Science of Nanofluidics and Energy Conversion

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ABSTRACT

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The emerging subject of nanofluidics, where solids and fluids interact closely at the nanoscale, has exhibited radically different from their macroscopic counterparts (and sometimes counterintuitive), and yet relatively less explored. On the other hand, the resulting unique properties may contribute to a number of innovative functions with fascinating applications. Among various exciting potential applications, an important and ever expanding one is to provide alternative solutions to energy conversion with high efficiency, including energy absorption, actuation and harvesting.

In this dissertation, we first report a novel protection mechanism of energy capture through which an intensive impact or blast energy can be effectively mitigated based on a nonwetting liquid-nanoporous material system. The captured energy is stored in nanopores in the form of potential energy of intercalated water molecules for a while, and not necessarily converted to other forms of energy (e.g. heat). At unloading stage, the captured energy will be released gradually due to the hydrophobic inner surfaces of nanopores through the diffusion of water molecules out of nanopores, thus making this system reusable. Several key controlling factors including impacting velocity, nanopore size, nanopore structure, and liquid phase have been investigated on the capacity of energy capture. The molecular mechanism is elucidated through the study of water molecular distributions inside nanopores. These molecular dynamic (MD) findings are quantitatively verified by a parallel blast experiment on a zeolite/water system.
During the transport of confined liquid molecules, the friction resistance exerted by solid atoms of nanopores to liquid molecules will dissipate part of energy, and is highly dependent of temperature of liquid molecules and wall morphology of nanopores. Using MD simulations, the effects of temperature and wall roughness on the transport resistance of water molecules inside nanopores are investigated in Chapter 3. The effective shear stress and nominal viscosity that dominate the nanofluidic transport resistance are extracted and coupled with the nanopore size, transport rate, and liquid property. The molecular-level mechanisms are revealed through the study of the density profile and hydrogen bonding of confined liquid molecules. A parallel experiment on a nanoporous carbon-liquid system is carried out and qualitatively verifies MD findings.

Motived by the well-known thermo- and electro-capillary effect, Chapter 4 and Chapter 5 present a conceptual design of thermal and electric actuation system by adjusting the relative hydrophobicity of a liquid-nanoporous system through a thermal and electric field, respectively. The thermally and electrically dependent infiltration behaviors of liquids into nanopores are analyzed by using MD simulations. The fundamental molecular characteristics, including the density profile, contact angle, and surface tension of the confined liquid molecules, are examined to reveal underlying mechanisms. The energy density, power density, and efficiency of both thermal and electric actuation systems are explored and their variations with pore size, solid phase, and liquid phase are evaluated. Thermally and electrically controlled infiltration experiments on a zeolite-water /electrolyte solution system are performed accordingly to qualitatively validate these findings. These energy actuation systems can also become high density thermal or electric storage devices with proper designs.
Energy harvesting by the flow of a hydrochloric acid-water solution through a nanopore is explored using atomistic simulations in the last chapter. Through ion configurations near the pore wall, an averaged ion drifting velocity is determined, and the induced voltage along the axial direction is obtained as a function of key material parameters, including the applied flow rate, environmental temperature, solution concentration and nanopore size. The molecular mechanism of ion hopping and motion is revealed. This study shed light on harvesting wasted thermal and mechanical energy from ambient environmental sources such as wasted heat in power plants.

Nanofluidics is a novel and thriving research area, whose couplings with other disciplines such as material, mechanical, physical, chemical, electrical engineering are open.
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Dedicated to my family
Chapter 1 Introduction and Motivation

1.1 Challenge of Energy Conversion

Global energy consumption is expected to increase by 53% over the next 25 years according to a released 2011 annual report from US DOE's Energy Information Administration (EIA)\(^1\). On the other hand, carbon intensive fossil fuels like oil, coal and natural gas will continue to remain the largest resource of energy worldwide (on the anticipation of 79.2% in 2035), and as a consequence, the carbon dioxide (CO\(_2\)) emission which is well recognized to be a major cause of global warming closely related with the use of carbon-based fuel energies will grow by 3% in 2035\(^1\). These urgent demands for energy and environmental sustainability have been considered the world’s most paramount challenge in the 21\(^{st}\) century, in particular, the second half of the century \(^2,3\).

In principle, there are two ways to address this challenge. The first alternative is to improve energy conversion efficiency, thus reducing energy consumption rate. Taking the oil consumption as an example, it is estimated that by improving the energy efficiency of the current technique, 64 million barrels of oil equivalent per day can be cut down\(^4\). The second alternative is to explore new renewable energy sources, such as wind energy, geothermal energy, solar energy and biomass energy. This can be a long-term solution with fossil fuels eventually shifted to green energies with a lower level of greenhouse gas emissions. Both ways will require scientific breakthroughs and truly revolutionary advances.

Nanotechnology, which deals with developing and manipulating materials and structures
with at least one dimension down to 100 nm thus leading to many novel functionalities and properties, represents the most exciting achievement over the past decades. Since the elementary step of energy conversion takes place at the nanoscale, the advances in nanotechnology have demonstrated a compelling potential for meeting such urgent requirements. From a fundamental perspective, the most crucial feature of material structures down to nanoscale is a tremendous increase in specific surface areas. Such excess large specific surface areas provide an excellent platform for energy conversion through contact interactions with other materials around. Based on states of matter, there are three common types of contacts in nature: solid-solid contact, liquid-liquid contact and solid-liquid contact. For the solid-solid contact, energy and mass transports are very difficult through the pure solid. For the liquid-liquid contact, the interface is very difficult to control and the performance cannot be tuned well. Thus, the only workable platform is through the solid-liquid contact. When seamlessly combined with functional liquids, with different solid surface structures and treatments, this platform is quite flexible, and can be extremely amplified through ultra-large specific surface areas provided by nanopores, which is underpinned by the science of nanofluidics.

1.2 Opportunity of Nanofluidics for Addressing Energy Challenge

1.2.1 Brief overview of nanofluidics

Nanofluidics is defined as a scientific study of the transport behavior of fluids confined to structures of the nanometer length (1-100nm) in one or more dimensions. In such small

* Note that despite the possible role played by gas molecules in nanoenvironments, inside a restrictive small space, the number of gas molecules is several orders of magnitude smaller than that of liquid molecules. And for the very small pores considered in the thesis, a couple of gas molecules can hardly affect the more dominant liquid behavior. Therefore, the gas-liquid and gas-solid interactions are not considered in the present dissertation.
dimensions, the scale of nanostructure itself is very close to the characteristic physical scaling lengths of the fluid. Besides, when structures are scaled down to nanometre dimensions, the surface-to-volume ratio increases and surface-related phenomena will become increasingly dominant. Consequently, a number of properties of liquids confined in these nanostructures and related phenomena which are insignificant in the macroscale exhibit unusual and unique in the nanoscale. Since the “birth” of nanofluidics, it has attracted many interests and lots of progresses from theories to applications have been made. A brief review will be given in this section.

Through transmission electron microscopy (TEM), the confinement of fluids in nanochannels such as carbon nanotubes (CNTs) has been observed directly. For example, Figure 1.1 shows a TEM micrograph of a CNT prior to and after water filling by autoclave treatment carried out by Naguib et al.\(^9\), indicating that water was successfully trapped inside the CNT. Figure 1.1 also shows there was not a clear meniscus shape between the water liquid and the gas, which is unlike the situation of water liquid occupancy in tube with a consistent shape at the micro- or macro-scale. The authors further observed a random movement of water molecules and vibration at the liquid-gas interface under electron beam heating, which demonstrates a mobility of water molecules in the nanoconfinement. Several other experimental studies also confirm these anomalous behaviors\(^{10-12}\), and further provide solid evidences of water confinement in CNTs. The random and complex meniscus suggests that water molecules at the liquid-gas interface in nanoconfinements may no longer exhibit bulk behavior, and the continuum fluid theory may break down.
Figure 1.1: TEM images of a CNT: (a) An empty nanotube with an inner diameter of 2.9 nm prior to water filling and (b) After autoclave treatment, water was observed in the nanotube channels.13

The whole dynamic process of water molecules filling in a nonpolar (6, 6) CNT (0.81 nm in diameter and 1.34 nm in length) has been studied by Hummer et al14. By using molecular dynamics (MD) simulation (Figure 1.2), they found that the empty CNT could be filled up continuously by water molecules within a few tens of picoseconds. Besides, the filled state remained occupied by about five water molecules over the entire simulation time (66ns). Another important feature in Figure 1.2 is that a one-dimensionally ordered chain of water molecules was formed in the CNT, which is never seen in bulk water. The formed hydrogen bonds were almost aligned along the carbon nanotube axis, suggesting a free rotation of water molecules about the aligned hydrogen bonds. After invasion of water molecules to the nanotube, Hummer et al. also found water passed the nanotube in pulse, and the burst-like motions could be as fast as 17 water molecules per nanosecond. To study the effect of attractive interactions between the carbon wall and water molecules, Hummer et al. further simulated the water filling behavior by reducing the carbon-water interaction potential, and found distinct transitions of water occupancy between empty and filled (Figure 1.2(b)), suggesting a very sensitive filling equilibrium to water-nanotube interaction parameters. Different from burst-like water filling phenomena in a short
nanotube, Joseph and Aluru\textsuperscript{15} showed that a net water transport could be attained in a long CNT when the orientation of the water molecules was maintained. Further, Joseph and Aluru\textsuperscript{16} simulated transport of water molecules at a larger CNT diameter, (16,16)CNT, and a similar velocity enhancement over prediction was observed.

**Figure 1.2:** MD simulations of water occupancy in a (6, 6)CNT. (a),(b) Number $N$ of water molecules inside the nanotube as a function of time (a) and reduced carbon-water attractions (b); (c) Structure of the hydrogen-bonded water chain inside the nanotube\textsuperscript{14}.

In order to focus on the transport behavior of water molecules, Kalra et al.\textsuperscript{17} performed MD simulations on water transport through a packed open-ended (6, 6) CNTs membrane under an osmosis pressure gradient. An average flow rate of 5.8 water molecules per nanosecond was observed, far exceeding predictions from macroscopic hydrodynamic theories. This high flow rate of water flux driven has also been found in other nanochannels like Boron-nitride (BNNT) and polymethyl methacrylate (PMMA)\textsuperscript{18}. These MD simulations have been verified by experimental studies. For example, Majumder et al.\textsuperscript{19} fabricated aligned array of multiwalled CNTs with pore sizes of around 7 nm, and measured the water transport at an applied pressure of 0.1MPa (1 atm). They found that the flow rates could be in the range of 43859 to 77017 times higher than that predicted from Newtonian flow. Besides, when the viscosity of the liquids
increased, the flow rate did not decrease, inconsistent with predictions from continuum hydrodynamics as well. A year later in 2006, Holt et al.\textsuperscript{19} designed a similar aligned CNT membrane but with pores size less than 2 nm. A less enhancement of flow rate in the range of 560 to 8400 times was reported.

In order to understand the filling mechanism, Hummer et al.\textsuperscript{14} compared water binding energy distributions between bulk and nanoconfinement states, and found that the binding energy decreased in the invasion of water molecules into the nanopores. A lower binding energy of water molecules in nanoconfinements tightens the hydrogen-bonding network of water molecules, leading to a high filling speed. This provides explanations from thermodynamic equilibrium points of view. For the steady state water filling a long CNT simulated by Joseph and Aluru\textsuperscript{15}, they attributed the pumping mechanism to the coupling between rotational and translational motions of formed molecular chain structures. When water molecules transport through the large (16, 16) CNT, Joseph and Aluru found that there was a velocity jump of water transport in a depletion layer at the interface between the nanotube wall and the water molecules, and attributed the enhancement of transport rate to the existence of the jump\textsuperscript{16}.

These dominant factors for understanding the unique transport behavior arise from distributions of confined water molecular structures. The water configurations in different diameters of CNTs were extracted by Lu et al\textsuperscript{20}. They found that at a smaller (6,6)CNT, the water configuration behaved a single-file chain, similar with Hummer et al.’s simulations. With the increase of tube diameters to (14,14)CNT, it would eventually evolve to a single file encircled by in a multi-layered water structures. Generally, as CNT diameters increase, the effect of CNT wall tends to be small, and water molecules located at the center of tubes behave like in bulk water. Further MD simulations showed that these single-file or layered models were rarely affected by
the nanotube helicity and dominated by tube diameter\textsuperscript{21}. Another important role of influencing the transport rate of water molecules is hydrogen-bond\textsuperscript{22,23}. For example, Wang et al. \textsuperscript{21} investigated the number of hydrogen-bond (HB) per water molecule, $n_{HB}$, in CNTs. Their calculations found that the $n_{HB}$ in all CNTs was lower than that in bulk water. Theoretically, the depletion of HB in a smaller tube will allow a single water molecule to move more freely, consistent with the enhanced transport rate.

Parallel with the study of unique nanofluidic properties and physical mechanisms through MD simulations and experiments, many efforts have been devoted to advancing theory of nanofluidics. For instance, it is well known that for a macro/microchannel filled by liquids at equilibrium, capillary effects can be described well by using the Laplace-Young’s equation\textsuperscript{24}:

$$P_{in} = \frac{4\Delta \gamma}{d}$$

(1.1)

Where $P_{in}$ is the pressure jump across liquid-gas interface, and used to overcome the initial energy barrier, $\Delta \gamma$ is the excess solid-liquid interfacial tension, and $d$ is the diameter of macro/microchannel.

At the nanoscale, when the liquids invade a nanochannel, with the increase of invaded liquid volume, in addition to the initial energy barrier, Qiao et al. \textsuperscript{25} found that an additional resistance needed to overcome, referred as a column resistance. Based on MD simulations and experiments, they proposed the additional pressure, $\Delta P$, can be expressed as:

$$\Delta P = \frac{4\eta L}{d}$$

(1.2)

Where $L$ is the infiltrated length, $\eta$ is the resistance per unit lateral surface area, and $\eta L$ is the column resistance.
Thus, at the nanoscale, by combing the infiltration pressure and the additional pressure, the pressure gradient of driving liquid flow can be written as:

$$\Delta P = P_{in} + \Delta P = \frac{4(\Delta \gamma + \eta L)}{d}$$  \hspace{1cm} (1.3)

Given the revised pressure gradient (Eq. 1.3), the transport velocity of nanofined liquids can be predicted by following the conventional fluid theory.

Inspired by Majumder et al.'s measurements on slip lengths, by coupling the slip length at the liquid-nanotube wall boundary, Thomas and McGaughey have directly estimated the liquid transport velocity in CNTs, and successfully predicted its enhancement compared with that calculated from conventional Hagen-Poiseuille relation. This is different from Qiao et al.'s strategy which focused on the infiltration process, and the main essences are summarized below.

Given the pressure gradient along the axial direction of a nanotube, $\partial P / \partial z$, the radial velocity profile, $u(r)$, of a liquid flowing steadily through a tube is:

$$u(r) = \frac{d^2}{16\mu} [1 - \frac{4r^2}{d^2} + \frac{4L_s}{d}] \frac{\partial P}{\partial z}$$  \hspace{1cm} (1.4)

where $\mu$ is the viscosity of the fluid and $L_s$ is the slip length at the liquid-solid wall boundary. The slip length, which describes the velocity discontinuity between the liquid and the solid, is defined as:

$$L_s = \frac{u(r)}{du/dr} \bigg|_{r=d/2}$$  \hspace{1cm} (1.5)

The volumetric flow rate with slip, $Q_s$, is then given by

$$Q_s = \frac{\pi[(d/2)^4 + d^3L_s] \frac{\partial P}{\partial z}}{8\mu}$$  \hspace{1cm} (1.6)

Equation (1.5) is the slip modified Hagen-Poiseuille relation; the no-slip Hagen-
Poiseuille flow rate, $Q_N$, can be found by setting $L_s$ equal to zero. The flow rate enhancement, $\varepsilon$, reported by Holt et al. and Majumder et al. can be defined as the ratio of the measured flow rate to $Q_N$ (evaluated using a bulk viscosity and the CNT diameter). If the measured flow is modeled using Equation (1.5), the enhancement becomes:

$$\varepsilon = \frac{Q_s}{Q_N} = [1 + 8 \frac{L_s(d)}{d}] \frac{\mu_\infty}{\mu(d)}$$

(1.7)

$$\mu(d) = \mu_i \frac{A_i(d)}{A_i(d)} + \mu_\infty [1 - \frac{A_i(d)}{A_i(d)}]$$

(1.8)

$$L_s(d) = 30 + \frac{352}{d^3}$$

(1.9)

where $\mu_\infty$ is the viscosity of bulk water, $L_s(d)$ is the diameter dependent slip length, and $\mu(d)$ is the diameter-dependent viscosity of the water inside the CNT. $\mu_i$ and $A_i(d)$ is the viscosity and area of the interface region, and $A_i(d)$ is the total cross-sectional area. Thomas and McGaughey’s predications agree well with their MD simulations and also fit within Holt et al.’s experiments.

Thanks to the absence of enough experimental data and accurate simulation results (e.g. limited by the accurate models, force field and computational scales of time and length), there is still no a generally accepted mechanism and theory for understanding the enhancement of transport behavior of liquid in nanoconfinements for far. More experimental verifications on various liquid phases confined nanopores are needed, which is very critical not only to understand and predict properties of liquids in nanoconfinements, but also to design nanofluidic devices.
1.2.2 Concept of nanofluidic energy conversion

Many applications have been explored owning to the unique properties of nanofluidics such as selective separations of mixing reactants\textsuperscript{29,30} in chemical analysis, analytical determinations of biomolecules like proteins and DNA\textsuperscript{31,32} in biological engineering, seawater desalination and water purification in environmental engineering\textsuperscript{33,34}. One of the more promising areas of nanofluidics is its potential for energy conversion, in particular, converting abundant natural resources (e.g. mechanical, thermal and electrical energies) cleanly and efficiently into a useable form of energy. This section will introduce fundamental principles of energy conversion based on nanofluidics with emphasis on conversion among three basic forms of energy in nature, thermal energy, mechanical energy and electrical energy (Figure 1.3). For example, when mechanical energy is converted to thermal energy, usually referred as energy absorption, it has been widely used in the protection of devices and personals from foreign object damages. When thermal or electrical energy is converted to mechanical energy, usually referred as thermal or electrical actuation, it has been employed to design actuation devices. On the other hand, energy harvesting from mechanical or thermal energy to useful electrical energy will provide a solution on energy generation and environmental sustainability.

Figure 1.3: Overview of energy conversion underpinned by the science of nanofluidics. The large surface of nanopores and unique interaction behavior between liquid molecules and solids enable high performance energy conversion among mechanical, thermal, and electrical energies.
1.2.2.1 Energy absorption/dissipation

When a nanopore is treated to be a hydrophobic inner wall, only when an applied external pressure is sufficiently high, called as infiltration pressure in the present thesis, $P_{in}$, the outside liquid molecules could overcome the capillary resistance and invade into the nanopore. During the infiltration process, the external work is in part converted to the excess solid-liquid interfacial tension and in part dissipated as heat through the “friction” between liquid molecules and solid wall (Figure 1.4). Due to the hydrophobic nature of the nanoporous wall, when the environmental pressure decreases to be lower than capillary force, the liquids inside the nanopore will defiltrate. The absorbed energy during the infiltration and defiltration can be estimated by timing infiltration pressure, $P_{in}$, with the infiltrated volume of liquid, $\Delta V$, (Figure 1.4), $E = P_{in} \cdot \Delta V$. Due to the large specific surface area of nanopore (~100-1000 m$^2$/g), the energy absorption/dissipation density can be 100 J/g or more, several orders of magnitude higher than that of conventional protective materials (e.g. polymer foams: 0.1-1 J/g; metal foams: 1-3 J/g; shape memory alloys: 0.3 - 2.0 J/g). Besides, with the help of liquid, the pressure may be distributed uniformly in all directions (similar to a liquid mattress or an air bag), thus avoiding shear localization. Theoretically, when the infiltrated liquid defiltrates from the nanopore with a hydrophobic wall, the liquid can invade again once the external pressure is high enough, thus the system with integration of this nanofluidic subpart can be used repeatedly.
Figure 1.4: Energy absorption mechanism based on nanofluidics: nonwetting liquid invades a hydrophobic nanopore and the external mechanical energy converts to interfacial energy and thermal or heat energy.

1.2.2.2 Energy actuation

When thermal or electrical energy is used to drive the motion of objects, it is generally referred as an actuation, where the thermal or electrical energy is converted to mechanical energy. In the science of nanofluidics, one typical example of such an energy conversion is to drive motions of liquid molecules past a nanopore by using an external thermal or electrical energy, which is different from the strategy of directly transporting the liquids through an osmotic or hydrostatic pressure gradient\(^\text{42,43}\). Several of these systems have been designed to pump liquid molecules transport along nanopores\(^\text{44-47}\). For example, Gong et al.\(^\text{48}\) designed a molecular water pump by the combination of static charges positioned adjacent to a nanopore. Under the charges-induced electrical field, Gong et al.\(^\text{48}\) observed a spontaneous and continuous unidirectional flow through the CNT. Wong-ekkabut et al.\(^\text{49}\) argued that that flow was an artifact caused by the incorrect use of charge groups, and thought that static charges could not drive a continuous flow of water molecules through a CNT. Another research from Zuo et al.\(^\text{50}\) thought...
that the unidirectional flow of water molecules inside a CNT could not be attained when the CNT length was below 10nm, thanks to the strong interactions of water molecules between inside and outside. The effect of electrical field on transport of liquid has been well recognized, but how to precisely control the flow of liquid by using electrical fields is so far unclear.

Similar with the electrical driven-flow of liquid through nanopores, a thermal gradient is also employed. For example, Liu and Li\textsuperscript{51} designed a composite nanochannel system and showed that the fluids could be continuously driven by a symmetric temperature gradient: the fluid moves from high to low temperature in the low surface energy part, while the fluid migrates from low to high temperature in the high surface energy part.

1.2.2.3 Energy harvesting

When an electrolyte is in contact with a solid surface, the ions experience different forces from the liquid molecules and solid atoms, forming a Helmholtz ion double layer at the liquid-solid interface, which polarizes the solid surface\textsuperscript{52}. The surface charge density is a function of temperature or flow rate, the variation of which can directly harvest thermal or mechanical energy into electricity, which can be amplified by nanopores\textsuperscript{53,54}. For example, van der Heyden et al\textsuperscript{55} measured an electrical current generated by a pressure-driven liquid flow in individual rectangular silica nanochannels (Figure 1.5). They found that the streaming current was proportional to the pressure gradient and increased with the channel height. Besides, the streaming current would reverse when the sign of the surface charge changed. Later, van der Heyden et al.\textsuperscript{56} studied the effect of ion concentrations in theory and revealed that the maximum energy conversion efficiency occurred at low salt concentrations. They further estimated that an electrokinetic energy conversion device could achieve a maximum efficiency of 12% for simple monovalent ions in aqueous solution.
Figure 1.5: (a) Nanochannels are fabricated by bonding two pieces of fused silica. The top piece contains an etched nanochannel and two 1 mm diameter holes for fluid connections; (b) Side view of the nanochannel; (c) Streaming current as a function of pressure for a 140 nm high channel at low- and high-salt concentrations; (d) Schematic illustration of the origin of the streaming current.

By carefully controlling the liquid flow through carbon nanotube bundles in experiment, Ghosh et al. found a logarithmic increase of the induced voltage with the flow speed (Figure 1.6), contrary to the streaming current led by the electrokinetic mechanism. The enhanced amplitude of flow-induced voltage was reported when the liquids flowed through multiwalled-carbon nanotubes by Liu et al. Ghosh et al suggested that the dominant mechanism involved a direct forcing of the free charge carriers in the nanotubes by the fluctuating Coulombic field of the liquid flowing past the nanotubes. This mechanism is argued later, and unclear now.
Figure 1.6: Variation of voltage developed as function of velocity of water. Inset shows experimental setup where R is the reservoir, L is the valve controlling the liquid flow, S is the cylindrical glass flow chamber, and G is the voltmeter\textsuperscript{54}.

1.3 A Novel Energy Conversion Platform Based on Liquid-Nanoporous Composite Material System

1.3.1 Nanoporous materials

Nanofluidics has exhibited many unique properties and prospective potentials in applications, in particularly, in energy conversion\textsuperscript{6,8,59}. These applications are challenging the batch productions of nanochannels or nanopores so that lab demonstration units of high energy conversion efficiency can be scaled up to industrial and commercial applications, although many fabrication techniques have been developed in the past decades, such as soft lithography\textsuperscript{60,61}, surface and bulk nanomachining\textsuperscript{62}, nanoimprint lithography\textsuperscript{63}, and others\textsuperscript{64}. Alternatively, as a subset of nanostructured materials, nanoporous materials comprise all kinds of porous solids with pore sizes in the range from 0.2nm to 50nm, and a high density of pores (10\textsuperscript{9}-10\textsuperscript{12} pores/cm\textsuperscript{3}) with small variations in pore sizes can be achieved\textsuperscript{65}. Some nanoporous materials have been used industrially for a long time. Typical examples are zeolites, silica, porous alumina,
activated carbon, etc. Figure 1.7 shows the SEM graphs of zeolites and porous alumina, where many nanopores are observed on their surfaces.

