy as $\gamma$ (surface tension of water in contact with vacuum), respectively, given
the non-wetting nature of the liquid phase, both $\gamma_{LS}$ and $\gamma$ should be positive and
thus the expansion of both interfaces should be energetically unfavorable. Note that as
the water front advances in a conical nanopore, the liquid-vacuum interface is
continuously reduced while the liquid-solid interface keeps expanding. This induces a
competition between the overall liquid-solid interfacial energy and the overall
liquid-vacuum interfacial energy, in which the apex angle plays a key role as it
determines the relative shrinking/expanding rates of the two interfaces. For example,
when $\alpha$ is sufficiently large, the reduction of the overall liquid-vacuum interfacial
energy should dominate, leading to spontaneous infiltration, and vice versa.

Mathematically, the equilibrium of a meniscuses inside a nanocone should take the form of

$$P = -4\gamma \cos(\theta - \alpha)/D$$

where $\alpha$ denotes the half apex angle, $\theta$ denotes the contact angle, $D$ is the diameter of
the cross-section reached by the water front, and $\gamma$ represents the liquid-vacuum
interfacial energy. This equation is slightly different from the Young’s relation shown
in eqn. (2), since two angle terms ($\alpha$ and $\gamma$) are involved and the energy term is
replaced by the liquid-vacuum interfacial energy (surface tension). Moreover, we note
that the pressure term in eqn. (15) is $P$, not $P_c$, as that involved in eqn. (2). In eqn. (2),
$P_c$ is referred to as the critical pressure required to infiltrate a liquid into a nonwetting
circular capillary. Eqn. (15), however, describes the pressure required to hold a
meniscus inside a cone-shaped capillary, which may vary as the meniscus moves; thus,
there is no critical pressure in this case so we use $P$ to generally denote the pressure.
Note that the sign of $P$ determines the mechanism of infiltration: $P \leq 0$ implies the
spontaneous infiltration while $P > 0$ indicates the pressure-assisted infiltration. From
eqn. (15) the sign of $P$ is governed by four variables, namely, $\alpha$, $\theta$, $\gamma$, and $D$ ($\theta$
should be between 90° and 180° given the hydrophobic nature of the solid phase). As $\theta$ and
$\gamma$ are largely determined by the adoption of materials and $D$ is varied in the conical
nanopore, $\alpha$ becomes the critical factor that determines the shape of the meniscus
(and the associated infiltration mechanism). According to eqn. (15), positive pressure
is needed when $\theta - \alpha > 90^\circ$, and spontaneous infiltration should occur when $\theta - \alpha \leq 90^\circ$. 

Figure 19. Size effects of the interfacial energy and contact angle. The inset shows a schematic illustration of the liquid intrusion into a cone-shaped nanopore.

This form of Young’s relation qualitatively matches the trend observed in Figure 18. First, $P$ is inversely proportional to $D$; second, in the case of pressure-assisted infiltration, larger $\alpha$ results in lowered pressure for any given $D$. Despite these qualitative agreements, one critical phenomenon remains unexplained. That is, for a given combination of the liquid and solid phases, once the cone apex angle $2\alpha$ is specified and the contact angle $\theta$ is assumed to take the bulk value (and thus a constant), according to the Young’s relation eqn. (15), the infiltration should be either spontaneous or pressure-assisted, and no transition like that observed in blunt nanocones should happen. This implies that the contact angle, $\theta$, may be size-dependent at the nanoscale.

3.1.4. Size Effects of Surface Tension and Contact Angle

In order to quantify the size effects involved in the current investigation, we first theoretically examine the infiltration into nanotubes of various characteristic sizes. Since any one nanotube corresponds to a unique critical pressure (Figure 17), the Young’s relation becomes $P_\alpha = 4\gamma_{LS} / D$ (eqn. (2)) by letting $\alpha=0^\circ$ and using the equilibrium relation,

$$\gamma_{LS} = -\gamma \cos \theta$$  \hspace{1cm} (16)

Based on MD simulation results (solid square symbols in Figure 18), $\gamma_{LS}$ can be obtained as a function of the tube size $D$, as plotted in Figure 19. Such variation results from the size effects of both the liquid-solid interaction (binding) energy and the surface energy of water.

In the second step, we rewrite eqn. (15) as $P = 4\gamma_{LS} \cos(\theta - \alpha) / D \cos \theta$. With
the $\gamma_{LS}(D)$ obtained above, $\theta$ becomes the only unknown, which is then fitted out and plotted in Figure 19 as a function of the pore size. The result reflects a significant trend of increasing contact angle with the decrease of pore size, which qualitatively matches the size effect of the contact angle of a water droplet resting on a flat graphene.[70] By incorporating the size effects of both $\gamma_{LS}$ and $\theta$, the Young’s relation (thin lines in Figure 18) shows good agreements with the MD simulation results (symbols in Figure 18), implying that the unveiled size effects of $\gamma_{LS}$ and $\theta$ are responsible for the observed mechanism transition between the spontaneous infiltration and the pressure-assisted infiltration in blunt nanocones.

3.1.5. Summary

Under ambient condition, when the apex angle of a nanocone is large, spontaneous infiltration initiates despite the hydrophobic nature of the solid phase; however, water molecules can only access a particular pore size and cannot wet the entire nanocone. This implies an interesting transition between the spontaneous infiltration (nominally hydrophilic) and the pressure-assisted infiltration (nominally hydrophobic) mechanisms. Thus, with the same blunt cone angle, a long nanocone and a short nanocone (with a pore opening smaller than the critical pore size that water can access under ambient condition) may exhibit distinct wetting properties. Further infiltration has to be assisted by applying an external pressure. A higher pressure is required for the water front to access a smaller pore size. Enlarging the apex angle always leads to lowered pressure and therefore easier infiltration. These phenomena can be explained by using the enriched Young’s equation, where both the liquid-solid interfacial energy and the contact angle are assumed dependent on the characteristic length (both increase as the pore size decreases).

The unique mechanisms revealed in this section may contribute to the understanding and prediction of nanofluidic infiltration into nanopores with more general cross-sections (slit-shaped, etc.), as well as help to design nanostructured surfaces with hydrophobic-hydrophilic (or wetting-nonwetting) transition capabilities. Note that although the solid is assumed to be graphene throughout the analysis of this section, the unveiled size and geometric effects are expected to be generally applicable in other nanopores of different compositions (e.g. polar nanopores). Nevertheless, when the pore size is reduced to a certain level, e.g. being close to the molecular size, the infiltration mechanism could be fundamentally altered, resulting in infiltration phenomena unique to the molecular-sized nanopore. This will be the focus of the next section, in which an interesting and counter-intuitive infiltration phenomenon is studied both experimentally and theoretically.
3.2. Fluidic Infiltration in Molecular-Sized Nanopores

Section 3.1 investigates the general size and geometric effects on the infiltration of water into nanopores. In this section, a different liquid phase, electrolytes, will be studied, which has drawn considerable attention owing to their key roles in biological transport, water purification, energy dissipation, conversion and storage, and many other promising applications of nanofluidics. The key distinction between pure water and electrolytes lies in the fact that, as solutions of salts, bases, or acids, electrolytes are essentially liquids containing multiple phases, and thus their fluid behavior must be more complicated. In particular, when ions transport inside a nanotube of the diameter comparable with the molecular size, the solvated configuration can be highly distorted. Thus, the resulting nanofluidic properties, such as the infiltration and transport behavior, must be strongly dependent on the characteristic length scale of the nanoconfinement.

In a small nanotube or nanochannel, liquid molecules and ions can form a quasi-one-dimensional chain. If the nanotube/nanochannel surface is effectively nonwettable, an external driving force must be applied to force the ions and liquid molecules to enter the nanoenvironment. That is, work must be done to increase the system free energy. It is envisioned that, for solvated ions of the same charge but different sizes, the required external work would be distinct, which depends on the variation in system free energy. It was generally predicted that for the same nanopore, if the solvent molecular or ionic size increases, the infiltration pressure should become higher because less pore volume is available. Even when the nanochannel wall is nominally wettable to the liquid phase, the channel size must be much larger than the solute molecules/ions; otherwise the repelling effect of the solid wall would prevent their infiltration; the required “free volume” can be a few times larger than the solute molecules/ions. This prediction, however, may break down for very small nanochannels where the effective channel diameter is only slightly larger than the ion size. Under the extreme confinement, all ions directly interact with the channel wall, which not only affects the solid-liquid interaction but also dominates the configuration of the confined clusters of electrolyte particles.

3.2.1. Counterintuitive Cation Size-Dependent Infiltration Pressure

To explore the unique transport behavior of electrolytes in molecular-sized nanochannels, we investigated a zeolite Y (ZY), which has an effective pore diameter of 0.7 nm. The as-received material was provided by Zeolyst (Part No.: CBV-901) in powder form, with the crystal size of 10-50 μm and the porosity of about 0.2 cm³/g. The relatively large crystal size assured that the ion transport could reach the steady state under a quasi-equilibrium loading. In order to minimize the defect density at
nanopore inner surfaces, the ZY crystals were first thermal treated in air at 175 °C for 6 h and then placed in a vertical quartz tube furnace. A nitrogen flow was conducted across the tube furnace, carrying saturated silicon tetrachloride vapor through the sample. The temperature was kept at 400 °C for 1 h, after which the ZY sample was cooled in air and thoroughly washed by distilled water, and then heated at 500 °C in air for 1.5 h and dried in vacuum at 50 °C for 8 h.

![Figure 20](image)

Figure 20. (a) Quasi-static sorption isotherm curves. (b) Infiltration pressure versus the Pauling cation size. The specific system volume is defined as the system volume normalized by the mass of the nanoporous material.

The sample was placed in a steel cylinder with an aqueous solution of chloride salt, with the ZY/liquid mass ratio of 1/10. The salt was either LiCl, NaCl, KCl, or CsCl, and the molarity of all the solutions was 4 M. During the infiltration experiment, the zeolite-liquid mixture was sealed in a stainless steel cylinder by a stainless steel piston (Figure 2). The piston was intruded into the cylinder at the rate of 0.5 mm/min by a type 5580 Instron machine, until the inner pressure reached 40 MPa. Further reducing loading rate would not cause any detectable change in the sorption isotherm curve, indicating that such a loading condition could be regarded as quasi-static. The system volume change was calculated as $A_p d_p$, where $A_p = 286 \text{ mm}^2$ is the cross-sectional area of the piston and $d_p$ is the piston displacement. The inner pressure was calculated as $F_p/A_p$, where $F_p$ is the intrusion force applied on the piston, measured by a 100 KN load cell.

The ZY material is hydrophilic. Therefore, if the liquid phase is pure water, nanopores can be soaked up spontaneously. As the electrolyte is added, the nanopore inner surface become effectively nonwettable, so nanopores remain empty under ambient pressure. As a sufficiently high external pressure is applied, pressure-assisted infiltration begins, leading to an infiltration plateau in Figure 20a. The liquid infiltration ends when the porous space is filled up. The width of the infiltration plateau reflects the accessible nanopore volume, which is close to the measured

![Diagram](image)
porosity, as it should be. The measured infiltration pressure, \( P_{cr} \), is shown in Figure 20b for the four solutions. For self-comparison purpose, \( P_{cr} \) is taken as the pressure at the starting point where the measured slope of the sorption isotherm curve is a constant afterwards. It is remarkable that \( P_{cr} \) decreases with the cation size. For the LiCl solution, \( P_{cr} \) was nearly 15 MPa; when the electrolyte is changed to NaCl, \( P_{cr} \) becomes 13.5 MPa; for KCl, \( P_{cr} \) is largely decreased to 4 MPa. In the system based on pure water and CsCl, the pressure-assisted infiltration could not be detected, indicating that the nominal \( P_{cr} \) is zero or below; namely, spontaneous infiltration dominated.

3.2.2. Quasi-Periodical Ion Couple Structure

In order to understand the unique ion behavior, atomistic simulations are carried out with the COMPASS (Condensed-phase Optimized Molecular Potentials for Atomistic Simulation Studies) force field\textsuperscript{155} in which a long, straight, and rigid silicon dioxide nanotube (Figure 21a) with the diameter of \( D_\theta = 7.4 \) Å (the distance between diagonal O atoms) is employed as a close analogue to a ZY nanopore. During the simulation, one end of the nanochannel is immersed in a liquid reservoir, which is bounded by two rigid planes (walls) in the axial direction. Periodic boundary conditions are imposed in the transverse directions (Figure 21a). To be consistent with the experiment, four solutions and pure water are considered. In the solutions, the molarity of salt concentration is considered to be 4 M. In the four solutions, cations are of the same partial charge but their Pauling ionic radii are different, equal to 60, 95, 133, 169 pm, respectively. After a system relaxation of 100 ps at the pressure of 1 atm and the temperature of 300 K, the ions are evenly solvated among the water molecules in the reservoir. All simulations are carried out sufficiently slow such that the process can be regarded as nearly quasi-static.

The MD simulation results are consistent with the findings from experiment. Pure water enters the nanopore under the ambient condition, which proves that the model nanochannel is hydrophilic. For three of the electrolyte solutions under investigation, LiCl, NaCl, and KCl, only at an elevated pressure can ions and water molecules infiltrate the nanochannel. The infiltration pressure, \( P_{cr} \), is calculated the highest for LiCl and the lowest for KCl. For the CsCl solution that has the largest cation, at the ambient pressure only water molecules enter the channel; no ion infiltration is observed even when \( P > 100 \) MPa, implying that the nominal \( P_{cr} \) for the CsCl solution is zero or below.
Figure 21. MD simulation of the electrolyte infiltration into a molecular sized silicon dioxide nanotube: (a) the computational model, where ion couples are formed right after the cations and anions enter the nanopore. (b-d) Molecular structures of three electrolytes confined in the nanotube; both the separation between two neighboring ion couples and the distance between two paired ions are found to be dependent on the cation size; (e) for the CsCl solution, no ion is found to intrude the nanopore.

Figure 22. Energy contours of individual cations and a water molecule moving within a cross-section of the nanotube: the energy value at the center is adopted as the ground state, and the diameter of the black circle equals to 4.5 Å.
3.2.3. Cation Size-Dependent Parameters

Owing to the strong confining effect of the nanochannel, the infiltrated water molecules and ions maintain a quasi one-dimensional chain, as shown in the MD snapshots (Figure 21b-d). It is remarkable that the distribution of ions is highly regular at the steady-state: each Cl\(^-\) ion pairs with a cation (Li\(^+\), Na\(^+\), or K\(^+\)), forming a number of anion-cation couples in an ordered sequence, and the neighboring ion couples are separated by a few water molecules. It is also noteworthy that in the nanotube under investigation, the infiltrated electrolyte chain (consisting of a number of ion couples) in Figure 21b-d is always led by a cation, and thus the electrolyte segment inside the nanopore is essentially non-neutral. Compared with the uniformly scattered ion distribution in the bulk electrolyte, the current atomistic simulation suggests that in a highly confining space, there is an energetic preference for cations and anions to aggregate, thus leading to the nanocrystalline-like structure. That is, as the space is insufficient for any solvated structure, the effective solubility of ions is greatly reduced. The detailed formation mechanisms of this unusual ion structure will be discussed in details in Section 3.2.6.

In the quasi-periodical ion structure shown in Figure 21b-d, we denote the separation between the cation and anion in an ion couple as \(a\), and the average spacing between neighboring ion couples as \(b\) (Figure 21b). Both of them show strong dependencies on the cation size. From MD simulations, \(a\) is measured 2.05Å, 2.39Å and 2.74Å, respectively, for the LiCl, NaCl, and KCl solutions. Ionic bonding is the dominant factor that influences the distance between the paired cation and anion. The ionic bond length\(^{**}\) is calculated 2.20Å, 2.55Å and 2.8Å, respectively, for the three electrolyte solutions, which are rather close to the values of \(a\) reported above. The small difference is attributable to the environmental factors (nanopore, water molecules, and other ions, etc.).

In essence, the value of \(b\) indicates the probability of an ion couple entering the nanochannel. According to our simulation results, smaller cation leads to larger \(b\). Theoretically, smaller cations should be more advantageous in the competition with other particles for invading the nanochannel; since the anion is the same among the considered electrolyte solutions, ion couples involving smaller cations would be more frequently infiltrated into the nanopore. As an illustration, in Figure 22 we plot the energy maps associated with the in-plane motion of a water molecule and four cations (Li\(^+\), Na\(^+\), K\(^+\), and Cs\(^+\)) inside the nanochannel. For Li\(^+\), a large plateau is found in the central region of the nanochannel, within which the energy is only slightly varied; by contrast, for Cs\(^+\), the radial gradient is much higher, which explains the non-infiltration of Cs\(^+\) (Figure 21e).

\(^{**}\) Ionic bond length is calculated as the separation between a cation and an anion after the geometric optimization in which no other atom is present.
3.2.4. Impact of the Unique Ion Couple Structure on Infiltration Pressure

These structural features and ion size dependent variables of the infiltrated electrolyte chain dominate the infiltration pressure, \( P_{cr} \).\(^{[18,59]} \) When the size of the nanochannel is fixed, \( P_{cr} \) is governed by the effective liquid-solid interfacial tension, \( \gamma_{LS} \). A known contribution to \( \gamma_{LS} \) arises from the difference between the free energies of a liquid volume in the bulk state and in the confined state, denoted as \( \gamma_{LS}^0 \). Energy analyses show that \( \gamma_{LS}^0 \) of water, LiCl, NaCl and KCl solutions are all of small negative values, indicating that, without considering other factors, all of them should be able to spontaneously enter the tube at the ambient pressure. However, both MD simulation and experiment show that, only pure water and the CsCl solution can spontaneously infiltrate the nanopore. Thus, there must be other mechanisms governing the infiltration of electrolytes into molecular-sized nanopores.

