ON THE PHYSICS OF FLUID TRANSPORT AND PHASE CHANGE IN NANOCONFINEMENTS

By

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To my lovely husband, Hamid

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ABSTRACT

Understanding the underlying physics of fluid behavior at nanoconfined geometries is essential to address many common challenges existing in science and engineering applications such as nanomedicine, energy conversion and storage, water purification, membrane science and electronics/photonics cooling. As the confinement dimensions shrink to nanoscale, the role of fluid/wall interactions as well as surface forces become more significant in the transport phenomena. These interactions result in the properties and behavior of the nanoconfined fluid to deviate considerably from those of the bulk, so that the classical theories no longer hold. In this dissertation, our focus is to study fluid behavior in nanoconfinements in the context of fluid transport and phase change. To this end, we developed nanofluidic devices, which consist of 2-D planner nanochannels with a height ranging from 180 nm to 10 nm, on silicon ship through the MEMS fabrication techniques. The simple and deterministic structure of our developed devices allow us to investigate the validity of classical equation and hydrodynamic properties at the nanoscale, to recognize the source of deviation, and to explore atypical phenomena (physics) emerging at this scale, such as extremely high evaporative heat flux, formation of interfacial viscous layer, breakdown of capillary wicking and the concept of surface tension nanogates.

To explore phase-change at nanoconfinements, we studied thin-film evaporation in nanochannels under absolute negative pressure in both transient and steady-state conditions. We demonstrated that thin-film evaporation in nanochannels can be a bubblefree process even at temperatures higher than boiling temperature, providing high reliability in thermal management systems. To achieve this bubble-free characteristic, the dimension of nanochannels should be smaller than the critical nucleolus dimension. In transient evaporative conditions, there is a plateau in the velocity of liquid in the nanochannels, which limits the evaporative heat flux. This limit is imposed by liquid viscous dissipation in the moving evaporative meniscus. In contrast, in steady-state condition, unprecedented average interfacial heat flux of 11 ± 2 kW cm⁻² is achieved in the nanochannels, which corresponds to liquid velocity of 0.204 m s⁻¹. This ultrahigh heat flux is demonstrated for a long period of time. The vapor outward transport from the interface is both advective and diffusion controlled. The momentum transport of liquid to the interface is the limiting physics of evaporation at steady state. The developed concept and platform provide a rational route to design thermal management technologies for high-performance electronic systems.

To investigate liquid transport at nanoconfinements, we studied capillary driven flow in nanochannels, and demonstrated the role of interfacial viscosity in capillary motion slowdown in nanochannels through a combination of experimental, analytical and molecular dynamics techniques. We showed that the slower liquid flow is due to the formation of a thin liquid layer adjacent to the channel walls with a viscosity substantially greater than the bulk liquid. By incorporating the effect of the interfacial layer, we presented a theoretical model that accurately predicts the capillarity kinetics in nanochannels of different heights. Non-equilibrium molecular dynamic simulation confirmed the obtained interfacial viscosities. The viscosities of isopropanol and ethanol within the interfacial layer were 9.048 mPa.s and 4.405 mPa.s, respectively (i.e. 279% and 276% greater than their bulk values). We also demonstrated that the interfacial layers are 6.4 nm and 5.3 nm-thick for isopropanol and ethanol, respectively. To examine the governing mass transport mechanism at sub-10 nm scale, both optical and electrical metrologies were utilized to identify the nature of fluid. we demonstrate that capillary wicking breaks down at a sub-10 nm scale for some fluids, changing governing physics of the mass transport and leading to a quasi-static liquid-vapor interface experiencing dynamic process of wetting and liquid fracture in a cyclic manner. The scale of capillary breakdown is a function of interfacial tension of the liquid and could be tuned based on the system requirements. The capillary breakdown results in surface tension nanogates that are turned on/off via external stimuli such as minimal temperature actuation or applied voltage. These nanogates are highly effective and tunable for ion transport playing a critical role in functionality of biological systems. The surface tension nanogates promise platforms to govern nano-scale functionality of wide spectrum of systems and foresee application in drug delivery systems, energy conversion, power generation, sea water desalination and ionic separation.

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NOMENCLATURE

Term	Definition
IPA	Isopropyl alcohol
LW	Lucas Washburn equation

I. INTRODUCTION

Fluid behavior at nanoconfined geometries departs in various aspects from bulk behavior leading to emergence of many unexpected phenomena at the nanometer-scale. The field of nanofluidics, which explores fluid and ion transport at such small scale, has emerged over the last 15 years to understand and explain the underlying physics of these phenomena. Indeed, at the nanometer scale, the continuum assumptions of hydrodynamic that considered for bulk fluid are no longer completely valid. This arises from high surfacearea to volume ratio which makes the surface forces and fluid interaction with boundaries more dominant in transport phenomena compared with the micro-meter and larger scales.

Atypical transports and irregular thermodynamics phenomena in nanoconfined fluid have been broadly investigated by computational studies. Undoubtedly, experimental exploration of mass/ and ions transport across the tight conduits is essential as it helps deeply understand the fundamentals of unusual behaviors, and thus leads to design and develop more efficient nanofluidic systems for applications in a variety of fields e.g., electronic cooling and thermal management, drug delivery and water sieving. To obtain experimental quantifications, nevertheless, one should overcome two main challenges; The first is creating the nanofluidic devices with well-defined size and geometry, and the second is developing dedicated techniques to collect data from ultra-small volume of liquid confined at nanostructures.

Emerging of Nanofluidic Systems

Advancement of nanofabrication techniques as well as development of new nanomaterials have significantly contributed to produce reliable nanofluidic devices for systematic fundamental investigations. The nanofluidic systems that have been developed so far include a wide variety of structures such as nanoporous membrane, nanotubes made from carbon or 2-D materials (in the form of individual or lipid membrane), and planar nanochannels (created by Vander Waals assembly of 2-D materials or fabricated by standard MEMS techniques).