Nanoporous materials are very common in biological systems and natural minerals. For example, Zeolite was discovered during rapidly heating the material stilbite in 1756, and as of 2010, over 40 naturally occurring zeolite frameworks were known. Besides, a great number of techniques have been proposed for synthesizing nanoporous materials, such as nanocasting, templating. For example, templating techniques have been developed to create activated nanoporous carbon with a uniform pore size by using silica nanoparticles. These advanced techniques have been commercialized by a very large number of companies, which not only reduces the cost of nanoporous materials greatly, but also helps their industrial applications with mass productions. More importantly, recent improvements in chemical treatments and manipulations make possible to control the pore size precisely. These advances also provide abilities to modify internal chemical characteristics of pores, like hydrophobicity, hydrophilicity, etc.

Given so many inherent advantages, in recent years, nanoporous materials have been recognized as promising candidates for multifunctional applications such as catalysis, sensor, gas storage, damage-protection, etc. Particularly, the large and sizeable interior surfaces and spaces of nanoporous materials is expected to provide an excellent platform for accepting liquid for energy conversion, discussed in the present thesis.
1.3.2 A novel liquid-nanoporous composite material system

By immersing nanoporous materials into non-wetting liquids, a liquid- nanoporous composite material system has been developed\textsuperscript{35,77-79}, shown in Figure 1.8. Thanks to ultrahigh specific surface areas of nanopores, typically in the range of 100-2000m\textsuperscript{2}/g, this system provides an ideal platform for energy conversion through surface interaction between solid nanopores and confined liquids. The pioneered experimental and multiscale numerical research on the similar system has demonstrated potentials in energy absorption\textsuperscript{80,81}: with increasing pressure, the liquid may overcome the capillary effect and infiltrate into nanopores. During this process, a large amount of energy is transformed into the solid-liquid interfacial tension and dissipated to heat energy through the friction applied by solid atoms. Besides, with an appropriate manipulation of the confined nanofluids inside the nanopores, the stored interfacial energy can also be released as a significant mechanical output/strain, making the system thermally or electrically controllable.
actuation capabilities.

1.3.3 Current research progress in nanofluidic energy conversion

Zhao\textsuperscript{82} investigated the energy dissipation by monitoring the temperature variation of the confined liquid - solid system in experiment. The experimental apparatus is shown in Figure 1.8. In his system, the nanoporous ZSM-5 zeolite was used and treated after series of chemical procedures so as to obtain hydrophobic inner wall surfaces of nanopores. The average pore size was 0.81nm around and the specific pore volume was 280mm\textsuperscript{3}/g. 3.0g of surface treated ZSM-5 zeolite was immersed into 5.0g of sodium chloride (NaCl) solution and the nanopore-liquid mixture was placed into a stainless steel cylinder. On the bottom of the cylinder, a piston was employed to compress the mixture and driven by a servo motor. The displacement of piston was recorded through a linear voltage differential transformer (LVDT). In order to monitor pressure and temperature variation of the mixture, a pressure transducer and thermal couple were employed to directly connect the mixture through a modified Tee connector.

Figure 1.9 shows a typical infiltration and defiltration isotherm curves under the loading rate of 0.2mm/min. As the pressure gradually increased, the liquid infiltrated into nanopores after the capillary resistance was overcome, leading to a decrease in the system volume. At the unloading stage, the infiltrated liquid molecules diffused out due to the hydrophobic nature of nanopores. During the whole process, a hysteresis was left and the enclosed area was the total absorbed energy by the nanopore-liquid system, which is on the order of infiltration pressure (or activation pressure) multiplied by the volume reduction, \(\approx 100\text{J/g}\), several orders of magnitude higher than conventional energy absorption materials. Further, when the second and third loadings were applied on this system, a good repeated the above stage was obtained,
demonstrating that the present nanopore-liquid system would work well under cyclic loadings and could be reused.

At the same time, Zhao also examined the variation of temperature (Figure 1.10). A monotonous increase was observed in the first three cycles, suggesting a heat generation during infiltration and deflation. The increase of temperature was expected from the transport of liquid past the nanopores through which parts of external mechanical energy was converted to heat energy and dissipated due to the “friction” slip of liquid molecules imposed by solid wall atoms, which implies an importance of transport resistance dependence of energy dissipation in the nanopore-liquid system.

![Image: Schematic setup of the Pressure-Volume Controller (PVC) fabricated in stainless steel that was used as the apparatus for the experiment on liquid-nanoporous material systems](image)

**Figure 1.8:** Schematic setup of the Pressure-Volume Controller (PVC) fabricated in stainless steel that was used as the apparatus for the experiment on liquid-nanoporous material systems.82
Figure 1.9: Graph of loading and unloading sorption isotherms expressed in normal (black solid line) and log scale (red solid line). Also included on this graph are the 2nd and 3rd periods of a cyclic loading test.  

Figure 1.10: Temperature variations during the first three cycles (for a system with a liquid that was saturated NaCl and a loading rate of 0.2 mm/min), including the raw measurements from the thermocouple and the pressure-dependency-corrected net increment. The blue and orange dash dot lines serve as dividing markers for the loading and unloading stages. The dash lines (in black and grey colors) indicate the general trend of temperature increments.
Likewise, the enormous specific surface area of nanoporous materials also amplifies the mechanoelectric and thermoelectric effects, even allowing a properly designed nanoporous system to simultaneously harvest electricity from ambient mechanical and thermal energies. For example, Qiao et al.\textsuperscript{83} designed a system consisting of nanoporous monel immersed into a 20 wt\% aqueous solution of NaCl (Figure 1.11). In their system, the nanopore diameter was around 460 nm, and the total pore surface area of each cylinder was 6.7 m\textsuperscript{2}. A counter electrode was placed 10-50 mm away from the monel cylinder. The monel cylinder and the counter electrode were connected by nichrome wires through a 1 Ω resistor, \( R_0 \), across which the potential difference was measured. The nanoporous monel cylinder was connected to the cathode of the DA board, and the counter electrode was connected to the anode. Figure 1.11(b) shows a typical measured result, and a significant output voltage was generated when the pump was turned on to allow electrolyte solution to flow through the nanoporous electrode. Besides, the generated voltage increases rapidly to \( \sim 68 \text{ mV} \) and is stabilized, independent of the flow rate.

**Figure 1.11:** (a) Schematic of the experimental setup; (b) A typical measurement result of the output voltage. The external resistance, \( R_0 \), is 1 Ω\textsuperscript{83}.

Inspired by Qiao et al.’s experiment, Liu\textsuperscript{84} investigated distribution of ions and atoms for NaCl solution confined a CNT through MD simulations, and calculated the net voltage output.
The MD model and results are shown in Figure 1.12. It can be seen that the ions and atoms exhibited a radial layer structural distribution near the interface between liquid and CNT wall. From the time averaged radial number density distribution of Na\(^+\) and Cl\(^-\) ions, and hydrogen and oxygen atoms, the charge density distribution could be computed. And then, the potential difference between the solid phase and liquid phase could be derived by solving the Poisson’s equation. The calculation shows that voltage between the central position of nanopore and wall could be as high as \(\sim 18\text{mV}\), which is on the same order of magnitude with that of Qiao’s experiment.

**Figure 1.12:** (a) MD model of an electrolyte solution confined in a nanopore; (b) Radial number density distributions of ions and atoms; (c) Radial distributions of net charge and deduced electrical potential.

1.4 Innovation of Present Research

Previous preliminary works have scratched the surface of the profound topic of nanofluidic energy conversion. Nevertheless, the detailed molecular mechanisms are lacking and the versatility of the platform needs to be expanded. For example, in the energy absorption system, the loading is quasistatic or low-rate, yet the perspective upon a high-rate loading like impacting or blast wave is unclear so far and the exploration may lead to new science of energy.
conversion. For another example, the interaction among liquid molecules and ions in nanorestrictive environments may bring about strong size effect which closely couples with other effects like temperature and electric field. The full explorations of which may provide useful guidelines for designing nanofluidic energy conversion devices.

1.4.1 A novel energy absorption mechanism of energy capture

Compared with a static loading shown in section 1.3.2, when the protection layer is subjected to a high impacting velocity such as high speed impacting and blast wave energy, if the energy-carrying medium can be “trapped”, and the wave energy cannot be transmitted out immediately, it will be effectively “captured”. Different from an energy dissipation process, the captured wave energy is not necessarily converted to other forms of energy, e.g. heat, and can be simply stored and isolated from the usual energy transmission path. Thus, the pressure that the target would receive would be much lowered with elongated duration and the target is protected, as illustrated in Figure 1.13. To achieve high energy capture (EC) efficiency, not only the energy-carrying medium needs to be confined, but also the energy should not go through the walls of the confinement. The EC capacity is expected to be estimated as $E = P \cdot V_r$, not $P_w \cdot V_r$. That is, the EC system can work at a low working pressure ($P_w$) and capture a high-pressure (P) wave.

![Figure 1.13](image)

**Figure 1.13:** Schematic of the expected protection mechanism to high speed impacting waves based on a nanopore-liquid composite system.
1.4.2 A concept of nanofluidic thermo- and electro-actuation

When a liquid droplet rests on top of the substrate, its geometry will change with wetting state on the substrate, usually characterized by contact angle and interfacial tension. With an external thermal or electrical field, the variation in interfacial energy renders the contact interface relatively more hydrophobic or hydrophilic, changing morphology of the liquid droplet. Hopefully, when hydrophobic nanoporous particles are suspended in a non-wetting liquid, the variation of the effective wetting properties with temperature may trigger a net motion of the liquid molecules into or out of the nanopores, illustrated in Figure 1.14. For example, if a monotonic temperature change can cause the liquid to spontaneously fill a nanoporous material, part of the thermal energy may be stored as the excessive solid-liquid interfacial tension; under a thermal cycle, the volume of the system may change back and forth and output mechanical work, and such a thermo-actuation system works like a thermal machine with high efficiency. Likewise, the solid-liquid interfacial tension is also a function of electric field, driving the liquid into and out of the nanopores.

Based on these principles, we design a nanofluidic thermo-and electro-actuation with high efficiency. That is, in the infiltration process, part of the thermal or electrical energy is effectively stored as the excess solid-liquid interfacial energy, and in the defiltration process with appropriate manipulation of the confined liquids, the stored interfacial energy can be released as a significant mechanical output/strain, making the system actuatatable.
1.4.3 Energy harvesting from thermal and mechanical energy

In a nanoconfinement, since most liquid molecules and ions belong to the “boundary layer”, their interaction with the solid atoms nearest the nanotube wall can be described by a frictional stick-slip and barrier-hopping model (illustrated in Figure 1.15) \(^{89}\). When a pressure gradient is applied, the hopping and moving velocity of ions along the flow direction is proportional to the induced flow velocity of liquid. Given the lateral velocity of ions, one can obtain the voltage along the flowing direction. This model has been used to understand the logarithmic variation of the generated voltage with the flowing rate measured by Ghosh et al. More importantly, the distribution of ions and molecules is a function of temperature or flow rate, the variation of which can directly harvest thermal or mechanical energy into electricity\(^{53,54}\). In the last chapter of this thesis, we will explore its temperature dependence of voltage generation induced by the liquid flow with flow velocity coupled, and thus demonstrate a possibility to harvest mechanical energy and thermal energy simultaneously to electrical energy.
1.5 Methodology

In nanoenvironments, the classical continuum fluid mechanics theory breaks down because the walls become more dominant and only fewer molecules are contained in fluids. Besides, experiments are very costly and many important questions remain puzzled\textsuperscript{90-92}. Numerical simulation may provide an alternative approach that could help to circumvent these problems. Molecular Dynamics (MD) simulation is the most common method for the study of nanofluidics because of relative high accuracy, low computational cost, etc.\textsuperscript{93-96}. In this section, the MD theory and application in nanofluidics will be viewed in brief.

1.5.1 MD theory

The MD technique was introduced by Alder and Wainwright\textsuperscript{97} and has been rapidly developed since then\textsuperscript{98,99}. It is a computer simulation of physical movements of atoms and molecules by describing the force interaction among atoms and molecules. The force interaction determines the motion of atoms and molecules through the classical mechanics (i.e. Newton’s second law), and is often called force field. According to the Newtonian equations of motion, in classical MD simulations the motion of atoms can be described via:
\[ m_i \frac{d^2 \mathbf{r}_i}{dt^2} = -\sum_{j=1, j \neq i}^{N} \frac{\partial U_{ \text{total} }^{i,j}}{\partial \mathbf{r}_i}, \quad i, 2, 3, \ldots, N \]  

(1.10)

where \( m_i \) is the mass of atom \( i \), \( \mathbf{r}_i \) is its position, and \( U_{\text{total}} \) is the total potential energy that depends on all atomic positions. The potential energy is the most crucial part in simulation, and must faithfully represent the interaction between atoms. Conceptually, the interaction potential is divided into \textit{intramolecular} and \textit{intermolecular} atomic contributions\(^{100}\). The former reflects interactions among nonbonded systems, and the latter describes pair terms between distant atoms. These contributions are presented in almost all force fields, overviewed below on the most common potential energy contributions.

### 1.5.1.1 Intramolecular terms

The intramolecular potential energy contains three terms in MD software LAMMPS which is employed throughout present simulations, and is expressed as\(^{101}\).

\[
U_{\text{intramolecular}} = U_{\text{stretch}} + U_{\text{angle}} + U_{\text{dihedral}}
\]  

(1.11)

\( U_{\text{stretch}} \) represents the potential energy required to stretch or compress each covalent bond in the system, and depends on the bond length and bond strength. When the bond is stretched from its equilibrium length \( r_0 \) to the new length \( r \) with bond force constant \( k_{\text{bond}} \), the required energy for the most popular Morse is written:

\[
U_{\text{stretch}} = k_{\text{bond}} \left[ 1 - e^{-\alpha(r-r_0)} \right]^2
\]  

(1.12)

\( U_{\text{angle}} \) represents the potential energy associated with the change of bond angle. When the angle \( \theta \) between two covalent bonds changes with respect to its equilibrium angle \( \theta_0 \) with angle force constant \( k_{\text{angle}} \), the required energy for cosine angle bending potential is expressed:
\[ U_{\text{angle}} = k_{\text{angle}} (1 + \cos \theta_0) \]  

(1.13)

\( U_{\text{dihedral}} \) describes the potential energy that deforms a planar group of atoms with at least three covalent bonds from its equilibrium angle \( \phi_0 \). The required energy for 2-fold torsion potential is written:

\[ U_{\text{dihedral}} = k_{\text{dihedral}} [1 - \cos(2\phi)] \]  

(1.14)

Usually, these potential parameters are determined from quantum chemistry calculations on small molecules and model molecules that represent pieces of larger molecules\(^{100}\).

### 1.5.1.2 Intermolecular term

Intermolecular term reflects attraction or repulsion interactions between pairwise additive potentials among atoms, molecules or ions. The deduced forces are weak compared to the intramolecular forces. In MD simulations, intermolecular potential energy generally includes contributions from van der Waals and electrostatics terms. The van der Waals term is usually modeled through the most popular 12-6 Lennard-Jones (L-J) potential for simplicity\(^{102}\):

\[ U_{\text{vdW}} (r_{ij}) = 4\varepsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{6} \right] \]  

(1.15)

where \( \varepsilon_{ij} \) is the depth of the potential well, \( \sigma_{ij} \) is the distance at which the potential is zero, and \( i \) and \( j \) denote the i-th and j-th atomic species, respectively. In this equation, there are only two adjustable parameters \( \sigma_{ij} \) and \( \varepsilon_{ij} \), which are usually obtained through experimental data fittings or theoretical considerations. For an unknown pair of atom species, the Lorentz-Berthelot mixing rules is widely employed to obtain the interaction parameters from the interaction parameters of the individual atom species\(^{103}\):
\[ \varepsilon_{ij} = \sqrt{\varepsilon_i \varepsilon_j}, \quad \sigma_{ij} = \frac{1}{2}(\sigma_i + \sigma_j) \]  

(1.16)

The electrostatic term often follows the well-known Coulomb law:

\[ U_{\text{coulomb}}(r_{ij}) = \frac{q_i q_j}{4\pi \varepsilon_0 r_{ij}} \]  

(1.17)

where \( q_i \) and \( q_j \) are the electrostatic charges of atom \( i \) and \( j \) respectively, and \( r_{ij} \) is the distance between them, and \( \varepsilon_0 \) is the dielectric constant of vacuum.

Since there is a fast decay of the L-J potential, a truncation beyond a certain cutoff radius is usually needed. Typical cutoff values are \( 1.5\sigma_{ij} \) for purely repulsive interactions, and \( 2.5\sigma_{ij} \) up to \( 10\sigma_{ij} \) for homogeneous and inhomogeneous systems, respectively\(^{104}\). Compared with the L-J potential, the decay of the electrostatic potential is not so sharp, but it can lead to certain problems especially when periodic boundary conditions are employed. In order to tackle this problem, specific summation techniques such as the particle-particle particle-mesh (PPPM) solver\(^{105}\) have been developed over the years and used in the present simulations.

### 1.5.2 Water molecules and carbon nanotubes (CNTs)

#### 1.5.2.1 Water model

Water is the most common solvent in nature and also crucial in biological reactions. Many different water models have been developed for MD simulations in the past few decades. These models can be categorized to three-site model (e.g. SPC, SPC/E, TIP3P) and four-site model (e.g. TIP4P, TTM2-F)\(^{100}\), but there is no accepted model which can reproduce all basic properties of water such as diffusion coefficient and viscosity. Today’s most popular model is a rather simple three-site model, SPC/E model, which is a slight reparameterisation of the SPC
model of water with a modified value for charge on oxygen\textsuperscript{106,107}. In this model, water molecule is modeled as a rigid isosceles triangle with a certain mass and charge for each atom and carries a single L-J site on the oxygen atoms. The configuration is kept fixed by rigid bond O-H bonds with the length of 1.0 Å and constrained H-O-H angle of 109.47°. The charges on the oxygen site and the hydrogen sites were chosen -0.8476 \textit{e} and +0.4238 \textit{e}, respectively\textsuperscript{108}.

\subsection*{1.5.2.2 Carbon nanotubes (CNTs)}

Carbon nanotubes (CNTs) are synthetic channels which can be formed simply through a nanosized rolled-up graphene sheet\textsuperscript{109}. By now, CNTs have firmly established itself as the iconic molecule of nanoscience due to a nanometer size range comparable to many biological channels, and offer the key platform to a world of nanometer size pores, which allows exploring the unique properties of nanofluidics, and manipulating the molecules\textsuperscript{27,100}.

Several potentials have been developed recently for CNTs. This is mainly motivated by the properties of novel carbon structures as fullerenes and CNTs. Table 1.1 lists the typical parameters based on a Morse bond, a harmonic cosine angle, and a 2-fold torsion potential\textsuperscript{110}. Often, carbon structures such as CNTs are not simulated in full detail. For example, in order to reduce computational cost, CNTs are modeled to be rigid and the intramolecular degrees of freedom are removed. In addition, some calculations show that the carbon-carbon bond deformations are small (on the order of magnitude 0.01 Å) and insensitive to the flexibility of CTNs in water. Since certain water properties (e.g. density, and hydrogen bond) are rarely dependent of flexibility of CNTs, CNTs are usually assumed rigid\textsuperscript{100}.
Table 1.1: Parameters for the carbon-carbon interaction potentials for a Morse bond, a harmonic cosine angle, and a 2-fold torsion potential\textsuperscript{110}

<table>
<thead>
<tr>
<th>Potential</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_{\text{bond}}$</td>
<td>114.46 Kcal Å(^2)/mol</td>
</tr>
<tr>
<td>$r_0$</td>
<td>1.1418 Å</td>
</tr>
<tr>
<td>$k_{\text{angle}}$</td>
<td>134.369 Kcal/mol</td>
</tr>
<tr>
<td>$\theta_0$</td>
<td>120°</td>
</tr>
<tr>
<td>$k_{\text{dihedral}}$</td>
<td>6 Kcal/mol</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>2.1867 Å(^{-1})</td>
</tr>
<tr>
<td>$\epsilon_{\text{C-C}}$</td>
<td>0.105 Kcal/mol</td>
</tr>
<tr>
<td>$\sigma_{\text{C-C}}$</td>
<td>3.851 Å</td>
</tr>
</tbody>
</table>

1.5.2.3 CNTs-water interaction

Traditionally, since the each carbon atom in model of pristine CNTs is neutral, Coulombic interactions are usually omitted for CNT-water interaction. In addition, the van der Waals interactions between hydrogen atoms in water molecules and carbon atom is not insignificant in the role of water-CNTs interactions, and thus a single L-J contribution between every carbon and oxygen atom for modeling the interactions between CNTs and water molecules is often employed in MD simulations\textsuperscript{111}. The parameters for these interaction potentials are either obtained directly from experimental fittings and quantum chemical simulations\textsuperscript{112,113} or calculated indirectly from other known interaction potentials by using Lorentz-Berthelot mixing rules (Eq. 1.16).

1.6 Outline of Dissertation

Nanofluidics is opening promising doors for either improving efficiencies of existing energy conversion or exploring new strategies of harvesting energy with the help of its unique phenomena. Through the present thesis, the fundamental mechanism of nanofluidics in energy conversion including energy absorption/capture/dissipation, actuation and harvesting is investigated. The thesis consists of six chapters:

In Chapter 1, an introduction of energy challenge in the next few decades, solutions underpinned by the science of nanofluidics and motivations of the present study are provided. A
brief overview is given to the science of nanofluidics and applications in energy conversion, from unique nanofluidic phenomena, mechanism, and commonly used methods of nanofludic study.

In Chapter 2, through numerical simulations and experiments, a proof-of-concept dramatically new protection mechanism of energy capture to the impact and blast energy wave is explored based on the nonwetting liquids-nanoporous material system. Several key factors such as impacting velocity, nanopore size, solid phase of nanopore, and confined liquid phase have been investigated on the capacity of trapping energy, and the molecular mechanism is also elucidated.

In Chapter 3, by using molecular dynamics simulations, the thermally responsive transport resistance of liquids in model CNTs is explored as a function of nanopore size, transport rate, and liquid property by employing the effective shear stress and nominal viscosity. Further, the effect of wall roughness on the transport resistance is investigated. The molecular-level mechanisms are revealed through the study of density profile and hydrogen bond of confined liquid molecules.

In Chapter 4, a conceptual design of a thermally controlled actuation system is proposed and realized by adjusting the relative hydrophobicity of a nanoporous material-liquid system. When the variation of wettability is amplified by the large surface area of nanopores, a mechanical work can output. The energy density, power density, and efficiency are explored and their variations with pore size, solid phase, and liquid phase are explored.

In Chapter 5, following the similar strategy in Chapter 4, we propose an electric-to-mechanical energy conversion system enabled by nanofluids. The infiltration and defiltration barriers of liquids flowing into and out of nanopores are related with the applied external electric
intensity, which is employed to control the actuation system. The working principle of the thermally responsive interfacial tension-driven actuation system is explored using MD simulations and experiments. High power density, energy density, and efficiency are demonstrated.

In Chapter 6, a liquid flow-induced voltage by flowing hydrochloric acid (HCl) water solution through nanopores is presented using MD simulations, and the molecular mechanism of ion hopping and motion is elucidated. The voltage dependence on flowing velocity, environmental temperature, pore size, and concentration of HCl solution is studied and sheds light on the design of high efficiency energy harvesting nanodevices.