As remarked earlier, the infiltrated quasi-periodical chain is always led by a cation. In other words, the electrolyte remaining in the reservoir must be non-neutral, which can be characterized by an effective negative charge near the pore opening. We note that, the effective negative charge outside the nanopore is closer to the cation in an ion couple than the anion in the same ion couple (Figure 21b-d). This leads to a strong net Coulomb’s attraction between the effective net charge and all infiltrated ion couples, which induces an additional energy barrier, \( \gamma_{LS}' \), against the liquid infiltration. Incorporating the new energy term, \( \gamma_{LS}' \), the overall interfacial energy takes the following form:

\[
\gamma_{LS} = \gamma_{LS}^0 + \gamma_{LS}'
\]

Suppose \( \Delta E \) is the energy barrier associated with one ion couple. The new energy barrier \( \gamma_{LS}' \) (per unit surface area) can be assessed by \( \Delta E \cdot n \), where \( n \) denotes the number of ion couples in an infiltrated segment that has the unit surface area. Notably, both \( \Delta E \) and \( n \) are ion size-dependent, where \( \Delta E \) is affected by \( a \) and \( n \) is influenced by \( b \).

Theoretically, \( \Delta E \) indicates the work required to transport an ion couple to the interior of the nanopore. In order to measure \( \Delta E \), three ion couples are moved inside the nanochannel, and the energy variations are plotted in Figure 23 as functions of the position of the ion couple. We note that the second derivatives of these curves are negative, implying that the work required for transporting ion couples keeps decreasing (since the Coulomb’s interaction is diminished as the distance between the effective charge and the ion couple increases). \( \Delta E \) is thus estimated as the total energy variation from the tube opening to about 500Å inside the nanotube, where the energy variation reaches a plateau. The K\(^+\)/Cl\(^-\) couple is found to have the largest \( \Delta E \), approximately 0.55 kCal/mol, followed by the Na\(^+\)/Cl\(^-\) couple with 0.53 kCal/mol, and then the Li\(^+\)/Cl\(^-\) couple with 0.45 kCal/mol. Such an ion size dependence of \( \Delta E \) is primarily due to the difference in \( a \) among the three ion couples. As \( a \) decreases, the
anion in the ion couple can offset more attraction between the cation and the effective charge, thus lowering the net force.

![Energy analysis of an anion-cation couple](image)

Figure 23. Energy analysis of an anion-cation couple (with an equilibrium separation, $a$) moving towards the interior of the nanopore.

The associated free energy change of the steady-state system is

$$\gamma_{LS} = \frac{\Delta E}{\pi b D}$$

where $D$ is the effective diameter of the nanopore. Then, the quasi-static infiltration pressure, $P_{cr}$, can be calculated by virtue of eqns. (2), (17), and (18). Since $\gamma_{LS}^0$ is negligible for the investigated cases, $P_{cr}$ is nearly proportional to $\Delta E$ and $1/b$. Although the KCl solution has the largest $\Delta E$, its $P_{cr}$ is still calculated the lowest, 8.85 MPa, due to the large $b$. The NaCl and LiCl solutions are calculated to have the $P_{cr}$ values of 14.64 MPa and 15.69 MPa, respectively. Using this model, the predicted ranking and values of $P_{cr}$ agree quite well with the experimental results.

3.2.5. Anion Size Effect and Concentration Effect

Although the model shown in Section 3.2.4 is developed to explain the cation size effect among the considered three electrolyte solutions, the model is expected to be widely applicable for other electrolyte solutions with different solutes and ion concentrations. As a verification, here we investigate a different set of salts (NaF, NaCl, and NaBr) and two representative ion concentrations (mole fraction, $X = 0.06$ and 0.08). The three solutes have the same cation but different anions. As expected, all of the three electrolytes form ion couple structures inside the nanopore, implying that the novel electrolyte structure is indeed a common phenomenon inside molecular-sized nanopores. Determined from MD simulations, the two geometric parameters, $a$ and $b$, again, show very strong dependence on the anion size. Quantitatively, $a$ is measured 2.13 Å, 2.55 Å, and 2.64 Å, respectively, for the NaF,
NaCl, and NaBr solutions (same for the two ion concentrations), which are rather close to the calculated ionic bond lengths (2.02 Å, 2.39 Å, and 2.52 Å, respectively). The corresponding values of $b$ are measured 14.75 Å, 19.16 Å, and 21.58 Å, respectively, when $X = 0.08$, and 26.75 Å, 36.29 Å, and 40.00 Å, respectively, when $X = 0.06$ (Figure 24). From an energy analysis similar to that shown in Figure 23, $\Delta E$ is calculated about 0.43 kCal/mol, 0.49 kCal/mol, and 0.53 kCal/mol, respectively, for the Na$^+/F^-$, Na$^+/Cl^-$, and Na$^+/Br^-$ ion couples.

![Figure 24](image_url)

Figure 24. The size and concentration effects on the predicted infiltration pressure ($P_{cr}$) and the separation between ion couples ($b$).

Using the model described by eqns. (2) and (17)-(18), $P_{cr}$ is predicted to be 11.61 MPa, 10.31 MPa, and 9.62 MPa, respectively, for the three electrolytes at $X = 0.08$. In essence, when the anion is smaller, the ionic bond length is shorter and thus $a$ is smaller and $\Delta E$ is smaller; however, when the anion size is smaller, the infiltration probability is higher, and thus $b$ becomes smaller. Again, the determination of the infiltration pressure is a competition between $\Delta E$ and $b$. For the cases under investigation, $b$ wins and thus $P_{cr}$ is larger for smaller anions. Due to the concentration effect on $b$, $P_{cr}$ must also dependent on the value of $X$. As shown in Figure 24, as the ion concentration is reduced by 25%, $P_{cr}$ is almost doubled. In a validation experiment with the Zeolite Y (ZY), the values of $P_{cr}$ are measured 250 kPa, 230 kPa, and 160 kPa for the NaF, NaCl, and NaBr solutions, respectively. It is evident that the infiltration pressure decreases as the anion size increases, which qualitatively agrees with the prediction of the proposed model.\textsuperscript{55}

\textsuperscript{55} The difference between the magnitudes of infiltration pressure measured in experiment and simulation is attributed to the effect of surface treatment and electrolyte concentration used in experiment.
3.2.6. Ion Couple Structure: Theoretical Verification

According to the previous part of this section, the quasi-periodical ion couple structure constitutes the basis of the new model developed by us which underpins the counterintuitive ion size-dependent infiltration of electrolytes into molecular-sized nanochannels. Such a novel structure can be verified by a number of energy analyses. Starting from an empty nanotube, we compare the energy variations associated with the entry of a cation and an anion in three successive stages (Figure 25a). Sodium bromide is taken as an illustrative example and all findings hold for the other two electrolytes. Stage 1 refers to the infiltration of the first ion, where “1C” illustrates the possibility that a cation would first infiltrate the nanopore, and “1A” corresponds to an alternative case that an anion would first infiltrate. In either case, a counter charge is placed outside the tube so as to neutralize the system. The examined ion is then perturbed by several Å along the axial direction, causing a variation to the system potential energy (Figure 25b). By comparing the energy variations of both possibilities, it is made clear that a cation should first infiltrate as it can decrease the system energy. In the subsequent stage 2 where a cation has already infiltrated, “2C” is found to be more energetically favorable than “2A” and thus another cation should enter the nanopore. Following the two previously infiltrated cations, the third infiltrated ion is found to be a Br⁻ anion.

Driven by an energetic preference, the Na⁺ cation infiltrated in stage 2 and the Br⁻ anion infiltrated in stage 3 should aggregate inside the nanopore. For verification, we consider two possible configurations of the confined Na⁺ and Br⁻ ions: a nanocrystalline-like structure which mimics the structure observed in simulation (Figure 26a), and a uniformly scattered ion structure (Figure 26b). The energy is calculated -710 kCal/mol and -216 kCal/mol, respectively, for these two configurations. That is, the formation of an ion couple could favorably reduce the system potential by ~90 kCal/mol. We note that, there is an energy barrier that needs to be overcome before the energetically favorable ion couple structure (Figure 26a) can be formed. That is, for a cation and an anion to approach each other, any water molecule in between must escape (Figure 26d); when a water molecule and an ion are about to switch their positions, however, a moderate energy barrier may arise given the limited space inside the nanopore. The energy barrier is computed about 5 kCal/mol for a water molecule to bypass a Na⁺, and about 94 kCal/mol for a water molecule to bypass a Br⁻. The former is lower, so the ion couples are formed by consecutively switching H₂O and Na⁺.

*** Water molecules may infiltrate the nanopore before/after the infiltrated ions.
Figure 25. Verification of the sequence of ion infiltration identified in simulation: in (a) three successive key stages, the (b) energy variations associated with the infiltration of a cation and an anion are compared.

Figure 26. Verification of the formation and stability of the ion couple structure: three possible ionic configurations inside the nanopore are compared: (a) a nanocrystalline-like structure that mimics the structure observed in MD simulation (Figure 21), where $a$ and $b$ are averaged from MD snapshots, approximately 2.5 Å and 21.5 Å, respectively; (b) a scattered structure that assumes no ion couple is formed and all ions are alternatively and uniformly distributed with a uniform spacing of 12 Å; and (c) an aggregated structure that assumes ion couples further aggregate to form a continuous ion strand with a uniform spacing of 2.5 Å. (d) As a cation and an anion approach each other to form a couple, water molecules in between, if any, have to switch position with a neighboring ion, which results in an energy barrier.
After the infiltration of the first three ions, there is only one net positive charge inside the channel and one counter-charge outside, which leads to a situation similar to the end of stage 1 ("1C" in Figure 25a). Thus, the subsequent infiltration of ions would repeat stages 2-3; more and more cations and anions would be driven into the nanopore and paired inside (which is consistent with the MD simulation shown in Figure 21). We further note that in MD simulation, the nanocrystalline-like structure (Figure 26a) is found to be very stable; there is no inclination for neighboring ion couples to aggregate to form a continuous ion strand shown in Figure 26c. Although an energy analysis shows that the aggregated structure has a lower energy (~880 kCal/mol) than the nanocrystalline-like structure, it is important to note that, for the aggregated structure to form, the bounded water molecules must switch their positions with Br⁻, which requires a prominent energy barrier (~94 kCal/mol per switch). Thus, from the energy point of view, the aggregation of ion couples is unlikely to occur, and the ion couple structure is rather stable.

With the continuous infiltration of ions and the formation of ion couples, eventually, a quasi-periodical chain of ion couples (led by a cation) is formed inside the nanopore. This holds for all the electrolytes under investigation. Although such an ion couple structure is discovered in a SiO₂ nanotube, it is envisioned to hold in other molecular-sized nanopores (e.g. a CNT of the same size).

3.2.7. Summary

In this section, we report an interesting phenomenon that, when other conditions remain the same, it requires a higher pressure to infiltrate an electrolyte solution of smaller ions into a molecular-sized nanochannel. MD simulation indicates that the confined ions tend to form crystalline-like ion couples; that is, inside the extreme confinement, the solubility of ions is essentially zero (similar to gas molecules[20]). As the nanopore is polar, there is a strong sequential preference for the ions to enter the nanopore, and thus a non-neutral and quasi-periodical chain of ion couples is formed. In order to sustain the infiltration, external work must be applied to the system, such that the infiltrated liquid segment could overcome the energy barrier imposed by the nonbonded interaction with the rest of the system. For smaller ions, although it requires less work to advance a unit ion couple, the spacing between ion couples is more dominant, so the infiltration pressure is larger. The ion size-dependent infiltration behavior is associated with the synergy and competition of a number of variables unique to the nanoscale confinement. It is envisioned that the unique ion couple mechanism revealed herein has important relevance to the studies on carbon nanotubes (especially those charged or surface treated), nanoporous membranes, and nanopipettes, etc.
3.3. Nanofluidic Transport: Viscosity, Shearing Stress and General Size and Loading Rate Effects

In the last two sections, nanofluidic infiltration is investigated in both normally sized nanopores and molecular-sized nanopores. The pore size and pore geometry, as well as the ion size and ion concentration are all found to play key roles in determining the magnitude of the critical infiltration pressure. The next two sections will be focused on the other physical process that governs nanofluidics, namely, the transport. Again, the investigation consists of two parts, one on the general size and rate effects of the nanofluidic transport (this section), and the other on the transport in molecular-sized nanopores (next section). Both are expected to provide useful guidelines for designing nanoporous composites of desired energy conversion performance (Section 1.2.2.1).

Viscosity is known to be a well-defined quantity at the macroscopic scale which indicates the external effort required to transport a liquid through a channel. The available results of the nanoscale viscosity are somewhat contradictory. Among prior experiments, Raviv et al. reported that when water molecules were confined between two curved mica surfaces (the water film thickness, \( h \), was 0.4-3.5 nm), the effective viscosity, \( \eta \), remained similar to its bulk counterpart.\(^{[140]}\) By contrast, when Li et al. studied the water film with a thickness \( h < 2 \) nm, they found that \( \eta \) was higher than its bulk counterpart by four orders of magnitude on hydrophilic surfaces (e.g. mica, glass), whereas no size effect on hydrophobic surfaces (graphite) was detected.\(^{[141]}\) In addition, Major et al. reported that \( \eta \) of water increased over seven orders of magnitude when \( h \) was less than 1 nm. Note that the scattered experimental results can only be partially attributed to the surface effect (e.g. defects and impurities).\(^{[137]}\) On the basis of atomistic simulations, Leng et al. found that the viscosity of a water film was close to that of bulk water when \( h = 2.44 \) nm, but increased by 2 orders of magnitude when \( h \) was decreased to 0.92 nm.\(^{[139]}\) Using the Green–Kubo relation from the linear response theory and a MD-based flux auto-correlation function, Liu et al. argued that inside a (16,16) CNT, the viscosity of water was the same as the bulk value, but it was nearly doubled in a (8,8) tube.\(^{[138]}\) In view of the controversies in the literature, viscosity (and transport) must be seriously reinvestigated at the nanoscale via a synergy between experiment and simulation. Indeed, at the nanoscale, the flow characteristics can be fundamentally different from those at the macroscopic scale (Section 3.3.1). In order to investigate the viscosity in the nanoconfinement, we start from an equally important yet more intuitive quantity, i.e. the shearing stress, whose size and flow rate effects will be systematically studied in Section 3.3.2. Then, in Section 3.3.3, the viscosity will be bridged with the shearing stress, and its intrinsic size and flow rate effects will be unveiled.

3.3.1. Plug-like Flow
Figure 27. (a) Water molecules in a model CNT. (b) The Radial Density Profile (RDP) of water molecules inside CNTs with different radii. (c) A representative Radial Velocity Profile (RVP) of water molecules inside a (60,60) nanotube. Both RDP and RVP are computed via the average of all water molecules in the computational cell.

Nonequilibrium molecular dynamics (NEMD) simulations are carried out using LAMMPS to explore the nanofluidic flow characteristics. The computational system consists of a number of water molecules (modeled by the TIP3P model) confined in a single-walled CNT (Figure 27a). The length of the computational cell is 300 Å and periodic boundary condition is applied along the axial direction. CNTs with the size ranging from (10,10) to (60,60) are selected (the radius, $R$, is varied from 0.675 to 4.053 nm). A specific number ($N$) of water molecules are placed inside the nanotube such that the initial water density is 0.998 g/cm$^3$ inside the occupied volume. After initial optimization, a constant acceleration is applied to each atom to initiate a uniform flow along the tube, until the desired flux (or velocity, $\nu$) is reached. The flow speed, $\nu$, is related with the flux $Q$ by $\nu = Q / (\pi R^2)$. Long range Coulomb interaction is handled by the Particle-Particle Particle-Mesh technique (PPPM).

††† We have verified that the computational results are insensitive to the variation of the size of the cell.
with a root mean square accuracy of $10^{-4}$. The time step in simulation is 1 fs. The initial structures are relaxed for 100 ps using the $NVT$ ensemble with the temperature kept at 298 K via the Nose-Hoover thermostat.

In the continuum modeling of fluidic transport, no-slip boundary condition is sometimes assumed, namely, the flow velocity at the tube wall is zero. For nanofluids, however, this assumption no longer holds. Indeed, nanofluidic flow usually exhibits partial slip against the solid surface, which can be characterized by the so-called slip length (around $3.4-68 \mu m$ for different liquids$^{[38]}$). The slip length, however, is not a physical quantity and is thus hard to be employed in a rigorous analysis. As an alternative, it may be more straightforward to extract the velocity profile directly from the MD simulation results. At a representative $v = 165$ m/s, Figure 27c shows the radial velocity profile (RVP) of water molecules inside a (60,60) nanotube. A typical plug-flow profile is found, which is consistent with the result shown in literature.$^{[61]}$

This unique velocity profile inspires us to reinvestigate the viscosity at the nanoscale.

### 3.3.2. Shearing Stress: Size and Rate Effects

Different from the viscous force in a macroscopic laminar flow, the “resistance” that a nanofluidic flow may encounter mostly comes from the “boundary layer”, i.e. the interface zone that separates the solid and liquid phases. Such a interface-induced “resistance” can be accounted for by a very intuitive physical term, i.e. the shearing stress, $\tau$. Due to the direct “contact” between the solid surface and the liquid column, this shearing stress is expected to dominate nanofluidic transport; and moreover, prominent size and rate effects may be involved.

In order to explore the shearing stress as well as the involved size and rate effects, a deceleration test is carried out in various CNTs and at different initial velocities. In a water flow that has reached the steady state (flowing at a constant velocity of $v$), we first remove the acceleration force that drives the flow, and then use the NVE ensemble to monitor the variation of the flow velocity in the next several picoseconds.$^{[4]}$ The instantaneous flow velocity ($\bar{v}$) is calculated at every time step by averaging the axial speed of all water molecules. From the results it is found that $\bar{v}$ decreases almost linearly with time. It is therefore possible to extract the deceleration ($a$) of the water flow, with which the effective shearing stress can be calculated as

$$\tau = Nma/(2\pi RL)$$

where $m$ is the mass of a water molecule and $L$ is the tube length. Denoting $n_0$ as the

$^\text{‡‡‡}$ The time period of the deceleration test varies case by case. In general, we want the variation of the flow velocity to be controlled below 3% throughout the deceleration test, such that the flow rate effect would not kick in, and the measured deceleration and the calculated shearing stress can be regarded as that for the starting velocity (because the shearing stress is dependent on the flow velocity).
number density of water (i.e. the number of water molecules in a unit volume), we can calculate the shearing stress as \( \tau = n_0 m R a / 2 \), which is a function of both the tube size and the average flow speed.