For instance, Holt et al.¹ developed sub-2nm vertically aligned carbon nanotubes membrane through following process; first, they applied catalytic chemical vapor deposition on the surface of a silicon chip to grow a dense array of CNT. Afterward, the grown CNT were encapsulated by a low-pressure chemical vapor deposition of silicon nitride. Finally, silicon nitride was removed from two side of the structure with ion milling and nanotubes were opened up through reactive ion etching. The researcher utilized the developed nanofluidic system to measure the gas and water flow within carbon nanotubes array. Another interesting type of transmembrane channel is bio-inspired carbon nanotubes porins which is developed by Tunuguntla et al.² to explore water and ion transport within nanoconfinemt. This nanofluidic system is formed by spontaneous insertion of 10-nm-long carbon nanotubes with 0.8-1.5 nm diameter into a lipid membrane.

Although experimental investigations performed in such nanoporous and nanotubes membranes offer valuable understanding of nanoscale fluid behavior, they essentially lack the accurate quantitative analysis since the probed transport phenomena in such systems is a result of averaged measurement over the entire membrane. To overcome this deficiency, one should utilize individual nanoconduits with well-defined geometry which can reveal detailed fluidic characteristic. For instance, Choi et al.³ built nanofluidic platform composed of single carbon nanotubes embedding between two micro-reservoirs to study ion transport through the individual carbon nanotube. In another study performed by Siria et al.⁴, the nanofluidic device was fabricated by insertion of a single boron nitride nanotube into a glass nanocapillary through nanomanipulator operating inside a scanning electron microscope. The fabrication procedure of these nanofluidic systems is complicated and needs sophisticated instruments to overcome the challenges related to manipulating and embedding of those single nanotubes. Nevertheless. rapid advancement micro/nanofabrication techniques has made the development of robust nanofluidic devices with individual 2-D planar nanochannels much easier⁵⁻⁸. These nanofluidic systems are mainly developed on a silicon wafer, and the fabrication process is composed of patterning nanochannels with standard photolithography and then etching them in nanometer scale with controlled reactive ion etching (dry etching) or sacrificial layer method (wet etching). It should be noted that the nanochannels width, which is defined by photomask in the patterning step, is in the range of few micrometers (less than 10 nm) to provide direct observation of fluid flow by optical microscopy. Finally, to seal the developed nanochannels and obtain final nanofluidic device, borosilicate glass is used to be bonded with silicon pieces through anodic bonding technique. Consequently, direct observation, simple and well-defined geometry of these nanochannels and the capability of integration with other micro/nanofluidic components make them the ideal platform for investigation of fluid behavior at nanoscale.

Dedicated Instruments and Techniques to Explore Mass/Ion Transport in Nanoconfinements

It is well known that fluid behavior at nanometer length scale deviates from that in bulk. Sophisticated instruments and techniques are essential to explore the mechanics of fluid and transport phenomena at such small scale. Various methods such as optical⁹ and fluorescence microscopy¹⁰, electrical conductance measurement¹¹, scanning and transition electron microscopy^{12,13}, mass spectroscopy and surface characterization technique such as AFM¹⁴ have been utilized to probe the transport properties and nature of fluid at nanofluidic devices.

Optical microscopy has been frequently used as the prevalent method to visualize the fluid dynamics inside transparent channels, **Figure 1a**. Indeed, real-time quantification of nanoscale fluid behavior is enabled by tracking the location of a moving liquid-vapor interface inside the nanochannels as a function of time. However, the optical contrast between liquid and vapor phase becomes negligible as the height of the channels drops to ultra-small nanometer (less than 10 nm) and sub-nanometer scale; where the optical path across the channel is too short to distinguish between liquid and vapor phases. Nonetheless, this situation can be improved by introducing an optical enhancement layer. Li et al.⁹ studied fluid flow in sub- 10 nm channels via direct visualization that was only possible after the deposition of silicon nitride on the bottom of the channels as the enhancement layer. The results indicated that LW equation holds for both polar and non-polar liquids even at sub-10 nm scale.



Figure 1. Dedicated instruments to study mass transport in nanoconfinements (a) Direct observation of liquid motion in silicon nanochannels through optical microscopy ^{7,15}. (b) Schematic of fluorescence dye stimulation in nanochannels ^{10,16}. (c) Schematic of environmental scanning electron microscopy and ESEM image of a water meniscus within a carbon nanotube¹². (d) Schematic of transition electron microscopy and TEM image of ultrathin water film absorbed on the inner wall of carbon nanotube ¹³.

Fluorescence microscopy is an alternative technique to probe the fluid behavior in nanoconfinements. Fluorescence imaging functions as a fluorescence dye dissolved in the liquid becomes excited and emits light within a specific wavelength. This technique is specifically useful for biological and physical research in nanofluidics due to its high signal-to-noise ratio and single-molecules sensitivity. It also overcomes the limitations caused by small fluid volume characteristic of these systems. For instance, Zhong et al.¹⁰ applied fluorescence microscopy to monitor fluid behavior at sub-10 nm nanochannels, **Figure 1b**. However, the intensity of the emitted light was very weak due to the small number of fluorescence molecules confined in the nanochannels. Hence, they also employed silicon nitride layer to build a Fabry–Pérot resonator that enhances both excitation and emission lights. Although many researchers have employed optical and fluorescence microscopy technique to study fluid behavior at nanoconfinements, these methods are insufficient when the confinement size shrinks to less than 5 nm. To the best

of our knowledge, there is no report regarding the direct observation of liquid at sub-5 nm scale.

Environmental scanning electron microscopy (ESEM) is a promising approach that can be used for in-situ studying of liquid transport at small scales. Unlike conventional SEM, this technique allows for imaging of hydrated material and does not require vacuum condition. In fact, imaging is carried out under pressures up to 20 Torr, maintained by circulating a gas (typically water vapor or nitrogen) inside the ESEM chamber. Also, ESEM chamber accommodates a Peltier plate which makes temperature and pressure adjustments possible. Rossi et al¹². utilized ESEM to study the filling and displacement of water inside CNTs with diameters between 200-300 nm and walls of 10-15 nm thickness. The ability of ESEM to see through the CNT walls was used to explore water evaporation and condensation inside CNTs, as well. Authors fabricated the CNTs through chemical vapor deposition of carbon in alumina membrane. The developed CNTs demonstrated strong hydrophilicity with water contact angles between 5 to 20 degrees, as shown in **Figure 1C**.