For each and every nanofluidic energy conversion function we study in the thesis (chapters 2-6), a synergy is pursued among modeling, simulation and experiment. First, a molecular model is established which could reflect the most essential conceptual working mechanism of the system under investigation. By varying key material and system parameters of the model, systematic all-atomic simulations based on MD are carried out to explore the functional outputs, as well as the effects and coupling among the variables. Upon clarification of the basic working mechanism of the energy conversion function, proof-of-concept experiments are performed through collaboration (with Professor Yu Qiao at the University of California-San Diego). The experiment not only proves the fundamental working mechanism, but it also provides critical parameters that are needed in modeling and simulation, and helps to improve the modeling effort. In turn, modeling could provide useful guidelines for experimental design and system optimization, which will eventually lead to the development of the high-performance energy devices. We also expect that, by integrating the various functionalities of the liquid/nanopore system, the multifunctional energy conversion can be realized for next-
In Chapter 7, the main findings are summarized, and the future work is discussed.
Chapter 2 Mechanical to Thermal Energy Conversion: Nanofluidic Energy Capture

2.1 Background

Conventional energy absorption materials, such as foams and honeycombs, dissipate energy through cell buckling and extensive plastic deformation\textsuperscript{114}. Recent improvements, including material selection and cell geometry optimization, are toward the goal of enhancing their capabilities for mitigating blast or impacting waves\textsuperscript{115-119}. For instance, Hutchinson et al. studied the buckling mechanism of sandwich plates of different cell structures\textsuperscript{120,121}. Tilbrook et al. developed an analytical model to elucidate the impulsive response of sandwich beams,\textsuperscript{122} and found that an overlap in time scale could enhance shock resistance. Evans et al. proposed that the energy absorption capability can be enhanced by using a hollow micro-lattice\textsuperscript{123}. Nevertheless, upon a high-speed impact loading or blast wave, due to the short timeframe and highly localized damage (e.g. shear localization and local softening), the failure stress may be quite low\textsuperscript{124} which significantly reduces the overall protection capacity\textsuperscript{125,126}, the system response may be quite slow and insufficient for blast/impact mitigation\textsuperscript{127,128}, and the system may not be used repeatedly after cell buckling or fracture.

Recently, nanoporous materials have become attractive for high-performance energy dissipation,\textsuperscript{129-131} in part because the nano-sized cells are smaller than shear band (thus cell collapse and condensation would provide a local hardening mechanism, instead of local softening) and have faster response time. Han et al. found that the energy dissipation density of a nanoporous silica was on the order of 300 J/g.\textsuperscript{132} Kazemi-Kamyab et al. carried out impact
experiments on nanoporous aluminum with various porosities\textsuperscript{133}, and argued that that energy absorption and stress attenuation depend on the porosity, pore structure, as well as the interaction between pore gas flow and solid wall. Moreover, when nanoporous materials are immersed in a non-wetting liquid, the pressure-induced infiltration process can convert part of the external mechanical work to solid-liquid interfacial tension, further enhancing energy absorption (with a density that exceeds 100 J/g).\textsuperscript{35,134,135} The process is reversible (such that the system may be used repeatedly), and the liquid phase helps to reduce localized damage, which achieves high energy density.\textsuperscript{41,136,137}

A major dilemma of the preceding energy absorption or dissipation mechanisms is the intrinsic conflict between the required high energy density (on mass or volumetric basis) and the desired low working pressure (for safety and comfort). That is, the total absorbed energy can be estimated (on the zero order) as $E = PV$, where $P$ is the pressure under which the energy mitigation mechanism works (e.g. for buckling, plastic deformation, or liquid infiltration, etc.) and $V$ is the associated system volume reduction. To achieve a high energy density ($E$ per mass or volume), $P$ must be as high as possible; but such a system becomes “hard”, not only uncomfortable, but also unsafe if $P$ exceeds the safety threshold of the personnel/devices to be protected (the pressure of the transmitted wave can never be lower than the working pressure, $P$). In order to solve this dilemma, novel energy mitigation mechanism that has at least one more degree of freedom needs to be discovered.

In this chapter, we report the novel nanofluidic energy capture (NEC) mechanism. We take advantage of the confined nanopore volumes and their large surface areas such that, upon a pressure wave loading, a non-wetting liquid phase can infiltrate into the nanopores to reduce the overall system volume, and the small ligament length and large impedance mismatch enables the
energy capture effect, where a significant portion of the incoming kinetic energy is temporarily trapped as the potential energy of invaded liquid molecules in nanopores. Furthermore, the surface area and confinement helps to “lock” the confined wave energy, weakening the incoming energy and leading to an unprecedented performance of impact/blast energy mitigation (which is also reusable). These will be demonstrated through atomistic simulations and experiments below.

2.2 Description of NEC Mechanism

The liquid-solid interfacial interaction is prominent at the nanoscale\textsuperscript{16,90,138}, which enables many unique nanofluidic behaviors (e.g. enhanced transport\textsuperscript{14,19}, strong size-dependence\textsuperscript{139}, etc.) and underpins novel devices such as the nanofluidic thermal machine\textsuperscript{45}, nanofluidic pump\textsuperscript{51}, nanofluidic energy harvester\textsuperscript{140}, etc. However, the intriguing nanofluidic intercalation behavior upon strong dynamic loading remains less explored.

With reference to the schematic Figure 2.1, a nanoporous material is immersed in a non-wetting liquid and the pores are empty initially. As an external wave pressure is applied on the system, when the pressure exceeds a threshold ($P_i$), the liquid molecules/ions can overcome the capillary resistance and rapidly infiltrate into the nanopores. The intercalated liquid phase carries the wave energy, and unlike in large pores, the confined energy may not transmit out through the nanopore walls and is effectively “captured” inside in the form of potential energy of the invaded molecules. This “nanofluidic energy capture” effect should be attributed to the nearly incompressible nanopore walls and the large impedance mismatch across the solid-liquid interface. The characteristic time of the pressure induced infiltration is around nanosecond, which also ensures a fast response of the system with respect to intense stress wave loading. Upon unloading, the confined liquid diffuses out of nanopores (at a much slower rate as compared to the infiltration rate) so that the captured energy is released slowly. Thus, the process
not only significantly reduces the peak load, but also elongates the impulse duration, and the system is fully reusable. This mechanism is therefore distinct from the impulse confinement phenomenon observed in granular materials.\textsuperscript{141,142}

The “captured” energy in the NEC process can be estimated as $E = P_w V_p$, where $P_w$ is the wave pressure and $V_p$ is the nanopore volume (typically 40-80\% in nanoporous materials). Thus, the more intense the wave is (i.e. the higher the $P_w$ is), the higher the wave mitigation efficiency would be. Meanwhile, the NEC activation/working pressure ($P_i$), i.e. the pressure at which the liquid intercalation takes place, is determined by the capillary effect (effective surface and interface energies) and is independent of $P_w$. That is, such a NEC system can capture high-pressure ($P_w$) wave energy at a low threshold pressure ($P_i$), attractive to mitigating intense stress waves. In what follows, atomistic simulations and parallel experiments are carried out to quantitatively understand the NEC mechanism.

\textbf{Figure 2.1:} Schematic of the nanofluidic energy capture (NEC) mechanism. Upon a blast or impact stress wave, the solvent molecules and solvated ions become highly compacted as they intercalate into the nanopores. The invaded molecules/ions rearrange themselves in a relatively ordered configuration while retaining high wave/potential energy. Within a short time frame, a large amount of impact/blast energy can be transferred into the potential energy of the confined liquid, leading to a substantial mitigation of the impact/blast stress wave.
2.3 Atomistic Simulation of NEC and Mechanism

2.3.1 Model and computational method

Figure 2.2 shows the computational cell which is developed on the basis of Figure 2.1. A carbon nanotube (CNT) is employed to model a smooth nanopore structure with length of $L_0$ and diameter of $D$. Its left end is open and immersed in a water reservoir; the initial density of water inside the reservoir is close to that of bulk water, $\rho_0 = 998.0 \text{ kg/m}^3$. The reservoir is bounded by two rigid carbon planes: the right one is attached to the nanochannel, and the left one is being impacted by a foreign object. The impactor is also modeled by a rigid mass and it collides the reservoir with a given initial velocity, generating a pressure wave traveling from left to right – if $P_w$ exceeds $P_i$, water infiltration would occur. The whole system would move to the right, and will hit a receiver (a rigid carbon plane that is fixed in space). Afterwards, the system may bounce back (and the impactor may detach from the reservoir). The force history transmitted to the receiver is recorded throughout the process, from which the transmitted impulse characteristics are obtained. Periodical boundary condition is imposed on the four lateral planes of the computational cell, mimicking an array of nanopores like that in a nanoporous material (Figure 2.1). For comparison, a reference system is also setup with almost identical characteristics, except that the left end of CNT is closed and water infiltration cannot occur.

The 12-6 Lennard-Jones (L-J) empirical force field and a Coulomb potential is used to describe the intermolecular potential between atoms:

$$U(r_{ij}) = 4\varepsilon[(\sigma/r_{ij})^{12} - (\sigma/r_{ij})^{6}] + q_iq_j/4\pi\varepsilon_0r_{ij}$$ \hspace{1cm} (2.1)

where $r_{ij}$ denotes the distance between atom $i$ and $j$, $\sigma$ and $\varepsilon$ are the energy and length parameters, respectively. $q_i$ and $q_j$ are the partial charge assigned to atom $i$ and $j$, respectively,
and $\varepsilon_0$ is the dielectric constant. The PPPM (Particle-Particle Particle-mesh) technique with a root mean square accuracy of $10^{-4}$ is employed to handle the long range Coulomb interactions among water molecules. The L-J interactions are truncated at a cutoff distance of 1Å suggested by Andrea et al.$^{143}$ The water model is the rigid extended simple point charge model (SPC/E)$^{106}$. It consists of a Coulomb potential acting between partial point charges on the oxygen (-0.8476e) and hydrogen atoms (+0.4238e) and an oxygen-oxygen L-J interaction with $\sigma = 3.166$ Å and $\varepsilon = 0.6502$KJ/mol. The CNT is assumed to be rigid since its flexibility has a minor influence on the water infiltration process$^{144}$, and that could also simulate a real “stiff” nanoporous material whose nanopore wall can effectively block lateral energy transmission. The carbon-water interaction is described by the L-J potential between carbon and oxygen atoms, with relevant parameters obtained from the experimental low-coverage isotherm data of oxygen adsorption on graphite which ensures the hydrophobicity of CNT$^{145}$.

Molecular dynamics (MD) program LAMMPS (large-scale atomic/molecular massively parallel simulator) is employed to carry out the numerical simulations$^{146}$. After initialization, the system is equilibrated for 100ps to minimize system energy with NVT ensemble at ambient condition. At this moment, the water molecules are outside the CNT due to hydrophobicity. During the subsequent impact process, the NVE ensemble is employed and the history of the transmitted force, $F$, as well as the number of intercalated water molecules, are obtained every 2.5 ps (the simulation time step is 0.5 fs).
**Figure 2.2:** The MD computational cell. This cell consists of an impactor, piston, water reservoir, boundary plane of reservoir, nanopore, and receiver (from left to right). The impactor is rigid to mimic a foreign impact loading or shocks parallel with the axial direction of the nanopore with a velocity of $v$; the movable piston is modeled by a rigid plane; the left open-end of the nanopore is inserted into the reservoir and is tied with the right rigid boundary plane of the reservoir, and the right end of the nanopore is closed; The receiver is fixed throughout the MD simulation and is used to deduce the transmitted force through the nanopore/water system. Periodical boundary condition is imposed to the four lateral planes of the cell.

### 2.3.2 Fundamental behavior of CNT/water system under an impact loading

Taking a representative system consisting of a (16,16) CNT ($D=2.17\text{nm}$ and $L_0=9.84\text{nm}$) whose opening is immersed in a reservoir with 1568 water molecules, we first investigate the response of water molecules under an impacting velocity of 50 m/s. The snap shots from MD simulations are given in Figure 2.3 (note that the system is rotated $90^\circ$ with respect to Figure 2.2 for presentation purposes). Right after the impact, the system (CNT and reservoir) starts to move toward the receiver, and the pressure in the reservoir builds up simultaneously. When the pressure wave arrives at the entrance of nanopore, the capillary resistance is overcome, and the highly compressed water molecules begin to invade the CNT and move toward the end of the CNT, weakening the impacting energy, as well as the magnitude and rate of transmitted force; during this process, part of the incoming kinetic energy is converted to the potential energy of the
intercalated water molecules. Owing to the confinement of the wall and pushing of the pressure wave, the infiltrated water molecules retain the highly compressed form until the pore is filled up. After the impactor bounces back, the pressure inside the water reservoir is reduced, and the transmitted force, $F$, begins to decrease; meanwhile, the confined water molecules recede due to the non-wetting surface of CNT, making the system fully reusable for repeated impact/blast loading.

Figure 2.4 (a) gives the history of transmitted force, which increases with infiltration, and it peaks at almost the same time when the CNT is filled with compacted water molecules, and then it decreases at a slower rate upon unloading. Comparing with the reference system, the peak load arrives later and the overall impulse time is longer, and the force reduction is prominent. In what follows, we explore the effect of impacting velocity and nanopore geometry, followed by a molecular mechanism analysis.
Figure 2.3: Snapshots of invasion and defiltration of water molecules into and out of the (16, 16) CNT and configurations inside during the whole impacting process. All water molecules are included in side views; while only water molecules inside CNTs are given in top views so as to highlight a clear layer structure. The diameter (D) and length (L₀) of the CNT are 2.17nm and 9.84nm, respectively; the impacting velocity (v) is 50m/s.
Figure 2.4: The history of transmitted force under impacting velocity ($v$) of (a) $v=50$ m/s and (b) $v=30$ m/s. In the reference system, water molecules are not allowed to flow into nanopore throughout simulations. The CNT size: $D=2.17$ nm, $L_0=9.84$ nm. $\tau$ is the ratio of impacting duration on the nanofluidic energy capture system ($\tau_{NEC}$) to the reference system ($\tau_{Ref}$).

2.3.3 Characteristics of NEC: effect of impact velocity ($v$)

2.3.3.1 Reduction of transmitted force and impulse energy

For the same the CNT/water system employed above, Figures 2.4(a) and (b) present the transmitted force (on the receiver) under $v = 50$ m/s and 30 m/s, respectively. Define the dimensionless reduction of the peak transmitted force as $\Delta F = \frac{F'_{\text{max}} - F_{\text{max}}}{F_{\text{max}}} \times 100\%$, where $F'_{\text{max}}$ and $F_{\text{max}}$ are the maximum transmitted force in the NEC system and reference system, respectively. The calculated $\Delta F$ is 72.09% and 67.6% for $v = 30$ m/s and 50 m/s, respectively. Figure 2.5(a) further plots $\Delta F$ as a function of $v$, where for the present CNT geometry, $\Delta F$ arrives maximum at the velocity of about 40 m/s, showing a nonlinear variation.

The total transmitted impulse energy (on the receiver) can be estimated as $W = \xi \int_0^\tau F'^2 dt$, which is integrated over the entire impulse duration (see below). Similarly, a dimensionless
reduction of the transmitted impulse energy is defined as \( \Delta W = \frac{W - W'}{W'} \times 100\% \) with respect to the reference system. Figure 2.5(a) shows that \( \Delta W \) has a similar nonlinear trend like that of \( \Delta F \), and reaches the maximum at about \( v = 30 \) m/s for the current CNT geometry.

**Figure 2.5:** (a) The reduction of the peak transmitted force, \( \Delta F \), and the total energy mitigation, \( \Delta W \), in comparison to the reference system counterpart upon impact loading; (b) The ratio between the trapped energy of the intercalated water molecules and the total impact energy, \( \frac{E_{\text{trap}}}{E_{\text{input}}} \), under different impacting velocities. The CNT size: \( D=2.17\)nm, \( L_0=9.84\)nm.

### 2.3.3.2 Elongation of impulse duration

Another parameter of interest is the total time of the transmitted impulse, which is longer with the NEC mechanism (Figure 2.4). We define the dimensionless ratio between the total transmitted impulse duration of the NEC system (\( \tau_{\text{NEC}} \)) and reference system (\( \tau_{\text{Ref}} \)) as \( \bar{\tau} \), the dash curve in Figure 6(a) shows that \( \bar{\tau} \) reaches maximum at about \( v = 30 \) m/s for the current CNT geometry, consistent with the maximum impulse energy reduction (dash curve in Figure 2.5(a)) as well as the maximum percentage of captured potential energy (see Figure 2.5(b), discussed below), and implies the best performance of energy mitigation.
The increased duration of transmitted impulse is directly related to the infiltration and defiltration processes of water molecules. The number of water molecules inside the CNT is examined and plotted in Figure 2.6(b). It can be seen that the infiltration process is rather quick, whereas the defiltration is much slower. The rates of infiltration and defiltration are also consistent with the impact velocity (despite that more water molecules invade the CNT at higher speed). The faster defiltration rate occurring at higher $v$ is likely caused by the larger potential energy trapped inside the hydrophobic CNT. According to Figure 2.6(b), another dimensionless parameter, $\tau_{de} / \tau_{in}$, can be defined as the ratio between the defiltration and infiltration times of water molecules. Figure 2.6(a) shows that $\tau_{de} / \tau_{in}$ increases with $v$, that is, for higher speed/energy impact, defiltration is relatively more difficult due to the resistance of potential energy of water molecules left in the reservoir.

![Figure 2.6](image)

**Figure 2.6:** (a) The ratio of impacting duration on the nanofluidic energy capture (NEC) system to the reference system, $\bar{\tau}$, and the ratio of defiltration time to infiltration time, $\tau_{de} / \tau_{in}$; (b) Number of water molecules in the CNT under different impacting velocity. The CNT size: $D=2.17\text{nm}$, $L_0=9.84\text{nm}$. 
2.3.3.3 Captured energy

To estimate the captured energy, we calculate the ratio between the variation of potential energy of the intercalated molecules (with respect to that of bulk water, and calculated at the instant of the peak transmitted force) and the incoming kinetic energy, $E_{\text{trap}} / E_{\text{input}}$. Figure 2.5(b) shows that $E_{\text{trap}} / E_{\text{input}}$ increases with $v$ when $v$ is relatively low, and it reaches a peak value (as much as 60% for the present CNT geometry) at about 30 m/s and then slowly reduces with further increase of $v$. Indeed, when the impact speed is low the intercalation process is less prominent and the CNT may not even be filled, and thus less energy is mitigated. With the increases of $v$, more water molecules and their associated potential energy are captured; moreover, the reordering of confined water molecules in nanopores may further increase the capacity of NEC, discussed later. Nevertheless, the maximum potential energy of water molecules that may get trapped in the nanopore depends on both pore geometry and impact speed. If $v$ is very high, although the confined molecules can be more compacted (and $E_{\text{trap}}$ is higher), however the incoming kinetic energy is even higher; thus, $E_{\text{trap}} / E_{\text{input}}$ becomes smaller. When the curve in Figure 2.5(b) is extrapolated to $v = 0$ m/s, there is no infiltration and no energy capture.

Note that from an energy point of view, when non-wetting liquids are forced to infiltrate a nanopore, part of the external work converts to the excessive solid-liquid interfacial tension, and there is also energy dissipation (i.e. the “friction resistance”) when the infiltrated liquid segment transports in the nanopore. For the system under study in the present paper, due to the weak hydrophobicity and smooth surface of CNT, the contributions of both terms are much smaller than $E_{\text{trap}}$, which is a distinctive characteristic of the NEC mechanism.
2.3.4 Characteristics of NEC: effect of nanopore length ($L_0$)

As discussed above, the nanopore volume is an important parameter determining the capacity of captured wave energy. The longer CNT is, the more water molecules may intercalate, the larger reduction of the transmitted force and impulse energy, and the longer invasion time leads to longer duration of the transmitted impulse. Once the CNT is filled, unless the ordering of confined water molecules is adjusted, it becomes somewhat difficult to accommodate more water molecules; even if reconfiguration is possible, the room for intercalating more liquid phase is limited within the nanoconfinement.

Consider a representative (16,16) CNT/water system under an impact velocity of 50 m/s, and $L_0$ varies from 4.92nm to 11.7nm. Figures 2.7(a) and (b) show the transmitted force history for two different $L_0$, and apparently both the transmitted force reduction and impulse elongation are more prominent with the longer nanochannel. In Figure 2.8(a), both the reduction of the transmitted peak force, $\Delta F$, and reduction of the transmitted impulse energy, $\Delta W$, increase with CNT length. For the same impacting energy, the pressure wave generated in the reservoir is the same, and thus the intercalated water molecules carry approximately the potential energy per molecule. This explains the essentially linear variation of $E_{\text{trap}} / E_{\text{input}}$ with $L_0$ in Figure 2.8(b), as well as the trend of $\Delta W$ in the dash curve Figure 8a, within the current space of parameters under study. Meanwhile, $\Delta F$ increases nonlinearly with nanochannel length. Figure 2.9(a) indicates that the dimensionless impulse time, $\bar{\tau}$, also increases monotonically with CNT length, which is associated with the time required to enter and exit the tube.

From the histories of confined water molecules in Figure 2.9(b), the infiltration rate is the same owing to the same impact velocity/energy. Likewise, the defiltration rates are close due to
the similar level of compression of confined water molecules; however, when the nanopore gets very long there are fewer water molecules remaining in the reservoir when the pore is filled and when defiltration gets started, which imposes less resistance to defiltration, leading to a relatively faster outflow. These observations are consistent with the plot of $\tau_{de} / \tau_{in}$ in Figure 2.9(a). Note that in this section, the initial reservoir volume is fixed. On the other hand, if the initial reservoir volume increases proportionally with pore volume as the pore length is increased, then the infiltration and defiltration rates will be essentially independent of pore length.

Figure 2.7: The history of the transmitted force measured in (16,16)CNTs/water system with the length of the CNTs ($L_0$) of (a) $L_0=4.92$nm and (b) $L_0=9.84$nm. The diameter of the CNTs, $D=2.17$nm, and impacting velocity, $v=50$m/s.
Figure 2.8: (a) The reduction of the peak transmitted force, $\Delta F$, and the total energy mitigation, $\Delta W$; and (b) The ratio between the trapped energy of the intercalated water molecules and the total impact energy, $E_{\text{trap}}/E_{\text{input}}$ with different lengths of CNTs. The diameter of the CNTs, $D=2.17$ nm, and impacting velocity, $v=50$ m/s.

Figure 2.9: (a) The variation of $\bar{t}$ and $\tau_{de}/\tau_{in}$ with the CNT length, and (b) Number of water molecules inside (16,16)CNTs with different lengths. The diameter of the CNTs, $D=2.17$ nm, and impacting velocity, $v=50$ m/s.

2.3.5 Characteristics of NEC: effect of nanopore diameter ($D$)

In this section, as we vary the diameter of CNT (with its length fixed at 9.84 nm), the length of reservoir is regulated so as to keep the same volume ratio between CNT and reservoir. This approach may help to reveal the pore size effect more clearly. The number of initial water
molecules in reservoir is adjusted accordingly. The impact velocity is fixed at 50 m/s.

As expected, with the increase of CNT diameter, more kinetic energy will be captured, leading to the reduction of the transmitted force and impulse energy, and the elongation of impulse duration. This is shown in Figures 2.10(a) and b for $D = 1.35$ nm ((10,10) CNT) and 2.17 nm ((16,16) CNT), respectively. Figure 2.11(a) gives the quantitative results of $\Delta F$ and $\Delta W$ as a function of $D$, where a nonlinear increasing trend is observed, and also similar for $\Delta E_{trap} / E_{input}$ in Figure 2.11(b). The nonlinear variation is related to the lateral diffusion effect that is more prominent in larger CNT. Note that with the increment of $D$, although more energy gets captured, the energy capture per unit volume does not necessarily increase, which will be discussed later. The dash curve in Figure 2.12(a) confirms that the dimensionless transmitted impulse time increases with CNT diameter.

Figure 2.12(b) presents the variation of the number of intercalated water molecules. Since the infiltration pressure (capillary resistance) is smaller at larger $D^{138,139}$, a higher infiltration rate is obtained. In a larger CNT, the initial defiltration rate is higher owing to the more prominent release of the captured energy, but later the defiltration becomes slower since more molecules need to be evacuated. Overall, $\tau_{de} / \tau_{in}$ increases with the increase of $D$, Figure 2.12(b).
Figure 2.10: The history of the transmitted force measured from the CNTs/water system with diameter of CNTs of (a) $D=1.35\text{nm}$, (10,10)CNT; (b) $D=2.17\text{nm}$, (16,16)CNT. The CNTs size: $L_0=9.84\text{nm}$ and the impacting velocity: $v=50\text{m/s}$.

Figure 2.11: (a) Variation of the peak transmitted force, $\Delta F$, and total energy reduction, $\Delta W$, with different diameters of CNTs. The length of CNTs is 9.84nm and the impacting velocity is 50m/s; (b) The ratio between the trapped energy of the intercalated water molecules and the total impact energy, $E_{\text{trap}}/E_{\text{input}}$. The CNTs size: $L_0=9.84\text{nm}$ and the impacting velocity: $v=50\text{m/s}$. 
Figure 2.12: (a) The variation of $\tau$ and $\tau_{de} / \tau_{in}$ with the diameter of CNTs, and (b) Number of water molecules in CNTs with different diameters. The CNTs size: $L_0 = 9.84\text{nm}$ and the impacting velocity: $v = 50\text{m/s}$.

2.3.6 Underlying molecular mechanism

As illustrated in Figure 2.1, once the potential energy-carrying water molecules invade into the nanopore, they may rearrange their configurations (in particular under higher speed impact) owing to the carbon-water interfacial interaction, which may potentially affect the capacity of energy capture and impact duration. The study of the axial and radial density profiles of water molecules may reveal some insights of the molecular mechanisms.