Figure 28 shows the relationship between \( \tau \) and \( R \) for different tube radii, in which \( \bar{v} \) is fixed at about 165 m/s. The shearing stress \( \tau \) increases with increasing \( R \), and the rate of increase is smaller for larger tubes. Overall, \( \tau \) is relatively small in the tube size range under investigation, implying that the tube surface is quite smooth and the water molecules can easily slip against it. In fact, the shearing stress is primarily contributed by the vdW interactions between the solid wall and the water molecules in the first solvation shell. The characteristic distance between the first solvation shell and the tube wall \( (d) \) depends on the equilibrium distance between the O and C atoms, the distribution of solid wall atoms, and the tube curvature. As a first order approximation, the magnitude of the first solvation shell scales with \( 1 - d_0 / R \), where \( d_0 = d_{R \rightarrow \infty}^{R=0} \). This trend qualitatively agrees with the computed radial density profile (RDP) of water molecules inside the nanotubes (Figure 27b). The magnitude of the first solvation shell increases with \( R \), suggesting that a larger tube wall can provide a stronger vdW constraint on the water molecules, and thus \( \tau \) is increased. The shearing stress is also dependent on the flow velocity (Figure 29). In the example of a (20,20) tube, \( \tau \) increases with \( \bar{v} \), with the rate of increase slowing down as \( \bar{v} \) increases. When \( \bar{v} \) is high, there is no much time for the moving water molecules to fully adjust themselves to the most energetically favorable positions/orientations, thus increasing the overall surface friction, i.e. the shearing stress.\[58\]
Figure 29. Flow velocity effect on the shearing stress (triangle) and the nominal viscosity (square) when \( R = 1.336 \) nm.

3.3.3. Nominal Viscosity: Size and Rate Effects

According to the classical fluid mechanics, with a pressure drop of \( P \) along a tube of length \( L \), the flow flux can be represented by eqn. (3) as \( Q = \pi R^2 P / (8\eta L) \). Due to system equilibrium,

\[
\tau = PR / (2L) \tag{20}
\]

a nominal viscosity of the liquid can be defined as

\[
\eta = \tau \cdot R / (4\bar{v}) \tag{21}
\]

Note that, although this equation is based on the continuum theory, it can be used to obtain the nominal viscosity of various nanofluids.\textsuperscript{[179,180]} Figure 29 shows the relationship between \( \eta \) and \( \bar{v} \) inside a (20,20) tube: \( \eta \) first sharply decreases with the increase of flow velocity, and after \( \bar{v} \geq 150 \) m/s, it starts to converge. For the considered tube size and range of flow velocity, \( \eta \approx 1 / \bar{v}^{0.5} \); such a trend arises from the \( \tau - \bar{v} \) relation shown in the same figure.

According to Figure 29, the rate effect is negligible when \( \bar{v} \) is relatively high. Figure 28 shows the relationship between the nanotube radius and the nominal viscosity (\( \bar{v} \approx 165 \) m/s). Since \( \tau \) increases with \( R \), \( \eta \) increases quickly in larger tubes by nearly 2 orders of magnitude as \( R \) is changed from 0.67 nm to 4.05 nm. The nominal viscosity of water inside the (10,10) tube is \( 8.5 \times 10^{-8} \) Pa \( \cdot \) s, which is about 4 orders of magnitude lower than the viscosity of the bulk water. This result is consistent with previous experimental and simulation results indicating that water can flow much faster at the nanoscale than at macroscopic scale.\textsuperscript{[38,63,111]}

\textsuperscript{555} This is for the purpose of self-comparison. The most intrinsic nanofluidic characteristic is still the shearing stress as discussed above.
3.3.4. Experimental Validation

To qualitatively validate the simulation results, we performed a pressure-assisted infiltration experiment on a nanoporous carbon (Horn BP2000), whose pore surface is hydrophobic\cite{181} and can be somewhat regarded as an analog to carbon nanotube clusters. The as-received material was in powder form, with the average particle size $D=10$ $\mu$m. Through a gas absorption analysis, the mean value of the micropore/mesopore radius was determined to be $2.2$ nm. The specific nanopore volume was $V_{\text{pore}} = 2.14$ $\text{cm}^3/\text{g}$, and the specific surface area was $1175$ $\text{m}^2/\text{g}$. The test sample was prepared by immersing $0.3$ g of the nanoporous carbon in $4$ g of glycerin. Glycerin was employed as the liquid phase since its viscosity was much higher than that of water, so that the influences of nanopore structure and the loading conditions could be amplified. The glycerin suspension was sealed in a steel cylinder by a steel piston with a gasket. By intruding the piston into the cylinder, an external pressure was applied on the liquid phase. The cross-sectional area of the piston, $A_p$, was $286$ $\text{mm}^2$.

![Figure 30](image)

Figure 30. (a) Typical sorption isotherm curves of glycerin infiltration and transport in a nanoporous carbon. The insert at the upper-left corner depicts the experimental setup. (b) Effective viscosity as a function of the nanopore radius and the loading rate.

Typical sorption isotherm curves are shown in Figure 30a. It can be seen that as the external pressure increases, the system volume decreases rapidly in a certain pressure range, leading to the formation of an infiltration plateau. When $P$ is relatively low, the capillary effect cannot be overcome, and thus the liquid does not enter the nanopores. With the increase of pressure, pressure-assisted infiltration begins, and once the nanopores are filled up, the system compressibility becomes small again. Due to the nanopore size distribution, the liquid infiltration starts with the largest nanopores, and the smaller nanopores can be involved in the infiltration process only
when the pressure is sufficiently high. The nominal flux in a nanopore with a radius of \( R \) can be estimated as \( Q = v_p A_p / N_p \), where \( N_p \) is the nanopore number density. The value of \( N_p \) can be evaluated by \( f V_{\text{pore}} / \pi R^2 L \), with \( L = D/2 \) being the effective infiltration depth and \( f \) the probability density of pore volume distribution as measured by the gas absorption analysis.

According to eqn. (3), the nominal viscosity can be calculated as

\[
\eta = \frac{\pi P R^4}{8 Q L}
\]  

The results are shown in Figure 30b. It is readily seen that the size and rate dependence of \( \eta \) agrees qualitatively with the results from the MD simulation. In all the cases under investigation, the value of \( \eta \) is much smaller than its bulk counterpart. When the nanopore radius is changes from nearly 1 nm to about 10 nm, the effective viscosity rises by one order of magnitude. A more significant change takes place as the loading rate increases from 0.1 mm/min to 100 mm/min, which causes a variation of \( \eta \) by 3-4 orders of magnitude. The mismatch between the simulation and testing data may be attributed to the differences in the nanoporous structure and the liquid species.

3.3.5. Summary

In this section, the transport behavior of water molecules inside a model carbon nanotube is investigated using NEMD. The result shows that the nominal viscosity of the confined liquid is not only a function of the tube size, but also strongly dependent on the flow velocity. A detailed analysis indicates that the repeatedly reported size effect and the newly discovered rate effect are directly related to the shearing stress between the liquid molecules and the solid atoms, which increases with the tube radius and/or the flow velocity. These findings are verified qualitatively via a pressure-assisted infiltration experiment of glycerin into a nanoporous carbon. The revealed size and rate effects are expected to hold generally for nanofluids confined in nanocavities within the same size range (even with different liquid and/or solid phases), though the magnitude of the size/rate effect may be varied. Moreover, the shearing stress can also be varied by changing the materials (e.g. ion species, ion concentration and solid composition).

3.4. Fluidic Transport in Molecular-Sized Nanopores

The last section investigates the general characteristics of the shearing stress and the nominal viscosity for nanofluids. Both of them show very strong dependence on the pore size and the flow velocity, and such dependence can be attributed to the
inhomogeneous molecular distribution inside the nanoconfinement. According to Section 3.2, when the pore size is reduced to the molecular level, the configuration of confined molecules and/or ions can undergo substantial changes, leading to fundamentally altered infiltration phenomena. It is therefore suspected that, the extremely small nanoconfinement may also induce unique transport characteristics. In this section, we will study the transport of water through molecular-sized nanopores via a synergy between simulation and experiment.

3.4.1. Two-Stage Transport

In experiment, we investigated a Zeolyst mobile-five-I (MFI) zeolite. The silica/alumina ratio was 280 and the nanopore surfaces were hydrophobic,\textsuperscript{[183]} which was verified by using a Micromeritics ASAP-2000 Gas Absorption Analyzer. According to its crystal structure, the surface-to-surface pore diameter was 0.83 nm. The nanoporous structure/size was confirmed to be highly regular through an x-ray diffraction analysis.\textsuperscript{[184]} The zeolite crystals were first dried in vacuum at 150 °C for 12 h and then treated in a nitrogen flow with silicon tetrachloride vapor at 400 °C for 1 h. After furnace cooling and thorough rinsing with deionized water, the material was hydrothermally treated in saturated water steam at 600 °C for 24 h, followed by vacuum drying at 120 °C for 12 h. The treated zeolite crystals were dispersed in distilled water and sealed in a stainless steel cylinder by a steel piston (inset of Figure 31). The cross-sectional area of the piston was 286 mm\textsuperscript{2}. The piston was driven into the cylinder with the loading rate ranging from 0.03 mm/min to 0.1 mm/min.

![Figure 31. Typical water sorption curves of a hydrophobic zeolite. The inset shows a schematic of the experimental setup.](image-url)
The measured sorption curves are shown in Figure 31, where the specific infiltration volume, $\Delta V$, is taken as the difference between the piston intrusion volumes of the testing sample and a reference system that contained only distilled water, normalized by the mass of zeolite, $m = 0.512 \text{ g}$. The corresponding temperature change at the center of the cylinder was measured by a type-E thermocouple insulated in a polyurethane cell (Table 4). The heat capacity of the water-zeolite suspension, $C$, was measured to be $3.4 \text{ J/g·K}$ through a differential scanning calorimetry analysis.

In Figure 31, the value of infiltration pressure ($P_{cr}$) is found to be quite small for the considered combination of solid and liquid materials. Once the infiltration starts to take place, the pressure rises almost linearly as the infiltration volume increases until $P$ reaches about $60 \text{ MPa}$. Then, a different transport slope is formed and $\Delta V$ rises more rapidly with the increase of $P$. Eventually, when the nanopores are filled up, the system compressibility is lost and the slope of the sorption curve tends to approach infinity. In such a bilinear sorption curve, while the first linear regime can be explained by frictional transport, the second (which has a different slope) is somewhat “intriguing”. Following the discussions in the last section, a unique shearing stress or viscosity should be identified if both the pore size and flow velocity are fixed. Then, what is the cause of this sudden change in the transport slope (right in the middle of the entire transport process)?

### 3.4.2. Structural Change: From Single Chain to Double Chain

In order to understand the experimental observation, MD simulation is carried out by using the COMPASS force field. A straight silicon dioxide nanochannel (Figure 32a) with a surface-to-surface diameter (distance between two opposite oxygen atoms) $D_0=0.83 \text{ nm}$ is employed as a close analogue to the MFI zeolite nanopore. One end of the nanochannel is closed, providing a simplified boundary condition for the symmetric compression of the liquid from both ends of a long nanopore. During simulation, the nanotube is immersed in a $45\text{Å} \times 45\text{Å} \times 200\text{Å}$ reservoir bounded by two rigid planes in the axial direction. Periodic boundary conditions are applied in the transverse directions. Initially, the reservoir is filled with water molecules with the density being maintained at 1 atm and 300 K. The liquid-to-nanopore mass ratio is set to be the same as that in the experiment.

With a rising pressure, the potential energy of the liquid in reservoir is continuously increased until the molecules are capable of overcoming the energy barrier to enter the tube. According to Section 1.2.2.1, the energy barrier includes two components, i.e. the surface tension ($\gamma$) and the liquid-solid interaction energy ($\gamma_{LS}$). Their summation indicates the total energy difference before and after the infiltration, i.e. the liquid-solid interfacial energy ($\gamma_{LS}$). For the current system, $\gamma$ and $\gamma_{LS}$ are calculated 117.10 Cal/mol/Å² and -116.86 Cal/mol/Å², respectively, and thus $\gamma_{LS}=0.24 \text{ Cal/mol/Å²}$, which implies that the nanochannel is hydrophobic.
Note that the effect of nanopore curvature has been incorporated in the calculation of \( \gamma \) and \( \gamma_{LS} \), and thus the reported value of \( \gamma_{LS} \) is valid for the current pore geometry. According to eqn. (2), the infiltration pressure, \( P_{cr} \), is calculated 1.11 MPa, which agrees well with the critical pressure calculated from MD simulation (Figure 33) and that measured in experiment.****

![Figure 32](image)

Figure 32. MD snapshots of the pressure-driven transport of water molecules inside (a) a model nanochannel: (b) the single-chain structure (\( P = 50 \) MPa); (c) the double-chain structure (\( P = 125 \) MPa).

![Figure 33](image)

Figure 33. MD simulation results of the pressure, \( P \) (solid symbol), and the temperature variation, \( \Delta T \) (open symbol), as functions of the specific infiltration volume, \( \Delta V \).

**** Note that the area accessible to the infiltrated molecules is smaller than that enclosed by the solid wall, and thus the effective diameter of the liquid segment, \( D \), is defined as \( (D_0 + D_1)/2 \), where \( D_0 \) is the surface-to-surface pore diameter and \( D_1 \) is the diameter of the ring formed by the O atoms in the outmost layer of the infiltrated water molecules. For the present MFI zeolite \( D = 0.6 \) nm.
Very importantly, Figure 32b shows that at moderate pressure, the infiltrated water molecules form a helical water chain inside the nanopore, which is compatible with the simulation results of the water conduction in CNTs of similar radii.\[63\] After the water segment reaches the capped end, starting from the pore opening, the water molecules in the original helical chain move along the radial direction so as to one-by-one accommodate the newly infiltrated water molecules. Such “dislocation-like” propagation finally leads to the formation of a second helical water chain (and thus the double helical structure shown in Figure 32c).

3.4.3. Impact of Molecular Structure on Shearing Stress

Figure 33 shows $P$ as a function of $\Delta V$, where the infiltrated water volume is normalized by the mass of the nanochannel (which is weighted to account for the geometrical difference between the model nanochannel and the real MFI zeolite nanopore). It is readily seen that initially, $P$ increases almost linearly with $\Delta V$ to counter the resistance caused by the shearing stress (or, the column resistance, which equals to the shearing stress times the area of the liquid-solid interface). After the double-helical structure is formed, the column resistance is slightly reduced, suggesting that the first water chain can ease the formation of the second chain like a “lubricant”. This observation echoes the bilinear infiltration curve shown in Figure 31.

Denoting the infiltration length as $L$, the column resistance can be represented by $\tau L$ where $\tau$ is the shearing stress. There are two ways of calculating $\tau$. First, according to eqn. (20), $\tau$ can be correlated with the transport slope of the $P-\Delta V$ curve (Figure 33) by

$$\frac{\partial P}{\partial V} = \frac{16\tau}{\pi D^3}$$

Alternatively, according to eqn. (19), $\tau$ can be calculated from a free deceleration test similar to that carried out in Section 3.3.2. In the single-chain regime, $\tau$ is calculated 3.09 MPa and 5.58 $\pm$ 0.4 MPa, respectively, via the two methods, which are rather close to each other. It is important to note that, in the zeolite nanopore, the column resistance, $\tau$, is orders of magnitude higher than that calculated in the last section for the CNT, which is largely owing to the electrostatic interaction between the solid atoms and the liquid molecules as well as the “roughness” of the solid channel. This suggests that the shearing resistance can be highly dependent on the solid phase; smooth and nonpolar surfaces (e.g. CNT) usually have lower shearing stress than rough and polar surfaces (SiO$_2$ tube).

3.4.4. Transport: An Exothermic Process

During the transport, the kinetic energy dissipated by the surface resistance is transferred to the thermal vibrations of the tube lattice and the water molecules, thus increasing the system temperature. This exothermic process can be verified by the
The calometric measurement results tabulated in Table 4, where the system temperature is shown to increase as the infiltration volume increases (from “A” to “C”). The temperature variation can also be calculated from MD simulation. As shown in Figure 33, when the pressure is low, $T$ increases almost linearly with $\Delta V$; when the double-chain structure is formed, another linear regime initiates, in which the $T-\Delta V$ slope is slightly lowered. At the end of the infiltration, the temperature is raised by about 1.3 K, comparable with that measured in experiment. Here, simulation and experimental results can be directly compared because they use the same liquid-to-nanopore mass ratio. In a parallel calorimetric experiment, a moderate temperature increase of the similar magnitude was measured as water infiltrates and transports through a hydrophobic ZSM-5 zeolite.

Theoretically, during the pressure-assisted infiltration, the mechanical work done to the system, $W_M$, is converted to two parts: the interfacial energy, $W_{in}$, and the thermal energy, $W_t$. The first part corresponds to the area below $P_{cr}$ in Figure 33, which increases linearly with the infiltration volume. The second part is to overcome the column resistance and thus is dissipated as heat. In Figure 33, $W_t$ corresponds to the area between the $P_{cr}$ line and the $P-\Delta V$ curve. Ideally, if all the induced thermal energy is used to heat the system, i.e. $\Delta T \cdot C = W_t$, one can estimate the temperature increase as $\Delta T = 1.1$ K, which is on the same order of magnitude as that measured in both simulation and experiment.

<table>
<thead>
<tr>
<th>Loading rate (mm/min)</th>
<th>Temperature (°C)*</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>“A”</td>
</tr>
<tr>
<td>0.1</td>
<td>20.8</td>
</tr>
</tbody>
</table>

* As shown in Figure 31, “A” indicates the onset of loading; “B” indicates the beginning of the secondary infiltration plateau; “C” indicates the end of the infiltration plateau; and “D” indicates the peak loading.