While ESEM can provide useful information about fluid dynamics, transport and phase change properties inside relatively larger CNTs, its spatial resolution is not sufficiently high to visualize liquid structure within nanoscale confinements. Transmission electron microscopy (TEM), on the other hand, enjoys higher, sub-nanometer spatial resolution. Notwithstanding, the ultra-high vacuum required for TEM operation, leads to fast evaporation of most fluids, making the study of nanoconfined liquid limited to closed cap CNTs or liquid cells, wherein a larger pressure can be maintained. The observations of Tomo et al.¹³, however, suggested that a thin layer of water remains stable on the walls of open hydrophilized CNT, as shown in **Figure. 1D**, and does not evaporate even under the extremely low pressures maintained during TEM visualization. The stability of this 1-7 nm liquid layer inside CNTs with diameters of tens of nanometer was attributed to a combination of curvature, nanoscale surface roughness, and confinement resulting in a lower vapor pressure for water, hence inhibiting its vaporization.

Beyond direct observation of nanoconfined fluid offered by optical and electron microscopy techniques, another way to probe unusual fluid behaviors at nanoscale is taking advantages of indirect approaches such as atomic force microscopy, weight loss measurement, mass spectroscopy, and electrical conductance measurement.

One innovative approach to analyze the properties of nanoconfined liquids is through the application of atomic force microscopy (AFM). Whereas, AFM commonly serves as an apparatus to characterize solid surfaces topographical properties e.g., roughness, alternative applications have taken advantage of this technology, as well.



Figure 2. Indirect techniques to study mass/ion transport and nature of fluid in nanoconfinements (a) Schematic of atomic force microscopy system and the corresponding AFM image¹⁴. (b) Weight measurement method used to investigate capillary evaporation in graphene nanochannels¹⁷. (c) Schematic of the electrical measurement set-up and the corresponding I-V characteristic results ¹⁶.

For example, Fumagalli et al¹⁴ employed AFM for dielectric imaging of nanochannels. They investigated the properties of water inside nanochannels fabricated via van der Waals assembly¹⁸ of atomically flat crystals of graphite and hBN; where graphite was used as a bottom layer for the assembly as well as the ground electrode in capacitance measurements. A hBN crystal served as the top layer that was separated from the graphite by a spacer layer of hBN in the form of parallel stripes. This striped hBN layer formed the channels and determined their heights. As shown in **Figure 2a**, AFM was utilized to scan over the channels and detect the electrostatic forces between the graphite layer and the AFM tip that served as the second electrode. **Figure 2a** demonstrates that the water filled nanochannels are easily distinguishable from channel walls made from hBN. It was observed that the out of plane dielectric constant of confined water was almost identical to its bulk value in channels with heights larger than 100 nm, but it dropped drastically to values as small as 2 for few nanometer tall channels.

Alternative innovative instruments and techniques have also been developed for mass transport analysis. For example in the study performed by Radha et al.¹⁷ evaporative mass flux in graphene nanocapillaries, where direct observation of a moving meniscus was not possible due to ultra-small-scale dimension of the confinement, was determined through precise weight loss measurement approach. They used van der Waals assembly method to fabricate graphitic channels with heights ranging from one to a few tens of atomic planes with atomic scale precision; where atomically flat top and bottom graphite crystals were separated by an array of spacers made from few-layer graphene. Precision gravimetry was used to explore the kinetics of water transport through these hydrophilic channels (contact angle $\sim 55^{\circ}-85^{\circ}$): the nanocapillary device was inserted into a Si nitride chip and mounted on top of a miniature container partially filled with deionized water. The variations in container mass by time was monitored for nanocapillary devices with different channel heights from which water transport rates were extracted. Figure 2b shows sample experimental data from weight measurement, where the container mass decreases linearly by time due the ongoing water evaporation and transport through the capillaries. The observations revealed unexpectedly fast transport of water through nanochannels (with velocities up to 1 m/s) that was attributed to high capillary pressures (ca. 1000 bar) and substantial flow slippage.

Electrical conductance measurement of confined liquid is also one of the most promising methods that have been extensively used in various studies to explore the nature of fluid as well as ion/mass transport phenomena. Electrical conductance measurement of confined liquid is also one of the most promising methods that have been extensively used in various studies to explore the nature of fluid as well as ion/mass transport phenomena. In these experiments, the nanochannel connects two micro-reservoirs at its opposite ends, as shown in **Figure 2c**. Once the reservoirs and the channel are filled with liquid, two electrodes are placed inside reservoirs and I-V curves are obtained.

Scope of the Present Work

The objective of this dissertation is to focus on 2-D planner nanochannels to experimentally explore the fundamental of phase change (evaporation) and mass transport mechanism inside the silicon nanochannels, and discover the corresponding unusual phenomena emerging in nanoconfinements such as extremely high evaporative heat flux, formation of interfacial viscose layer, breakdown of capillary wicking and the concept of surface tension nanogates. To achieve the goal, the nanofluidic device was developed through MEMS fabrication techniques. The simple and deterministic structure of our developed device allow us to employ optical microscopy approach to track the liquid-vapor interface within the nanochannels. In addition, we used confocal microscopy and electrical conductance measurement approaches to detect the nature of confined liquid, and explore the new physics emerging at this scale. In chapter 2, we will describe the unusual nanoscale fluid behavior in the context of liquid transport and gating characteristic, and briefly mention the application of these phenomena. In chapter 3, we will study thin-film evaporation of a confined liquid in nanochannels under negative pressure at transient and steady state conditions. In the transient experiment, it is demonstrated that phase change (evaporation) at nanoconfinements could be a bubble free process at temperatures higher than boiling temperature. In the steady-state experiment, the concept of absolute negative pressure is utilized to achieve extremely high evaporative heat flux of $11 \pm 2 \text{ kW cm}^{-2}$ which opens the new path for thermal management technologies of electronic systems. In chapter 4, we will investigate capillary flow of liquid in nanochannels and discuss the role of interfacial viscosity in reduced liquid transport within nanoconfined geometries. In chapter 5, we will demonstrate the breakdown of capillary wicking at sub-10 nm scale for some liquids and prove that the scale of this unexpected phenomena depends on the interfacial tension of a liquid. Capillary breakdown leads to emergence the concept of surface tension nanogates which can be a promising platform for a variety of applications in drug delivery, energy conversion, and ionic separation.

II. ATYPICAL TRANSPORT PHENOMENA IN NANOCHANNELS

This chapter discuses atypical transport phenomena occurring in nanofluidic systems in the contexts of liquid transport and gating behavior. likewise, the emerging application of these unusual behavior is briefly described with focusing on energy harvesting and separation.