Taking the (16,16) CNT/water system as a representative example, Figure 2.13(a) gives the density profile of water molecules along the axial direction of CNT under the impact velocity of 30 m/s. During the infiltration stage, the water density is pretty high near the entrance of the CNT, which is the pressure wave which overcomes the capillary resistance and that keeps feeding water into the CNT. On the other hand, for water molecules that have invaded the CNT, the axial density is approximately a constant (along the axial direction) and much higher than that of bulk water – this suggests that the excessive potential energy carried by every intercalated
water molecule is about the same. The axial density is also almost the same at different instants of infiltration (as well as when the pore is filled up and during defiltration), indicating the cluster movement of compacted water molecules.

At a higher impact velocity (50 m/s), the axial density increases as the infiltration proceeds, which indicates that under stronger pressure wave and confinement of nanopores, the intercalated molecules becomes more compacted (which requires the reordering of the molecules); on the other hand due to the volumetric constraint, there is an upper limit of the maximum captured energy (and the axial density is the highest when the pore is filled up) for a given pore geometry. Likewise, the axial density decreases with defiltration (and at any instant, the density remains fairly uniform in the axial direction). In other words, the energy is captured and released through continuous “clusters” of compressed molecules, and the capture and release rates are different.

Figure 2.14 gives the radial density profile of water molecules inside the CNT. A fluctuation is observed due to competition between water-water and water-carbon interactions, showing a layer distribution of water molecules, similar to that at equilibrium\textsuperscript{14,23,112}. Such a layered structure can also be seen from Figure 2.3 (top view). The magnitude of the first solvation shell (FSS) becomes smaller with the increase of velocity\textsuperscript{16,23}, implying the water molecules are more closely-packed with stronger pressure waves, leading to higher trapped potential energy. The decreased FSS also echoes with that under high nanofluidic transport rate\textsuperscript{148}. The radial density profile upon defiltration is more uniform than that during infiltration (which is consistent with the less ordering of confined molecules during defiltration in Figure 2.1), indicating a more “uniform” releasing of the trapped energy.

In addition, the density profiles in Figure 2.13 indicates that the compaction level is
approximately constant along the axial direction, and thus the captured energy varies almost linearly with $L_0$, consistent with the findings in Section 2.3.4.

The reduction of transmitted force and impulse energy with the increase of CNT diameter can also be understood by the ordering of intercalated water molecules. Figure 2.15 gives the axial and radial density profiles of water molecules at different $D$. In the smaller CNT, despite fewer captured molecules, the axial density is higher, with more captured energy per volume. The result implies that higher porosity (with smaller pore size) will in general benefit the overall performance of energy mitigation.

**Figure 2.13:** Normalized density profile, $\rho(L)/\rho_0$, of water molecules at different moments along the axial direction of the CNTs/water system (i.e. the impacting direction) under the impacting velocity of (a) $v=30\text{m/s}$ and (b) $v=50\text{m/s}$. The CNT size: $D=2.17\text{nm}, L_0=9.84\text{nm}$. 
Figure 2.14: Normalized average radial density profile, $\rho(r)/\rho_0$, of water molecules inside CNTs at the (a) infiltration process and (b) defiltration process under different impacting velocity. The CNT size: $D=2.17\text{nm}$, $L_0=9.84\text{nm}$.

Figure 2.15: (a) Normalized average density profile, $\rho(L)/\rho_0$, of water molecules along the axial direction of the CNTs/water system; (b) Normalized average radial density profile, $\rho(r)/\rho_0$, of water molecules inside CNTs at the infiltration process with different diameters of CNTs. The CNT size: $L_0=9.84\text{nm}$; the impacting velocity: $v=30\text{m/s}$.

### 2.3.7 Extend to silica nanopores

In this section, the CNT is replaced with a silica nanotube (SNT) in order to study effect of solid-liquid interaction on NEC. A larger SNT with $D = 2.05 \text{ nm}$ and a smaller SNT with $D =$
0.84 nm are investigated – their diameter are analogous to that of a (16, 16) CNT and a (6, 6) CNT, respectively. When the diameter of SNT is varied, the reservoir volume is regulated accordingly, like that in Section 2.3.5. The length of all tubes is fixed at 9.8 nm in this section.

For the larger tube diameter, Figure 2.16(a) shows the transmitted force history, with $\Delta F = 69.09\%$ and $\Delta W = 72.44\%$, and for the smaller tube in Figure 2.17(a), the $\Delta F = 41.6\%$ and $\Delta W = 45.69\%$. The trends are similar to the size effect of CNT. The corresponding simulation results of the CNT systems are given in Figures 2.16(b) and 2.17(b), where $\Delta F$ and $\Delta W$ are 64.98% and 75.22% respectively for the larger CNT, and 42.90% and 52.75% respectively for the smaller CNT. Thus, in the silica system the reduction of transmitted force is larger than the CNT counterpart, whereas the reduction of transmitted impulse energy is smaller. The partially charged surface of SNT results a stronger interfacial interaction with water molecules\textsuperscript{44}, leading to fewer intercalated water molecules and thus less reduction of transmitted impulse energy. Meanwhile the stronger interfacial interaction of SNT results in a higher effective shear stress, and that could reduce the transmitted force. The differences between SNT and CNT, however, are relatively small since the NEC mechanism is more dominant.
**Figure 2.16:** Comparison of the transmitted force measured from (a) (16,16)SNT/water system and (b) (16,16)CNT/water systems. The diameter of CNT and SNT is 2.17nm and 2.08nm, respectively and is considered match each other in size. Lengths of both tubes are 9.8nm. The impacting velocity: \( v = 50\text{m/s} \).

**Figure 2.17:** Comparison of the transmitted force measured from (a) (6,6)SNT/water system and (b) (6, 6)CNT/water systems. The diameter of CNT and SNT is 0.81nm and 0.84nm, respectively and is considered match each other in size. Lengths of both tubes are 9.8nm. The impacting velocity: \( v = 50\text{m/s} \).

### 2.3.8 Extend to electrolyte solution

In addition to the solid phase, liquid phase is another key material parameter for affecting
the soli-liquid interface interactions, thus system performance. In this section, two typical liquid phases, NaCl and KCl electrolyte solutions, are chosen as representatives. The nanopore is the (16, 16) CNT with the diameter and length of 2.17nm and 9.8 nm, respectively, and the impacting velocity is 50m/s.

Figures 2.18 (a) and (b) show the history of transmitted force for the NaCl solution and KCl solution with the same molar concentration of 2.0M (M = 1.0 mol/l), respectively. Both show a similar trend with that for the liquid phase pure water (Figures 2.7(b) or 2.17(b)). When the NaCl solution is employed, the calculations show the force and energy reductions are $\Delta F = 73.53\%$ and $\Delta W = 78.16\%$, respectively, larger than that of pure water; whereas when the KCl solution is employed, they are $\Delta F = 68.58\%$ and $\Delta W = 75.27\%$. There is a decrease in $\Delta F$ while $\Delta W$ remains approximately the same compared with that of pure water phase. Further, as the concentration changes, $\Delta F$ and $\Delta W$ vary accordingly (Figures 2.19 (a) and (b)): the $\Delta F$ decreases linearly with the increase of the KCl solution concentration, and varies nonlinearly with the NaCl solution concentration; whereas there is a slow increase in $\Delta W$ with the increase of either KCl or NaCl solution concentrations. Further comparisons demonstrate that both $\Delta F$ and $\Delta W$ are larger for the employment of NaCl solution than that for the same concentration of KCl solution.

Generally speaking, when an electrolyte solution is employed, the number of infiltrated water molecules in the nanotube will decrease, leading to a less captured energy, and thus a smaller $\Delta F$ and $\Delta W$. On the other hand, the formation of solvated ions increases interactions among water molecules, leading to a stronger and closer configuration of clusters of infiltrated water molecules$^{82,149}$, which enhances the captured energy, and thus $\Delta F$ and $\Delta W$. In addition,
during the transport of liquid molecules, the addition of ions will increase the transport resistance (see Chapter 3), leading to an decrease of $\Delta F$ and $\Delta W$. With the increase of concentration, there will be less numbers of infiltrated water molecules, but a stronger configuration of clusters of infiltrated water molecules and enhanced transport resistance. All these factors will affect the system performance. From Figure 2.19, it can be concluded that the number of infiltrated water molecules dominates the variations of $\Delta F$ and $\Delta W$. Besides, with the same concentration, a bigger size of $K^+$ makes a number of infiltrated water molecules even less, leading to a smaller $\Delta F$ and $\Delta W$ in the KCl solution over the NaCl solution.

**Figure 2.18:** Transmitted force measured from (a) (16,16)CNT/2M-NaCl solution system and (b) (16,16)CNT/2M-KCl solution systems. The concentration of both NaCl and KCl solutions is 2mol/l. The CNT size: $D=2.17\text{nm}$, $L_0=9.84\text{nm}$. The impacting velocity: $v=50\text{m/s}$. 
2.3.9 Extend to charged CNTs

During the fabrication of CNTs, surface treatments are often used to change surface properties of tube walls. The injection of electric charges into CNTs is one of popular strategies, and as a result the induced charge on each carbon atom on CNTs provides a finite overall surface charge density $^{150,151}$. In this section, we will consider the effect of electrostatic charge distributions of CNTs on system performance. For simplification, we assume that an extra charge is uniformly distributed on each carbon atom of CNTs, where the (16, 16) CNT with the length of 9.8nm is chosen as a representative. The liquid phase is pure water, and the impacting velocity is 50m/s.

Figure 2.20(a) shows the history of transmitted force when the surface charge density is $+0.037aC/nm^2$ ($1aC = 10^{-18} C$). Compared with the reference system counterpart, an obvious force reduction is observed, similar with that of uncharged CNT/water molecules system. The calculation shows that the force and energy reduction are $\Delta F = 60.3\%$ and $\Delta W = 68.31\%$, 

**Figure 2.19:** Effect of concentration $(c)$ of (a) NaCl solution and (b) KCl solution on the force and energy reduction in the CNT/electrolyte solution system. The CNT size: $D=2.17nm$, $L_0=9.84nm$. The impacting velocity: $v=50m/s$. 


respectively. When the surface of the (16, 16) CNT is uniformly decorated by the same density but negative charges, -0.037aC/nm², and other conditions are kept, a similar force reduction is also observed (Figure 2.20(b)), corresponding to ΔF = 54.28% and ΔW = 64.2%, but a little bit lower than that of a positive charged CNT/water system. Compared with uncharged (16,16)CNT/water system (Figures 2.7(b) or 2.17(b)), both charged (16,16)CNTs/water systems show a lower force and energy reductions when other conditions are the same.

Series of calculations are performed with different surface charge densities and signs, and their variations with the force and energy reductions are plotted in Figure 2.21. As the surface charge density increases, both force and energy reductions decrease. Besides, given the same surface charge density, there is a higher force and energy reduction for a positive charge distribution in comparison to a negative charge density, indicating an asymmetric dependence of energy capture performance on surface charge states of CNTs. When the CNT surface is charged, either hydrogens or oxygens in water molecules are attracted by carbon atoms due to the Coulombic effects, resulting in interatomic interactions between CNT wall and water molecules. Such attractions will drive water molecules closer to the charged CNT wall compared to uncharged wall, and loosen the confined structures and distributions of water molecules in CNTs, thus decreasing the force and energy reduction. More specifically, when the surface charge of CNT is positive, it will attract oxygen atoms while repel hydrogen atoms in water molecules, leading to distribution of confined water molecules with oxygen atoms closer to CNT wall than hydrogen atoms, which has a relative close-packed state than that hydrogen atoms closer to CNT wall than oxygen atoms at a negative charged surface wall. And thus, a higher force and energy reduction is observed in CNT/water system with positive charge distributed.
Figure 2.20: Transmitted force measured from (a) (16,16) charged CNT with surface charge density of +0.037aC/nm$^2$-water system and (b) (16,16) charged CNT with surface charge density of -0.037aC/nm$^2$-water system. The CNT size: $D=2.17$nm, $L_0=9.84$nm. The impacting velocity: $v=50$m/s.

Figure 2.21: Effect of surface charge density of on the force and energy reduction in the charged CNT/electrolyte solution system. The CNT size: $D=2.17$nm, $L_0=9.84$nm. The impacting velocity: $v=50$m/s.

2.4 Experimental Verification

In order to verify the energy capture mechanism, in this section, an impact test on nanoporous zeolites-liquid system was performed. Through a gas absorption analysis, the nanoporosity was about 0.24 ml/g and the nanopore surface area was 700m$^2$/g. The as-received
material was in particle form with the size of 10-30µm. The processing and post-processing treatment procedures have been employed to obtain a slightly hydrophobic inner surface of nanopores, and discussed elsewhere. The after-treated nanoporous particles were compressed to a disk-like geometry, and put into polypropylene pad. After deionized water was added into this polypropylene pad at its mass ratio to nanoporous particles of 1:2.5, the pad was thermally sealed for a testing sample. The overall thickness of one testing sample was 2.3 mm. By using adhesives, the sample was strongly glued to the surface of an aluminum supporting platform, as illustrated in Figure 2.22.

In order to generate a high impacting wave, a blast chamber setup was designed, shown in Figure 2.22. This high-pressure chamber was made of 2.54 mm thick solid aluminum alloy with cross-sectional diameter in 203 mm and depth in 254 mm. A high pressure up to 1.2 MPa could be generated in the chamber by using a 1.6 hp Craftsman A13277 compressor. A vinyl diaphragm with thickness of 0.4 mm was placed at the front of the chamber to trigger a blast wave. When the generated pressure inside the chamber reached the limit of the diaphragm, the diaphragm would break up, generating a Friedlander wave. The wave would propagate through the guide tube, and impact on the testing sample which was placed about 10 cm away. The transmitted force when the impacting wave transported through the testing sample could be measured by a pressure transducer which connected with the testing sample behind. The input pulse was directly measured by a similar pressure transducer that was mounted 25.4 mm away in the mounting stage, open to the air. In addition, a testing sample of standard 6-lb expanded polystyrene (EPS) was employed for comparisons as a representative of conventional energy absorption materials (EAM).
Figure 2.22: The blast chamber setup. A high intensive pressure will be generated in the pressure chamber, and propagate along the guide tube after breaking the diaphragm, and then arrives at the testing sample. The testing sample is tightly attached on the supporting platform (green). The transmitted force of input pulse through the sample can be collected through the red pressure sensor.

Figure 2.23 shows typical measurement results of the input and transmitted waves. When the wave propagates through the EPS sample, at the beginning stage, the profile of the wave is nearly identical with the input pulse, implying that buckling deformation of cells does not occur at such a short time to coordinate a so fast input impacting wave energy, and usually takes a few milliseconds\textsuperscript{132,153}. After the first 1.5 milliseconds, the pressure reduction takes place evidently compared with generated pressure (input pulse), indicating that energy absorption happens. During the following overpressure plateau, the maximum pressure is reduced by about 20-30%.

When the wave transmits through the mixture of nanopore/liquid testing sample, the pressure reduction takes place almost immediately at onset of pressure rising. At the overpressure stage, a much pressure reduction is observed compared with both the input and EPS curve and the peak pressure is only 0.035MPa. The maximum pressure reduction is about 85% and 80% of that input pulse and EPS sample, respectively, showing that the developed nanopore-liquid system can absorb energy more efficiently and much faster. More importantly, the transmitted
pressure curve is quite smooth including the major low-pressure valleys. As a result, the transmitted wave profile consists of only a single phase, with a slowly-rising, non-shock front, followed by a slowly-decreasing plateau, implying that part of input energy is captured by the liquids, which qualitatively verifies above MD simulations.

![Figure 2.23: Typical blast impacting pulse and measured transmitted pressure through polystyrene (EPS) and nanopore-liquid composite samples.](image)

**2.5 Summary**

We have shown a new protection mechanism of energy trapping to the impact and blast energy wave based on the non-wetting liquids-nanoporous composite material system by using the MD simulations. Upon an impact loading or blast wave on this composite material system, the incoming kinetic energy can be converted to the potential energy of water molecules quickly and is trapped, and then confined into the CNTs for a while. MD simulations show that both impacting force and energy will have much of decrease when traveling through this composite material system via the energy trapping mechanism. At the same time, the duration is extended, weakening the stress wave gradient. The trapped energy will be released gradually at unloading.
stage due to the inherence of non-wetting surface wall of CNTs through the defiltration of water molecules out of CNTs. The defiltration time depends on the trapped energy and solid-liquid interfacial tension. MD simulations further demonstrate that the trapped energy will not always increase with impacting velocity due to the filling up of CNTs; while a linear increase with length of CNTs is obtained with the same trapped energy per length. The study of size dependence trapped energy shows a more total trapped energy in larger CNTs due to more number of intercalated water molecules in CNTs. The density profiles of water molecules at the axial and radial direction of CNTs are examined to understand the mechanism of energy trapping. A “cluster-like” energy trapping and releasing model is put forward.

The study also extends to the effect of solid phase-silica nanotube, surface charged state of CNTs, and liquid phase-NaCl and KCl electrolyte solutions on the system performance. A little increase in the reduction of transmitted force and yet decrease in the reduction of transmitted impulse energy is found when the silica nanotubes are employed compared with CNTs. For charged CNTs, independent of sign of electric charge, both the transmitted force and energy will decrease. Furthermore, both show a larger sensitivity to negative charges compared with positive charges. The transmitted force also shows a little decrease with the increase of electrolyte concentration, and the transmitted energy remains almost the same. These extensions shed some light on the optimization of system performance by changing the material and systemic parameters. Finally, a parallel blast experiment on a nanopore zeolite/water composite material is carried out and the results quantitatively verify these MD findings.
Chapter 3 Mechanical to Thermal Energy Conversion: Nanofluidic Energy Dissipation

In Chapter 2, a novel energy capture mechanism is presented when liquid molecules are rapidly compressed into a nanopore. Afterward, the highly compressed liquids will transport through the nanochannels, and part of kinetic energy will be dissipated through the “friction” force exerted to the liquid molecules by solid wall atoms (See Figure 1.7 in section 1.2.2.1). This “friction” force reflects a nanofluidic transport resistance, and strongly depends on interfacial interactions between the confined liquid molecules and solid wall of nanochannel, which can be attributed to surface hydrophobicity of nanopores and their atomic smoothness. As one of critical parameters of controlling hydrophobicity, temperature has been used to pump nanofluids\(^{46,51,154}\). However, the temperature dependent transport behavior of nanofluids still remains unexplored. On the other hand, many nanoporous materials have prominent wall surface features in practice, either by natural crystallographic appearance (e.g. porous silica, zeolite, etc.) or by synthesis or fabrication\(^{155,156}\). During nanofluidic transport, since the solid “surface” atoms and confined liquid molecules interact closely at the interface, the surface roughness of nanopore is expected to play a crucial role.

In this chapter, the temperature and surface roughness dependent characteristics of nanofluidic transport resistance is investigated by using MD. In section 3.1, for a system of water transport in a model CNT, the thermal dependence of the effective shear stress and nominal viscosity are explored with the CNT size and flow velocity coupled. The thermal effect of electrolyte liquid transport is also studied and the behaviors are compared with that of pure
water. The underlying molecular mechanism is elucidated by the temperature dependence of radial density distribution and hydrogen bonding. A parallel experiment on a nanoporous carbon/water system is carried out to qualitatively verify the MD simulation findings. In section 3.2, a carbon nanotube (CNT) is perturbed with a sinusoidal surface morphology (inspired by that observed in CNT fabrication\textsuperscript{157}), and taken to be a model rough nanochannel. By carrying out MD simulations, we investigate the effect of nanopore wall roughness on the water transport resistance, where the effective shear stress encountered by water molecules during transport\textsuperscript{136} is also employed to characterize the solid-water interaction.

### 3.1 Temperature Dependence of Fluid Transport Resistance

#### 3.1.1 Computational model and method

A segment of CNT is employed to model a smooth nanopore structure (Figure 3.1). The axial length of the CNT, $L$, is chosen to be $8R$, where $R$ is the radius of the CNT. Since the number of water molecules inside a CNT remains approximately constant when flowing with a constant flux\textsuperscript{14,158}, thus, in the present study, the number of water molecules is constant for a given CNT with specific diameter and length. The surrounding environment is assumed vacuum in order to highlight the transport behavior of water molecules inside. The density of water molecules inside the occupied volume of CNTs is close to that of bulk water, $\rho_o = 998.0$ kg/m$^3$, at 300 K and 0.1 MPa. During the computation of the density of confined fluid, the accessible volume of CNT to water molecules is deduced from its effective radius, which can be effectively estimated as $R_{\text{eff}} = R_o - \sigma_c$, where $\sigma_c$ is the commonly used van der Waals radius of carbon (1.7 Å)\textsuperscript{159,160}. Periodical boundary condition is imposed in the axial direction of the computational
cell so as to mimic an infinite long pore and minimizing the entrance and exit effects on the transport behavior\textsuperscript{161-163}. The periodic length of $8R$ has been verified to be long enough for robust data collection.

The simulation is performed using LAMMPS (large-scale atomic/molecular massively parallel simulator)\textsuperscript{146}. Although the flexibility of CNT affects the free energy of water filling and emptying\textsuperscript{161,164}, for the current model where the CNT is already filled with water, the effect of nanotube flexibility is significant only for self-diffusion at a low pressure loading. As the pressure gradient increases, such an effect will become smaller and can be negligible\textsuperscript{165,166}. In the present study the nanopore wall is assumed rigid. The water molecules are modeled by the extended Simple Point Charge (SPC/E) potential\textsuperscript{106}, and constrained by the SHAKE algorithm. The 12-6 pairwise L-J potential and Coulomb interaction, \[ U(r_{ij}) = 4\varepsilon_{ij} \left[ (\sigma_{ij}/r)^{12} - (\sigma_{ij}/r)^{6} \right] + q_i q_j / (4\pi\varepsilon_0 r), \] are used to model the water-water interaction and carbon-water interaction, where $r_{ij}$ denotes the distance between atoms $i$ and $j$, $\varepsilon_{ij}$ and $\sigma_{ij}$ are the energy and length parameters for a $i$-$j$ pair atoms, respectively, $q_i$ and $q_j$ are the electric charge counterpart, and $\varepsilon_0$ is the permittivity of vacuum. When other electrolyte solutions are employed, this governing potential equation is also used to describe the interaction between ions and atoms. The cross interactions are obtained by using the Lorentz-Berthelot mixing rules, \[ \varepsilon_{ij} = \sqrt{\varepsilon_i \varepsilon_j}, \] and \[ \sigma_{ij} = (\sigma_i + \sigma_j) / 2 \]. The relevant L-J parameters are taken from ref.\textsuperscript{108,167}. These parameters have been confirmed to reproduce the experimental information such as contact angle of water droplet on a graphite surface\textsuperscript{145} and the binding energies of ion-water interactions\textsuperscript{167}. All L-J interactions are truncated at a cut-off distance of 1.0 nm to calculate the short range van der Waals forces\textsuperscript{143}, and the particle-particle particle-mesh (PPPM) solver with a
root mean-square accuracy of $10^{-4}$ is applied to account for the truncation of the long-range electrostatic force. In the present study, the temperature varies between 300~360 K, and within such a moderate range, it is generally assumed that the force field parameters can be kept the same throughout simulation. Besides, within this temperature range, there is no phase transition for the employed CNTs (with the diameter between 0.81~2.71nm) under the pressure of 1 atm.

Several methods have been developed to simulate nanofluidic behaviors using MD techniques, such as gravity-driven flow, dual control volume grand canonical molecular dynamics, and fluidized piston-driven flow, among others. The gravity-driven flow is particularly attractive because of its computational simplicity, and it also allows us to focus on the properties of the fluid. In this approach, a homogeneous stable flow is generated by applying an analog of gravity force to each molecule in the flow direction. When a steady flow with a desired flow rate is reached, in order to better measure the flow resistance (in comparison with the thermal noise), the applied gravity force is removed to allow the molecules to flow and decelerate freely.

The simulation procedure consists of two steps: In the first step, after initialization at a desired temperature, the NVT ensemble is employed for 0.1 ns to equilibrate the system, and then a constant gravity-acceleration is applied on each water molecule along the axial direction of the CNT so as to initiate a uniform flow inside the nanotube. During this stage, the temperature is maintained by using a Nose/Hoover thermostat with a time constant of 0.2 ps, and it is only applied to the liquid phase since the CNT is assumed to be rigid. To avoid artificial heating caused by the imposed axial displacements, the mean axial velocity of the liquid mass center is subtracted from the axial component of the velocity of each liquid molecule during the
calculation of temperature. After a desired transport velocity, $\bar{v}$, is reached, in the second step, the applied acceleration is removed and the molecules are allowed to flow freely and only subjected to the transport “friction” resistance from carbon wall. Afterwards, the NVE ensemble is employed to monitor the velocity and deduce fluidic characteristics (see below).