### 3.4.5. Summary

In a molecular-sized MFI zeolite nanopore, most of the infiltrated water molecules are in direct contact with the solid surface, thus leading to a significant flow resistance. During the transport, a part of the external work is converted into the liquid-solid interfacial energy, and the rest is dissipated as heat. Both experiment and simulation show that the second part is dominant in the investigated case, which is partially attributable to the polar nature of the solid phase. Moreover, it is discovered that when the applied pressure is relatively high, the single-chain structure of the confined water molecules is no longer stable; a double-helical structure can be formed.
Such a conformational change perturbs the energy barrier related with the transport, thus lowering the flow resistance as well as the energy dissipation rate.

3.5. Defiltration: A Short Remark

Nanofluidic motion in contact of a solid nanopore typically consists of three key frames: infiltration (when the liquid enters the nanopore), transport (when the liquid flows inside the confined space), and defiltration (when the liquid leaves the nanopore). While the first two elements have been intensively discussed in Sections 3.1-3.4, the third (namely, defiltration) is not considered a focus of this dissertation for two reasons.

First, although defiltration is an indispensable part of nanofluidics, its importance is not as significant as the other two, i.e. infiltration and transport. With reference to the two typical sorption hysteresis curves shown in Figure 3a-b, obviously it is the infiltration and transport that determines the size of the enclosed area (or, the energy absorbed during the loading-unloading loop): the infiltration pressure marks the initial height of the plateau while the shearing stress (viscosity) determines the slope of the plateau; both of them contribute prominently to the shape of the hysteresis. By comparison, the contribution from defiltration is marginal. Thus, defiltration cannot be compared with infiltration and transport in terms of the contribution to the energy absorption.

Second, compared with infiltration and transport where a number of characteristic quantities (such as the infiltration pressure, shearing stress, and the viscosity) can be varied in a wide range by changing the various system and materials parameters, defiltration is a physical process that has only two critical states, i.e. full-defiltration and non-defiltration. Hence, defiltration is of less scientific sophistication, and has been relatively well understood. According to Section 1.2.2.1, defiltration is governed by the competition between the capillary force and the surface friction. Full-defiltration should occur if the capillary force dominates, while non-defiltration should be the case if the surface friction wins. Therefore, the defiltration behavior largely depends on the adopted solid and liquid phases. For instance, the Fluka 100 C₈ reversed phase mesoporous silica/water system often exhibits non-out-flow phenomenon upon unloading, whereas zeolite/water system usually shows full defiltration.

We note that such a competition may be profoundly influenced by an additional factor that is ignored in most nanofluidic studies - the gas phase preexisting inside the nanopore. MD simulation reveals that, in a nanopore, even a single gas molecule can significantly promote defiltration by disturbing the molecular configuration of the confined liquid. More specifically, the effective gas solubility in a
small nanopore (Figure 34) is extremely low (similar to the zero ion solubility in a molecular-sized nanochannel as analyzed in Section 3.4); during infiltration, the trapped gas molecules are clustered inside the nanopore, which, upon unloading could expand and significantly assist the outflow. In larger nanopores, nevertheless, the gas phase is well dissolved in the solvent, so there is essentially no gas cluster present to assist defiltration; thus, if the friction term wins over the capillary term as mentioned above, the infiltrated water molecules tend to get stuck inside the nanopore, leading to the observation of non-outflow.

Figure 34. (a) MD simulation results of water infiltration, transport and defiltration in a small CNT: preexisting gas phase promotes the defiltration. Two cases are considered: (b) the interior of the CNT is initially in vacuum state, and (c) a single CO$_2$ molecule (blue) preexists in the CNT.

Despite its marginal contribution to the energy absorption (or, shape of the loading-unloading hysteresis), defiltration is not a process of no importance. In fact, it has a unique practical significance – determining the reusability of the nanoporous energy absorption system. As discussed in Section 1.2.2.1, a nanoporous energy absorption system could be reused or applied in cyclic loading conditions only if the infiltrated liquid could fully defiltrate after unloading; otherwise, the system can only be used for only once, after which the compressibility is lost although the functionality may be recovered by using selected chemical treatments.

3.6. Implications for Energy Absorption
As one of the important functionalities of the nanoporous composite, nanofluidic energy absorption features a unique advantage over conventional energy absorption materials/systems – the superior energy density (Table 1) enabled by the ultra-large liquid-solid interface in nanoporous materials. According to Section 1.2.2.1, the energy absorption performance is governed by two physical processes (Figure 35a): the infiltration (which is characterized by the infiltration pressure, $P_{cr}$) and the transport (which is characterized by the slope of the transport plateau, $\partial P/\partial V$, or the shearing stress, $\tau$; $\partial P/\partial V$ and $\tau$ are correlated in eqn. (23)). Both of them contribute significantly to the shape of the $P-\Delta V$ hysteresis, and thus they determine the amount of energy absorption/dissipation during a loading-unloading loop. Larger infiltration pressure and/or larger shearing stress would lead to larger energy absorption. As discussed in the last section, defiltration contributes only marginally to the energy density, though it is critical to the reusability of the system.

As introduced in Sections 3.1-3.4, both $P_{cr}$ and $\tau$ are functions of a number of system and material variables, such as the pore size, pore geometry, liquid phase, ion concentration, temperature, and the flow velocity (Figure 35b; note that some of these effects may be coupled, such as the pore size and ion size effects, and that may lead to more complicated phenomena as shown in some examples earlier in this dissertation). As such, by changing those parameters, the overall energy absorption of the nanoporous composite can be adjusted in a very large range to suit various target applications.

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Figure 35. (a) Schematic of the loading-unloading hysteresis of a nanoporous energy absorption system: regime I – linear compression of the liquid and empty nanoporous materials; regime II – infiltration followed by a transport plateau; regime III – compression of the liquid and filled nanoporous materials; IV-1 – linear unloading stage; IV-2 – nonlinear unloading stage which may result in full-defiltration (dash line) or non-defiltration (solid line). (b) The infiltration pressure ($P_{cr}$) and transport slope ($\partial P/\partial V$, or, shearing stress, $\tau$) may be fine-tuned by a number of system and material variables, including the pore diameter ($D$), the conical half apex angle ($\alpha$), the flow velocity ($v$), and the temperature ($T$).
Indeed, the requirement for protection materials can be varied significantly among different applications. For example, in applications where the external load is relatively low (e.g. damping or vibration proof), $P_c$ is desired to be low enough such that the energy absorption mechanisms can be activated; in some others where the peak load is extremely high (e.g. blast protection, body armor or car bumper), it is hoped that both $P_c$ and $\tau$ could be as high as possible such that a large amount of energy can be absorbed and dissipated. In view of this complexity, we suggest an Object-Oriented Design (OOD) of the nanoporous energy conversion system, in which the various system and material parameters are optimized to achieve the performance desired in target applications. The study presented in this chapter serves as the first step in establishing a database that relates the various system and material variables with the system performance, which is critical to the success of OOD.

As illustrated in Figure 35b, in general, in order to increase $P_c$ (or, the hydrophobicity of the nanopore), one can decrease the diameter of a circular nanopore, decrease the apex angle of a conical nanopore (Section 3.1), decrease the temperature (Section 4.1), or increase the loading rate.\textsuperscript{[156]} Using a different solid material may largely affect the interfacial energy, $\gamma_{LS}$, and thus the magnitude and even the sign of $P_c$ may be changed; however, the general size and geometric dependence should hold as predicated by the enriched Laplace-Young equation (Section 3.1). If the liquid phase is changed, $\gamma$ may also be varied and so may $P_c$. In particular, electrolytes can form a quasi-periodical ion couple structure in molecular-sized nanopores, leading to the counterintuitive ion size and ion concentration dependent infiltration phenomena (Section 3.2).

For transport, in general, the shearing stress can be increased by increasing the flow velocity or the pore size (Section 3.3), decreasing the temperature, or making the pore surface more rough. Again, the general size and loading rate effects should hold for different liquid phases and different solid phases, though the magnitude of the shearing stress may be varied. For example, the shearing stress of a polar nanopore could be orders of magnitude higher than that associated with a nonpolar nanopore of the same size (Section 3.4). Moreover, if electrolytes are considered as the liquid phase, the shearing stress should also depend on the ion concentrations and ion size.\textsuperscript{[182]}

The dependences of $P_c$ and $\tau$ on a few selected system and material parameters are shown in Figure 35b. We note that, in real cases, those parameters as well as some others that are not shown are often interrelated and coupled. For example, as one increases the pore diameter ($D$), $P_c$ increases while $\tau$ decrease; in other words, the strengthened capillary effect (i.e. enhanced energy absorption) can be largely traded off by the diminished surface friction (i.e. diminished energy dissipation). Moreover, as will be shown in Section 4.2, when the surface charge is sufficiently large, the general size effect on $P_c$ can be largely affected and even reversed. This cautions the use of the effects of independent variables in the system
design. In complicated cases where many parameters and mechanisms are coupled, we suggest use the molecular/multi-scale simulation and experiment to precisely analyze and design the system performance.
Chapter 4.
Field Effects on Nanofluidic Infiltration – Fundamentals and Implications for Actuation

According to the well known thermocapillary and electrocapillary effects, the interfacial property at a solid-liquid interface (which is often characterized by the contact angle, $\alpha$) can be varied significantly as the ambient temperature is changed or an electric field is applied.\cite{187,188} As such, a liquid phase might be actuated when subjected to a thermal gradient or an electrical potential gradient. This enables the manipulation of fluids via external fields, which have been evidenced in microfluidic channels\cite{189,190} and on flat/patterned surfaces.\cite{187,191}

Given this principle, we consider a nanochannel immersed in a nonwetting liquid with $\alpha > 90^\circ$. Due to the nonwetting nature, an external pressure is required to infiltrate the liquid into the nanochannel. From eqns. (2) and (16), the critical infiltration pressure should take the form of

$$P_{cr} = -\frac{4\gamma \cos \alpha}{D}$$

where $\gamma$ is the surface tension of the liquid, $\alpha$ the contact angle, and $D$ the pore diameter. Since both $\gamma$ and $\alpha$ are functions of temperature, $P_{cr}$ should also be a temperature-dependent quantity. It is then possible to use temperature as a “switch” to control the infiltration/defiltration of the liquid (or the wetting/dewetting of the channel). For example, assume the liquid is loaded under a fixed external pressure of $P$, and the system’s $P_{cr}$ is larger than $P$ at one temperature, $T_1$, and it is below $P$ at an elevated temperature, $T_2$ (i.e. we assume the system becomes relatively more hydrophilic when heated). Apparently, the nanopore would stay unwetted at $T_1$ and be spontaneously filled at $T_2$. Hence, if we cyclically change the temperature between the two bounds, the liquid phase would be forced to move back and forth inside the nanochannel, leading to varied system volume and energy conversion between the interfacial energy and the mechanical work output. This is the basis of a nanofluidic thermal machine, and similarly, an electrical machine could be enabled if $P_{cr}$ can be varied by the electric field.

The mechanism introduced above can be easily extended to materials that have numerous nanochannels, i.e. the nanoporous composite materials introduced in Section 1.2. Amplified by the ultra-large surface area of nanoporous materials, such systems may achieve ultra-large energy density and/or strain output compared with
conventional smart materials (Table 2). In order to fulfill the promise of the nanoporous thermal/electrical machine, it is of fundamental value to understand the thermally and electrically responsive behavior of nanofluids inside nanopores, which will be the focus of this chapter.

4.1. Effect of Temperature on Nanofluidic Infiltration

4.1.1. General Thermal Effect on Infiltration Pressure

Figure 36. The computational model. One end of a long carbon nanotube (CNT) is immersed in a reservoir filled with water molecules. The upper rigid plane is fixed while the lower one is movable for adjusting the pressure inside the reservoir. Periodic boundary conditions are applied to the four lateral planes of the computational cell.

We first explore the fundamental thermal effect on nanofluidic infiltration characteristics. A flexible carbon nanotube (CNT, illustrated in Figure 36) is adopted as a model nanochannel. One of its openings is immersed in a reservoir filled with water molecules. The top and bottom surfaces of the reservoir are bounded by two rigid planes. The upper one is fixed and the lower one is movable to mimic a piston. Periodic boundary conditions are imposed on the four lateral planes of the computational cell. In MD simulation, the interatomic vdW (van der Waals) interaction is described by the Lennard-Jones (LJ) empirical forcefield. The Amber96 LJ parameters\textsuperscript{[152]} are adopted for carbon atoms. The flexibility of CNT is addressed by a Morse bond, a harmonic cosine angle and a 2-fold torsion potential\textsuperscript{[151]} Water molecules are modeled by the extended simple point charge potential (SPC/E)\textsuperscript{[150]} The
carbon-oxygen LJ parameters are extracted from the experimental low-coverage isotherm data of oxygen adsorption on graphite.\cite{154} By using these molecular models and parameters, the graphene as the raw material for constructing CNTs is ensured to be hydrophobic.\cite{70} A 10 Å cutoff is assumed for the vdw interaction. The Nose/Hoover thermostat\cite{192} with a damping parameter of 0.1 is employed to regulate the temperature at 300 K. Long range electrostatic interaction is estimated by the Ewald summation technique. Time step is set to be 1 fs.

Four representative CNTs, (10,10), (13,13), (15,15), and (20,20), are considered, whose diameter, $D$, equals to 13.56 Å, 17.63 Å, 20.34 Å, and 27.12 Å, respectively. The ambient temperature, $T$, is varied and assumed to take four representative values, 300 K, 320 K, 340 K and 360 K, respectively. For a given temperature, a specific number of water molecules are placed in the reservoir such that the initial pressure is close to the ambient (zero) after equilibrium. Next, the water phase is pressurized by moving the piston upwards. In order to rule out possible dynamical effects, we carefully load the system in a stepwise and quasi-static manner. In each step, we move the piston by 0.05 Å, after which the position of the piston is temporarily fixed and the system is allowed a sufficiently long time to reach equilibrium (where the temperature distribution is close to uniform). Note that the equilibrium time varies throughout the process, on the order of 1 ns after water intrusion and shorter before. Pressure is evaluated every step from the immediate density of water inside the reservoir via eqn. (14).

As an illustrative example, Figure 37 plots the number of infiltrated water molecules in response to the applied pressure for a (10,10) armchair nanotube, at the...
temperature of 300 K. \( P_{cr} \) is found to be equal to about 153 MPa. Upon unloading, no hysteresis is observed as the loading and unloading paths overlap exactly. This may be attributed to the quasi-statically applied load and the defect-free (nearly frictionless) carbon nanotube. For other nanotubes studied at different temperatures, the overall shape of the continuous water intrusion isotherm is similar to that shown in Figure 37, yet the most critical parameter, \( P_{cr} \), exhibits strong dependence on the temperature and pore size. As depicted in Figure 38a, for all considered nanotubes \( P_{cr} \) decreases with the increase of temperature, indicating that the energy barrier for water to enter a hydrophobic confinement is effectively reduced at elevated temperatures. If the temperature is fixed, the infiltration pressure is found to vary nonlinearly with the pore size, echoing the Young’s equation (eqn. (24)) where \( P_{cr} \) is inversely proportional to \( D \). Interestingly, in Figure 38b, the critical density of water, \( \rho_{cr} \), is shown to be almost linear with the temperature, and the slopes, \( k \), are quite close for all examined CNTs as tabulated in Table 5. The thermal dependency of \( P_{cr} \) is attributable to the interplay of multiple physical quantities, including the contact angle, surface tension, hydrogen bonding, among others, elaborated on in the next section.

![Figure 38](image)

Figure 38. Effects of temperature and pore size on the infiltration of water into carbon nanotubes: (a) infiltration pressure, \( P_{cr} \); and (b) water density inside the reservoir, \( \rho_{cr} \). The diameters of CNTs are 13.56 Å, 17.63 Å, 20.34 Å, and 27.12 Å, respectively.

The linear \( \rho_{cr} - T \) relationship revealed in simulation provides an alternative route to building nanothermometers. Inside a partially wetted nanotube immersed in a volume-fixed reservoir (at an appropriate pressure level), the advancement and recession of the water front is linearly related to the temperature variation, as described by \( \Delta h = k \Delta T V_r / m_0 \bar{N} \), where \( \Delta h \) is the height variation of the confined water in the nanotube, \( \Delta T \) the temperature change, \( V_r \) the volume of the reservoir,
the slope of the $\rho_{cr} - T$ relation as tabulated in Table 5, $m_0$ the density of a water molecule, and $\overline{N}$ the line number density of confined water molecules as tabulated in Table 6. Apparently, with a sufficiently large reservoir (large $V_r$) and a small nanopore (low $\overline{N}$), a considerably high sensitivity ($\Delta h/\Delta T$) may be achieved, making the proposed nanothermometer superior to those purely based on the thermal expansion mechanism.\[194\]

Table 5. $\rho_{cr} - T$ relation (Figure 38b) described by $\rho_{cr} = -kT + \rho'$.  

<table>
<thead>
<tr>
<th>CNT</th>
<th>(10,10)</th>
<th>(13,13)</th>
<th>(15,15)</th>
<th>(20,20)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k$ [10^{-3}g/(cm^3·K)]</td>
<td>0.6687</td>
<td>0.6195</td>
<td>0.6293</td>
<td>0.5998</td>
</tr>
<tr>
<td>$\rho'$ [g/cm^3]</td>
<td>1.2272</td>
<td>1.2195</td>
<td>1.2265</td>
<td>1.2350</td>
</tr>
</tbody>
</table>

4.1.2. Thermal Effect on Surface Tension, Contact Angle, and Various Molecular Quantities

According to the Young’s equation, two quantities are directly related to the thermally responsive infiltration behavior discovered above, namely the contact angle, $\alpha$, and the surface tension, $\gamma$. In order to quantify their thermal dependencies in the nanoconfinement, a (20,20) CNT is considered as a representative cavity for accommodating water molecules: 1220 water molecules are placed inside the flexible nanotube to form a discrete water drop, and simulated for 10 ns at a fixed temperature (without any external load). Molecular trajectories are output every 0.1 ps for statistical purposes. Shown in Figure 39a is the density map for the case with $T=300$ K, where it is readily seen that a convex meniscus is formed on top of the liquid drop due to the hydrophobic nature of the considered nanotube. In order to effectively characterize the water front, the spatial positions of boundary water molecules are averaged over all recorded time frames (squared symbols in Figure 39a), which are further fitted by a circular arc shaped curve (the black curve, which represents the water front). $\alpha$ is subsequently deduced as the angle of the tangent of the water front where it meets the lateral surface of the water drop. Further, with the measured $\alpha$ and $P_{cr}$, $\gamma$ is calculated according to the Young’s equation (eqn. (24)) for the present tube and the temperature.