Liquid Transport in Nanoconfined Geometries

Liquid transport phenomena in nanoscopic confinement has been investigated both by molecular dynamics simulations and experiments. In some cases, the results show slower flow in nanoconduits compared to the predictions from classical theories, whereas , sometimes the flow rate of the confined liquid exceeds the theoretical predictions^{19,20}. These apparently contradicting results for flow behavior in nanochannels are, in fact, due to different types and strengths of the liquid/wall interactions. These interactions that play a crucial role at small scales can be categorized according to the degree of affinity between the liquid and the wall surface. Wetting and non-wetting are two broad categories that surfaces with weak and strong affinity with liquids fall into, respectively. Therefore, there can be a significant difference in properties and transport behavior of liquid in nanochannels with non-wetting walls and those with wetting wall surfaces²¹. In nonwetting confinements, liquid molecules can slip on walls, and consequently, the classical assumption of no-slip boundary condition is no longer valid $^{22-25}$. In fact, the weak liquid/wall interactions lead to formation of a depletion layer near the wall surfaces wherein the liquid viscosity is substantially less than bulk viscosity. This phenomenon results in higher mobility of water molecules and can be characterized in terms of true slip length²⁶.

However, the situation in wetting confinements, where liquid molecules undergo a notable epitaxial ordering, is quite different. That is, the strong liquid/wall interactions immobilize a very thin liquid layer adjacent to the walls leading to a significant increase in local and average viscosity; that in turn, slows the fluid flow. This phenomenon, known as multilayer sticking, has been reported in several studies.

Reduced Liquid Flow in Nanoconfinements

Unlike liquid flow within non-wetting confinements, the transport of water through wetting nanoconduits is slower than the theoretical predictions from classical flow rate equations. The strong liquid/wall affinity i.e., the considerable long-range interactions between liquid molecules and the surface of the walls leads to an apparent increase in the liquid viscosity near the walls that is to blame for the slow flow rate²⁷. Kelly et al.²⁸ used reflected differential interference contrast microscopy to visualize the imbibition of isopropanol (IPA) in siliceous 2D nanochannels. Their observations yielded that IPA permeation into these nanochannels under ambient conditions was consistently at least 5 times slower than the Lucas-Washburn equation prediction. They attributed this slower flow to the formation of a relatively thick quasi-crystalline layer (10-25 nm) near the walls, wherein molecules are strongly organized and structured. As shown schematically in **Figure 3a**, the velocity profile inside the channels is highly affected by these layers that results in a decrease in overall flow rate.



Figure 3. Deviation of liquid transport in nanochannels from bulk (a) Organic liquid (IPA) transport in nanochannels deviates from bulk due to nucleation of structured boundary layer and increased viscosity ²⁸. (b) Interfacial viscosity of water increases as contact angle reduces. In fact, strong affinity between liquid and wall (smaller contact angle) causes dense hydrogen bonding network and ordered structure in the interfacial region resulting in increased viscosity ²⁶.

Alibakhshi et al.¹⁵ designed a hybrid nanochannel device for precise measurement of water transport through 2D hydrophilic silica nanochannels. They measured the hydrodynamic resistance against the flow and compared it against the resistance predicted from classical LW equation. The variation in ratio of the actual resistance to the theoretical resistance for different nanochannel demonstrated that for larger channels no significant deviation from predictions is observed. However, the difference increases with decreasing channel height and reaches 45% in the case of 7 nm channels. Formation of a stagnant layer of water (hydration layer) on the silica surface with the thickness up to 7 Å is believed to explain the increased resistance. Li et al.²⁹ fabricated nanochannels with height of only 8 nm and used high contrast optical microscopy to directly visualize the real-time fluid dynamics of capillary filling for different polar and non-polar liquids through silica nanochannels. The results indicate that while the filling rate is consistently smaller than predictions from the original LW equation, it still follows the square root relationship suggested by LW equation. In addition, the modified LW was shown to successfully predict the experimental results.

To characterize the overall effect of the liquid/wall interactions on flow rate, an interfacial layer in close proximity of the channel walls can be defined within which the liquid viscosity is greater than the bulk viscosity³⁰. Experimental observations confirm the existence of such a layer, as well. For example, Tomo et al.¹³ reported the formation of super-stable ultra-thin water film on hydrophilized CNT walls observed via transition electron microscopy. These films with thicknesses of 1-7 nm, were surprisingly stable even under vacuum conditions. The wall roughness and the strong liquid/wall adhesion were identified as the key parameters for the stability of the ultrathin water films.

The increased viscosity within the interfacial region is primarily due to reorientation and structuring of liquid molecules in response to long-range forces exerted from the walls. Hence, the interfacial viscosity highly depends on liquid/wall affinity as it determines the strength of the interactions. Wu et al.²⁶ also highlighted that water viscosity within interfacial region (0.7 nm thick) strongly depends on the contact angle, since contact angle represents the strength of the liquid/wall interactions. They proposed a linear relationship between the ration of interfacial viscosity to bulk viscosity and the liquid/wall contact angle; an assumption that was supported by experimental and simulation data from previous studies^{28,31,40,41,32–39}, as shown in **Figure 3b** Shaat and Zhang²⁷ used a hybrid continuum-molecular mechanics (HCMM) technique to study the variations of viscosity and velocity across nanotubes cross section. As shown in **Figure 4a**, a clear peak in viscosity profile was observed near the wall. This is because a solid phase of water (ice)

with viscosity multiple times higher than the one of bulk water was observed at the first water layer. They calculated the interfacial water viscosity for different values of water/wall interactions strength: the viscosity increased to ~10 times the bulk water viscosity when water/wall interaction strength was increased from 0.1 to 10 kJ/mol. They also demonstrated that velocity profile for water flow in nanotubes is neither parabolic nor plug-like.



Figure 4. Distribution of liquid viscosity and density in nanoconfinements (a)Velocity profile and distribution of water viscosity within 5 nm nanotubes for various water-wall interaction. (b) The density profile of water flowing between two walls with oppositely charged surfaces⁴².