### 3.1.2 Fundamental transport behaviors upon different temperatures

We first examine the velocity profile of water molecules inside the CNT. For a representative (20,20) CNT/ water system, the average axial velocity of water molecules across the CNT section (at the temperature of $T$=300 K) is plotted in Figure 3.1. The overall velocity profile is plug-like, featuring almost uniform velocity except the reduction near the pore wall, consistent with literature $^{136,174}$.

![Figure 3.1](image_url)

**Figure 3.1:** The average axial velocity distribution (in the radial direction) of water molecules inside a (20,20) CNT at 300 K. The diameter of the (20,20) CNT is 2.71 nm.

After a desired $\bar{v}$ is reached, the liquid molecules are allowed to freely decelerate.
average flow rate is recorded to identify an initial linear decelerating window (about 0.1 ns), during which its magnitude drops by a small percentage; at the same time, the system temperature is closely monitored to make sure that there is no sudden rise in system temperature. Upon the deduction of the average deceleration, $\bar{a}$, the effective shear stress at the liquid-solid interface can be defined as $\tau \big|_{r=R} = \tau = \left( \sum m_i \bar{a} \right) / (2\pi R' L)$, where $\sum m_i$ is the total mass of all water molecules inside the tube, and $R'$ is the accessible radius of liquid molecules occupied in the tube.\(^{161}\) As an “overall” measure of the transport resistance of nanofluidic flow, the direction of $\tau$ is opposite to the axial flow direction. During the computation of $\bar{a}$, the system temperature is closely monitored to make sure that there is no sudden rise in system temperature.

In a nanofluidic system, the most dominant characteristic is the interaction between solid wall and liquid molecules immediately near it, and the conventional Newton’s law of viscosity may be invalid for highly inhomogeneous nanofluid\(^{26,163}\). The effective shear stress $\tau$, whose majority is exerted by the carbon wall to water molecules, is perhaps a more reliable measure of the transport resistance. Based on the obtained the shear stress $\tau$, we further define a nominal viscosity, $\tilde{\nu} = \nu^{136,175}$, a quantity that has the same dimension as conventional viscosity. It is largely based on the solid-liquid interaction and reflects the “easiness” of water transporting through a nanochannel. Although the present nominal viscosity is different from the conventional bulk liquid viscosity, it is still useful for revealing the size, rate, and temperature effects of nanofluids. In what follows, these two parameters ($\tau$ and $\tilde{\nu}$) are employed to study the temperature dependent transport behavior, and the primary focus is given to $\tau$.

At $\bar{v} = 100 \text{m/s}$, the effective shear stress $\tau$ and nominal viscosity $\tilde{\nu}$ for water molecules transporting in a (20, 20) CNT are obtained at different temperatures, shown in solid square
curves in Figure 3.2, and both of them decrease with the increase of $T$. The error bar arises from the small uncertainty of determining the deceleration. When Figure 3.2 is replotted in a semi-log coordinate system (not shown here), it can be verified that $\dot{r}$ varies as $\exp(1/T)$, a characteristic that is somewhat similar to the viscosity of bulk water,\textsuperscript{176,177} although it is reminded that the nominal $\dot{r}$ for nanofluidic transport is largely caused by the liquid-solid wall interaction, yet the viscosity of bulk fluid is dominated by the interaction among liquid molecules.

In addition, the pore size effect is coupled with the temperature effect. By studying three other CNTs with chirality (16, 16), (10, 10), and (6, 6) (whose diameters are 2.17, 1.36, and 0.81 nm, respectively), it is found that the values of $\tau$ and $\dot{r}$ in smaller tubes are lower than their counterparts in larger tubes. That is, smaller CNTs may benefit higher water flow rate, consistent with refs.\textsuperscript{14,19} More importantly, in a smaller tube, as the temperature increases, there is a faster decreasing trend of $\tau$ and $\dot{r}$ (than that in a larger tube), indicating that the transport resistance is more sensitive to temperature variation in a smaller tube. This phenomenon is consistent with the increasing role of liquid-solid interaction on nanofluidic transport with the decrease of CNT size.\textsuperscript{91,136}
Figure 3.2: Effect of temperature on the (a) effective shear stress and (b) nominal viscosity for different CNT sizes at the transport rate of 100 m/s.

The influence of transport rate is also coupled with the thermal effect. In Figure 3.3, a (20,20) CNT and a (6,6) CNT are chosen as representatives of a large and small tube, respectively, and $\overline{v}$ varies as 100 m/s, 150 m/s, and 200 m/s. In general, the transport resistance increases with the increase of $\overline{v}$, while the nominal viscosity, $\overline{\eta}$, decreases with the increase of flow rate. At a higher transport rate, since there is no sufficient time for the molecules to fully adjust their positions to minimize the system energy, the overall van der Waals repulsion is more prominent, leading to a higher shear stress. Again, if the CNT diameter is smaller, the temperature sensitivity of the effective shear stress and nominal viscosity is more prominent, which may benefit relevant applications in the design of thermomechanical nanofluidic devices.
3.1.3 Molecular mechanism of temperature effect coupling with size and transport rate effects

Nanofluidic transport behavior is underpinned by the liquid-solid wall interaction. In essence, the transport behavior reflects the non-bond force imposed by the solid wall on liquid molecules, and a stronger van der Waals’ constraint will lead to a larger effective shear stress. The radial density profile and hydrogen bonding may help to reveal the configuration and structural distribution of confined water molecules inside a CNT. Both of them are employed to reveal molecular mechanism of the temperature dependent transport behavior coupling with pore size effect and transport rate effect, and explored below.

Figures 3.4(a) and (b) give the effect of temperature on the radial density profile in (20, 20) CNT and (10,10) CNT /water systems at the transport rate of 100 m/s, respectively. The fluctuations indicate the annular layered-structures of water molecules inside CNTs\textsuperscript{23,136}. The maximum density near the wall is usually referred as the first solvation shell (FSS), whose...
spacing to the wall is the equilibrium distance. With the increase of temperature, both the amplitude of FSS and equilibrium distance decrease, which imply a weaker solid wall-water interaction. Moreover, under such a circumstance, the radial confinement effect imposed on the water molecules is less severe, and thus the axial component of the velocity of water molecules is relatively more prominent, leading to smaller transport resistance and effective shear stress. When the diameter of CNT decreases (Figure 3.4(b)), the effect of temperature on the variations of both the FSS amplitude and the equilibrium distance becomes more prominent, which qualitatively echoes with the coupling between size effect and temperature effect (i.e. the transport resistance in smaller tubes is more thermally responsive).

Figure 3.4 gives the variation of the number of the averaged hydrogen bond per water molecule, $N_{HB}$, is calculated by dividing the total number of hydrogen bonds by the total number of water molecules in each annual layer along the radial direction. The calculation of $N_{HB}$ is based on geometry\textsuperscript{178}, where two water molecules are assumed to be hydrogen-bonded only if (a) the oxygen-oxygen distance is smaller than 3.5 Å and simultaneously (b) the bond angle between the oxygen-oxygen direction and one of the oxygen-hydrogen directions is less than 30°. From Figure 3.4, $N_{HB}$ arrives maximum at the center of CNT, close to that calculated for bulk water (3.78), and decreases away from the center. Overall, at a higher temperature, or higher transport velocity, the value of $N_{HB}$ is smaller, which leads to a lower transport resistance, consistent with simulations. The drop of $N_{HB}$ near the water-CNT interface indicates the local depletion of hydrogen bond and a weakened water network structure near the solid wall, consistent with previous studies\textsuperscript{14,16,112}. In addition, a larger CNT shows a more significant drop of $N_{HB}$ near the water-CNT interface, leading to larger transport resistance and larger effective shear stress,
which also agree with above simulations.

\[ \frac{\rho}{\rho_0} \]

\[ N_{HB} \]

\[ R, \, \text{Å} \]

\[ \frac{\rho}{\rho_0} \]

\[ N_{HB} \]

\[ R, \, \text{Å} \]

\[ \frac{\rho}{\rho_0} \]

\[ N_{HB} \]

\[ R, \, \text{Å} \]

**Figure 3.4:** Normalized radial density profile, $\rho / \rho_0$ (solid curves), and the number of hydrogen bond per water molecule, $N_{HB}$ (dash curves), in the (a) (20, 20) CNT/water system and (b) (6, 6) CNT/water system at different temperatures, all at the same transport rate of 100 m/s; and (c) (20, 20) CNT/water system at different transport rates and the same temperature of 300K.

### 3.1.4 Water transport vs. electrolyte solution transport

The preceding study on the water/CNT system shows that the effective shear stress and nominal viscosity depend primarily on the solid-liquid interfacial interaction. When the liquid phase changes, the transport behavior is expected to vary $^{161,179-181}$, and in this section, we focus
on the thermal effect of electrolyte transport in CNT. The NaCl and KCl solutions are chosen as substitutes of the water liquid phase, whose concentration is maintained at 2.0 mol/L. Following the same simulation procedure above, taking a (20, 20) CNT and a (6, 6) CNT as representatives of a large and small pore, respectively, the variations of the effective shear stress and nominal viscosity with temperature (at $\bar{v} = 100$ m/s) are given in Figures 3.5(a) and (b). Both of them decrease with the increase of temperature, similar with those of water/CNT system, but are larger in respective amplitudes. Besides, they also show intriguing ion size dependence: a larger ionic size ($K^+ > Na^+$) leads to a higher effective shear stress and nominal viscosity because of a stronger interaction between a larger ion, water and CNT. With the decrease of CNT size (Figure 3.5(b)), the deviation of the effective shear stress between electrolyte solution and pure water system increases.

The corresponding radial density profile of water molecules and $N_{HB}$ are plotted in Figure 3.5(c). Both the amplitude of FSS and the equilibrium distance are larger in the system with electrolyte solution (compare with that of pure water phase). When electrolyte solutions are employed, owing to the electrostatic interaction of ions with water molecules, the water molecules tend to become more cohesive (which can also be validated from the increase of $N_{HB}$ in the CNT/electrolyte solution system), leading to the increase of amplitude of FSS and equilibrium distance, with more prominent radial confinement effect, and thus a higher effective shear stress.
Figure 3.5: Temperature dependent transport behavior in CNT/electrolyte solution system. Effect of temperature on the effective shear stress(solid curves) and nominal viscosity(dash curves) in (a) (20, 20) CNT/ electrolyte solution system; (b) (6, 6) CNT/electrolyte solution system; (c) the normalized radial density profile, $\rho / \rho_0$ (solid curves), and the number of hydrogen bond per molecule, $N_{HB}$ (dash curves), at 300 K. The transport velocity is 100m/s.

### 3.1.5 Comparison with experimental data

A pressure induced infiltration (PII) experiment was carried out on a nanoporous carbon/water system, and its data are qualitatively compared with the above MD simulation results. The material under investigation was Cabot BP-2000 nanoporous carbon, with the smallest nanopore radius of about 1.0 nm and the largest nanopores around 100 nm. Through a Brunauer-Emmett-Teller (BET) analysis, it was measured that the specific nanopore surface area...
was 1400 m²/g. The as-received material was in powder form, with the particle size of about 50 μm. For the nanoporous carbon materials, the inner surface of nanopores was hydrophilic as received. If the untreated nanoporous carbon was immersed into the liquid phase (deionized water), the water molecules would spontaneously enter the nanopores, which makes it extremely difficult to deduce the nominal viscosity. Therefore, prior to the PII experiment, the nanoporous carbon was treated by silyl groups to modify the properties of the inner pore surfaces and achieve hydrophobicity, the details of which has been given elsewhere\textsuperscript{175}.

In a stainless steel cylinder, 0.3 g of the surface modified nanoporous carbon and 5.5 g of deionized water were sealed by two stainless steel pistons. The pistons were equipped by reinforced o-rings. The schematic of the experimental setup is shown in Figure 3.6. The cross-sectional area of the piston was $A_p = 286$ mm². The temperature of the testing cell was kept at 293K, 308K, 328K, or 348K by using an Aldrich DigiTrol II Z28 water bath.

\textbf{Figure 3.6:} Schematic of experimental setup. Due to the non-wetting of liquid phase to nanopore carbon, the liquid will not intrude into nanopores. As the external pressure, $P$, increases, the solid-liquid interfacial capillary force is overcome and the liquid starts to infiltrate into nanopore, leading to the decrease of system volume. The continuous transport of liquid inside nanopore can be employed to study the interfacial property between the solid wall and liquid phase.
By using a type 5580 Instron machine, the upper piston was continuously intruded into the cylinder at a constant rate and an external pressure was applied on the water liquid phase. The piston displacement rate, \( v_p \), was 5 mm/min. The PII process starts from the largest nanopores, and as the pressure increased, more and more smaller nanopores were involved in the liquid infiltration. Eventually, as the liquid infiltration volume reached the nanopore volume, the system became nearly incompressible. The Instron machine measured continuously the piston pressure and the piston displacement (\( d_p \)).

The liquid infiltration volume can be assessed as \( d_p A_p \). 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 obtained through \( fV_{pore}/(\pi R^2 \xi) \), where \( V_{pore} \) is the specific nanopore volume, \( \xi \) is the effective liquid infiltration depth, and \( f \) is the BET analysis result of the probability density of pore volume distribution. According to the equation of \( \tilde{\eta} = (8QL) \), the nominal viscosity can be estimated as \( \tilde{\eta} \), where \( L \) is assumed half of the nanoporous particle size. The \( P \) is the pressure acting on the infiltrating water liquid phase and can be measured from the sorption isotherm curve at corresponding temperature and loading rate following the analysis procedure discussed in refs\(^{136,182} \). The calculated results are plotted in Figure 3.7. It is seen that the nominal viscosity decreases with the increase of temperature. Besides, the smaller nanopore radius is, the lower viscosity is, which agrees qualitatively with the results of MD simulations (despite the different working conditions in experiment and simulation).
Figure 3.7: Calculations of the nominal viscosity with temperature and pore size from a pressure induced infiltration (PII) experiment on a nanoporous carbon/deionized water system.

Note that there are several factors making it prohibitively difficult for quantitative matching between simulation and experiment: (1) the nanoporous carbon used in experiment has some variations in its pore size; (2) the pore network in nanoporous carbon is quite complicated; (3) the porous carbon surface is modified by silyl groups, which makes it difficult to analyze or reproduce the exact surface structure in simulation; (4) the loading rate in experiment cannot be very high yet the simulation in MD cannot be very slow. The MD simulation in the present paper is focused on an “idealized” nanofluidic model so as to reveal some intrinsic trends and molecular mechanisms. Nevertheless, the qualitative matching trends shown in Figures 3.2 (simulation) and 3.7 (experiment) have demonstrated the feasibility of the current numerical approach and experimental setup in the present preliminary study. We envision that the qualitative trends reported in this paper are applicable to all nanoporous materials. More quantitative coordination between simulation and experiment will be reported in the future, including the effect of surface group in experiment and modeling more complicated surface functional group structure.
3.1.6 Summary

The temperature dependent transport behaviors of water molecules inside CNTs are studied by using MD simulations. Both the effective shear stress and nominal viscosity decrease with the increase of temperature, owing to the relatively less severe confinement effect. The thermal effect is coupled with the tube size and transport rate effects, where in smaller tubes or at higher flow rates the transport resistance is more temperature sensitive. Moreover, with the addition of ions, the shear stress of electrolyte transport is higher (compare with that of pure water) owing to the more prominent liquid-solid wall interaction. The findings are qualitatively verified by a pressure-induced infiltration experiment on a nanoporous carbon/water system.

The thermally dependent nanofluidic transport behaviors may provide insights for designing temperature controlled nanodevices. For example, a low transport resistance can be beneficial for nanoconductors; whereas a high shear stress can be employed for high-performance energy dissipation nanomaterials whose energy density can be controlled through temperature. Besides, the system performance can be further optimized by take into account the pore size effect, transport rate effect, variation of the liquid phase, or surface modification. Since the transport behavior changes when ions are added to the liquid phase, the study may also shed some light on separating molecules or ions.

3.2 Effect of Wall Roughness on Fluid Transport Resistance

3.2.1 Computational model

A similar CNT with that employed in section 3.1 is employed but it is modified with a sinusoidal wall profile along the axial direction (z-direction) to mimic a rough nanopore. The
schematic is given in Figure 3.8(a). The roughness profile is described by
\[ R = R_0 + A \sin(2\pi z / \lambda), \]
where \( R_0 \) is the radius of the smooth “baseline” CNT, and \( R \) is the local radius at \( z \). \( A \) is the amplitude of roughness, and \( \lambda \) is the wavelength. According to the accounts of degree of roughness of graphene\(^{183-185}\), \( A \) is taken to be less than 0.5nm. The axial length of the CNT, \( L \), is chosen to be at least several times of \( \lambda \). Based on the conventional characterization of dimensionless roughness in pipes\(^{186}\), the present relative roughness is characterized by two dimensionless parameters, \( A / R_0 \) and \( \lambda / R_0 \).

In addition to the same considerations for the employment of a rigid CNT in section 3.1, more importantly, if the CNT is flexible, after initial optimization, the surface roughness profile may deviate from the designed sinusoidal geometry (especially when the roughness is prominent), which makes it difficult to quantitatively correlate the roughness and transport resistance. Therefore, the CNT remains rigid in this section such that we can implement the “ideal” surface roughness profile, characterized by \( A / R_0 \) and \( \lambda / R_0 \) in the presumed sinusoidal geometry. \( A / R_0 \) and \( \lambda / R_0 \) are chosen to be within moderate ranges, such that the modified tube profile is relatively stable. The other conditions such as boundary conditions and water model remain the same with these used in section 3.1.
3.2.2 Results and discussion

After initialization at temperature of 300K, the water molecules show a harmonious distribution with respect to the wall profile, as shown in Figure 3.8(b). Owing to the liquid-solid interaction, the “free” OH bonds of water molecules point to the wall, which is consistent with that reported by Mittal and Hummer\textsuperscript{187}. Next, a constant acceleration is applied on each water molecule along the axial direction of the CNT, so as to initiate a homogeneous flow inside the nanotube. The mean axial velocity of the liquid mass center is subtracted from the axial component of the velocity of each liquid molecule to avoid artificial heating caused by the imposed axial displacements. During this period, NVT ensemble is used with temperature of 300K, and the temperature is maintained by using a Nose/Hoover thermostat with a time
constant of 0.2 ps. After a desired flux is reached (the average transport speed is fixed at about 250 m/s in the present study), the gravity force is removed to allow the water molecules to flow (decelerate) freely, and NVE ensemble is employed to monitor the fluid velocity. Note that during this deceleration period, the temperature will vary and in order to minimize such an impact, we only obtain the deceleration of fluid during the initial stage of free flow for 100ps (during which the variation of temperature is confirmed to be negligible). Upon the deduction of the average deceleration, \( \bar{\alpha} \), the effective shear stress at the liquid-solid interface can be defined as \( \tau = \sum_{i} m_{i} \bar{a} / S \),\(^{136}\) where \( S \) is the surface area of CNT including roughness effect, and \( \sum m_{i} \) is the total mass of all liquid molecules inside the tube.\(^{161}\)

Taking the (20, 20) CNT/water as a representative system (\( R_{0} = 13.56 \) Å) with roughness parameters \( \lambda / R_{0} = 1.0 \) and \( A / R_{0} = 0.1 \), the effective shear stress, \( \tau \), and nominal viscosity, \( \tilde{\eta} \), are determined and plotted in Figure 3.9(a). Both \( \tau \) and \( \tilde{\eta} \) increase nonlinearly with the density and amplitude of the roughness. Similar trends can be observed in a smaller (10,10) CNT (\( R_{0} = 6.78 \) Å) in Figure 3.9(b), where the enhancement of transport resistance is more pronounced at the same level of relative roughness (compared to the larger nanochannel). That is, the effect of wall roughness is more prominent in a smaller tube.
Figure 3.9: Effect of relative roughness of CNT on the effective shear stress (left axis) and nominal viscosity (right axis) of (a) rough (20,20) and (b) rough (10,10) CNT nanochannels.

Intuitively, the rough “extrusions” on the CNT wall may serve as ‘stumbling blocks’ for water transport, perturbing the uniform axial flow and enhancing the radial movement of water molecules near the wall. The representative snapshots of the velocity profile of the confined water molecules inside a (20,20) CNT are given in Figure 3.10. Along the smooth wall of CNT, a small radial velocity component is observed which is consistent with the observation of the non-zero radial velocity by Joseph and Aluru\textsuperscript{16}. With the increase of $A / R_0$ or decrease of $\lambda / R_0$, the radial movement is more prominent and water molecules near the center of the tube are also affected. Such radial movements enhance the collision possibility of water molecules with carbon wall, leading to an increased transport resistance in the axial direction.
In order to further understand the molecular mechanism behind the transport resistance induced by nanochannel roughness, the commonly used physical parameters, the radial density profile and hydrogen-bonding of water molecules inside CNT, which represent the configuration of confined water molecules and their interaction with solid wall, are examined. The results are illustrated in Figures 3.11(a) and (b) for the rough (20,20) CNT/water system. The fluctuations in radial density profiles indicate the annular layer-structures of water molecular orderings, consistent with previous findings\textsuperscript{25,136}. The maximum density near the wall is referred as the first solvation shell (FSS), and its distance to the wall is referred as the equilibrium distance. With the same roughness wavelength, $\lambda / R_0$, as the roughness magnitude, $A / R_0$, increases, it can be seen from Figure 3.11(a) that the magnitude of FSS decreases, and the equilibrium distance becomes smaller. On the other hand from Figure 3.11(b), if $A / R_0$ is fixed, with the decrease of $\lambda / R_0$, both the magnitude of FSS and equilibrium distance decrease, which implies a weaken gradient of water density toward the rough surface wall (in contrast to a steep density profile at the smooth wall), consistent with ref.\textsuperscript{187}. 

**Figure 3.10**: Representative flowing velocity field of water molecules in an axial plane of (20,20) CNT with different relative roughness.
Generally, a smaller magnitude of FSS and equilibrium distance indicates a relatively weaker hydrophobicity of the CNT wall to water molecules, and that results in an increase in resistance\textsuperscript{16,138}. These trends are consistent with the variations of the effective shear stress and nominal viscosity with relative roughness in Figure 3.9. Moreover, with respect to such a relative hydrophilicity, water molecules are closer to the CNT wall, leading to an enhancement of the radial movements of water molecules\textsuperscript{188,189}, also consistent with transport velocity profile in Figure 3.10 and hence the trends of resistance. Similar characteristics can be found for the smaller rough (10,10) CNT/water system in Figure 3.11, where the variations of the FSS and equilibrium distance are more prominent, suggesting a stronger effect of the wall roughness in a smaller tube, consistent with the results of $\tau$ and $\bar{r}$ in Figure 3.9. Therefore, the analysis of FSS serves explains in part the molecular mechanisms of the effect of surface roughness on nanofluidic transport resistance.

Next, the characteristics of the hydrogen bonding of the nanoconfined water molecules are explored. Along the same rule of calculating hydrogen bond in section 3.1.3, the number of the averaged hydrogen bond per water molecule, $N_{HB}$, inside the rough (20,20) CNT and (10,10) CNT systems under consideration is plotted in Figures 3.11. The value of $N_{HB}$ is close to that of bulk water (3.78) near the channel axis, and it decreases away from the center of the tube. Overall speaking, when the relative roughness is higher (i.e. with larger $A/R_0$ and smaller $\lambda/R_0$), $N_{HB}$ is smaller, which is consistent with the lower density distribution. In addition, the drop of $N_{HB}$ near the water-CNT interface indicates the local depletion of hydrogen bond. The degree of depletion increases with the increase of relative roughness. This significant loss of $N_{HB}$ near the rough wall surface, as well as its variation trend with surface roughness, are also
consistent with Mittal and Hummer’s MD simulation\textsuperscript{187}. In essence, the depletion of hydrogen bond indicates a weakened water network structure near the rough wall, which helps to enhance the radial movement of water molecules. Besides, in a smaller CNT, with the same relative roughness a more serious depletion of H-bond is observed (compared with the larger CNT counterpart), which is in part responsible for the higher transport resistance deduced from MD simulation (Figure 3.9). Therefore, the molecular mechanism of transport resistance in rough nanochannel can be understood via the studies of the flowing velocity field, radial density profile, and H-bond of confined liquid molecules.