As plotted in Figure 39b-c, both $\alpha$ and $\gamma$ are found to decrease at elevated temperatures. According to the Young’s equation, both terms contribute to the reduction of $P_{cr}$ with respect to the increasing temperature. The descending trend discovered for $\alpha$ agrees well with the result for a water droplet resting on a graphene.\[195\] The result for $\gamma$ qualitatively matches the temperature-induced
variation of the surface tension of bulk water in contact with air, $\gamma_{\text{bulk}}$. Importantly, in Figure 39c $\gamma$ shows a faster decreasing trend than $\gamma_{\text{bulk}}$, suggesting that the surface tension is more sensitive to thermal perturbation when confined in a nanoenvironment.

From an atomistic perspective, the uncovered thermal dependencies of surface tension and contact angle are underpinned by the thermally induced variations of multiple quantities. First, hydrogen bonding as an attractive interaction between water molecules is critical to determining water properties such as boiling and surface tension. Two water molecules are considered hydrogen bonded if (1) the O-O distance is below 3.5 Å, and (2) the angle between the O-O axis and a O-H bond is smaller than 30°. The average number of hydrogen bond per molecule, $N_{\text{HB}}$, may serve as a numerical indicator of the hydrogen bonding. Besides $N_{\text{HB}}$, two other parameters are associated with the strength of hydrogen bonding and thus effectively depict the interaction among water molecules: (1) water density, $\rho$, which is an indication of the average intermolecular distance; and (2) dipole orientation, $\theta$, which quantifies the orientation of the dipole moment with respect to the tube axis. The thermal dependencies of these three quantities are pursued via MD simulations, for a water drop confined in various nanotubes and at various temperatures, elaborated on below.

Figure 39. A water segment confined in a (20,20) carbon nanotube. (a) Density map where darker color refers to higher density and lighter color corresponds to lower probability of occupation of water molecules. The left axis overlaps the tube axis and the right axis indicates the tube surface. The black line fitted from the open squared symbols depicts the statistically averaged water front, based on which the contact angle is determined. The yellow curve represents the radial density distribution of water molecules (far away from the meniscus), and the variation is consistent with the color gradient in the density map. (b) Contact angle, $\alpha$, versus temperature. (c) Surface tension $\gamma$ and the ratio of $\gamma / \gamma_{\text{bulk}}$ versus temperature.
Figure 40. The radial distribution of the average number of hydrogen bond per molecule, $N_{HB}$ (the dashed curve), and the normalized water density, $\rho/\rho^*$ (the solid curve), at four representative temperatures for (a) (10,10) CNT; (b) (13,13) CNT; (c) (15,15) CNT; (d) (20,20) CNT. In each figure, the left axis overlaps the tube axis and the right axis indicates the tube surface. Two reference horizontal lines are shown: the purple one refers to the bulk water density ($\rho/\rho^*=1.0$) and the green one corresponds to the value of $N_{HB}$ measured in the bulk water at room temperature (approximately 3.81).
Figure 41. The probability of dipole orientation with respect to the tube axis, $\theta$, at four representative temperatures for (a) (10,10) CNT; (b) (13,13) CNT; (c) (15,15) CNT; (d) (20,20) CNT. Two groups of water molecules are analyzed separately: one group (the solid curve) refers to the outmost layer in the multilayered water structure (the first wave to the right axis in the density profile, Figure 40), which is usually the most concentrated region, and the other (the dashed curve) includes all of the rest water molecules.
Figure 40 plots the radial distributions of $N_{HB}$ (the dashed curve) and $\rho / \rho^*$ (the solid curve, where $\rho$ is normalized by $\rho^*$, the bulk water density). Compared with their counterparts in the bulk phase, $N_{HB}$ in the confined water is always smaller, whereas $\rho$ moderately fluctuates about $\rho^*$. Interestingly, the fluctuations of $N_{HB}$ and $\rho$ conform to opposite trends; that is, a crest of $N_{HB}$ often corresponds to a trough of $\rho$ and vice versa. This implies that a higher concentration of water molecules may to some extent distort the angle between the O-O axis and the O-H bond, leading to lower probability of forming hydrogen bonds.

Table 6. The line number density, $\overline{N}$, of water when confined in carbon nanotubes [1/Å].

<table>
<thead>
<tr>
<th>CNT</th>
<th>(10,10)</th>
<th>(13,13)</th>
<th>(15,15)</th>
<th>(20,20)</th>
</tr>
</thead>
<tbody>
<tr>
<td>300 K</td>
<td>2.4194</td>
<td>4.8246</td>
<td>6.9218</td>
<td>13.9458</td>
</tr>
<tr>
<td>320 K</td>
<td>2.3417</td>
<td>4.7126</td>
<td>6.7595</td>
<td>13.6293</td>
</tr>
<tr>
<td>340 K</td>
<td>2.2147</td>
<td>4.5374</td>
<td>6.6256</td>
<td>13.2642</td>
</tr>
<tr>
<td>360 K</td>
<td>2.1448</td>
<td>4.4065</td>
<td>6.3836</td>
<td>12.9141</td>
</tr>
</tbody>
</table>

With the temperature increased from 300 K to 360 K, $N_{HB}$ decreases almost linearly at all radial positions, whereas $\rho$ decreases in crests and increases in troughs (and thus its fluctuation is reduced). Very importantly, the thermal effect is found to be more significant in confined water than in the bulk. For instance, from 300 K to 360 K, the density of water in the (20,20) CNT is reduced by 21% at the outmost peak and increased by 14% at the second peak; by contrast, the density of bulk water only shows a 2.9% reduction in response to the same thermal perturbation. Another example is the thermally induced (for temperature increased from 300 K to 360 K) variation of the line number density of water molecules (namely, the number of water molecules confined in a nanotube of unit length), $\overline{N}$, which according to Table 6 is estimated to be 11.4%, 8.7%, 7.8% and 7.4%, respectively, for CNTs of increasing sizes. This further verifies that the thermal effect is more prominent in a narrower nanoconfinement. The enhanced thermal effect shown in the confined water indicates that fluidic properties should be more sensitive to thermal factors in nanoconfinement than in the bulk, which echoes our findings about the surface tension in Figure 40b.

With reference to the multilayered density distribution of water molecules inside the CNT, Figure 41 plots the probability of $\theta$ for two groups of water molecules separately. One group (the solid curve) refers to the outmost layer of the water column, and the other (the dashed curve) includes all of the rest water molecules. The two groups of water molecules exhibit distinct dipole orientations. In the outmost layer, primarily due to the direct and strong interaction with solid atoms,
water molecules are less uniformly orientated than the inner molecules, which show a strong tendency to align with the tube axis. Figure 41 also shows that the dipole orientation is much less sensitive to the thermal variation than other quantities investigated in this section, implying less contribution from $\theta$ to the apparent thermally responsive nanofluid behavior.

4.1.3. Experimental Validation

In order to verify the discovered thermal effect on the infiltration pressure, an infiltration experiment with a Norix nanoporous carbon was performed. The as-received material was in the form of 50-100 $\mu$m powders. About 2 g of the material was placed in a steel mold and compressed in a type 5580 Instron machine at either 0.5 MPa (sample A) or 15 MPa (sample B), forming densely packed powder cluster disks. The disks were milled back to the powder form, and the nanoporous structure was characterized by a Micromeritics ASAP-2000 gas absorption analyzer. The average nanopore size of sample A was 50 Å, and that of sample B was 30 Å. The specific surface areas of both samples were around 550 m$^2$/g.

![Figure 42. Measurement results of infiltration pressure for nanoporous carbon immersed in water. The average nanopore size of sample A is 50 Å, and that of sample B is 30 Å.](image)

About 0.25 g of the treated material (the detailed surface treatment process was described elsewhere\cite{198}) was sealed in a steel cylinder with 6 g of deionized water. By using the Instron machine, a steel piston was intruded in the cylinder at a speed of 1 mm/min (the loading rate was confirmed to be sufficiently slow so as not to introduce any rate effect). The diameter of the piston was 19 mm. Because the nanopore inner surfaces were hydrophobic, only when the applied pressure was sufficiently high (beyond $P_{cr}$) could a large number of water molecules be forced into the nanopores. The medium pressure associated with the pressure-induced
infiltration was measured by a 2 kN load cell. During the testing process, the temperature of the sample was maintained by a water bath around 270 K, 290 K, 310 K, or 330 K.

The measured results are plotted in Figure 42, which qualitatively agree with the computational results shown in Figure 38a, both suggesting decreasing $P_{cr}$ with increasing $T$ or $D$. Note that, the experimental measurements might be affected by surface treatment$^{[46,198]}$ and nonuniform pore size$^{[199]}$ among others, which effectively lowered the infiltration pressure and led to the data scattering in the $P_{cr}-T$ curves. Nevertheless, the trends of the variation of infiltration is qualitatively consistent between the experiment and simulation, and experiments with better controlled surface structure/treatment and pore size will be carried out in future.

A word of caution is that our finding of the temperature effect may not be extrapolated to extremely small nanopores, e.g. silicalite-1 zeolite with the diameter of about 5.4 Å.$^{[85]}$ Inside such a small nanopore whose cross-section may accommodate only one water molecule, the invaded water molecules are expected to have molecular behavior (e.g. hydrogen bonding,$^{[63]}$ dipole orientation,$^{[66]}$ and thermal vibration characteristics) very different from those confined in larger pores. Furthermore, under this circumstance the polarization of nanopores must play an important role on the infiltration/transport behavior of confined liquids.$^{[124]}$ The detailed temperature effect on water infiltration into very small nanopores will be carried out in future.

4.1.4. Summary

This section investigates the fundamental thermal effect on the infiltration of water molecules into hydrophobic nanopores. Both MD simulation (on CNT) and experiment (on nanoporous carbon) confirm that the critical infiltration pressure increases with either lowered temperature or reduced pore size. The reduced hydrophobicity at elevated temperature is underpinned by the thermally induced variations of multiple quantities, such as the surface tension, contact angle, hydrogen bond, intermolecular distance, and the dipole orientation. The thermal dependencies of these parameters are systematically quantified via MD simulations. A general finding is that the thermal effects on these atomic/fluid variables are more significant in a confined nanoenvironment than in the bulk. Increasing the temperature can reduce the contact angle, surface tension, hydrogen bond number density, and water line number density, and make the water radial density distribution less fluctuating.

Although the findings are extracted from the model system of the infiltration of water molecules into carbon nanotubes, the overall thermal effect is expected to be prominent for other nanofluidic phases confined in different nanochannels. Different details of the thermal effect for different solid-liquid combinations are envisioned to enrich the relevant applications of thermally responsive nanofluidic devices.
4.2. Effect of Surface Charging on Nanofluidic Infiltration

According to the previous sections, nanofluid behavior is in essence dominated by the solid-liquid interfacial characteristics. Since an external electric field may strongly influence the configurations of polar liquids in nanoevironments, thereby affecting the liquid-solid interfacial energy,\(^{[200]}\) it becomes attractive to control nanofluid behavior using electric fields.\(^{[13,14]}\) Practically, a nanofluidic system may be electrically modified by several means – it can be placed in between two electrodes, or directly charged by external power, or chemically modified to carry functional groups. All these treatments can prominently affect nanofluid behavior, and if well designed, such influences may facilitate novel applications of nanofluidics or enhance the performance of existing nanofluidic systems. For example, in a single-file reverse osmosis system, applying an electric field in the direction of reverse osmosis can help maintain the dipole vectors towards the same direction, thus enhancing the water flux through a molecular-sized nanotube;\(^{[201]}\) in a Y-junction CNT confining an electrolyte, if the two side branches are oppositely charged, cations and anions would be preferentially absorbed into different branches, leading to two solutions of separated cations and anions;\(^{[202]}\) by functionalizing the openings of aligned CNTs embedded in a membrane, ions can be effectively rejected from the flow transporting to the other side of the membrane.\(^{[32]}\) In view of all these advances, this section explores the variation of the infiltration pressure as a function of externally applied electric fields, which has tremendous implications for the electro-actuation and energy absorption with nanoporous composites.

4.2.1. Intensity Effect

In this section, we consider the electric field induced by surface charging. The computational model follows the one shown in the last section (Figure 36), except that the temperature is fixed at 300 K and the surface atoms of the carbon nanotube are assumed to carry partial charges. In our analysis, the partial charge per atom, \(Q\), is varied to reflect different charging intensities. Nine representative values of \(Q\) are considered, ±0.004e, ±0.003e, ±0.002e, ±0.001e and 0e. The last case is considered as a reference where no charge is applied. Four carbon nanotubes, (10,10), (13,13), (15,15), and (20,20), are considered, whose diameter, \(D\), equals to 13.56 Å, 17.63 Å, 20.34 Å, and 27.12 Å, respectively.

As plotted in Figure 43, the infiltration pressure exhibits a very strong dependence on the surface charge – for all the carbon nanotubes under investigation, \(P_c\) decreases substantially as the magnitude of \(Q\) increases. In other words, the energy barrier against the intrusion of a nonwetting liquid can be remarkably lowered while surface charge is applied. Take the (13,13) CNT (\(D=17.63\) Å) as an example. \(P_c\) is originally larger than 100 MPa but reduced to about 40 MPa when \(Q=±0.004\)e, which reflects a reduction of 60%. Such a reduction caused by surface charging is found to be
larger than that can be achieved by thermal perturbation (Figure 38, where temperature is elevated by from 300 K to 360 K).

Figure 43. Infiltration pressure, \( P_{cr} \), versus the partial charge applied on each atom, \( Q \). Four carbon nanotubes are considered, whose diameter, \( D \), equals to 13.56 Å, 17.63 Å, 20.34 Å, and 27.12 Å, respectively.

Compared with the thermal effect, another distinction of the charge effect is that it is somewhat more irregular among the nanopores of different sizes. According to Figure 43, the dependence of \( P_{cr} \) on \(|Q|\) is close to linear in the (15,15) CNT, whereas in other cases, the reduction rate, \( \frac{dP_{cr}}{d|Q|} \), is a bit small from 0 to \( \pm 0.001e \) but becomes larger thereafter. By contrast, the \( P_{cr} - T \) relation shown in Figure 38 is close to linear for all the four CNTs. We note that, a major difference between thermal perturbation and surface charging lies in the fact that, the former is applied to the entire volume of the system while the latter only modifies the solid surface. As a consequence, although the charge density (per unit surface) is the same among the four CNTs, the charge density per unit volume, or per unit length, is actually varied. This complicates the charge effect with respect to the pore size, leading to the observed irregularity among the four CNTs.

The irregular charge effect also causes the irregularity of the size effect. According to the Young’s relation, \( P_{cr} \) is inversely promotional to \( D \), and thus increasing pore size should lead to reduced \( P_{cr} \). In Figure 43, this rule is well obeyed when \(|Q|=0 \) and 0.001e. Nevertheless, when \(|Q| \) is increased to 0.002e, the (15,15) CNT and the (20,20) CNT show very close values of \( P_{cr} \); when \(|Q| \) is further increased over 0.002e, \( P_{cr} \) for the (20,20) CNT slightly exceeds that for the (15,15) CNT, which is contradictory to the prediction of the Young’s equation. In Section 1.2.3, it is introduced that nanofluidic infiltration may be affected by a number of system and material variables (including pore size and surface charge), and the effects of these variables could be coupled. The calculation in this section serves as a representative
example that demonstrates the coupling effect – when the charge effect is present, the general size effect may be largely affected and even break down in some cases.

4.2.2. Sign Effect

As the magnitude of the partial charge plays the most important role in determining the value of $P_{cr}$, according to our calculation, the sign of $Q$ also makes some effects. Overall, the hydrophobicity of a negatively charged nanotube is always slightly larger than its counterpart carrying positive charges. Considering the (13,13) CNT as an example, when negatively charged, $P_{cr}$ is calculated to be 63.22 MPa, 47.80 MPa, 35.39 MPa and 20.69 MPa, respectively, for increasing charging intensities. All these numbers are a bit larger than their counterparts for positively charged nanotubes (61.89 MPa, 47.59 MPa, 28.78 MPa and 15.01 MPa, respectively).

![Radial distribution of the O atom and the H atom in the water molecules confined in a (20,20) CNT. RDF denotes the Radial Distribution Function, which describes how the atomic density varies with respect to the tube axis. Mathematically, RDF = $\rho_{\text{local}} / \rho_{\text{av}}$, where $\rho_{\text{local}}$ is the local density of the specified atom and $\rho_{\text{av}}$ is the density averaged in the entire volume.](image)

This finding is attributable to the bipolar nature of the liquid phase – water. In the last section, it has been revealed that water molecules are not uniformly distributed in CNTs; they tend to concentrate close to the solid surface, forming the outmost peak in the radial distribution profile. Shown in Figure 44, if the H atom and the O atom of water molecules are separately considered, the outmost layer of concentrated water molecules is in fact also layered. The first peak (red curve, at $r = 10.5$ Å) is comprised of O atoms, implying that the O atom is more favored by the solid atom than the H atom. As the surface charge effect kicks in, positive surface charge can attract more O atoms (oppositely charged) to the outmost O shell, which is...
favorable by the C atom. If the tube surface is negatively charged, nevertheless, the O atom would be repelled and the H atom would be attracted, which is however not favored by the C atom. Simply put, the negative surface charge tends to dampen the preference of C atoms, thus leading to relatively higher infiltration pressure compared with its positive counterpart.