A study by Wu et al.⁴³ showed that temperature can be used as a stimulus to manipulate liquid fluidity in nanoconfinements. They experimented both hydrophobic and hydrophilic nanopores. The temperature increase appeared to restrain water fluidity in hydrophilic confinements, but it improved water transport by at least four orders of magnitude in hydrophobic confinements. These observations can be explained as the affinity between water and hydrophilic wall strengthens at higher temperatures, whereas an increase in temperature adversely affects the interactions between water and

hydrophobic walls. In fact, interfacial resistance and viscous resistance are the main forces slowing water transport. It is shown argued that interfacial resistance plays the main role in determining the water flow behavior in water/hydrophobic nanopore systems, while the viscous resistance dominates in water/hydrophilic systems.

The electrostatic effects rising from interactions between liquid and charged walls can impact the transport properties, as well. Geng et al.⁴² used MD simulations to investigate the combined effect of surface charge and wettability on flow in nanoconfinement. They modeled water flow between two oppositely charged solid planar surfaces for different values of surface charge density and solid/liquid interaction energy (wettability). They used a positively charged upper surface and a lower surface with negative charge. As expected, the slip length decreased for larger solid/liquid interaction energies (more wettable surfaces). But, interestingly, at the largest surface charge density, the slip length became nearly independent of the water/solid interaction energy. Increasing the surface charge density also resulted in shrinkage of the slip length and increased molecular structuring near the walls. However, the impacts from positively and negatively charged surfaces on water structuring within the interfacial layer and slip length was different: at small surface charge densities, the positively charged surface induces less ordering structure and larger slip than that by the negatively charged surface; whereas, for large surface charge densities, the opposite correlation was observed. These differences can also be seen in Figure 4b, a representative density profile of water under different surface charge densities and water/solid wettabilities. Note that the first peak in density profiles near the walls is closely related to the magnitude of slip length; it also, increases for larger surface densities.

Gating Behavior of Nanofluidic Systems

Transport of ions and liquid in nanochannels can be controlled by various gating mechanism. Gating behavior in nanochannels is achieved by physical, chemical or physical-chemical regulations. This phenomenon plays a critical role in different natural and industrial applications e.g., molecular and ionic fluxes for metabolic and signaling purposes, semi-conductor industry etc. Gating can be triggered through a variety of stimuli i.e., physical, chemical and physicochemical. Smirnov et al.44 demonstrated an example of application of physical stimulus to induce gating. In their work, they mimicked the functioning of biological voltage-gated channels by applying voltage across membranes with hydrophobic nanopores. In fact, the transition between wetting/non-wetting states in nanopores acts as the switch between open and close modes of the membrane. Figure 5a, depicts two possible mechanisms to induce wetting in hydrophobic pores i.e., electrowetting and meniscus overlap. Hou et al.⁴⁵ designed a liquid-based gating mechanism, where a capillary-stabilized liquid as a reversible, reconfigurable gate that fills and seals pores in the closed state, and creates a non-fouling, liquid-lined pore in the open state, Figure 5b. These types of gates are very versatile and the absolute and relative pressures for gases or liquids to pass through can be tuned by using membranes with different materials and/or pore sizes. The gates feature a combination of differential tunability and reversible opening and closing that enables fast and repeatable control over multiphase flows in both micro/macro-fluidic systems by simply adjusting the system

pressure.



Figure 5. Physical stimuli. (a) Transition between wetting and non-wetting state in the hydrophobic nanochannel is achieved by applying a voltage across them. The left figures depicts the movement of the contact line, while the right one indicates decreasing the contact angle ⁴⁴. (b) Demonstration of liquid-based gating channels ⁴⁵.

Chemical stimuli can be used to trigger gating mechanisms, as well. Cheng et al.⁴⁶ produced nanochannels with gating capability by controlling the wettability of the inner surface of nanochannels of mesoporous silica nanoparticles, **Figure 6a**. The nanochannels constitute a biomimetic on demand delivery system analogous to the aquaporins in nature, where the transport of water and ions is controlled by regulating channel wettability, which results from the transition between the intrinsic hydrophobic state and the stimulus-induced hydration state.



Figure 6. Chemical stimuli. (a) Schematic of changing inner surface wettability of mesoporous silica nanochannels⁴⁶. (b) Local flow in nanofluidic channel is controlled by regulation of well-tailored thermoresponsive polymers ⁴⁷.

Xu et al.⁴⁷ also employed chemical stimulus for gating mechanism activation. They achieved active gating through the self-assembled stimulus-responsive polymeric brushes that were planted inside nanochannels to act as valves, as shown in **Figure 6b**. In this case, poly(N-isopropylacrylamide) (PNIPAM) that is a thermoresponsive polymer, i.e., it exhibits a reversible phase transition at its lower critical solution temperature (LCST) was used. When heated above LCST, the hydrated extended PNIPAM chains instantaneously convert into dehydrated compact aggregates. A quick valving performance in respond to temperature change was observed owing to the sharp phase transition temperature of PNIPAM brushes. The results revealed that the nanoscale PNIPAM brushes locally self-assembled in the nanofluidic channels can act as active valves to regulate femtoliter-scale fluids with quickly responding to the external temperature change.



Figure 7. Physicochemical-chemical stimuli. (a) Wetting behavior in hydrophobic nanochannels is controlled by light emission⁴⁸. (b) The sub-10 nm hydrophobic PET nanochannels is transferred from non-conductive to water conductive state by electrostatic charge variation and applied electric field⁴⁹.

Xie et al.⁴⁸ designed functionalized hydrophobic nanopores using azobenzenederivatives-modified polymer and employed light and electric field to control wettability and regulate mass transport. In fact, nanopore surface wetting was adjusted to switch between conducting and non-conducting phases. Mass and ion transport was regulated by applying ultraviolet (UV)/visible light and different voltages. They found a threshold voltage beyond which the hydrophobic Azo-modified nanopores can be wetted by the electrolyte solution i.e., become completely open for transmembrane transport. As shown in **Figure 7a**, when exposed to visible light, the hydrophilic reaction products cover the hydrophobic surface of the nanopores allowing for transport across the membrane. Xiao et al.⁴⁹ used electrostatic charge and electric field to trigger gating mechanism for water transport, **Figure 7b**. They successfully regulated the surface charge density and external electric field through a process involving alternating capillary evaporation and capillary condensation to enable switching between open (conductive) and closed (non-conductive) states.