\textbf{Figure 3.11:} Normalized radial density profile, $\rho / \rho_0$ (solid curves), and the number of hydrogen bond per water molecule, $N_{HB}$ (dash curves), in the (a) and (b) rough (20, 20) CNT/water system, and (c) and (d) rough (10, 10) CNT/water system, with different relative roughness.
3.2.3 Summary

We study the influence of wall roughness on the transport resistance of water molecules inside rough nanopores by using MD simulations. A CNT whose surface is modified with a sinusoidal morphology is employed to mimic an “idealized” rough pore. It is shown that as the wavelength of roughness decreases, or the magnitude of roughness increases, both the effective shear stress and the nominal viscosity increase. That is, the transport resistance is larger when the relative roughness is higher. In addition, the effect wall roughness becomes more prominent in a smaller nanopore. The underlying molecular mechanisms are explored through the velocity profile, radial density profile, and hydrogen bonding of water molecules inside the nanopores.

The present study may provide several promising applications for nanofluidic devices by adjusting the wall roughness of nanopores. For example, a larger resistance can also be employed to increase the energy density of nanofluidic energy absorption or dissipation devices. In addition, the larger transport resistance may be useful for separating ions and molecules, as predicted by Chu.$^{190}$
Chapter 4 Thermal to Mechanical Energy Conversion: Nanofluidic Thermal Actuation

In chapter 3, the transport resistance shows temperature dependence when the confined liquid molecules flow through a nanochannel. In principle, this thermal dependence of transport behavior results from a variation of solid-liquid interface tension with thermal fluctuation. For example, for temperature variation associated with typical low grade heat ($\Delta T=30-50 \degree C$), the solid-liquid interface tension can vary by 20-50$, or on the order of 10-100mJ/m$^2$. Such a variation, when multiplied by the ultralarge specific surface area of a nanoporous material ($A\sim100-2000 m^2/g$), can lead to a significant energy conversion/storage and power output. As the relative wetting-dewetting transition occurs, the liquid molecules could enter into or be repelled out of the nanopores at a high speed, enabling a promising nano-propulsion system with considerable energy and power density. Inspired by this phenomenon, a conceptual design of such a thermo-capillary effect-based nanofluidic thermal actuation system is demonstrated using both atomistic simulations and experiment in this chapter.

In the beginning, MD simulation is employed to reveal the fundamental thermal-dependence of the infiltration characteristics of liquid molecules into hydrophobic nanopores, and the underlying molecular mechanisms are elucidated. And then, based on the variation of the effective solid-liquid interfacial tension on temperature, a conceptual thermally responsive energy conversion system (also referred to as thermal machine, propulsion, or thermal actuation system in this thesis) is proposed. The performance indices are obtained using MD simulations, which demonstrate that the liquids can be continuously pumped in and out of nanopores by
adjusting the system temperature. Finally, an infiltration experiment on a zeolite/water system is performed to qualitatively validate these findings.

4.1 Fundamental Thermal-Dependence of Infiltration Characteristics

4.1.1 Model and computational method

The computational cell consists of a model nanochannel (e.g. a single-walled carbon nanotube, CNT) and a reservoir with model liquid (e.g. water), Figure 4.1, and periodical boundary condition is imposed on the four lateral planes of the computational cell. One end of the nanotube is closed, and the open end is inserted into the reservoir. The reservoir is bounded by two rigid planes, with the upper one fixed and the bottom plane acts like a piston and is moveable in the axial direction.

MD simulations are carried out using LAMMPS\textsuperscript{146}. The initial water molecule density in the reservoir is close to that of bulk water, $\rho_0 = 998.0$ kg/m$^3$ at 300K and 1 atm. Since the effect of CNT flexibility is small on the infiltration behavior\textsuperscript{144}, the CNT is treated as a rigid channel. The steric and van der Waals (vdW) carbon-carbon interaction is accounted for by employing the 12-6 Lennard-Jones (L-J) potential, $U(r_{ij}) = 4\varepsilon[(\sigma/r_{ij})^{12} - (\sigma/r_{ij})^6]$, where $r_{ij}$ denotes the distance between atoms, and $\varepsilon$ and $\sigma$ are the energy and length parameters, respectively. The water is modeled by the rigid extended Simple Point Charge potential SPC/E\textsuperscript{106}, which consists of a Coulomb potential between partial point charges on the oxygen and hydrogen atoms and an L-J potential between oxygen atoms; a cutoff distance of 10Å chosen\textsuperscript{143}. The P3M (Particle-Particle Particle-mesh) technique with a root mean square accuracy of $10^{-4}$ is employed to...
handle the long range Coulomb interactions among water molecules. The carbon-water interaction is described by the L-J potential whose parameters are obtained from the experimental low-coverage isotherm data of oxygen adsorption on graphite $^{145}$. By using these molecular models and parameters, the inner surface of CNT is ensured to be non-wetting to water and an external pressure is required for infiltration. As alternative solid and liquid phases, silica nanotube and NaCl/water solution are also chosen, whose force fields as well as the interaction with water molecules are described in similar fashion, ref.$^{161}$.

![Figure 4.1](image.png)

**Figure 4.1:** The MD computational cell of the model nanopore/liquid system. One end of a long nanotube is inserted into a liquid reservoir, and the other end is closed. The water reservoir is bounded with a fixed upper plane and movable bottom plane. An external pressure is applied on the piston-like bottom plane. Periodical boundary condition is imposed to the four lateral planes of the cell.

The system pressure can be adjusted by moving the piston, either quasi-statically or dynamically. By sampling a region near the entrance of CNT, the instantaneous effective applied pressure, $P$, is calculated based on the intermolecular potential among water molecules through
the Virial expression, \( P = N' k_B T / V + \sum_{i}^{N'} \frac{f_i}{3V} \), where \( N' \) is the number of water molecules inside the sampling region, \( k_B \) is the Boltzmann constant, \( T \) is the water temperature, \( V \) is the volume of sampling region, and the second term describes the contribution from the pair wise body interaction among the \( N' \) water molecules. \( V \) is taken to be sufficiently large to insure a nearly isotropic density distribution of water. At each time step, the information of atoms/molecules inside the sampling region is collected to calculate the instantaneous effective pressure. The Nose/Hoover thermostat with a damping parameter of 0.1 is employed to regulate the desired water temperature, which is a main variable in this chapter.

### 4.1.2 Infiltration behavior and thermal dependence

We first explore the fundamental quasi-static infiltration behavior of water molecules into a representative (12,12) CNT. Figure 4.2(a) shows the variation of the number of intruded water molecules with applied pressure at the temperature of 300K. When the pressure reaches a critical infiltration pressure, \( P_{in} = 121 \text{MPa} \) in this case, a large number of water molecules start to invade the CNT after the capillary resistance (which is related to the solid-liquid interfacial energy) is overcome. Afterwards, the infiltration plateau remains quite flat, suggesting that the inner surface of CNT is quite smooth and the “frictional” dissipation is very small. At different temperatures, the thermal dependence of the infiltration pressure is given in Figure 4.2(b), which is also coupled with the pore size effect. It is seen that the system becomes relatively more hydrophobic (with higher \( P_{in} \)) when the pore gets smaller or when the temperature is cooler, and that is largely related to the enhancement of the interfacial tension between solid and liquid. The molecular mechanism in the confining nanoenvironment is discussed next.
Figure 4.2: (a) Variation of the number of infiltrated water molecules into a (12,12) CNT as a function of the applied quasi-static pressure (at the temperature of 300K). From the plateau of the infiltration curve, the critical infiltration pressure, \( P_{in} \), can be deduced; (b) The effect of the CNT diameter, \( D \), and temperature, \( T \), on the critical infiltration pressure, \( P_{in} \).

4.1.3 Underlying molecular mechanism

During quasi-static infiltration, the equilibrium between the applied pressure and the imbibing pressure of water into CNT can be described by the classic Laplace-Young’s equation,

\[
P_{in} = -4\gamma \cos \theta / D,
\]

where \( \gamma \) is the surface tension of water molecules, \( \theta \) is the contact angle of the confined water molecules, and \( D \) is the accessible diameter of water molecules inside the CNT. Note that, in Figure 4.2(b) \( P_{in} \) does not vary with pore diameter as \( 1/D \), this implies that both \( \gamma \) and \( \theta \) are size-dependent. If the system is warmer, as will be shown below, both \( \gamma \) and \( \theta \) reduces significantly yet \( D \) enlarges slightly, leading to the observed reduction of \( P_{in} \).

First, some qualitative insights of the confined liquid molecules can be learned from their average radial density distributions in Figure 4.3, where the CNT radius is also varied. The fluctuations indicate that the water molecules form a layered structure, and the interaction is the most prominent in the first solvation shell (FSS) near the tube wall. With the increase of CNT
diameter, the smaller fluctuations imply that the water molecules become more cohesive and the water-CNT interaction is weaker, which reduces the infiltration threshold. As temperature rises, the position of FSS moves closer to the tube wall which helps to increase the effective $D$, and contributes to a small part of the reduction of $P_{in}$. Meanwhile, the amplitude of FSS is decreased and that suggests the effective interfacial tension ($\gamma \cos \theta$) is reduced.

Next, we quantify the contributions of $\gamma$ and $\theta$. The contact angle can be determined from an independent analysis by following Werder et al.\textsuperscript{112} For liquid molecules confined in a cavity, at the equilibrium state the spatial positions of the molecules at the meniscus front are averaged over a long computational time, and from such an averaged meniscus profile the contact angle can be deduced, illustrated in the inset of Figure 4.4(a). Figure 4.4(a) also shows the variation of $\theta$ with temperature and two different pore sizes, which indicate that the contact angle is smaller in a warmer system or in a smaller pore, consistent with experimental results\textsuperscript{191}. The current result of contact angle is also close to that calculated by Werder et al.\textsuperscript{160}, and the small difference is due to the different water molecule model and CNT flexibility. Based on the values of $\theta$ (Figure 4.4(a)) and $P_{in}$ (Figure 4.2(b)), from the Laplace-Young’s equation, the surface tension $\gamma$ can be calculated (Figure 4.4(b)), which shows a decreasing trend in a warmer system or a larger pore. Thus, the thermal dependences of $\gamma$ and $\theta$ are primarily responsible for the relative wetting transition of the nanochannel, as the temperature varies.
Figure 4.3: (a) The normalized density profile distribution of water, $\rho(r)/\rho_0$, in the confined CNT along the radial direction, as the temperature is elevated. $\rho_0 = 998.0 \text{kg/m}^3$. (a) (10,10) CNT; (b) (12,12) CNT; (c) (16,16) CNT; (d) (18,18) CNT. The left and right axes are aligned with the tube axis and inner surface, respectively.
Figure 4.4: Thermal variation of (a) contact angle, $\theta$, of the confined water inside CNT; and (b) surface tension, $\gamma$. The CNT size is also varied.

4.1.4 Variation of solid and liquid phases

The analyses above are based on the model CNT/water system. Apparently, when different solid and liquid phases are employed, the interfacial tension and thus the infiltration characteristics also vary. A substitute silica nanotube (SNT) with $D=24.56$ Å, whose size matches with that of a (18, 18) CNT, and a substitute liquid phase, NaCl/water solution of concentration 2.0mol/L, are explored in this section. Partial charges of 0.89e and -0.445e are imposed to each silicon and oxygen atom, respectively, and the SNT is neutral overall. For the NaCl solution, in the initial stage, certain water atoms are replaced by ions of Na$^+$ and Cl$^-$ to reach the concentration of 2.0mol/L.

Following the same quasi-static simulation procedure, Figure 4.5(a) plots the variation of $P_{in}$ as a function of temperature. Upon the same $T$, the $P_{in}$ in SNT/water or CNT/NaCl solution system is slightly higher than that in CNT/water system, implying stronger solid-liquid interactions. The corresponding contact angle, $\theta$, and surface tension, $\gamma$, are given in Figures
4.5(b) and 4.5(c), respectively. To infiltrate the NaCl-solution, an extra work is needed to break the hydration shell, and thus $P_{in}$ is higher compared with that of pure water. For SNT, the solid-liquid interaction is stronger than the CNT system, owing to the partially charged surface of SNT and polar water molecules, and therefore its infiltration process requires a larger work. The similar findings have been reported for fluidic transport in nanochannels\textsuperscript{161}, which may provide a feasible strategy of improving the energy absorption capacity of nanofluidic devices/systems.

**Figure 4.5:** The thermally-dependent infiltration characteristics of different solid/liquid systems (a) Infiltration pressure, $P_{in}$; (b) Contact angle, $\theta$; (c) Surface tension, $\gamma$. 
4.2 A Conceptual Thermal Actuation System

4.2.1 Working principle and MD realization

For a nanoporous material with given pore size immersed in a non-wetting liquid, the infiltration pressure decreases monotonically with the increase of temperature, which enables a thermally controlled fluidic actuation system. Denote \( P_{in}^{T_0} \) and \( P_{in}^{T_1} \) as the critical infiltration pressure under \( T_0 \) (ambient temperature) and \( T_1 \) (elevated temperature), respectively. We apply a fixed external pressure \( P_{app} \) on the piston throughout the actuation/propulsion process, with \( P_{in}^{T_1} < P_{app} < P_{in}^{T_0} \). When the working temperature is \( T_1 \), liquid intrudes into the nanopores and the system volume is reduced, and part of the thermal energy is converted to mechanical energy. When system temperature returns to \( T_0 \), the nanopore becomes relatively hydrophobic and the liquid molecules defiltrate from the nanopores, thus part of the excessive interfacial energy is converted to mechanical work. Both processes are similar to that of a thermal machine, except that the present model is driven by the thermo-capillary effect of nanofluids.

In practice, one may employ two strategies to set \( P_{app} \): the first one is to make \( P_{app} \) just below \( P_{in}^{T_0} \), and the second one is to make \( P_{app} \) just above \( P_{in}^{T_1} \). The first approach is applicable to a wide range of working temperature \( T_1 \), and when \( T_1 \) is higher the output work and power are larger. The second strategy works for a fixed working condition (pre-designed) \( T_1 \) in a quasi-static manner. In this study, we only focus on the first strategy (with \( T_0=300K \)) and evaluate its output work, power, as well as thermal efficiency.

The actuation system is first illustrated using a representative (18,18) CNT/water system, where the length and diameter of the CNT is 4.9 nm and 2.4nm respectively, and the reservoir...
(58Å×58Å×20Å) initially contains 2312 water molecules. The piston position is adjusted in-situ during the dynamic infiltration/defiltration processes, such that \( P_{\text{app}} \) is fixed as a constant just below \( P_{\text{in}}^0 \). When the system temperature is elevated, the water molecules enter the CNT (Figure 4.6): The higher the temperature, the higher the infiltration flow rate (driven by the pressure difference, \( P_{\text{app}} - P_{\text{in}}^T \)). When the system is cooled to ambient, the confined water molecules defiltrate at a rate slower than infiltration.

During the infiltration process, the effective work output can be calculated as \( W_{\text{eff}} = P_{\text{app}} \cdot \Delta V \), where \( \Delta V \) is the volume reduction of the reservoir. The work reaches a maximum \( W_{\text{max}} \) when the CNT is filled up. Since the constraining effect of water molecules is different at different \( T \) (Figure 4.3), \( W_{\text{max}} \) varies slightly with temperature. For the current model (18,18) CNT/water system with specified dimensions, Figure 4.7(a) gives its maximum energy density (\( W_{\text{max}} \) per mass of the entire system), which is on the order of 10J/g and much higher than conventional actuation materials such as shape memory alloys.

The second performance index of the actuation system is its power density (\( P \) per mass during infiltration), which is almost a constant during infiltration. Due to the strong dependency of the flow rate with temperature difference, the average power density is a function of \( \Delta T \), as shown in the down triangle curve in Figure 4.7(b) for the representative (18,18) CNT/water system.

The system’s thermal efficiency can be estimated as, \( \eta = W_{\text{eff}} / (W_{\text{eff}} + W_T) \times 100\% \), where the total consumed thermal energy (\( W_T \)) can be estimated via the temperature variation and specific heat capacity of the system (note that for the low grade heat or small temperature
variation considered herein, one may assume that the specific heat capacity is invariant with respect to temperature or pressure). Figure 4.7(c) gives the efficiency of the (18,18) CNT/water system (down triangle curve). The system efficiency is enhanced at higher temperature due to the more pronounced reduction of the solid-liquid interaction.

**Figure 4.6:** For a representative thermo-actuation system with (18,18) CNT and water, under a fixed $P_{\text{app}}$, the water molecules continuously invade into the tube with the increase of temperature. Water starts to flow out of the CNT 0.8ns after the temperature is reduced to ambient.
Figure 4.7: (a) the maximum energy density, $W_{\text{max}}$ per mass; here the error bar represents the small variation of $W_{\text{max}}$ with respect to the temperature range considered; (b) the output power density, $P$ per mass; (c) the thermal efficiency, $\eta$, of the thermo-actuation system.

### 4.2.2 Parametric study of thermal actuation system

In terms of the performance indices (maximum energy density, power density, and efficiency), a parametric study can be carried out to obtain some insights on improving the system performance. First, we explore the pore size effect: as the CNT diameter is changed, we keep the ratio between the pore volume and reservoir volume a constant. Figure 4.7 shows that
with the help of the higher surface-to-volume ratio and stronger carbon-water interfacial tension, in general a smaller CNT can lead to better performance indices. Nevertheless we caution that if the CNT size is too small such that the infiltrated water molecules form a single-file\textsuperscript{161,192} the system performance may decrease. Our study indicates an optimum pore size of about 1nm, which may be achievable as high-density nanopore arrays in practice\textsuperscript{19,193,194}.

Likewise, one may also adjust the liquid and solid phases. When the water phase is replaced by a 2.0mol/L NaCl-solution while the same (18,18) CNT is employed, although the system mass is increased, the stronger solid-liquid interaction (Figure 4.5) renders an increase in the energy density, power density, and efficiency. When the CNT is replaced by a SNT of same diameter while keeping the same water phase, despite the stronger SNT-water interaction (Figure 4.5), SNT is considerably heavier than CNT, leading to lower energy and power densities in the present study. A more systematic parametric investigation may be carried out in future to optimize the material and system parameters, such as the pore phase, pore structure, surface treatment, liquid phase, liquid concentration, temperature variation rate, etc.

In all numerical examples discussed above, the overall efficiency (calculated at $t_0$) is on the order of half of the Carnot efficiency, which indicates a decent performance of the proposed nanofluidic-based propulsion system.

### 4.3 Experimental Verification

To validate the feasibility of the nanofluidic propulsion system, we performed a thermally controlled infiltration test on Zeolyst ZSM-5 zeolite. A series of treatments were carried out to control the degree of hydrophobicity of the pore surfaces, the details of which were given in ref.\textsuperscript{195}. The average pore diameter was about 1.26nm with a standard deviation of 0.2nm, and the
overall nanopore volume was about 17%. About 1.0 g of zeolite was suspended in 7.0 g of de-ionized water. The suspension was sealed in a poly(methyl methacrylate) cylindrical cell by a steel piston (Figure 4.8, inset). By compressing the piston which is controlled by a type 5580 Instron machine in a quasi-static manner, an external pressure was applied. The temperature was maintained by an Aldrich DigiTrol II Z28 water bath.

The typical sorption curves at elevated temperatures are shown in Figure 4.8(a). It clearly shows that the infiltration process took place when the applied pressure reached a critical pressure (i.e. $P_{in}$) and afterwards the infiltration plateau was formed. The width of the infiltration plateau is related to the specific pore volume, and the small slope of the infiltration stage is resulted from the slightly nonuniform pore size distribution; at the end of infiltration when the pores are filled up, the pressure increases again.

With the increase of temperature, $P_{in}$ decreases almost linearly, which is qualitatively consistent with the simulation result in Figure 4.2(b). Such an temperature-sensitive infiltration behavior implies that if the applied pressure is kept as a constant just below the ambient $P_{in}^{T_0}$, as the temperature increases, the liquid would infiltrate spontaneously into nanopores, converting part of the thermal energy to mechanical work. Following this principle and the measurement of infiltration pressure in Figure 4.8(a), we let $T_0= 278K$ as an illustrative example, and the measured power output, $P$, of such a conceptual thermal actuation system is given in Figure 4.8(b) at elevated temperatures. It can be seen that the power output increases with temperature, qualitatively consistent with MD simulations. Note that due to several limitations such as the assumptions and parameterization adopted in the “idealized” computational model, as well as the specific pore structure used in experiment, the present comparison between simulation and
experiment is rather qualitative, and more quantitative coordination will be pursued in future.

**Figure 4.8:** (a) Experimental result of the sorption isotherm curves at different temperatures. The variation of the deduced infiltration pressure with temperature is also given. The experimental setup is illustrated at the corner inset; (b) Variation of output power of the experimental thermal actuation system.
4.4 Summary

The thermally dependent infiltration behavior of nanofluids underpins high performance thermal actuation (or propulsion) and storage systems. Using MD simulations, we show that in a system containing a hydrophobic nanochannel and non-wetting liquid, with the increase of temperature or pore size, the critical infiltration pressure decreases, which is resulted from the reduced solid-liquid interfacial tension. The molecular mechanisms are elucidated through the thermal dependence of fundamental variables, including the radial density profile, contact angle, and surface tension of the confined liquid molecules. Moreover, the interactions between the thermal effect and pore size, pore phase, and liquid specie are illustrated. It is found that the relative hydrophobicity is stronger with the employment of smaller pore, partially charged nanopore, or electrolyte.

Based on the thermally adjustable infiltration characteristics of liquids into nanopores, we put forward a conceptual design of a thermal actuation system. As the temperature is increased, the system becomes relatively more hydrophilic and thus the liquid could infiltrate the nanopores, converting part of the thermal energy into the excessive solid-liquid interfacial tension. When the temperature is reversed, the effective hydrophobicity enhances and the system volume increases as the liquid molecules are repelled out of nanopores. Through a constant pressure applied on the system, a significant mechanical work can be output with the volume reduction/expansion, similar to a thermal machine. The output power density and efficiency increase with the increase of temperature. For solid/liquid systems illustrated in the present study, the energy density is about 10J/g, and the efficiency is on the same order of the Carnot efficiency. The parametric study shows that the system performance can be further improved by optimizing the pore size, solid phase, and liquid phase. A parallel thermally controlled infiltration
experiment on a zeolite/water system is carried out, which qualitatively verifies the working principles and simulation findings.

We remark that the thermally controllable infiltration/defiltration process of liquids into/out of nanopores may also facilitate the development of high-density thermal storage devices. That is, the thermal energy may be effectively stored as the excessive liquid-solid interfacial energy, which can be on the order of 100J/g. The detailed working mechanism and optimization will be reported in the future.
Chapter 5 Electrical to Mechanical Energy conversion: Nanofluidic Electric Actuation

In the presence of an external electric field, because of its dipole and quadrupole moments, water molecules feature strong interactions with the electric field next to the charged or polar solutes, and they are attracted to the field exposed regions, which may affect the effective surface tension of water molecules on nanopore wall\textsuperscript{196,197}, and thus may be employed to control the nanofluidic motion. Besides, compared with the thermal control, the electrical control is in particular attractive because it is relatively simple and straightforward, maintains the inherent characteristics of nanopores such as their mechanical strength and surface morphology, while affecting the nanofluidic behavior by influencing the configurations of polar liquid molecules in nanoenvironment.

Similar with the design of nanofluidic thermal actuation system in Chapter 4, this chapter proposes a simple electroactuation system based on nanofluidics, and is structured as follows. First, the infiltration of liquid molecules into nanopores in the presence of an external electric field is studied, in particular, the dependency of the infiltration pressure on the external electric field and pore size. Both liquid and solid phases are varied: the working fluid includes water and electrolyte, and both carbon and silica nanotubes are taken as model nanochannels, so that the different influences of electric field can be revealed. Second, The contact angle, surface tension, and liquid distribution density are employed to describe the solid-liquid interfacial characteristics. Third, the basic working mechanism of an electrically controlled actuation system based on nanoporous materials and liquids is designed and verified by using the MD
simulations. Finally, an electric-induced infiltration experiment is employed to justify the simulation findings.

5.1 Model and computational method

The computational cell is illustrated in Figure 5.1, similar with Figure 4.1. Here a uniform external electric field, $E$, is applied along the axial direction of the nanopore, whose magnitude varies between $10^{-2} \text{ V/Å} < |E| < 0.4 \text{ V/Å}$ which on the same order of that for biological channels and membranes$^{198,199}$. Within the range of this electric intensity, as will be shown below, the hydrophobility will decrease, nevertheless, the system will not switch to hydrophilic. In addition, the applied electric field does not include the field reduction due to water polarization, and this assumption has been rationalized for the SPC/E water model$^{197,200}$. Other conditions including model descriptions, simulation technical issues and pressure calculations can refer to Chapter 4.
Figure 5.1: The computational cell of the model water/CNT system: One end of a carbon nanotube (CNT) is inserted into a water reservoir; the CNT is sufficiently long so that no water molecule will flow out from the other end during simulations. Pressure is applied through the piston-like bottom plane of the reservoir. The loading is quasi-static. A periodical boundary condition is imposed to the four lateral planes of the cell. An external electric field, $E$, is applied in the cell along the length direction of CNT (the current direction is positive).