4.2.3. Summary

In this section, the effect of electric field induced by surface charging is analyzed for nanofluidic infiltration. In general, it is found that infiltration pressure decreases as the magnitude of the surface charge increases. Comparing positive charging and negative charging with the same intensity, the energy barrier against liquid intrusion is usually larger when the tube is negatively charged. Such a surface charge effect is shown to be strongly coupled with the size effect. When the surface charge is sufficiently large, the general size effect (namely, $P_{cr}$ decreases as $D$ increases) could be affected and even reversed. This cautions the use of general effects of independent variables for designing a nanofluidic system governed by several parameters simultaneously.

4.3. Effect of Charged Channel Opening on Nanofluidic Infiltration

In the last section, we have shown that electric field can play a crucial role in determining the effective wetting property of solid surface. By charging the solid phase, the positive/negative charges carried by solid surface atoms can strongly disturb the configurations of liquid molecules situated near the surface, leading to much lowered infiltration pressure. In addition to surface charging, though, there exists an alternative method that has been widely adopted to locally modify the electric field in nanoenvironment, namely, the chemical functionalization.\textsuperscript{203} Compared with surface charging, functionalization is of much more flexibility as it can selectively charge surface atoms, and thus a number of novel applications have been enabled. For example, by positioning charges at designed sites, a CNT can pump water molecules at an extremely high rate,\textsuperscript{120} by functionalizing the openings of aligned CNTs embedded in a membrane, ions can be effectively rejected from the flow transporting to the other side of the membrane.\textsuperscript{32} In view of these attractive applications enabled by local chemical modifications, this section investigates the pressurized flow in a selectively charged nanochannel. The role of selective charging in nanofluidic infiltration will be quantified, and the relevant molecular mechanisms will be elucidated.
Figure 45. Computational model: (a) charges are anchored to the opening of the nanotube; (b) top view of the charge arrangement.

4.3.1. Enhanced Infiltration Barrier

A (15,15) CNT, which is nominally hydrophobic with a radius of 10.2 Å (Figure 45a), is employed as a model nanopore. Initially, the reservoir (55 Å × 55 Å × 35 Å) is filled with 3542 water molecules such that the normal water density at 1 atm is maintained. We study two embodiments of the system - one is selectively charged while the other is not. In the former case, twelve point charges are placed at the bottom end of the tube, all of which are fixed at 0.8 Å away from the nanopore boundary in the radial direction, forming a charge ring attached to the nanopore (Figure 45b). The same absolute value of 2e is assumed for all charges, with sign altering between neighboring charges, so as to keep the designed system electrically neutral. MD simulations are carried out at 300K by using COMPASS force field. Figure 45a shows a snapshot of the profile of infiltrated water molecules as the piston is moved up by 2.8 Å from its original position.

From our simulations, it is remarkable to find that with the charges anchored to the tube opening, the critical pressure, $P_{cr}$, is increased by 100 MPa compared with the uncharged system. Following the discussions in Section 1.2.2.1, the increased $P_{cr}$ may contribute the enhancement of the energy density of nanofluidic energy absorption. Theoretically, as a water molecule enters a nanopore, it tends to lose hydrogen bonds (characterized by the surface tension) and interact with the solid atoms (characterized by the interaction energy). While the energy associated with the loss of hydrogen bonds is essentially invariant, the interactions energy must be varied significantly near the charged sites. For verification, in Figure 46 we plot the interaction energy map for both systems - within the region shown in the insert of
Figure 46, a water molecule is moved, and at each position its interaction energy with the nanopore is assessed via molecular simulation.†††† The contours imply different potential energy barriers that a water molecule needs to be overcome in order to reach different positions inside the nanochannel. In Figure 46a, it is readily seen that, along the radial direction, the potential energy is the lowest near the solid surface, which echoes the formation of the concentrated water shell illustrated in Figure 40. On the other hand, a prominent energy gradient is found along the axial direction, implying that in order for the water front to proceed towards the interior of the tube, the external assistance has to be continuously increased (near the opening). In Figure 46b, due to the presence of the anchored charges, the modified system shows distinct potential energy characteristics. A deep potential energy well is found near each of the attached charges; that is, any water molecules situated in the region may face much difficulty escaping. In other words, water molecules may be stuck near the charged sites, which, presumably, would “block” the subsequent entrance of H₂O molecules, thereby affecting the infiltration phenomenon.

![Figure 46](image)

Figure 46. Interaction energy map of a single water molecule inside the tube: (a) without anchored charge; (b) with anchored charge.

4.3.2. The “Blocking Mechanism”

To verify the hypothesized “blocking mechanism”, the trajectories of all water molecules were tracked.†††† The O atom of the examined water molecule is fixed and the two H atoms are positioned by minimizing the system potential energy (which is the same as minimizing the interaction energy since the potential energy of a single water molecule is negligible and all other energies are unchanged).
molecules are analyzed throughout the infiltration process. Figure 47b-c shows the positions of water molecules when penetrating an entry plane defined in Figure 47a. Each point in Figure 47b-c represents the position of a H₂O molecule when it penetrates the entry plane, and every infiltrated molecule should leave such a mark. Very interestingly, we find that near any one of the charged sites (in the cycled regions in Figure 47c), the entry positions of water molecules almost overlap. This suggests a strong attraction exerted by the anchored charge (the origin of the “potential well”), which forces the water molecules to stay in the most energetically favorable positions. In order to quantify the influence of the stuck molecules on the flow characteristics, a flux analysis is further carried out. Table 7 tabulates the flux across the entry plane at different radii. It is readily seen that, when charges are present, the flux near the tube surface is highly suppressed and water molecules are seemingly more inclined to infiltrate through inner regions. In other words, due to the “potential well” induced by the charged sites, water molecules flowing in the boundary layer may be impeded and stuck near the charged sites, thus reducing the subsequent flow in the region. As such, water molecules are forced to seek alternative routes to circumvent the stuck water molecules, so the flux through the inner region is much enhanced.

In light of the blockage effect of stuck molecules, the effective entrance for water infiltration must be shrunk substantially in the charged case. From Figure 47, the diameter of the effective entrance, D, is estimated 3.52Å for the unchanged case and 2.68Å for the charged case, respectively. Given D and Pcr, the interfacial energy, γls, is evaluated via the Young’s relation to be about 0.0273 N/m for the uncharged case and 0.0268 N/m for the charged case. The two values are found very close to each
other, which is seemingly contradictory to one of our remarks made at the beginning of this section (i.e. when the nanopore is charged at the opening, the interaction energy is varied and the surface tension remains unchanged, which implies varied interfacial energy). In fact, there is no contradiction here because the statement only applies within the region close to the charged opening. In the interior, however, both energetic terms should be the same for the charged and uncharged cases, and so should their sum, $\gamma_{LS}$. The successful application of the Young’s equation serves as another proof of the discovered “blocking mechanism”, because only if the shrinkage of the entrance (which is caused by the blockage of stuck molecules) is considered can matching results be achieved between the charged and uncharged cases.

Table 7. Water flux through different subregions of the observation plane.

<table>
<thead>
<tr>
<th>Inner and outer radii of annular subregions (Å)</th>
<th>0-1</th>
<th>1-2</th>
<th>2-3</th>
<th>3-4</th>
<th>4-5</th>
<th>5-6</th>
<th>&gt;6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Modified system</td>
<td>0.08</td>
<td>0.13</td>
<td>0.18</td>
<td>0.16</td>
<td>0.21</td>
<td>0.11</td>
<td>0.13</td>
</tr>
<tr>
<td>Original system</td>
<td>0.14</td>
<td>0.19</td>
<td>0.13</td>
<td>0.14</td>
<td>0.13</td>
<td>0.07</td>
<td>0.2</td>
</tr>
</tbody>
</table>

4.3.3. Summary

When the opening of a nanopore is charged, the applied charges tend to interact strongly with water molecules, forming a number of penitential wells near the charged sites. The existence of the penitential well substantially reduces the mobility of water molecules situated near the charged sites. Hence, subsequent flow in the boundary layered is largely suppressed which shrinks the entrance area for water intrusion and increases the infiltration pressure.

4.4. Implications for Field-Responsive Actuation

At the beginning of this chapter, we propose the concept of a thermally/electrically responsive nanosystem based on nanofluidics. The mechanism is straightforward: suppose $P_{cr}$ is different at two temperatures ($P_{cr}(T_1)$ and $P_{cr}(T_2)$) and the system pressure ($P$) is fixed at an intermediate value between the two values of $P_{cr}$. A nonwetting liquid would spontaneously intrude the nanopore at one
temperature and defiltrate at the other. †‡‡‡ Hence, by cyclically varying the temperature between the two bounds, the liquid can be actuated to move back and forth inside the nanochannel, leading to substantial volume change of the system. It is readily seen that the proposed smart system has a key: the dependence of infiltration pressure on the externally applied field. As long as there is such a dependence, one can use the relevant field to control nanofluid behavior.

In this section, we investigate three types of external field – the thermal field, the electric field induced by surface charging, and the electric field induced by chemical functionalization. All of them are found to have profound effects on the nanofluidic infiltration. In the analyzed cases, $P_{cr}$ decreases as temperature increases, decreases as surface charge increases, and increases as the nanopore opening is functionalized in the way shown in Section 4.3. At first glance, the trends for the two electric fields are inconsistent. In fact, there is no contradiction here because the two electric effects are based on distinct mechanisms. First, in the functionalization-induced charge effect, the underlying “blocking mechanism” is a consequence of the potential wells surrounding the selectively charged sites. When all solid atoms are charged, nevertheless, no single atom would be “special” enough to form deep potential wells, and thus the basis of the “blocking mechanism” no longer exists. Second, also in the functionalization-induced charge effect, the interfacial energy, $\gamma_{LS}$, is regarded invariant compared with the uncharged case (the charged sites are too local to affect the surface property far away from the opening). This is obviously not the case under the surface charging condition, where all atoms are charged so $\gamma_{LS}$ must be varied. In essence, considering the two variables that determine $P_{cr}$ in the Young’s equation, $\gamma_{LS}$ and $D$, the effect of surface charging is caused by the variation of $\gamma_{LS}$, while the effect of charged opening is induced by the decrease of $D$.

The discovered correlation between the external fields and the nanofluidic infiltration enables the actuation functionality of the nanoporous composites. According to the Carnot cycle analysis, the net output energy density of such an actuation system can be approximated by $P \cdot \Delta V$, where $P$ is the working pressure and $\Delta V$ is the pore volume density. Apparently, considering the output, it is desired that both $P$ and $\Delta V$ are as high as possible. While $\Delta V$ is solely determined by the porosity of the adopted nanoporous material, $P$ is bounded by two values of $P_{cr}$ determined by the range of variation of the applied field. For example, for a thermally responsive system working between $T_1$ and $T_2$, the working pressure, $P$, can be any

†‡‡‡ Note that, in order for infiltration and defiltration to happen, surface friction as discussed in Sections 3.3 and 3.4 have to be overcome, which presumably also depends on the various external fields. For simplicity, in this chapter, we assume the difference between $P_{cr}(T_1)$ and $P$ and the difference between $P$ and $P_{cr}(T_2)$ are all sufficiently large such that the surface friction would not disrupt the functioning of the field-responsive system. The detailed analysis of the field effects on nanofluidic transport will be a subject of future study.
intermediate value between $P_{cr}(T_1)$ and $P_{cr}(T_2)$. $P$ would be large if both $P_{cr}(T_1)$ and $P_{cr}(T_2)$ are large. Note that, the difference between $T_1$ and $T_2$, i.e. $\Delta T$, is an indication of the consumption of input thermal energy. Apparently, from efficiency point of view, low $\Delta T$ is desired. However, too small $\Delta T$ may result in some issues in practice. For example, small $\Delta T$ is usually associated with small difference between $P_{cr}(T_2)$ and $P_{cr}(T_1)$ (or, small $\Delta P_{cr}$). Systems designed with such parameters could be highly susceptible to environmental perturbations. Any small changes in the environment (e.g. electric field and vibration) may cause unexpected system response. Moreover, as discussed above, too small difference between $P$ and $P_{cr}(T_1)$ or between $P$ and $P_{cr}(T_2)$ may fail to assist the liquid to overcome the surface friction such that infiltration and defiltration can occur as desired in the field-response system. Hence, in order to enhance the robustness of the actuation system, large $\Delta P_{cr}/\Delta T$ is desired, such that a large enough $\Delta P_{cr}$ can be achieved even with a relatively small $\Delta T$. $\Delta P_{cr}/\Delta T$ (thermally controlled) or $\Delta P_{cr}/\Delta Q$ (electrically controlled) as well as $P_{cr}$ are thus usually regarded as the design objectives of the nanoporous actuation system, which may be fine-tuned by a number of system and material variables shown in Figure 8.

In order to demonstrate the energy density of the proposed nanoporous actuation materials, we use the mixture of nanoporous carbon and water as an example (Section 4.1). For sample B in Figure 42, the energy density is estimated as 0.4 J/g, much larger than that of Ti–Ni alloys, 50 mJ/g. The output energy density of the nanoporous system may be further enhanced by enhancing either the working pressure or the pore volume density. As a perspective example, based on the simulation results of the (13,13) CNT where the pore volume density is about 0.3 cm$^3$/g, a working pressure of 100 MPa (which is below $P_{cr}$ at 300 K but exceeds the threshold at 310 K, according to Figure 38a) can, theoretically, yield a considerably high output mechanical energy at the level of 10 J/g. In addition, we note that varying the liquid and solid phases may also affect the efficiency of the proposed nanoporous actuation system. For example, it is envisioned that silica nanotubes cannot work as well as carbon nanotubes for thermo-actuation applications (in terms of $\Delta P_{cr}/\Delta T$), and electrolytes are typically more suitable than water for electro-actuation applications (in terms of $\Delta P_{cr}/\Delta Q$).
Chapter 5.

Inhomogeneous Charge Distribution in Nanofluids – Fundamentals and Implications for Energy Harvesting

Nanofluidics\textsuperscript{[45,46,54,173]} has attracted considerable interest in the past decade owing to its profound implications for molecular separation,\textsuperscript{[205]} detection,\textsuperscript{[206]} biological transport,\textsuperscript{[32]} energy absorption and damping,\textsuperscript{[13,28]} as well as drug delivery and others.\textsuperscript{[28-31,207-209]} Most of these applications are enabled by the unique molecular,\textsuperscript{[63]} energetic,\textsuperscript{[160]} and flow\textsuperscript{[59,60]} characteristics of liquids when confined in extremely small space.\textsuperscript{[160,210-214]}

Despite these advances, nevertheless, the application of nanofluids for energy harvesting has not yet received necessary attention. As an electrolyte solution contacts an ideal polarizable solid, the ions and atoms situated in the vicinity of the interface are subjected to different forces from the solid phase and liquid phase. This induces a layered structure of the electrolyte solution (Figure 9): in the Helmholtz layer (namely, the layer closest to the solid surface), ions are highly compact and less mobile due to the intimate contact with the solid surface; the Gouy-Chapman layer (which is also known as the diffuse layer), by comparison, has relatively higher ion mobility and lower ion density. Such a layered structure of solvated ions, together with the reorganized dipole orientations (if any), reflects the electrification of the electrolyte when contacting a solid surface, which further induces an electrical potential difference, $\phi$, between the solid phase and the liquid phase. Importantly, the solid-liquid potential difference, $\phi$, is not only a function of the adopted materials (e.g. the ion species and concentration, the solvent, as well as the pore size and the solid composition), it also strongly depends on the environment in which the liquid-solid biphasic system operates (e.g. the temperature and the flow velocity of the electrolyte solution). Thus, by connecting two of such biphasic systems governed by different environmental variables, a potential difference is generated and a voltage can be output. For example, assume that in system A, the electrolyte is driven to flow at a velocity of $v_A$ whereas in system B, the electrolyte solution has a flow velocity of $v_B$. The generated potential difference can be readily assessed by $\Delta \phi = \phi_A - \phi_B$, where $\phi_A$ and $\phi_B$ denote the solid-liquid potential differences in both systems. This enables the mechanical-to-electrical energy conversion where an electrical output is generated.
from the mechanical input of pressure. Based on a similar mechanism, electrical energy can also be generated from a thermal input, i.e. temperature difference.

It is readily seen that the interface structure of the electrolyte, in particular, its dependence on the temperature and flow velocity, plays a central role in the described energy conversion process. Nevertheless, when the electrolyte is confined in extremely small environment such as nanopores, the liquid phase may be so severely squeezed that the layered structures at opposite boundaries would overlap and strongly affect each other. Arguably, this may cause ionic and molecular distributions that can hardly be predicted by closed-form or exact solutions. Molecular simulation therefore becomes the tool that can be counted on to elucidate the atomistic mechanisms of the nanofluidic energy conversion process and to quantify the relevant electrical output and energy conversion efficiency. In this chapter, the interface structure of nanoconfined electrolytes is extensively studied at various temperatures and flow rates. The induced electrical potential, , is correlated with the temperature difference and the flow rate difference between two connected cells. The simulation results are further verified by parallel experiments, which show reasonably good agreements.

5.1. Electrical Output Induced by Temperature Difference

5.1.1. Inhomogeneous Charge Distribution

In this study, we consider a 12 wt% aqueous solution of sodium chloride (NaCl), and four carbon nanotubes of different diameters, , including a (06,06) CNT with \( D = 8.14 \) Å, a (10,10) CNT with \( D = 13.56 \) Å, a (15,15) CNT with \( D = 20.34 \) Å, and a (20,20) CNT with \( D = 27.12 \) Å. Each of the CNTs is filled with a specific number of water molecules and ions such that the prescribed ion concentration is retained at the ambient temperature and pressure. Periodic boundary condition is applied in the axial direction to ensure the continuity of the computational model. The system is first relaxed by a dynamic simulation of 100 ps, and then simulated for another 5 ns, during which the atomic positions are output every 50 fs for statistical purposes. Note that, for each of the CNTs, 50 initial configurations of the confined electrolyte are sampled and independently simulated. Any of the MD results shown in this study is in fact an average among these sampled systems.