Application of Nanofluidic Systems

Beyond exploring the unusual fluid behaviors at nanoscale such as non-linear transport mechanism and reduced/enhanced liquid flow, researchers have focused on emerging applications of these new physics which leads to innovative solutions in energy harvesting and separation.



Figure 8. Application of nanochannels in Energy harvesting. (A) Single boron nitride nanotube connecting two reservoirs with different concentration. (B) Concentration gradient across a single-layer MoS₂ nanopore induces huge current leading to 10³ kWm⁻² power density ⁵⁰. (C) Ultra-thin (500 nm) nanofluidic power generator is made from separation of two block copolymers⁵¹.
Nanofluidic channels have shown great promise for applications in energy harvesting facilities from electrical power generation to ion pumps. Interestingly, the transport phenomena in nanochannels can take place due to a gradient in concentration. Often, mass/ion transport through the channels is maintained by salinity gradient between two reservoirs at the opposite ends of the channels, which can be harvested as electricity. For example, as shown in **Figure 8a**, very large electric currents with power densities up to 4 kWm⁻² can be achieved as the liquid moves through a single boron nitride nanotube connecting two reservoirs with different concentration⁴. In another study, Feng et al.⁵⁰ utilized the concentration-driven (osmotic pressure-driven) flow to harvest energy and were able to obtain power densities of ca. 106 Wm⁻². These large amounts of energy were generated through the application of single-layer molybdenum disulfide (MoS₂) nanopores as osmotic nanopower generators, Figure 8b. Since water transport through a membrane is inversely proportional to membrane thickness, the atomically thin membrane of MoS_2 plays a substantial role in making these large currents achievable. Zhnag et al.⁵¹ also utilized the blue energy i.e., the osmotic potential in the fluids to generate power with densities as large as ca. 2 Wm⁻². To this end, they designed ultrathin and ion-selective Janus membranes prepared through phase separation of two block copolymers, Figure 8c. They also, analyzed the effect of membrane thickness and channel structure on ion transport via both experiments and continuum simulations.

Nanofluidics have also demonstrated great potentials for separation applications. CNTs, boron nitride nanotubes and nanoporous graphene are few examples of membranes that can be utilized for such purposes. For instance, scientist have been inspired by ion channels existing in natural organisms to create artificial nanochannels that can separate water from hydrate ions and small gas molecules. Such gas-rejecting water-conduction nanochannels are good candidates for application in catalysis or CO₂ conversion. Recently, Li et al.52 reported in-situ water removal through gas-impeding water-conduction nanochannels composed of NaA zeolite crystals, Figure 9a. To fabricate Zeolitic nanochannels, they assembled Zeolite crystals into a continuous separation membrane; where a porous ceramic support was dip coated by 50-200 nm NaA nanocrystals, and then thermally annealed to the membrane to form a chemical bond between physically loaded nanocrystals and the surface of the support. The possibility of simultaneous waterconduction and gas-rejection through fabricated membrane arises from gating effect of sodium ion in NaA zeolite crystal structure. The structure of NaA zeolite with a channel diameter of ~ 4.2 Å, consists of 8-oxygen ring and sodium ion (Na⁺) located in the aperture of zeolite nano-cavity to neutralize the negative charge of the framework. Therefore, this positively charged ion can affect the passage of small molecules not only by reducing the effective channel size but also based on their electric charge. Hence, it enhances the transport of water molecules due to their small size and polarity; while, it does not allow larger and less polar molecules such as CO₂ or H₂ to pass.



Figure 9. Application of nanochannels in separation. (A) Water conducting nanochannels made of NaA Zeolite crystals⁵². (B) A nanobubble trapped in the hydrophobic section of the nanochannels acts as a separation membrane for sea water desalination 53,54.

Nanoconfined gas bubbles can act as osmotic membranes for separation applications, as well. In fact, as shown in Figure 9b, liquids such as water can cross the gas barrier i.e., a bubble trapped inside a channel through evaporation/condensation; however, the bubble remains impermeable to ionic solutes. The main advantage of gas bubble-based semipermeable membranes is that the sub-nm pores needed for separation via liquid-phase transport-based membranes is no longer necessary and membranes with pores as large as tens of nanometer can be used. Lee at al.54 used a hydrophobic coating to selectively functionalize the entrance of the pores in a 50 μm thick alumina membrane, and thus, created a nanoporous composite membrane with a hydrophilic core and a short hydrophobic entrance that traps a gas bubble when the membrane is immersed in water solutions. This configuration enabled them to verify and systematically study the vaporphase transport of water across opposing liquid menisci. The experiments were conducted at different temperatures, osmotic pressures and pore aspect ratios. The results indicated that the existence of a mass transport regime is determined by the resistance of the liquid/vapor interface that in turn depends on the transmission probability of water molecules across the nanopores and on the condensation probability of a water molecule incident on the liquid surface. While this setup seems a very promising design to advance separation technology, there are still a few challenges that need to be overcome before it can declare itself as a viable technology in the market. Bocquet⁵³ lists topics such as the long-term mechanical and chemical stability of the nanobubbles, the resistance of the membrane to pollution and fouling and the feasibility of design for reverse osmosis as the main fields that require careful investigations.

III. Ultrahigh Evaporative Heat Fluxes in Nanoconfined Geometries

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Title: Ultrahigh evaporative heat fluxes in nanoconfined geometries

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Introduction

Miniaturization has been the hallmark of electronic and photonic instruments in the last few decades. The miniaturization efforts span in an enormous range of dimensions from nanoscale transistors to thumbnail-sized chips, smartphone, vehicle electronic and server farms. This miniaturization accompanied by enhanced functional density necessitates enhanced heat dissipation, which has been the bottleneck of further advancement in these technologies^{55,56}. The current CPU power densities have reached to several hundred Watts per square centimeter. This constantly growing CPU power density has introduced a high demand for advanced cooling systems⁵⁷. A range of approaches has