5.2 Fundamental Infiltration Characteristics in the Presence of an External Electric Field

5.2.1 Effect of electric field on infiltration pressure in CNT/water system

Without an external electric field, from Chapter 4, when the applied pressure exceeds a critical value (referred as infiltration pressure, $P_{in}$), the capillary resistance is overcome and water molecules will burst in to a CNT (Figure 4.2). The $P_{in}$ shows a strong size dependence of nanopores, and will decrease with the increase of pore diameter.

With an applied electric field, the infiltration isotherm of the water-(16,16) CNT
reference system is distinct. Figure 5.2 indicates that more water molecules can easily enter the CNT (at lower $P_{\text{in}}$) with the increase of electric field, as the system becomes effectively less hydrophobic. An interesting phenomenon can be found when the direction of the electric field is switched. In Figure 5.3 (a), when $|E|=0.06$ V/Å, there is a small asymmetry for positive and negative electric intensities, where the $P_{\text{in}}$ of a small (10,10) CNT is slightly smaller (and the system is a bit less hydrophobic) upon a positive electric intensity than that with a negative electric intensity. Such a nanoconfinement-induced asymmetry is more obvious if the magnitude of the applied electric intensity is increased to $|E|=0.1$ V/Å, Figure 5.3(b). If the CNT gets larger, such as (18,18), then in case of a small magnitude of electric intensity (0.06 V/Å), the difference between the positive and negative electric intensity is negligible (Figure 5.4(a)); when $|E|$ is increased to 0.1 V/Å the asymmetry is apparent (Figure 5.4(b)) but the difference in infiltration behavior is still less prominent than that in the smaller (10,10) CNT.

![Figure 5.2](image_url)

**Figure 5.2:** The effect of electric intensity on the infiltration behavior for a (16,16)CNT/ water system.
Figure 5.3: The effect of the direction of the external electric field on the infiltration characteristic of water molecules into a (10,10) CNT. (a) $\pm 0.06 \, \text{V/Å}$, and (b) $\pm 0.1 \, \text{V/Å}$.

Figure 5.4: The effect of the direction of the external electric field on the infiltration characteristic of water molecules into a (18,18) CNT. (a) $\pm 0.06 \, \text{V/Å}$, and (b) $\pm 0.1 \, \text{V/Å}$.

Figure 5.5 plots the effect of electric field on $P_{in}$ for six different CNT radii. It is readily seen that the $P_{in}$ decreases with the increase of electric intensity. The asymmetry in positive and negative electric field is more obvious if the electric field is stronger, or when the CNT is
smaller, and the system is slightly more non-wetting (with a higher $P_{in}$) in the presence of a negative electric field. These features are consistent with parallel experiment discussed below.

The underlying mechanism for electric field-dependent infiltration behavior is attributed to the inherent physical characteristics of solid-liquid interaction, such as the contact angle, surface tension, and density profile of confined liquid molecules, which are influenced by not only the electric field but also the size of nanopore, elaborated in the next section.

![Figure 5.5: The coupled effect of pore size and electric field strength on the critical infiltration pressure, $P_{in}$.](image)

**5.2.2 Molecular mechanism of electrically driven infiltration**

Along the similar analysis procedure in Chapter 4, the surface tension, $\gamma$, between water molecules inside CNT and vapor (vacuum in this study), and contact angle, $\theta$, continue to be employed to study the molecular mechanism in the present of an external electric field, first qualitatively and then quantitatively. When there is no an external electric field (i.e. the reference system where $\gamma = \gamma_0$, $\theta = \theta_0$, and $D = D_0$), The analysis in Chapter 4 shows that the more
constriction of water molecules in a smaller CNT subjects a stronger solid-liquid interaction, which leads to a lower $\theta_0$ and a higher $\gamma_0$.

When an external electric field is applied, according to the insight from classic electrochemistry theory, $\gamma \cos \theta = \gamma_0 \cos \theta_0 - C \phi^2 / 2$, where $C$ is the interfacial capacity, and $\phi$ is the applied potential difference $^{201}$. This equation indicates that regardless of the sign of the applied voltage, the effective interfacial tension $\gamma \cos \theta$ always decreases with the magnitude of $\phi$, and that would reduce the critical infiltration pressure, $P_{in}$; these observations are qualitatively consistent with MD simulation results (Figure 5.5). Meanwhile, the classic theories cannot directly explain the size dependence of infiltration behavior (and its coupling with electric field dependence) and the asymmetry of positive and negative electric fields.

In order to quantify the molecular mechanism of water-carbon interaction in the nanoconfinement, two different model nanochannels, (10,10) and (18,18) CNTs, are chosen as representative cavities for accommodating water molecules. Figure 5.6 shows the density profile of water, $\rho(r)$, along the radial direction of a (10,10) CNT at the equilibrium after the water molecules have intruded the nanopore. The fluctuation of density profile is due to the hydrophobic nature of the considered nanotube, where most of the water molecules are confined in concentric rings/layers inside the tube; the similar characteristic of water distribution in CNTs has also been observed in other previous MD studies $^{14,23,160,174}$.

From Figure 5.6, under the applied electric field, the fluctuation amplitude of the density profile decreases; moreover, the difference of the density profile under the negative and positive electric fields indicates that the wetting properties are different. These features echo the above MD simulation results. Figure 5.7 shows the radial density profile of water molecules confined in
the larger (18,18) CNT: it can be seen that the water structure contains more concentric layers with smaller amplitude (density) than that in the (10,10) CNT, and the smaller fluctuations in the density profile suggest a weaker solid-liquid interaction and thus less sensitivity to the external electric field (as well as the asymmetry of positive and negative electric fields). With further increase of CNT diameter, it is envisioned that the radial density profile distribution will become homogenous and deduces to that of the classic fluid behavior.

Another important feature that can be obtained from the radial density profile is the position of the first solvation shell (FSS). In the absence of the external electric field, the distances from FSS to the nanotube wall (referred as the equilibrium distance here) are 2.280 Å and 2.305Å for (10,10) and (18,18) CNTs, respectively. Both of them are close to the measured value of water drop on a graphene (2.5Å) \(^{202,203}\), and the small difference is resulted from the curvature confinement effect \(^{112,204}\). With the increase of the applied electric intensity, Figures 5.6 and 5.7 indicate that the position of FSS moves away from the nanotube axis, and reduces the equilibrium distance. This is consistent with the electrowetting characteristic of water on a grapheme observed by Daub et al. \(^{205}\). For a given nanotube, a smaller equilibrium distance implies a larger effective diameter \(D\), and according to the Laplace-Young equation, that is another factor contributing to the reduction of \(P_{\text{in}}\) for the system under electric field.
Figure 5.6: The normalized radial density profile of water, $\rho(r)/\rho_0$, confined in a (10,10) CNT where $\rho_0 = 998.0 \text{kg/m}^3$. (a) $E=\pm0.06\text{V/Å}$, and (b) $E=\pm0.10\text{V/Å}$. The left axis is aligned with the tube axis.

Figure 5.7: The normalized radial density profile of water, $\rho(r)/\rho_0$, confined in a (18,18) CNT where $\rho_0 = 998.0 \text{kg/m}^3$. (a) $E=\pm0.06\text{V/Å}$, and (b) $E=\pm0.10\text{V/Å}$. The left axis is aligned with the tube axis.

Besides the effective pore size $D$, the surface tension $\gamma$ and contact angle $\theta$ affect the infiltration behavior in a more profound manner. We first deduce the quantitative information of
\( \theta \) through an independent analysis. Following the technique proposed by Werder et al. \(^{112}\), for water molecules confined in a given CNT, at the equilibrium state the spatial positions of the molecules at the meniscus front are averaged in a long computational time frame, and from that averaged meniscus profile, the contact angle is deduced, illustrated in Figure 5.8(a) for the example of (18,18) CNT subjecting to an electric intensity of 0.1 V/Å. In Figure 5.8(b) \( \theta \) is presented as a function of electric strength, and the coupled pore size effect is also shown. For (10,10) and (18,18) CNTs, the contact angle \( \theta_o \) is 106.6\(^{\circ}\) and 112.4\(^{\circ}\), respectively, in the absence of electric field, consistent with the hydrophobic nature. With an applied electric field, the contact angle \( \theta \) decreases, and such a reduction of hydrophobicity is also larger for positive electric strength than the negative one, consistent with the trend in \( P_{in} \) (Figure 5.5). The anisotropy in water molecule response to the direction of an applied electric field indicates possible new electrochemistry mechanisms in a confining nanoenvironment.

Finally, based on the Laplace-Young equation, \( P_{in} = -4\gamma \cos \theta / D \) and Figure 5.8(b), the electric field-dependent and size-dependent \( \gamma \) can be calculated in Figure 5.8(c), where the variation and dependence of \( D \) are taken into account. It can be seen that the surface tension of water in the (18, 18) CNT is \(~0.11\) N/m without electric field, and it increases with the reduction of CNT diameter due to the effect of CNT curvature and density of confined water molecules \(^{206,207}\). The result is consistent with that of MD results of \(0.1269\) N/m\(^{208}\) on the water-carbon system at 300 K. Like the contact angle, the surface tension also decreases with the external electric intensity. The field-induced reduction of both \( \gamma \) and \( \theta \) contribute to the decrease of hydrophobicity (reduction of \( P_{in} \)) in the electrically controlled nanopore-liquid system. The variation trend of surface tension and contact angle with respect to the applied electric field also
agrees with the experiment for a water droplet resting on a graphene\textsuperscript{205}, yet we note that in the present study, the electric field effect is closely coupled with the pore size effect.

![Diagram](image)

**Figure 5.8:** (a) Illustration of determining the contact angle in a (18,18) CNT upon an external electric intensity of 0.1V/Å; the left axis is aligned with the tube axis, and the right axis is at the tube surface. The red dash line indicates the statistically averaged spatial positions of the water molecule front in the CNT, based on which the contact angle is determined. (b) Variation of the contact angle, $\theta$, with the external electric intensity; (c) Variation of the surface tension, $\gamma$, with electric intensity.

### 5.2.3 Extend to other nanopores and liquid phases

In previous sections based on a model CNT/water system, we have revealed some basic mechanisms of the effect of electric field on infiltration behaviors. Apparently, with different
solid phase and liquid composition, the infiltration characteristics are distinct. For example, in the absence of electric field, the infiltration pressure may be favorably elevated through the introduction of electrolyte as well as using silica nanotube\textsuperscript{161,209,210}.

To demonstrate the influence of electric field on other systems, a silica nanotube (SNT) with pore size very close to that of (18,18) CNT and aqueous solution of sodium chloride (NaCl) (with molar concentration of 2.0mol/l) are chosen as substitutes of the solid pore and liquid phase, respectively. Here the diameter of the (18,18) SNT (24.56 Å) is measured as the distance between two opposite oxygen atoms.

Following the same computational procedure above, Figure 5.9(a) plots the effect of the external electric field on $P_{in}$. In comparison to the CNT/water system under the same electric intensity, with the employment of SNT or aqueous solution of NaCl, the system becomes more hydrophobic with a higher $P_{in}$, with the electrolyte have a bigger impact. The corresponding contact angle, $\theta$, and surface tension, $\gamma$, are plotted in Figures 5.9 (b) and (c), respectively: the results indicate that the increment of surface tension is mainly responsible for enhancing the hydrophobicity when the liquid/solid phases are changed. In case of the employment of electrolyte (in comparison with that of pure water), the additional work required to break the hydration shell for liquid infiltration makes $P_{in}$ higher; with an applied electric field, the cations and anions tend to move toward different directions and that is added to the electric strength-dependent infiltration barrier. In case where the SNT is used, the partially charged surface has a stronger interaction with the polar water molecule and that could lead to a stronger solid/liquid interfacial tension\textsuperscript{161}, which is also sensitive to the electric field. These findings could improve the energy absorption efficiency of nanopore-liquid system.
Figure 5.9: Comparison of different solid and liquid phases; the effect of external electric intensity on the (a) critical infiltration pressure, $P_{in}$, (b) contact angle, $\theta$, (c) surface tension, $\gamma$.

5.3 An Electro-actuation System Based on Nanofluids

5.3.1 Design strategy and MD realization

Figure 5.5 implies that for a given pore size, there is a one-to-one correspondence between the $P_{in}$ and $E$. Therefore, an electro-actuation system can be designed as follows. Let $P_{in}^0$ and $P_{in}^E$ to be the critical pressure without and with $E$, respectively. An external pressure $P_{app}$, whose magnitude is fixed throughout the process and $P_{in}^0 > P_{app} > P_{in}^E$, is imposed on the piston.
Once the electric field is applied, the system becomes relatively more hydrophilic, and with the water invasion into the nanopore the system volume decreases, and mechanical work is produced. When $E$ is removed, the system becomes relatively hydrophobic again and the water defiltrates, and part of the stored interfacial tension will be converted to mechanical energy.

We first investigate the performance of a representative actuation system, whose unit cell contains an end-capped (18,18) CNT of length 4.9 nm and initially there are 2312 water molecules in the reservoir. Throughout the simulation, the piston’s position is adjusted in-situ such that the reservoir pressure $P_{\text{app}}$ is kept as a constant just below $P_{\text{in}}^0$. As expected (Figure 5.10), with the application of electric field, the water starts to flow into the CNT. During the operation, the effective work output, which can be evaluated as $W_{\text{eff}} = P_{\text{app}} \cdot \Delta V$ with $\Delta V$ the volume reduction of reservoir, increases almost linearly with time – this implies that the power output $P$ is almost a constant during actuation. When $E$ is larger, the water infiltration flow rate, $q$, is higher, and thus with higher power. Similar to the classic pipe flow, the flow rate is found to be proportional to the pressure difference, $q = \zeta \cdot (P_{\text{in}}^0 - P_{\text{in}}^E)$, and $\zeta$ depends on material and system parameters (and independent of $E$). After $E$ is removed, the outflow rate is almost the same since that process is driven by the same solid-liquid interfacial tension.
Figure 5.10: For a (18,18) CNT/water system, when $P_{\text{app}}$ is fixed and upon employment of electric field, the number of infiltrated water molecules varies dramatically with time.

The maximum work ($W_{\text{max}}$) that can be output by such a system is reached when the CNT is just filled. Since the infiltrated water molecule configuration depends only slightly on $E$, so does $W_{\text{max}}$. In Figure 5.11(a), the down triangle curve gives the relationship between the available energy density ($W_{\text{max}}$ per mass, where the mass is that of the entire system) and $E$ for the current (18,18) CNT/water system with specified dimensions.

The average power density ($P$ per mass during infiltration) is shown in the down triangle curve in Figure 5.11(b), which is a strong function of $E$. The system efficiency can be estimated as, $\eta = \frac{W_{\text{eff}}}{(W_{\text{eff}} + W_e)} \times 100\%$, where $W_e$ is the input required to maintain the static uniform electric field. In Fig. 3b the average efficiency of the present system is shown to increase with $E$ due to the reduced solid-liquid interaction.

5.3.2 System parameter optimization

The performance of electro-actuation depends on characteristics of the system, such as
pore phase, pore size, pore length, liquid phase, liquid volume, working temperature, electric field direction, etc. To illustrate, we first study several CNT/water systems with different pore sizes. In these systems the CNT length and reservoir height are fixed, and the ratio between the pore volume and reservoir volume keeps a constant. Corresponding results in Figure 5.11 show that in general a smaller CNT diameter is more welcome for enhancing the energy density, power density, and efficiency, thanks to the higher surface-to-volume ratio and stronger interfacial action between carbon and water molecules. Nevertheless, it is cautioned that if the CNT is small, the infiltrated water molecules may be constrained in a single-file\textsuperscript{161} and that reduces the system performance. When other parameters are fixed, our study indicates an optimum pore size of about 1nm.

The CNT can be replaced by other nanochannels, for example a silica nanotube (SNT), with diameter 24.56 Å that matches with that of CNT (18, 18) and with other conditions fixed. Although the interaction between SNT and water is stronger\textsuperscript{161}, SNT is considerably heavier than CNT and thus having lower energy and power densities. When the water phase is replaced by 2.0mol/L aqueous solution of sodium chloride (NaCl), for the same (18,18) CNT system, the solid-liquid interaction becomes stronger\textsuperscript{161}, yet the mass is not significantly increased. Thus for the systems under investigation the energy density, power density, and efficiency are all increased compare with the pure water counterpart.

There are many other factors that can affect actuation. For instance, in all examples above the ratio between the volumes of the pore and reservoir is fixed. If less liquid is used, the energy/power densities and efficiency will improve. The variation of temperature and electric field direction (or pore alignment) will also influence the solid-liquid interfacial tension,\textsuperscript{160,161} and a more systematic parametric study will be carried out in future.
Figure 5.11: Variation of (a) the energy density, $W_{\text{max}}$; (b) the normalized output power density, $P$ (normalized by that of a 1.0nm$^3$ water at $E=0.08V/\text{Å}$), and (c) the efficiency, $\eta$, of the electrically controlled actuation system. The applied $E$, pore size, pore phase, and liquid phase are varied.
5.4 Comparison with Experimental Data

To qualitatively validate the computational results, we performed an electrically-induced infiltration test on a nanoporous silica crystal. The nanoporous material under investigation was a nanoporous silica crystal, which was surface treated to increase the degree of hydrophobicity of the inner surfaces of nanopores. The nanopores were confirmed to be open through a gas absorption analysis by using a Micromeritics Tristar-3000 Analyzer; the average pore diameter was about 14.6 nm. An aluminum foil was repeatedly folded to form aluminum layers, and treated silica disks of about 16.5 mg were inserted between the adjacent layers (Figure 5.12). The extra aluminum layers were connected together, forming an electrode and counter-electrode respectively. The silica disks and the electrode were insulated by porous Teflon membranes, and thus a nanoporous layer stack is formed. This stack was placed at the bottom of a steel cylinder, inside which 10g of 15% aqueous solution of potassium chloride (KCl) was sealed by another steel piston from the top. The inner surface of the cylinder was insulated from the liquid phase and aluminum layers by a Teflon layer. By using a direct current (DC) power source, an open-circuit voltage, $\phi$, was applied between the lower and a counter-electrode, which was separated from the silica-aluminum layer stack by a porous polystyrene membrane. The present applied voltage created an electric field parallel to nanopore walls was approximately obtained. The value of $\phi$ was in the range of -380 V to +420 V. By using an Instron machine, the piston was intruded into the cylinder at a constant rate of 0.5 mm/min (the loading rate was confirmed to be sufficiently slow so as not to introduce any rate effect). Since the nanopore inner surfaces were hydrophobic, only when the applied pressure was sufficiently high (beyond $P_{in}$) a large number of water molecules could be forced into the nanopores.
Figure 5.12: Schematic of the experimental setup. Disk-like porous silica samples were inserted into the adjacent folded aluminum layers. The silica disks and the electrode were insulated by porous Teflon membranes. The silica stack and the anode were separated with a porous polystyrene membrane, and placed at the bottom of a steel cylinder and immersed in aqueous solution of potassium chloride (KCl), sealed with a steel piston from the top, and properly insulated in the interior. The upper and bottom extra aluminum layers were connected to form electrodes and counter-electrodes, respectively, through them a direct current (DC) power source with voltage, $\phi$, was applied to obtain an electric field parallel to nanopore walls in proximity.

The measured $P_{in}$ as well as the deduced effective interfacial tension are given in Figure 5.13 as a function of the applied voltage, where the trend is qualitatively consistent with the computational results (Figures 5.5 and 5.8), suggesting that $P_{in}$ decreases with increasing $|E|$, despite the difference between the experimental and simulation systems. In addition, the direction of the electric field has some effect on $P_{in}$, and a lower $P_{in}$ is observed in the presence of the positive electric field, which is also consistent with predictions in Figure 5.5. All these phenomena again suggest that the conventional electrochemistry theory should be enriched the nanoscale. The power output of the thus designed electro-actuation system is deduced in Figure 5.14, which shows that $P$ increases nonlinearly with $\phi$. The energy density is about 4.7J/g,
which, as discussed above, can be significantly improved by using less liquid. The results are qualitatively consistent with simulation, despite of different nanopore structure, solid, and liquid used.

Note that the current agreement between simulation and experiment is rather qualitative, owing to several practical challenges that have not yet been overcome. First, the experimental system is much larger than the simulation cell, with the pore size larger and length longer. Second, the diameter of nanopores in the experimental systems is not quite uniform, and the pore structure is also quite complex. Third, the surface treatment used in experiment is difficult to incorporate into simulation. Last but not least, due to the size and time scale accessible to MD simulation, the electrical strength applied in simulation is much higher than that in experiment. A more quantitative coordination between simulation and experiment will be reported in future.

![Graph](image)

**Figure 5.13:** Experimental result on a nanoporous silica/aqueous solution of potassium chloride (KCl) system. The infiltration pressure, $P_{in}$, and the deduced solid-liquid interfacial tension, $\gamma \cos \theta$, in response to the applied external voltage, $\phi$. 
5.5 Summary

By taking advantage of the large specific surface area of nanoporous materials, a number of nanofluidic devices have been proposed whose functionality critically depends on the ability to control the effective solid-liquid interfacial tension. In this chapter, we investigate the possibility of adjusting the liquid-solid interactions by using electric field, and explore the electric strength-dependent infiltration behaviors of water molecules into hydrophobic nanopores. Systematic MD simulations of CNT/water systems show that the critical infiltration pressure reduces with the increase of electric intensity or pore size. The factors contributing to the reduced hydrophobicity include the electrical induced variations of surface tension, contact angle, as well as radial density profile of confined liquid molecules. An interesting phenomenon of asymmetric response to positive and negative electric fields is discovered, which is associated with the asymmetry in radial density profile and contact angle. The coupling between the electric field effect and pore size effect is elucidated, as well as the effect of using electrolyte and polar nanopore.
Based on the critical influence of the electrical field on the nanofluidic behavior, a concept of an electrically controlled actuation system is proposed by adjusting the effective hydrophobicity of a nanoporous material/liquid system. In the presence of an external electric field the infiltration threshold is reduced, and with liquid intrusion the reduction of system volume leads to work output. The power density and efficiency increases with higher electric strength, and for the current system under investigation, the energy density is about 10J/g and higher. The system performance, such as power density, energy density, and efficiency, also varies with pore size, solid phase, liquid phase and a few other parameters. The working principles are verified qualitatively by experiment. The study also shed some light on the perspective applications of controlling nanofluidic properties with electric field as well as the design of other electrically controlled nanoscale actuation devices.
Chapter 6 Mechanical/Thermal to Electrical Energy Conversion: Nanofluidic Energy Harvesting

The liquid-nanoporous composite material system has demonstrated an excellent capacity with high efficiency in energy absorption/capture for protecting objectives from impacting loads and energy thermo-electro-actuations for outputing mechanical work in the previous chapters. Likewise, the enormous specific surface area provided by nanopores is expected to amplify the mechanolectric and thermoelectric effects, allowing harvesting electricity from ambient mechanical and thermal energies. Since the unique nanofluidic behaviors are underpinned by the distribution and evolution of confined liquid molecules, as well as the strong intimate interaction between liquid molecules and solid wall. In this chapter, we will study the voltage generation induced by hydrochloric acid (HCl) water solution flowing through CNTs using the MD approach. The molecular mechanism is elucidated via the hopping motion and number density of ions in the first solvation shell. The voltage dependences of flowing velocity, environmental temperature, CNT size, and concentration of HCl solution are investigated. The results may be helpful for developing prospective energy harvesting nanodevices from ambient waste mechanical and thermal energy.

6.1 Model and Computational Method

The computational cell is shown in Figure 6.1. In this example, a segment of (20,20) CNT is employed to model a smooth nanopore, whose diameter is $D=2.712$ nm and length is $L_0=10.7$ nm. The CNT is assumed to be rigid according to the theoretical analysis by Král and
Shapiro. The CNT contains a HCl/water solution with a desired concentration, where the H$^+$ is combined with water molecule via one monovalent with the form of H$_3$O$^+$. The number of total water molecules, $N$, is chosen such that the density inside the CNT is close to that of bulk phase, 998.0 kg/m$^3$, at 300 K and 0.1 MPa. The extended Simple Point Charge (SPC/E) potential is used to model water molecules, as well as that for the O-H bonds and H-O-H angles of the H$_3$O$^+$ ion. The O and H atoms in H$_3$O$^+$ ions are charged with -0.554e and +0.518e, respectively, and each Cl$^-$ is charged with -1.0e, such that the total liquid system is electric neutral. The proton transfer is not considered in MD simulations. The 12-6 pairwise L-J potential and Coulomb interaction, $U(r_{ij}) = 4\varepsilon_{ij}[(\sigma_{ij}/r)^{12} - (\sigma_{ij}/r)^6] + q_i q_j / (4\pi\varepsilon_0 r)$, are used to model the short-range van der Waals and electrostatic interactions among ions as well as that among atoms, respectively, where $r$ denotes the distance between atoms $i$ and $j$, $\varepsilon_{ij}$ and $\sigma_{ij}$ are the energy and length parameters for a $i$-$j$ pair atom, respectively, $q_i$ and $q_j$ are the electric charge counterpart, and $\varepsilon_0$ is the permittivity of vacuum. All L-J interactions are truncated and shift to zero at 10 Å. Additionally, to account accurately for the long-range electrostatic interactions of the charges and their periodic images, the Particle-Particle Particle-mesh technique with a root mean square accuracy of $10^{-4}$ was employed. The L-J parameters and partial charges are taken from refs., and listed in Table 6.1. The cross interactions are obtained by using the Lorentz-Berthelot mixing rules, $\varepsilon_{ij} = \sqrt{\varepsilon_i \varepsilon_j}$, and $\sigma_{ij} = (\sigma_{ii} + \sigma_{jj}) / 2$. 
Figure 6.1: An example of computational model of HCl solution (0.9mol/l) flowing inside a (20,20) CNT (green, Cl⁻; red, O; white, H or H⁺).