Lennard-Jones (LJ) empirical forcefield is adopted to describe the interatomic van der Waals interaction. Water molecules are modeled by the extended simple point charge potential (SPC/E). Carbon atoms are modeled by the Amber96 LJ parameters, and the flexibility of CNT is addressed by a Morse bond, a harmonic cosine angle and a 2-fold torsion potential. The LJ parameters for ions are taken from free energy perturbation simulations. All the other interatomic parameters
are evaluated by the Lorentz combining rule. A 10 Å cutoff is assumed for the vdw interaction. Long range Coulomb interactions are handled by the Particle-Particle Particle-Mesh technique (PPPM)\textsuperscript{[178]} with a root mean square accuracy of $10^{-4}$. The Nose-Hoover thermostat\textsuperscript{[192]} with a damping parameter of 0.1 is employed to regulate the temperature.

Figure 48. The radial distribution of the four species of atoms and ions (O, H, Na\textsuperscript{+}, and Cl\textsuperscript{-}) in an aqueous solution of NaCl when confined in: (a) a (06,06) CNT with $D=8.14$ Å; (b) a (10,10) CNT with $D=13.56$ Å; (c) a (15,15) CNT with $D=20.34$ Å; and (d) a (20,20) CNT with $D=27.12$ Å. The insets show snapshots of confined atoms and ions (red sphere: O; white sphere: H; purple sphere: Na\textsuperscript{+}; green sphere: Cl\textsuperscript{-}). Temperature is fixed at 300 K in all simulations. The number density is defined as the number of the specified ion/atom in a unit volume. Only half the $r$-$z$ plane is plotted, where $r$ denotes the radial direction and $z$ is the axial direction. The left axis is therefore the tube axis ($r=0$), while the right axis indicates the solid surface (where the carbon atoms are situated).
Shown in the insets of Figure 48a-d are the snapshots of the NaCl solution confined in four representative CNTs. Note that the diameters of these CNTs are just a bit larger than the interatomic equilibrium distance, and thus only a few ions and atoms can be accommodated in the same cross section of the CNT simultaneously. Hence, almost all ions and atoms can be regarded within the boundary layer, and very probably opposite boundary layers can overlap and strongly affect each other. In light of these unique characteristics, it is envisioned that the atomic and ionic distributions in nanofluids could be distinct from conventional predictions and strongly dependent on the size of the nanoconfinement.

Figure 48 plots the radial density distribution (RDD) for the four atoms and ions involved in the NaCl electrolyte: O, H, Na+, and Cl-. Similar to the density profile of pure water revealed in the last chapter (Figure 40), the RDD curves of the H and O atoms in the solution also concentrate at the boundary layer and exhibit large fluctuations there. The cation and anion, by contrast, show very low densities in the region, which may be attributable to two reasons: first, the equilibrium distance between Na+/Cl- and C is relatively larger than that between a H$_2$O molecule and C; and second, the high concentration of H$_2$O molecule close to the solid surface can largely suppress the occurrence of ions in the region. Given the high density of water and the low densities of ions at the boundary region, the ion concentration at the interface must be subjected to a significant variation, which may further affect the hydration of ions and relevant nanofluid behavior.

Figure 48 also reveals profound size effects. In the (20,20) CNT, for example, three full waves (only the waves in the half r-z plan are considered) can be identified in the RDD curves of both H and O (Figure 48d). When the tube diameter is reduced by about 6.78 Å, nevertheless, only the outer two waves persist while the inmost one shifts to the center of the CNT, forming a half wave together with its image about the central axis in the (20,20) case. As the tube size keeps decreasing, the waves keep shifting and overlapping, eventually leading to the extremely high concentration of H (about 0.32 /Å$^3$) at the center of the (06,06) CNT (where only one full wave exists in the RDD curve).

On the other hand, in the three cases with $D$ over 10 Å, the first peak of density is all found about 3.3-3.5 Å away from the solid surface, comprised of O atoms (i.e. the outmost O shell, which is closer to the solid surface than the outmost H shell). In the (06,06) CNT, however, H takes over; a shell of concentrated H atoms is found only 2.3 Å away from the solid surface.$^6$ It is very important to note that, no matter it is H or O that is closer to the solid surface, their RDDs are far from matching: a peak of O does not correspond to a peak of H, and neither does a trough of O overlap

$^6$ In fact, this H shell does not just disappear suddenly as the confinement is enlarged. In fact, its peak is still observable in Figure 48b-d (right to the outmost O shell), though the peak is much smaller than that of the O shell.
a trough of H. This implies that, in solvent molecules, different atom species are subjected to different unbalances at the interface, leading to radical reorientation of the dipoles (which is however random in the bulk). For example, considering the outmost O and H shells defined in Figure 48b, a separation of $\Delta r$ is found between the two peaks in the radial direction. That is, on average, there is a preferential dipole orientation within this boundary region, which can be characterized by an “effective dipole”. The effective dipole is defined to connect an O shell and a neighboring H shell (pointing from the H shell to the O shell), and thus the distance between the two shells determines the separation between the two poles in the effective dipole. Among the four cases under investigation, the outmost effective dipole points to the tube axis in the (06,06) case, and points to the solid surface in the other cases. The separation between the two poles in the effective dipole, $\Delta r$, also shows strong size dependency: as $D$ increases, $\Delta r$ is measured 0.74 Å, 0.17 Å, 0.16 Å, and 0.13 Å, respectively, for the four cases under investigation. Importantly, the preferential dipole orientation is bound to induce a net charge distribution in the boundary region (and in other regions as well), which, together with that contributed by the cations and anions, would lead to an overall net charge distribution that determines the electrochemical properties of the interface (elaborated on below).

5.1.2. Solid-Liquid Potential Difference: Size Effect

Due to the perturbed force field in the vicinity of a solid-liquid interface, not only ions would form layered structures, the dipoles in solvent molecules might also adopt new orientations. As a consequence, the density profiles of ions and atoms usually exhibit large fluctuations at the interface region, leading to a prominent net charge distribution. Given the time-averaged density profiles obtained above, the net charge density can be readily assessed by

$$C_\rho = \sum_{i=1}^{n} \rho_i \cdot C_i$$

Here, $n$ represents the number of atom and ion species in the electrolyte solution, $\rho_i$ denotes the local density of the $i$-th species and $C_i$ represents the partial charge carried by the species. The calculated net charge distribution is plotted in Figure 49 for the four cases investigated in this study (blue curves). In general, $\rho_c$ is found substantially varied in the entire volume of the electrolyte. We note that, in the ultra-small nanoconfinements under investigation ($D=1$ nm), almost all atoms and ions can be regarded within the boundary layer; thus, the density profiles and the net charge distribution must be subjected to substantial fluctuations throughout the entire confinement, leading to profound impact on the interfacial electrochemical properties. It also deserves mention that, despite the large variation of $\rho_c$ with respect to $r$, the volume integration of the net charge density must equal to zero as there is no excess charge present in the electrolyte or in the solid.
Figure 49. The variations of the net charge (blue) and the electrical potential (red) in the NaCl solution confined in four representative CNTs. The diameters of the CNTs are (a) 8.14 Å, (b) 13.56 Å, (c) 20.34 Å, and (d) 27.12 Å, respectively.

Figure 50. The solid-liquid potential difference versus the size of the nanotube.
According to the Poisson’s equation, the electrical potential, $\varphi$, has a differential relationship with the pointwise charge density, $\rho_c$:

$$\nabla^2 \varphi = -\frac{\rho_c}{\varepsilon_0 \varepsilon}$$

(26)

where $\varepsilon_0$ and $\varepsilon$ are the vacuum permittivity and the dielectric constant of the medium, respectively. In this study, the dielectric constant, $\varepsilon$, is taken as that of the bulk 12 wt% aqueous solution of NaCl (about 44.30)\cite{215}, though it is known that the dielectric constant could be affected to some extent at the interface.\cite{216} The electrical potential, $\varphi$, is thereby calculated via eqn. (26) and plotted in Figure 49 (red curves and right axis). Similar to $\rho_c$, $\varphi$ also exhibits large fluctuations, but the fluctuations in $\rho_c$ and $\varphi$ are different in details. For example, in the (10,10) case, three peaks are found for $\rho_c$ but only one is identified for $\varphi$. After all, the electrical potential is an integral of the spatial net charge distribution, and thus there must be many distinctions in their variations.

Due to the considerable variation of $\varphi$ in space, a potential difference can be generated between the solid phase and liquid phase. Denoted by $\phi$, the solid-liquid potential difference conforms to the following equation

$$\phi = \varphi|_{r=R} - \varphi|_{r=0}$$

(27)

where $R$ is the radius of the circular confinement, $\varphi|_{r=R}$ and $\varphi|_{r=0}$ represent the electrical potentials at the solid surface and the center of the confined liquid, respectively. Figure 50 plots the solid-liquid potential difference for the four cases under investigation. As the size of the confinement decreases, $\phi$ is shown to first gradually ascend, attaining the maximum of 38.04 mV at $D=13.56$ Å; when the pore size is reduced to 8.14 Å, however, $\phi$ suddenly drops to an extremely low value, 3.61 mV, which is about 90% lower than the peak value. Why does the solid-liquid potential fall so severely when the diameter of the CNT is reduced from 13.56 Å to 8.14 Å? First, the diameter of a (06,06) CNT is only 8.14 Å. Deducting twice the equilibrium distance between the C atom and any atom/ion in the electrolyte (which is typically larger than 2Å), the space accessible to the intruding atoms/ions is rather limited. As illustrated in the inset of Figure 48a, the electrolyte ions and atoms can only access a small circular region in the center, whose diameter is about half that of the CNT. Indeed, under such a circumstance, only a single chain of ions and atoms***** may be accommodated, which can strongly affect the various quantities investigated in this section that determine the solid-liquid potential difference. For example, inside the (06,06) CNT (Figure 48a), the density profiles of H and O are found to have

***** More atoms and ions (e.g. forming a double helical chain) may be accommodated when the pressure in the liquid phase is sufficiently large.
different numbers of peaks; two are identified for H but only one is found for O (and
the O peak is sandwiched in between the two H peaks). Such a phenomenon is not
observed in all the other CNTs of larger diameters, where the peak number is always
the same for O and H. Following the above definition of the effective dipole, there
should be two effective dipoles in a (06,06) CNT, one pointing from the outer H shell
to the O shell, and the other pointing from the inner H shell to the O shell. It is
important to note that the directions of these two effective dipoles are opposite. In
other words, the inner effective dipole would counteract the influence of the outer
effective dipole, and thus the potential difference across the solid-liquid interface is
effectively lowered, which echoes the observation in Figure 50.

5.1.3. Solid-Liquid Potential Difference: Thermal Effect

As noted in the introductory section of this chapter, if the solid-liquid
potential difference has a prominent dependence on the temperature, a voltage would
be generated by connecting two cells operated at difference temperatures. It is
therefore of much fundamental value and practical interest to study the effect of
temperature on both the structural and electrical aspects of the electrolyte confined in
nanopores. There are four quantities that have been extensively discussed in the
previous part of this section, namely, the atomic/ionic density ($\rho$), the charge density
($\rho_c$), the electrical potential ($\varphi$), and the solid-liquid potential difference ($\phi$). Indeed,
all these four variables are intimately interrelated: $\rho$ determines $\rho_c$ via eqn. (25); $\rho_c$ is
correlated with $\varphi$ via the Poisson’s eqn. (26); $\phi$ is defined as the potential difference
between the solid surface and the inmost region of confined electrolyte. Hence, it is
envisioned that, if any of these four variables is found dependent on the temperature,
all the others would have similar thermal dependences.
Figure 51. Effect of temperature on the charge density and the electrical potential: the radial distribution of the charge density in (a) a (15,15) CNT and (b) a (20,20) CNT; the radial variation of the electrical potential in (c) a (15,15) CNT and (d) a (20,20) CNT.

Figure 52. (a) The solid-liquid interfacial potential difference versus temperature in the four representative CNTs. (b) Effect of temperature difference on the potential difference between two (20,20) CNTs containing the same NaCl solution.
Figure 51a-b plots the effect of temperature on the charge density profile in a (15,15) CNT and a (20,20) CNT, respectively. In both cases, the variation of temperature is found just slightly affecting the charge density. For example, at the peak closest to the solid surface, $\rho_c$ is increased by only 8% as the temperature is elevated from 280 K to 340 K. Although marginal, the thermal effect on $\rho_c$ implies that $\phi$ should also change as the temperature varies. According to Figure 51c-d, the thermal effect on $\phi$ does not just exist, but in fact, it is very prominent. Considering the (20,20) case as an instance, as the temperature is reduced by 60 K, the electrical potential at the solid surface, $\phi_{r=R}$, increases by about 38%, implying that the electrical potential is more sensitive to the temperature variation than the charge density. This is reasonable because $\phi$ is in essence an integration of $\rho_c$, and thus, any small variation in $\rho_c$ could be much amplified in the variation of $\phi$.

With the apparent thermal dependence of the electrical potential, the solid-liquid potential difference must also be temperature-dependent. According to Figure 52a, in the (20,20) case, as the temperature increases, $\phi$ decreases almost linearly. Nevertheless, when the size of the CNT is further decreased, the variation of $\phi$ with respect to the temperature is no longer monotonous, but rather somewhat fluctuating. Again, in extremely small CNTs, the confining effect is so dominant that all atoms, ions and dipole orientations are significantly affected. Hence, as the temperature varies, the structural response of the confined electrolyte could be less monotonous. Such a non-monotonous structural response, when amplified by the spatial integration, would lead to complicated variations in the electrical potential as well as the solid-liquid potential difference. This increases the difficulty of using extremely small nanopores for the proposed thermal-to-electrical energy conversion. The (20,20) CNT (which has a diameter of 27.12 Å) is thus among the smallest CNTs that may be utilized for such applications. For example, by connecting two of the (20,20) CNT-electrolyte systems operated at different temperatures, a potential difference, $\Delta\phi$, would be generated. As plotted in Figure 52b, $\Delta\phi$ increases almost linearly with $\Delta T$ (the temperature difference) at a rate of 0.084 mV/K, which is comparable with that measured in experiment (Figure 6). The discrepancy may be attributable to many factors, but the difference in pore structure (between the “ideal” smooth CNT employed in this study and the porous carbon in experiment which may has rough, irregular, and interconnected pore structure) is believed to be the most important because it can largely affect the structural and electrical characteristics of the confined electrolyte.

5.1.4. Summary

Each of the curves is a time-averaged statistical result among all the 50 sampled systems.
Due to the perturbed force field in the vicinity of a solid-liquid interface, not only ions would form layered structures, the dipoles in solvent molecules might also adopt new orientations. As a consequence, the density profiles of ions and atoms usually exhibit large fluctuations at the interface region, leading to a prominent net charge distribution and electrical potential variation. A potential difference is thus induced between the solid phase and the liquid phase, which exhibits a prominent dependence on the temperature. Due to the thermal dependence of the solid-liquid potential difference, a voltage can be generated by connecting two cells operated at different temperatures. It deserves mention that, the proposed system behaves similar to a capacitor. The calculated $\Delta \phi$ represents only the initial potential difference between the two cells. The output potential decays as the new system equilibrium is approached, and the decay rate depends in part on the resistance in between the two cells, and in part on the pore structure (which may govern ion diffusion rate). However, after the two cells are disconnected and grounded (for typically several seconds), the initial equilibrium can be restored in both cells. Then, by connecting the two cells again, the output voltage is recovered and the energy conversion process can be repeated. We envision that by using two nanoporous energy harvesting systems that are alternatively connected and disconnected (e.g. one is grounded while the other outputs power), a quasi-continuous energy harvesting can be realized.

In extremely small CNTs, the confining effect is so dominant that all atoms, ions and dipole orientations are significantly affected. Hence, as the temperature varies, the structural response in the confined electrolyte could be much less monotonous, leading to complicated variations to the solid-liquid potential difference. This increases the difficulty of using such nanopores for the proposed thermal-to-electrical energy conversion. The (20,20) CNT (which has a diameter of 27.12 Å) is thus found one of the smallest carbon nanopores that may be utilized for such applications, which outputs the voltage at a rate of 0.084 mV/K, comparable with the experimental result.

5.2. Electrical Output Induced by Flow Rate Difference

When situated near a solid surface, ions and molecules are forced to adopt new positions and orientations, leading to a non-zero net charge distribution and a fluctuating electrical potential at the interface. As a consequence, the solid phase and the liquid phase are usually subjected to distinct electrical potentials, and in the last section, this potential difference has been shown to have prominent size effect and thermal dependency. This section aims to study the effect of flow rate on the interface molecular structure and the associated electrical characteristics. Since the liquid ions
and molecules are known to have different mobilities near and far from the interface, when the electrolyte is driven to flow, the molecular structure must be disturbed to different extents at different distances from the solid surface, thus leading to the flow rate effect on the various nanofluidic characteristics.

The computational model and simulation techniques are similar to that adopted in the last section, except that the confined electrolyte is no longer stationary, but flows along the nanochannel at different velocities. The (15,15) CNT is considered in this section as an illustrative case. Due to the apparent shearing stress at the liquid-solid interface and the intrinsic nominal viscosity of the liquid phase, a driving force (e.g. pressure drop or thermal gradient) is required to initiate and sustain the liquid flow. In this study, mechanical driving force is adopted so as to decouple the flow rate effect from the thermal effect. A constant external acceleration, \( a \), is applied along the channel direction on all liquid particles. We note that, under such a driving force, it usually takes hundreds of picoseconds for the liquid flow to reach steady state. Thus, in this study, each system is simulated for 12 ns but only the last 10 ns is used in gathering the statistics of various quantities (steady-state flow rate and radial density profile, etc.). Moreover, in order to rule out possible effects of initial molecular configurations (atom positions), 50 initial structures of the confined electrolyte are sampled and independently simulated. All the results shown in this section are obtained by averaging the statistical results from all these sampled systems.