been studied to address this high heat dissipation challenge including jet impingement, sprays and microchannels^{58,59}. However, thin film evaporation with nanometer fluid thickness is considered as one of the most promising approaches to address the future technological demands^{60–65}. The thickness of liquid film in this phenomenon should be in the order of nanometers to reduce thermal resistance for heat transfer. Thin film evaporation in micro/nanostructures is a coupled multi-physics momentum transport, energy transport, and gas kinetics problem. The momentum transport governs the liquid flow to the liquid-vapor interface; the energy transport governs the heat transfer to the interface, and the gas kinetics governs the evolution of molecules from liquid phase to the vapor phase. Depending on time scale, length scale, and the thermodynamic properties of the liquid-vapor interface, each of these physics imposes a limit on the kinetics of thin film evaporation discussed in Appendix A, A1. On the momentum transport aspect, miniaturization of the electronic devices and consequent cooling systems increases hydraulic resistance of the fluid flow. As the radius of confinement for the fluid flow decreases, the fluid transport to the liquid-vapor interface becomes limited. On the energy transport aspect, the energy transport to the liquid-vapor interface is a function of solidliquid thermal conductance, liquid-vapor thermal conductance and thermal diffusivity of the thin film of liquid. On the gas kinetics aspect, thin film evaporative mass flux is limited by the net flux of molecules from the liquid-vapor interface to the vapor phase. There are three main theories on the net flux of molecules at the liquid-vapor interface namely Hertz-Knudsen model (kinetic theory)^{66,67} (HK), Statistical rate Theory (SRT)⁶⁸⁻⁷¹ and Nonequilibrium thermodynamics (NET)^{72–75}. Summary of these theories are discussed in the Appendix A, A1. As shown by Plawsky et al.⁶² the predicted limit of heat flux through

kinetic theory is in order of 10⁵ Wcm⁻². Among these limits, momentum transport is the current limit of thin-film evaporation. Early in the development of micro/nanostructures for thin film evaporation, research studies only focused on transcending the momentum transport limit by optimizing geometry of micro/nanostructure of the thermal spreader. These include superhydrophilic micro and nanostructures such as micro-pillar arrays^{76–81}, copper micro-posts, sintered wick microstructures⁸², multi-artery, nanotubes⁸³ and nanomembrane⁸⁴ to transport the liquid via capillary force⁸⁵⁻⁸⁷. In capillary-driven fluid flow, the capillary pressure and viscous pressure are coupled to each other. As we move to smaller pore radius, the hydraulic resistance increases, and eventually fluid flow will stop. Thus, the maximum liquid flow rate with optimized geometry on the micrometer scale is limited with capillary pressure in the order of 10 kPa. However, development of bi-porous approach^{88–90} allowed raising the limit imposed by the momentum transport. In this approach, the viscous pressure of fluid flow is divided into two parts, (I) a long length of fluid flow occurs in microchannels with small hydraulic resistance (II) a short length of fluid flow occurs in the nanochannels with high hydraulic resistance. Thus, the overall small hydraulic resistance allows raising the limit of heat flux imposed by the momentum transport. Several other strides have been made to achieve higher limits of heat fluxes. For instance, the calculations by Xia et al.⁸⁸ show that with 1 µm length scale of fluid flow in a nano-membrane with porosity of 24%, interfacial heat flux with a value of 5000 Wcm⁻² could be achieved. In another interesting work, Li et al.⁸ explored limits of evaporation in nanoscale conduits which were composed of a nanochannel with a step in its height. The authors found a limit of evaporation, which was independent of outward diffusion of vapor molecules and pressure of the vapor phase. As shown by previous studies^{75,91,92}, low

pressure of the vapor phase does not necessarily lead to higher mass flux as the liquid temperature drops significantly under vacuum condition. In contrast with other predictions, they suggested that this limit of ~ 8500 Wcm^{-2} corresponding to flow velocity of 0.04 ms⁻¹ is imposed by kinetics of molecules motion from liquid to vapor phase. In another study, by Radha et al.⁹³ limits of capillary evaporation in nanochannels with height in the range of angstroms are explored. A multi-layer of graphene is used to develop these nanochannels. With water contact angle of 55-85° on these graphene sheets, flow velocity of 0.1 ms⁻¹ was achieved. The authors found that momentum transport is the limiting factor not diffusion and kinetics of liquid molecules transformation to vapor phase. Recently, Xie et al.⁵ explored fast transport of water in graphene nanochannels and predicted velocities in the order of 1-100 ms⁻¹ could be achieved. Although great strides have been made, much work remains to be done to overcome the momentum transport limit and explore other limits of evaporation.

Motivation and Scope

Here, we utilized the concept of liquid absolute negative pressure^{94,95} in nanochannels integrated with micro-reservoir to achieve unprecedented heat fluxes through thin-film evaporation. For a curved interface, the Young-Laplace equation governs pressure discontinuity across the interface and is written as $P^V - P^L = \sigma^{LV}(C_1 + C_2) +$ Π , where P^L denotes the liquid pressure, P^V is the vapor pressure, σ^{LV} is the liquid-vapor surface tension, and C_1 and C_2 are two principal curvatures of the interface and Π is the disjoining pressure. The disjoining pressure describes that the water-surface interaction dominates at scales < 100 nm⁹⁶, but rapidly decreases at a larger scale. For a hydrophilic solid-liquid-vapor combination, as the curvature of the liquid-vapor interface increases, the liquid can adopt negative absolute pressure. That is, the liquid is under tension, which is a metastable thermodynamic state, but a stable mechanical state ($\partial P/\partial V < 0$). At the centerline of the liquid-vapor interface, the principle curvatures are written as $C = \cos \theta/r$, where θ represents the contact angle and r the radius of a confinement. High curvature interfaces can be developed in nanoconfined geometries (i.e. small r). The negative pressure at the liquid-vapor interface provides a substantial driving force for liquid flow to the interface for evaporation, which raises the limit of momentum transport. We studied both transient and steady-state characteristics of thin-film evaporation under negative pressure in nanoconfined geometries and demonstrated that heat flux in the order of 11 ± 2 kWcm⁻² is achieved in steady-state condition.