Table 6.1: The 12-6 L-J potential parameters used in the MD simulation

<table>
<thead>
<tr>
<th>Atom/ion</th>
<th>ε (kcal/Å)</th>
<th>σ (Å)</th>
<th>q (e)</th>
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<tr>
<td>C</td>
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<td>3.215</td>
<td>0</td>
</tr>
<tr>
<td>H (in H₂O)</td>
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<td>0</td>
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<tr>
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<td>-0.8476</td>
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<tr>
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<td>-0.554</td>
</tr>
<tr>
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<td>+0.518</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>0.4184</td>
<td>4.404</td>
<td>-1</td>
</tr>
</tbody>
</table>

MD simulation is performed using LAMMPS (large-scale atomic/molecular massively parallel simulator) with a time step of 1.0 fs. Periodical boundary condition is imposed in the axial direction of the computational cell so as to mimic an infinite long pore. The simulation procedure is the following: after initialization, the NVT (canonical) ensemble is employed for 100ps to minimize the system energy. To simulate a steady flow, a thin liquid slab (2Å in axial length) in the middle of the CNT is assigned a constant velocity, $v_0$. Note that $v_0$ is much larger than that used in experiment so as to minimize the effect of thermal noise on motion of ions and water molecules. The temperature is controlled by using the Nose-Hoover thermostat with a time constant of 1.0 ps. At the same time, to avoid artificial heating caused by the imposed load, the
mean axial velocity of the liquid mass center is subtracted from the axial component of the velocity of each liquid molecule during the calculation of temperature. The ion motion is monitored via the accumulated displacement to deduce their drift velocity.

6.2 Results and Discussion

6.2.1 Fundamental ion distributions and thermal dependence

Taking a representative example of (20,20) CNT containing 0.9 mol/l HCl solution, we first examine the distribution of Cl\(^-\) and H\(^+\) (or H\(_3\)O\(^+\)) ions inside the CNT at 300K. Figure 6.2 shows their number densities along the radial direction. It can be seen that the density of Cl\(^-\) ions oscillates and arrives at maximum near the CNT wall, implying a layered structure in the radial direction. The shaded region in Figure 6.2 and inset indicates the outermost layer, which is often referred as the first solvation shell (FSS). In other words, most Cl\(^-\) ions are confined in the FSS due to their strong interaction with carbon atom. In contrast, the oscillation for H\(^+\) is less prominent due to a weaker interaction between H\(_3\)O\(^+\) and CNT.

6.2.2 Voltage generation: transport rate and thermal dependences

Upon a steady flow, the Cl\(^-\) ions may hop and move forward near the wall thanks to their strong interaction with carbon atoms and adjacent water molecules\(^{89,216}\) showing a stick-slip motion. Meanwhile, the more uniformly distributed H\(_3\)O\(^+\) ions follow the flow without hopping, since their combination with water molecules is rather stable. The ion drift may thus be responsible for voltage generation, and such a mechanism was theoretically proposed to flow through CNT bundles\(^{89}\) and by graphene\(^{216}\) inducing a current opposite to the flow direction. In
the present study, we use MD simulations to validate the mechanism and explore the ion drifting effect inside the CNT, as well as its dependence on flow speed, pore size, ion concentration, and temperature. Note that the contribution of H$_3$O$^+$ on voltage generation is negligible since the cations circulating inside nanotube will not generate a net current. Thus, we focus on the hopping and moving mechanisms of Cl$^-$ ions near the wall, which makes the distribution of Cl$^-$ nonuniform along the flow direction. Moreover, simulation shows that the drift velocity of each Cl$^-$ ion inside FSS is almost a constant, where the drifting velocity is calculated from the accumulated displacement of respective ion. Figure 6.3(a) gives the average drifting velocity of Cl$^-$ ions, $v$, as a function of the applied flow velocity, $v_0$, at 300K, and a nonlinear increasing trend (close to logarithmic) is found.

![Figure 6.2: Radial number density of Cl$^-$ and H$_3$O$^+$ ions, where the inset shows the top view of distribution of water molecules and ions. The concentration of HCl solution is 0.9mol/l. The left axis is aligned with the tube axis.](image)

With the aforementioned mechanism of energy harvesting, the voltage induced by the nanofluidic flow can be estimated as $V = RA\sigma v$, where $R$ is the CNT’s resistance, $\sigma$ is the
average charge carrier density, $e$ is the electronic charge and is $1.6 \times 10^{-19} \text{C}$, $A$ is the cross section area of CNT, and $v$ is the average drifting velocity of Cl$^-$ ions in FSS. Based on previous experimental results,$^{218,219}$ the resistance, $R$, is related to the CNT geometry as $R = 4R_0L / (\pi D^2)$ where $R_0$ is the reference resistance of $400\ \Omega \cdot \text{nm}$. The temperature dependence of resistance is negligible (for the range of 300-360K considered in this paper).$^{219}$ With reference to Figure 6.3(b), a nonlinear increase in the induced voltage with the increase of flux is obtained, and the trend qualitatively agrees with the experiments of Ghosh et al.$^{54}$

Nanofluidic behavior is temperature-dependent, and so is the energy harvesting capacity. Figure 6.2(a) shows the thermal variation of the number density of Cl$^-$ ions, whose FSS amplitude decreases at elevated temperatures, indicating a weaker interaction among water molecules, ions and CNT wall;$^{45,160}$ consequently, the pinning force of Cl$^-$ ions to FSS decreases, and a few of them may migrate to the center of nanochannel. Likewise, the distribution of H$_3$O$^+$ ions also shows a smaller oscillation and smaller FSS amplitude at a higher temperature. The temperature dependence of the average drifting velocity of Cl$^-$ ions in FSS (Figure 6.3(a)) shows that under the same $v_0$, $v$ increases with temperature. The resulting temperature-dependent voltage is plotted in Figure 6.3(b), which also increases with temperature. That is, despite the lower number density of Cl$^-$ ions in FSS at elevated temperatures, the enhancement of the drifting velocity is more dominant (consistent with the more “active” hopping effect). This strong temperature dependence also verifies the prediction by Persson et al.$^{89}$ On the other hand, with further increase of temperature, the increase of voltage becomes slower, indicating a nonlinear thermal dependence which is mainly caused by the reduced number density of Cl$^-$ ions in the FSS.
Figure 6.3: Variation of (a) the drifting velocity of Cl\textsuperscript{-} ions in FSS and (b) induced voltage in axial direction, as a function of the flow rate and at different temperatures. The results are specified for a (20,20) CNT containing 0.9mol/l HCl solution. The error bar indicates the range of fluctuation of the drifting velocity, which propagates to the deduced voltage.

6.2.2 Response of voltage generation to ion concentration

Ion concentration clearly affects the anion hopping mechanism and therefore the voltage generation. Take a (20,20) CNT at 300K and with flow rate $v_0=9$ m/s as an illustrative example. Figure 6.4 shows that $v$ decreases with the increase of concentration, possibly due to the enhanced resistance to hopping and motion of ions. Nevertheless, such an effect is offset by the more dominant term of the higher number density of Cl\textsuperscript{-} ions in FSS, resulting in an overall increase of the induced voltage with ion concentration. Meanwhile, the voltage tends to saturate at very high concentration of ions, due to the competition between the increase of number density of Cl\textsuperscript{-} ions and decrease of drifting velocity. These trends are in qualitative agreement with experimental results reported by Dhiman et al \textsuperscript{57} and Ghosh et al \textsuperscript{54}. Note that when the concentration of HCl solution is zero, there is no ion-hopping mechanism, and the energy harvesting by flowing of pure water through the CNT is attributed to polarization,\textsuperscript{220,221} which
generates less prominent voltage and such a mechanism is not considered in the present paper.

![Graph showing variation of drifting velocity of Cl\(^-\) ions in FSS and induced voltage as a function of concentration of HCl solution in a (20,20) CNT. The temperature is 300K, and \(v_0=9\text{m/s}\).]

**Figure 6.4:** Variation of the drifting velocity of Cl\(^-\) ions in FSS and induced voltage, as a function of the concentration of HCl solution in a (20,20) CNT. The temperature is 300K, and \(v_0=9\text{m/s}\).

### 6.2.3 Size dependence of voltage generation

Following the similar procedure, we investigate the influence of CNT diameter which would affect the degree of nano-confinement. Figure 6.5(a) shows that the radial number density of Cl\(^-\) ions in FSS decreases with the increase of diameter, suggesting that a weak interfacial interaction among ions, water molecules and carbon atoms.\(^{45}\) The structural distribution of water molecules and ions (inset in Figure 6.5(a)) further indicates that in a smaller CNT, Cl\(^-\) ions tend to gather in the FSS and there is no ion left in the middle of CNT. Under the applied flow rate of \(v_0=9\text{m/s}\), the drifting velocity of Cl\(^-\) ions is plotted in Figure 6.5(b), which decreases with the increase of CNT size, consistent with the lower transport velocity and larger resistance in larger CNTs.\(^{136,222}\) The deduced voltage is thus smaller in a larger CNT (Figure 6.5(b)), owing to the smaller number density of Cl\(^-\) ions in the FSS and lower drifting velocity. The strong size dependence could be used to optimize energy harvesting performance.
Figure 6.5: (a) The radial distribution of ions inside CNTs of different sizes and (b) variation of the drifting velocity of Cl⁻ ions inside FSS and induced voltage, as a function of CNT diameter. The inset in Figure 5a shows anion distribution of in smaller and larger CNTs. The temperature is 300K, concentration of HCl solution is 0.9mol/l, and v₀=9m/s.

6.3 Summary

When an acid solution flows through a nanotube, the stick-slip motion of anions induces an ion gradient along the axial direction, enabling energy harvesting. We employ MD simulations to study the voltage generation by flowing a HCl solution through a model CNT. The molecular mechanisms of ion hopping and motion are elucidated via the study of the anion configurations in FSS, from which the average drift velocity of Cl⁻ is deduced and subsequently used to obtain the voltage. The voltage increases with applied flow velocity, temperature, and ion concentration, and decreases with pore size increment, and these trends (which agree with previous experimental studies) are underpinned by the competition between the number density of anions in FSS and drifting velocity of these ions. The thermal, size, concentration, and flow rate dependences may be employed to design high efficiency energy harvesting nanodevices. For instance, the waste heat (~320-370K) from the exhaust of a power-plant may be circulated through nanopores, and part of the relevant kinetic and thermal energies may be scavenged.
Chapter 7 Conclusions and Future work

7.1 Concluding Remarks

In this dissertation, by seamlessly tailoring nanoporous materials with functional liquids, we have demonstrated in experiments and simulations that the formed liquid-nanoporous composite material system provides an ideal platform for energy conversion with high efficiency, including energy absorption, actuation and harvesting.

We start with the energy absorption protection mechanism based on nanofluidics through MD simulations. Upon an impact loading or blast wave on the formed liquid-nanoporous composite material system, a new protection mechanism of energy capture to the impact and blast energy wave is discovered. That is, the incoming kinetic energy can be quickly converted to the potential energy of water molecules and is captured, and then confined into slightly hydrophobic nanopores for a while, leading to an obvious reduction in both transmitted force and energy. The captured energy will be released gradually at unloading stage due to the inherence of non-wetting surface wall of nanopores through the diffusion of liquid molecules out of nanopores. The characteristic time of the process is around $10^{-9}$-$10^{-7}$ second, making it ideal for mitigating a highly nonlinear stress wave such as blast energy wave. Since the captured energy is not necessarily converted to other forms of energy (e.g. heat) and can be released gradually upon unloading, it is totally distinct from conventional energy absorption or dissipation mechanism, thus making the system reusable. MD simulations further demonstrate that the captured energy will not always increase with impacting velocity, and depends on the material parameters, such as nanopore size, solid composition, liquid phase, and charged state of nanoporous wall, and
external conditions, such as impacting velocity, which have been studied systematically. Under the same impacting velocity, the transmitted force and energy reduction, energy capture and duration show an overall increase with the increase of nanopore length and diameter, but the energy capture per volume decreases for an increased nanopore diameter. Given a certain nanopore, the transmitted force and energy reduction, energy capture and duration increase till arriving at a maximum first and then decrease due to the filling up of the nanopore. For the same pore size and impacting velocity, if the carbon nanopore in the system is replaced by a silica nanopore, the transmitted force reduction will increase, while the energy reduction will show a little drop; if the surface wall of the carbon nanopore is uniformly charged, independent of the sign of charge, or the liquid phase of water molecules changes to a electrolyte solution (NaCl or KCl solution), both transmitted force and energy reduction will decrease. The density profiles of water molecules at the axial and radial directions of nanopores are examined to understand the mechanism of energy capture. The axial density shows approximately the same during all stages of infiltration and defiltration process, and the relative uniformly layered-structure distribution in radial direction is observed, implying a “cluster-like” energy trapping and releasing mechanism. These MD findings are verified through a parallel blast experiment on a zeolite-water composite material system.

We then study the energy dissipation during transport of confined liquid molecules through nanopores, where the kinetic energy is dissipated due to the transport “friction” resistance exerted to the nearest liquid molecules by solid wall atoms. The temperature of confined liquids and wall roughness of nanopores are considered two key factors of affecting friction resistance, and investigated. The effective shear stress and nominal viscosity which represent an “overall” resistance the wall exerting to the flow are employed to characterize the
flow resistance. As the temperature of confined liquids rises, both the effective viscosity and the nominal viscosity decrease. The coupling effects of thermal effect between the nanopore size and transport rate effects are further studied, showing that the transport resistance is more sensitive to temperature in a smaller nanopore or higher transport rate. In addition, when the ions are added to the confined liquids, due to the enhanced liquid-solid wall interaction, the effective shear stress shows an enhancement compared with that of pure water molecules. When water molecules transport through a rough nanopore, MD simulations indicate that both the effective shear stress and the nominal viscosity increase with the decrease of wavelength of roughness or the increase magnitude of roughness. Besides, the roughness effect becomes more prominent in a smaller nanopore. Velocity profile, radial density and hydrogen bond of water molecules inside nanopores are employed to understand these findings and provide an underlying molecular mechanism. Either a lower temperature or a rougher nanopore shows a stronger solid wall-water interaction and an enhancement in the radial movement of water molecules near the wall, thus leading to a higher transport resistance. These findings are qualitatively verified by a pressure-induced infiltration experiment on a nanoporous carbon-water system.

Next, we develop a thermal actuation system based on nanofluidics with high energy output and conversion efficiency, allowing converting thermal energy to mechanical energy. When liquid molecules invade a hydrophobic nanopore, the infiltration pressure shows a thermal dependence. By using MD simulation, we systemically investigate the fundamental thermal infiltration behaviors of liquid molecules into hydrophobic nanopores. When the applied pressure arrives at a critical value beyond which the capillary resistance is overcome, water molecules start invading the nanopores, where the critical infiltration pressure decreases with the increase of temperature. The thermal dependence of infiltration pressure results from reduced interfacial
tensions between water molecules and nanopores, and is elucidated by studying the distribution of confined water molecular structures through the radial density profile, contact angle, and surface tension. In addition, the infiltration pressure is also a functional of pore size and solid phase as well as liquid phase. The infiltration pressure decreases with the increase of pore size; while increases when either solid phase carbon atoms or liquid phase water molecules are substituted by silica and NaCl-solution counterpart due to a stronger interfacial tension in comparison to carbon-water system. Based on the thermally tunable infiltration pressure of liquid molecules into CNTs, a conceptual design of thermal actuation system is proposed and realized through MD simulations. The working principle is summarized here: as environmental temperature varies, the system transits between a relatively stronger and weaker hydrophobicity, through which the liquids outside nanopores can be compressed into or the confined liquids inside nanopores can be repelled out of, leading to a variation of system volume. When an external mechanical pressure is applied on the system, the variation of system volume can lead to an output of mechanical work, similar to a conventional thermal machine. As temperature increases, the output power density and efficiency increase. The energy density can be as high as about 10J/g. The system performance can be further improved by optimizing systemic and material parameters such as the pore size, solid phase, and liquid phase. Parallel with MD simulations, a thermally controlled infiltration experiment on a zeolite-water system is performed. Both the thermal infiltration behavior of liquids into nanopores and the working principle of proposed thermal actuation are qualitatively verified.

Closely following the strategy of designing the thermal actuation system, we study the electric infiltration characteristics of liquid molecules into hydrophobic nanopores and conclude that it can also be adjusted by an external electric field. As the applied electric intensity
increases, the critical infiltration pressure decreases. Similar with the mechanism at evaluated temperatures, it can also be attributed to a reduced hydrophobicity which has been elucidated through the employment of surface tension, contact angle, as well as radial density profile of confined liquid molecules. Besides, further MD simulations indicate an asymmetric response to the sign of the applied electric field with the same magnitude: the critical infiltration pressure in the presence of a positive electric field is a little higher than that in the presence of a negative electric field, indicating that the conventional electrochemical theory may break down in nanoenvironments. The electric infiltration behavior is also coupled with the pore size, polar silica nanopore and electrolyte solution. Generally, in a smaller nanopore, the electric infiltration behavior is more sensitive, and the employment of polar silica nanopore and electrolyte solution shows the same trend. Given this clear molecular adjustable mechanism of electrically controlled nanofluidic infiltration behavior, a concept of electrically controlled actuation system is proposed. As the external electric intensity changes, the infiltration pressure changes, leading to a variation of system volume during the liquid into or out of nanopores, and thus the mechanical work can output. Both the output power density and the efficiency increase with the increase of electric intensity. The energy density is about 10J/g with the present parameters, and can be higher by optimizing the pore size, solid and liquid phase of systemic parameters. These MD findings are verified qualitatively by an electrically controllable infiltration experiment on a zeolite-KCl solution material system, providing a solid fundament on the application of electroactuation in practice.

Using MD simulations in the last chapter, we explore voltage generation mechanism by passing hydrogen chloride (HCl) solution through nanopores. MD simulations show that the accumulated displacement of Cl− ions nearest the nanoporous wall increases linearly with
simulation time, and a constant drifting velocity is obtained, responsible for voltage generation. The contribution from H$_3$O$^+$ can be neglected due to a quite uniform and stable distribution. The voltage generation mechanism of the ion hopping and moving forward nearest nanoporous wall is confirmed. Given an ion density distribution nearest the nanoporous wall and their drifting velocity, the generated voltage along the flow direction can be deduced. Further MD calculations show a nonlinear increase of voltage with the increase of the applied flowing velocity, consistent well with experiments in literatures. More importantly, the induced voltage is very sensitive with a small temperature fluctuation, which can be employed to harvest energy from low-grade heat. In addition, other critical factors of such as pore size and liquid concentration are also studied, through which an enhanced system performance can be achieved.

7.2 Recommendations for Future Work

Nanofluidics is a truly interdisciplinary research area encompassing aspects of mechanics, material, physics, chemistry, biology, etc. and its many unique behaviors remain unclear for far. On the other hand, such unique behaviors provide unexpected promising applications. Both are worthy of future study.

On the fundamental aspects, for example, both MD simulations and experiments in chapter 5 show that an infiltration process is dependent of the sign of an external applied electric field, in contrary to the conventional electrochemical theory. How to describe this asymmetric behavior with respect to the sign of the electric field? Will the water polarization affect the applied electric field? Which is the most proper water model at the nanoscale in the present of an electric field? Does this asymmetric response hold for any kind of polar liquid molecules? Can this electric asymmetric behavior be used to design alternating current actuation? These
works are expected to be helpful for building electrochemical theory at the nanoscale.

The confined liquid molecules like water molecules at nanoenvironments behave somewhat differently from macroscopic predictions, such as viscosity, thermal conductivity, and phase change. How to precisely define them remains unclear. More importantly, the unique behavior of water molecular transport is often attributed to an ordered configuration of the hydrogen bond network. Actually, many physical properties of water depend on the coherence and the number of the hydrogen bonds. What is the accurate relationship between the hydrogen bonds and fluidic properties such as viscosity, density and phase change? With the recent achievement that a single water molecule has been successfully encapsulated into a C60 cage, insulating it from any hydrogen-bonding environment, this provides an opportunity for quantitatively studying the effect of hydrogen bonds on nanofluidics and intrinsic behavior of water molecules. Future study can be carried out with emphasis on: (I) studying nanofluidic transport process of H$_2$O@C60 and closely relating it to the findings of pure water molecules in macrochannels down to nanochannels through several key physical indexes, such as diffusion, viscosity, and thermal conductivity; (II) investigating the transport response of H$_2$O@C60 to an external field, such as pressure, electric field, and thermal gradient; (III) exploring applications of H$_2$O@C60 in the detection and storage of one single molecule; (IV) probing characteristics of a single water molecule in this totally isolated state and its “communication” with the liquids surroundings.

Parallel with the studying properties of H$_2$O@C60, another effort can be devoted to encapsulating molecule like a water molecule into an opened-fullerene (C60) which can be deemed a nanopore with a unique interior space, which is similar with the infiltration of liquid molecules into a CNT. The future work can include: (I) mimicking the whole process of one
water molecule into the opened-C60 structures and obtaining the characteristic parameters, e.g. infiltration time; (I) studying the effects of the opening diameter and functional groups around the opening edge, and designing proper functional groups to allow the water molecule to infiltrate bow-like C60 spontaneously at room temperature and atmospheric pressure; (III) employing electrolyte solutions and other mixtures (e.g. CHCl₃) to investigate their effects on infiltration of water molecule, and obtaining the key controlling parameters (e.g. the ratio of mixtures to water molecules); (IV) investigating effects of an external field on infiltration behaviors such as pressure, electrical and thermal fields; (V) designing adjustable “switch” functional groups through which the trapped molecule can freely flow in or out of the opened-C60. This proposed structural design of the opened-C60 has also the potential to open up fertile areas of far future research for manipulating and counting one single molecule.

On the practical applications, for example, solar energy has been acknowledged a huge energy form for longer-term benefits in addressing energy crisis and environmental sustainability. Nanostructured materials have been employed to increase solar-energy conversion efficiency through the use of surface plasmons (SPs) in the past few decades. With the encouraging results on energy conversion enabled by nanofluids in this thesis, the nanostructured materials coupled by nanofluidics, which can be referred as nanofluidics-integrated nanophotonics, is expected to improve sensitivity and resolution of SPs, where the addition of liquid molecules offers great freedom to manipulate electromagnetic fields, thus enhancing the solar-energy conversion efficiency. The nanofluidics-integrated nanophotonics technique is also expected to provide a reliable approach for detecting low-concentration components with a high resolution by flowing them through a photonic nanochannel, such as the emerged Perchlorate (ClO₄⁻) contaminant (~10-100 mg/L) in water, which is urgently needed for environmental
protection and sustainability\textsuperscript{226}. Hopefully, such studies can be carried out soon.

This prospective application based on this new scheme will challenge conventional modeling and theory, such as finite-difference time-domain (FDTD) method for studying SPs. A new theory and modeling approach involving multiscale and multiphysics, where the interaction among light, nanofluidics and nanostructures are coupled, needs to be developed. The modeling of nanofluidics-integrated nanophotonics should include a realistic description of the medium and of its nonlinear dielectric response, especially for a random nanofluidic medium. At the same time, the re-organization feedback in the field of dynamics is also needed by coupling internal interaction potentials of particles in the media. This research for new modeling technique is expected to provide a design optimization tool which will help design nanostructures, and components of media in the search for new engineered nanostructures with enhanced SPs relevant to solar energy and molecular detection.

Finally, we want to point out that through the interaction of fluid and solid mechanics at the nanoscale, the unique characteristics of nanofluidics have offered compelling advantages for enhancing energy conversion efficiency and environmental sustainability. When nanofluidics is combined with other disciplines like chemical, electrical, and biomedical engineering, such its fantastic behaviors are expected to provide unprecedented opportunities and even open new areas in both theories and applications.
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