In Figure 53a, the solid-liquid potential difference, \( \phi \), is shown to have an apparent dependence on the flow velocity, \( v \): in general, as \( v \) increases, \( \phi \) increases. According to the discussions in the last section, the ions and atoms have different affinities with the solid surface; water molecules are more concentrated at the boundary layer while ions tend to stay in the middle. Despite the strong inclination of H2O to stay close to the solid surface, there exists an upper limit on its density in the outmost layer (since too high density can be energetically unfavorable). As the electrolyte is driven to flow, nevertheless, the disturbance caused by the flow velocity can assist water molecules to go beyond the density limit; and thus, more water molecules are able to enter the boundary region, which contribute to the further densification of the outmost boundary layer (Figure 53c-d). On the other hand, as water molecules are increasingly attracted to the boundary layer, the occurrence of ions in the region is further suppressed; more and more ions choose to stay far away from the solid surface, leading to increased ion densities in the middle of the electrolyte column (Figure 53e-f). Due to these structural changes (in response to the mechanically driven flow), the net charge distribution is much affected (Figure 53b), thus leading to the flow-rate dependent potential difference between the solid and liquid phases (Figure 53a).

Further, the effect of the flow rate is found more prominent when the flow velocity is large. According to Figure 53a, when \( v \) is below 125 m/s, \( \phi \) increases almost linearly with \( v \) at a rate \( \frac{d\phi}{dv} \approx 0.003 \text{ mV s/m} \); when \( v \) is raised above 125
m/s, another linear regime is identified, in which \( \frac{d\phi}{dv} \) is calculated five times larger, about 0.016 mV s/m. Such a nonlinear flow rate effect is attributable to the nonlinear response of the confined electrolyte to the mechanically driven flow. Figure 53b plots the net charge distribution at three representative velocities, 16 m/s, 83 m/s, and 168 m/s. We note that, the first two velocities are in the low \( \frac{d\phi}{dv} \) regime while the last velocity is in the high \( \frac{d\phi}{dv} \) region; moreover, the velocity difference between the first two velocities (16 m/s and 83 m/s) is close to that between the last two velocities (83 m/s and 168 m/s). In Figure 53b, the outmost peak in the net charge density profile (which affects the potential variation the most) exhibits very strong nonlinearity with respect to the flow rate. When the flow velocity is increased from 16 m/s to 83 m/s, the local net charge density is decreased by just 0.0055 C/mm³; by comparison, when the flow velocity is further increased by just 85 m/s to 168 m/s (which is a velocity above 125 m/s, though), the local net charge density is prominently reduced by 0.0233 C/mm³, much larger than 0.0055 C/mm³. That is, when confined in nanoenvironment, the interface molecular structure is highly sensitive to the mechanically driven flow when \( v \) is large, but less sensitive when \( v \) is relatively low (Figure 53b). This explains the nonlinear flow rate dependence of \( \phi \) shown in Figure 53, i.e. low dependence (low \( \frac{d\phi}{dv} \)) at relatively low flow velocity and high dependence (high \( \frac{d\phi}{dv} \)) when the flow velocity is high. The nonlinear nanofluidic response is also apparent in the density profiles of individual atoms and ions (Figure 53c-f), where the curve for \( v=168 \text{ m/s} \) is always separated from the curves for the other two velocities.

The value of \( \frac{d\phi}{dv} \) has important implications for the proposed mechanical-to-electrical energy conversion. Recall that a typical mechanoelectric nanoporous system consists of two identical nanofluidic units. Once a difference is established between the flow velocities in the two units (either only one unit is loaded, or both are loaded but at different loading rates), a potential difference can be output, i.e. \( \Delta\phi = \phi(v_1) - \phi(v_2) \), where \( v_1 \) and \( v_2 \) are the flow velocities in the two nanofluidic units. Consider the output potential difference, \( \Delta\phi \), as the gain, and the two velocities, \( v_1 \) and \( v_2 \), as an indication of the energy consumption (since the flow is driven by mechanical force and the resistance, i.e. the shearing stress, is dependent on the flow velocity). Apparently, larger \( \frac{d\phi}{dv} \) (which can be achieved at high flow velocity) can make the nanoporous mechanical-to-electrical energy conversion more cost-effective, and thus should be pursued in the system design.
Figure 53. (a) The solid-liquid potential difference versus flow velocity in a (15,15) CNT. (b) The net charge distribution at three representative velocities, 16 m/s, 83 m/s, and 168 m/s. The effect of flow velocity on the number density of (c) O, (d) H, (e) Na⁺, and (f) Cl⁻, respectively.
5.3. Implications for Energy Harvesting

Due to the perturbed force field in the vicinity of a solid-liquid interface, the density profiles of ions and atoms usually exhibit large fluctuations, which induces a prominent potential difference between the solid phase and the liquid phase. Since this solid-liquid potential difference is a function of temperature and flow velocity, a voltage can be generated by connecting two nanofluidic systems operated at different temperatures or different flow rates, through which thermal/mechanical energy is converted into the electrical energy. This makes the nanoporous composite a very promising candidate for harvesting or scavenging energy from various otherwise wasted ambient energy sources, including low grade heat, vibrations, and human motion. As long as there exists a temperature/loading rate difference, electricity can be generated.

In extremely small nanopores, the confining effect becomes so dominant that all atoms, ions and dipole orientations are significantly affected. Hence, as the temperature varies, the structural response of the confined electrolyte could be much less monotonous, leading to complicated variations to the solid-liquid potential difference, which increases the difficulty of using such nanopores for the proposed thermal-to-electrical energy conversion. The (20,20) CNT (which has a diameter of 27.12 Å) is thus considered one of the smallest nanopores that may be utilized for thermoelectric applications, which outputs the voltage at a rate of 0.084 mV/K, comparable with the experimental result. More influences from other material and system parameters, such as the effects of solid phase, pore structure, liquid phase and concentration on the thermal sensitivity of the potential difference, will be studied in future.

For the proposed mechanical-to-electrical energy conversion, it is found that the solid-liquid potential difference is more sensitive to the flow velocity (which is favored in designing cost-effective systems) when the flow velocity is sufficiently large (larger than a critical value that varies with the pore size). However, we note that in order to drive the confined liquid to flow above such a critical velocity, a large driving force is required to counter the surface resistance (since the shearing stress increases as the flow velocity increases). The benefit achieved by increasing the flow velocity over the critical velocity may be largely traded off by the increased energy dissipation. Hence, an optimal balance must be sought so as to maximize the system efficiency, which requires detailed mechanical, thermal, electrical analyses of specific systems. The results presented here provide useful hints for the future work of designing and optimizing ultra-efficient nanoporous energy harvesting systems.
Chapter 6.
Energy Dissipation Using Nanoporous Materials without Liquid

Energy absorption is of immense importance for assuring the safety of people and the reliability of devices and infrastructures. To achieve enhanced energy absorption capabilities, this dissertation proposes a novel nanocomposite that combines nanoporous materials and functional liquids. Although the proposed material has been shown to have superior energy density together with other exciting functionalities, it may not be favored in all applications. For example, in applications involving extreme temperature (e.g. blast protection), insurmountable issues may be caused by the liquid phase contained in the nanoporous composite. Moreover, the corrosion and the incompatibility between the liquid phase and the packaging materials may pose additional concerns. In light of these inherent limitations of the proposed nanocomposite, it is of immense value to develop advanced solid energy absorption materials that can complement the proposed nanoporous composite in some applications. This chapter briefly reviews two of our studies on the liquid-free energy absorption technology, one based on the irreversible collapse of zeolites, and the other based on the reversible buckling of CNT clusters. Both of them involve nanoporous materials, which have been attracting much interest as promising and alternative candidates of energy absorption materials.\[217,218\]

6.1. Energy Dissipation using MFI zeolite under Dynamic Loading

Inspired by natural materials and structures, energy dissipation/absorption materials with micro or nanoporous structures are attracting growing interests.\[217,218\] Kyriakides et al. systematically studied the energy absorption of honeycombs\[219,220\] and other porous materials,\[221,222\] concluding that upon external loading, porous materials usually undergo a number of structural changes (including cell buckling, shear slip, and crushing), through which a large amount of energy can be dissipated.\[223\] When the pore size is reduced to sub-nm level, e.g. MFI zeolite, it is envisioned that the energy absorption may be further enhanced by the ultra-large
specific surface area and the ultra-fine pore structures.\cite{33,59,224} Despite these advances, nevertheless, it remains unclear whether the energy absorption mechanism of nanoporous materials is exactly the same as that of conventional porous materials, and whether the energy absorption involves any intriguing orientation effect and/or rate effect.

These questions are pursued by atomistic simulation in this study. MFI zeolite is adopted as an illustrative material, and the loading direction and rate are varied to explore their respective effects. There are two distinct nanochannel systems coexisting in the MFI zeolite (Figure 54):\cite{225} zigzag channels along [100] and straight channels along [010]; along [001], the pore path is rather tortuous, with the contribution from both zigzag and straight nanopores. After geometric optimization, the size of the unit cell of MFI zeolite is 18.1286Å, 20.4136Å and 14.5949Å, respectively, along the [100], [010] and [001] directions. Because of the direction-dependent atomic structures, MFI zeolite is in essence an anisotropic material so its mechanical properties (including energy absorption) must also be direction-dependent. Hence, this section studies the crushing responses of zeolite along three directions, i.e. [100], [010] and [001]. A specific number of zeolite unit cells are stacked along a certain direction to form a film of desired orientation and thickness. Periodic boundary conditions are imposed in all the lateral directions to ensure the continuity. During the simulation, the bottom layer of the film is fixed and a compressive loading is applied through a moving rigid plane (with a controlled displacement rate) in contact with the top surface of the film. The applied pressure is computed by summing up the interactions forces between the atoms on the rigid plane and those in the zeolite film. MD simulations are carried out in Materials Studio\cite{226} using the COMPASS force field.\cite{185} Simulation temperature is fixed at 300 K via the Berendsen thermostat.

Figure 54. The atomic structure of MFI zeolite: views from three principal directions.

Three typical crushing (pressure-strain) curves are shown in Figure 55a for different loading rates along the [001] direction. In general, when the compressive
strain is low, an elastic response is identified where the pressure increases almost linearly with the deformation. As the strain is increased beyond a critical value, a fluctuating plateau is formed, signaling the inelastic deformation of the material (the fluctuation is caused by the sequential collapse of the nanopores). Interestingly, in the elastic regime, the slope is found rather close among the three curves, implying that the elastic constants of the MFI zeolite is in essence independent of the loading rate along this direction. In the inelastic regime, however, the mechanical response shows very strong dependence on the loading rate. If define the pressure at the onset of the inelastic deformation as the critical crushing pressure ($P_{crush}$), $P_{crush}$ always increases as the loading rate increases (Figure 55a), and such a rate dependency remains if the load is applied along different directions (Figure 56d).

The crushing of the MFI zeolite is also direction-dependent. For example, at the highest loading rate of 500 m/s, $P_{crush}$ is calculated to be 18 MPa, 48 MPa, and 75 MPa, respectively, along the three directions under investigation, i.e. [100], [010] and [001]. The direction-dependency of $P_{crush}$ must be attributable to the different nanochannel geometries in different directions. Figure 56a-c shows the atomic structure of the MFI zeolite when compressed by 28% along three different directions and at three different loading rates. Despite the various loading directions and loading rates, the inelastic deformation of the MFI zeolite seems to be governed by two mechanisms, namely, shear slip and densification (honeycombs also have these two mechanisms\cite{219,220}). When the load is applied along [100], for example, the MFI zeolite shows considerable lateral deflections, implying that shear slip dominates. In the other loading directions, nevertheless, shear slip is found to be dominant only at relatively low loading rates, e.g. 20 m/s in the current study; when the loading rate is high, densification takes over and becomes the dominant mechanism (the densification region can be found near the surface of the nanofilm).

Figure 55b gives more details of the effect of loading direction on the pressure-strain curve (loading rate is fixed at 50m/s). In the elastic regime, the MFI zeolite shows different elastic constants along different orientations. The Young's modulus ($E$) is calculated about $1.6 \pm 0.1$ GPa along [100] and [010], which is on the same order as that measured in a quasi-static experiment\cite{227} along [001], though, the Young’s modulus is lowered to about $0.9 \pm 0.05$ GPa, indicating that MFI zeolite is more compliant in this direction. The effect of loading direction is prominent also in the inelastic regime. According to Figure 55b, when the load is applied along [100], pressure continuously increases with the deformation; in the other two directions, however, pressure is kept almost a constant as the deformation increases. From the above discussions, it is known that the inelastic deformation of the MFI zeolite is dominated by shear slip along [100] and densification in the other two directions (at 50m/s). These results collectively suggest that, the development of shear slip requires increasing pressure. By contrast, the densification mechanism does not require the applied pressure to be continuously increased; keeping the pressure at the critical crushing pressure can continuously collapse the nanopores and densify the material.
Figure 55. Typical pressure-strain curves: (a) the MFI zeolite is subjected to the compressive (crushing) loading along [001] at three loading rates; (b) the loading is applied along three representative directions at the same rate of 50m/s. In all cases, the thickness of the undeformed zeolite, $t$, is 16.05 nm along the loading direction.

Figure 56. The atomic structures of the MFI zeolite when compressed by 28% at three representative loading rates (20, 50, and 500 m/s): the load is applied along (a) [100], (b) [010], and (c) [001], respectively. (d) $P_{\text{crush}}$ for different loading directions and different loading rates.
Accompanying the irreversible deformation of the MFI zeolite under compression, a large amount of mechanical energy is absorbed, which can be assessed by the area enclosed by the hysteresis in the pressure-strain curve (assuming it is not affected by fracture). At a compressive strain of 28% and a loading rate of 50 m/s, for example, the energy density of MFI zeolite is calculated about 1.58, 2.01 and 2.08 KJ/g, respectively, along the three loading directions. These values are comparable with the experimental results[,] and significantly higher than that of conventional energy dissipation materials such as composites and shape memory alloys[,] as well as some of the nanoporous composites proposed in this dissertation.[] It deserves mention that, the [001] direction always leads to higher $P_{\text{crush}}$ owing to the complexity of the tortuous nanochannels, which should be favored in energy absorption applications.

6.2. Energy Dissipation using CNT Cluster under Quasi-Static Loading

Thanks to the unique combination of superior mechanical and electrical properties, carbon nanotubes (CNTs)[72] have been widely applied as conducting or semiconducting wires in nanoelectronic devices,[] probes in scanning-probe microscopy,[] gas detectors,[] hydrogen storage materials,[] electrodes,[] and nanotweezers[,] among others. In addition to these exciting applications, CNTs are also promising for energy absorption. Consider an isolated multi-walled CNT with one of its ends clamped on a solid surface. During a compressive loading-unloading loop, the CNT sequentially undergoes four deformation mechanisms (Figure 57): (1) linear compression, (2) snap buckling, (3) post-buckling and (4) unloading. Different from the MFI zeolite discussed in the last section, after unloading, a CNT can fully recover its shape owing to the extremely large stretchability of the C-C bond. Despite this recoverability, however, a large amount of mechanical energy is dissipated as indicated by the area enclosed by the hysteresis shown in Figure 57.

The unloading behavior is almost linear with a slope close to that of the initial loading stage, and the recovery of the elastic energy is rather small. The energy absorption is thus evaluated by integrating the pressure-strain curve shown in Figure 55.
Figure 57. The force-strain relationship for a (5,5)-(10,10)-(15,15) MWCNT under compressive loading.

Figure 58. Compression of a (8,0) CNT and three (8,0) CNT clusters of different tube numbers: (a) $F$-$\delta$ curves; (b) top and side views of the deformed clusters.

When a number of CNTs are vertically aligned to form a cluster, an additional mechanism would kick in, i.e. the frictional sliding between neighboring CNTs. Considering two CNTs that are positioned sufficiently close, as the snap buckling occurs, both of them tend to bend towards a certain direction. During this process, the contacting atoms on the two CNTs are, however, subjected to relatively different displacements; thus, the atoms on one CNT would slide against the atoms on the other, and a net friction force would be generated between the sliding surfaces. The significance of this frictional sliding is twofold: first, a certain amount of energy would be dissipated directly through the atomic sliding; second, the net frictional force would pose an additional barrier against the snap buckling, thus increasing the critical
buckling load as well as the critical buckling strain. Both effects are expected to enhance the energy absorption of CNTs when forming a cluster, which will be quantitatively studied in this section.

Molecular mechanics (MM) with the COMPASS force field\(^{[185]}\) is employed to explore the structural responses of CNT clusters under compressive loading. Simulations are performed at 0 K, so as not to involve the kinetic energy term, which otherwise may largely affect the intrinsic buckling behavior of CNTs.\(^{[235-240]}\) The compressive load is applied via a flat rigid plane consisting of diamond atoms. During the simulation, this plane is aligned perpendicular to the tube (or tube cluster) and continuously moved downwards with a stepping of 0.05 Å. The effect of frictional sliding is quantified by comparing the structural responses of isolated CNTs and CNT clusters consisting of different numbers of CNTs. Considering an \(n\)-tube cluster as an example, the calculated compressive force, \(F\), is averaged by the tube number, \(n\), leading to the compressive force per tube, \(F/n\); by comparing \(F\) for the cluster and \(F\) for an isolated CNT, the clustering effect can be unveiled as a function of \(n\).

In Figure 58a, the \(F-\delta\) curve of a 7-tube (8,0) CNT cluster is compared with that of an isolated (8,0) CNT, as well as those of a 12-tube cluster and a 19-tube cluster. The buckled configurations of the clusters are shown in Figure 58b. By comparing the \(F-\delta\) curves, the aforementioned strengthening effect induced by the frictional sliding is apparent: as \(n\) increases from 1 to 19, both the critical force per tube, \(F_{cr}\), and the critical deformation, \(\delta_{cr}\), are increased by more than 100%. Since both \(F_{cr}\) and \(\delta_{cr}\) contribute to the area enclosed by the loading-unloading loop (which indicates the amount of energy absorption), by forming a cluster of 19, the energy density of CNTs is remarkably increased by three times. The resulting energy density, about 80 J/g, is very competitive among the available energy absorption materials. We envisioned that, by clustering more CNTs, the energy density can be even more improved, which makes the CNT cluster a very promising energy absorption platform that features several desirable attributes, e.g. superior energy density, full reusability, and simple composition (liquid-free), among others.
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