Experimental Section

Device fabrication: The fabrication process consists of four main steps including patterning, etching, thermal oxide growing and anodic bonding presented in **Figure 30ak**. First, a positive photoresist was uniformly dispersed on a silicon wafer by using a spin coater (Brewer Cee 200) and then backed on a hot plate at 130°C for 90s. In order to create an optical mask, the geometric pattern of nanochannels was designed in SolidWorks (Dassault Systemes) and transferred onto a chrome mask with a resolution of 1 μ m. The optical mask was utilized to pattern the photoresist by exposing it to UV irradiation through mask aligner (ABM). Afterward, the sample was immersed into a photoresist developer, washed with deionized water and dried with nitrogen flow. Our structure includes 9 sets of nanochannels bridging two micro-reservoirs. Each set of nanochannels consists of 11 individual nanochannels. The width and length of each nanochannel is 5 μ m and 500 μ m, respectively. The nanochannels' patterns were etched into the silicon wafer with different depths using controlled reactive ion etching (Oxford Plasma Lab ICP 180 RIE). To remove the photoresist after etching, the sample was washed with acetone, alcohol and deionized water, and then dried with nitrogen flow. The channels height is in the range of 10 nm to 500 nm, which can be defined by the etching recipe of silicon. All the steps of standard photolithography and reactive ion etching were repeated to pattern and etch two microreservoirs perpendicularly located at the two ends of nanochannels. The micro-reservoirs are squares with length of 4 mm and height of 20 µm. In the next step, 300 nm oxide was thermally grown on the developed micro-nanochannels. This thermal oxide acts as an insulating layer which decreases the high electro-static forces in nanometer distances between silicon and glass and prevents channel collapse during anodic bonding. We confirmed the thickness of thermal oxide layer through ellipsometry method. The last step of nanofluidic device fabrication is sealing the developed micro-nanochannels with borosilicate glass through anodic bonding process. Initially, two holes were drilled on the glass in order to facilitate the introduction of liquid to the micro-reservoirs. Next, the silicon wafer and borosilicate glass were dipped into piranha solution (H_2SO_4 : $H_2O_2=3:1$) for 15 min. After cleaning, the silicon wafer and borosilicate glass were bonded together by anodic bonding process carried out for 10 min at 400°C with a voltage ranging from 300V to 700 V. To check nanochannels survival after anodic bonding, first we observed the bonded nanofluidic chip with optical microscope. The successful bonding indicated a uniform color across the whole length and width of nanochannels (an example of partially collapsed channels is shown in Figure 31. We also measured electrical conductance of nanochannels filled with liquid to further explore channel survival. In open channels, changing current as a function of voltage was observed, while no current could be detected for the blocked channels. It should be noted that 300-nm thermal oxide prevented current leakage through our nanofluidic chip during conductance measurement.

Evaporation experiments: The experiments were conducted at isothermal condition for transient evaporation and locally heated conditions for steady-state evaporation. The experimental setup for the isothermal experiment is shown in **Figure 11a**. A silicon rubber heater (Omega, SRFG-101/10-P), connected to a direct current power supply, was used in all experiments. Isothermal evaporation experiments were performed at different temperatures (ranging from 25 to 100 °C). Temperature was measured through a K-type thermocouple connected to the thermometer. The thermocouple was fixed on the silicon wafer using a thermal paste (PELCO conductive silver paint). The developed nanofluidic device was cleaned through plasma cleaning before each set of experiments to avoid any contamination, and then it was filled with isopropyl alcohol (IPA) and installed on top of the heater. We should add that one thick insulator layer (Buna-N/PVC foam) was put underneath the heater to reduce the heat loss. The outlet of one micro-reservoir was covered by tape to minimize the evaporation at that reservoir. Note that the taped micro-reservoir was not airtight. Therefore, evaporation took place faster at the uncovered micro-reservoir and continued to the nanochannels from one side until it dried out completely. A highspeed camera (AMETEK, VR0315, 70 frames s-1) connected to the optical microscope (Nikon, ECLIPSE LV100ND) was used to monitor the liquid-vapor interface movement. The experimental set-up for the locally heated evaporation experiment, which is similar to the transient experiments, is presented in Figure 37. We should add that during the steadystate experiments, a droplet of IPA was placed on top of the cold reservoir to make sure a sufficient supply of liquid to the interface was provided.

Results and Discussion

To achieve negative pressure at the liquid-vapor interface, we used a nanochannel geometry shown schematically in Figure 10a and fabricated a closed array of nanochannels shown in Figure 10b. The developed structure is made up of 9 sets of nanochannels and two micro-reservoirs placed perpendicularly along the two ends of the nanochannels. Each set of nanochannels consists of 11 separate channels with a width of 6 μm, depth of 180 nm and length of 1.6 mm (see Appendix A, A4). The reservoirs are 2 mm in width, 4 mm in length, and 25 µm in depth. These micro-reservoirs pump the liquid to the nanochannels via capillary force for evaporation. We developed five sets of nanochannels in each Si wafer, as shown in Figure 10c, to boost the number of samples and reduce error in our measurements. The geometry of the channels was examined with scanning electron microscopy (SEM) and scanning probe microscopy (SPM), as shown in Figure 10e-f, respectively. As demonstrated, the developed channels are highly uniform and consistent. This consistency allows us to have a sound interpretation of the experimental results. Borosilicate glass with a thickness of 1.1 mm was used to seal the channels through anodic bonding.



Figure 10. Schematic and characterization of the developed nanofluidic systems (a) Schematic of thin-film evaporation in nanochannels. (b) Developed nanochannels and micro-reservoirs on Si wafer after anodic bonding. The scale bar is 1 mm. (c) Five sets of channels on a Si wafer. The scale bar is 5 mm. (d) SEM image of the nanochannels. The scale bar is 2 μm. SPM characterization of (e) two nanochannels and (f) one individual nanochannel before anodic bonding.

The developed nanochannels were cleaned thoroughly before the experiments through plasma cleaning. We chose isopropyl alcohol as the working liquid in all experiments as it provides complete wettability of Si nanochannels and contact angles close to zero $(1-7^{\circ})$ (see **Appendix A, A5**). Two length scales should be considered in the nanochannels, to determine principal curvatures, width and depth. Considering these scales, the liquid pressure at the liquid–vapor meniscus is –158.5 to –108.6 kPa (see **Appendix A, A6**).

Once the nanochannels were developed, we studied thin- film evaporation under negative pressure in two regimes: isothermal experiments (i.e., transient evaporation) and locally heated experiments (i.e., steady-state evaporation). In the transient evaporation, the liquid–vapor interface was mobile, whereas in the steady-state evaporation, the liquid–vapor interface was stationary.

Isothermal Experiment

The schematic of the experimental set-up for isothermal experiments is shown in **Figure 11a**. More detail about the experimental setup is given in Experimental Procedures.

In these experiments, the nanochannels were heated uniformly and motion of the liquid– vapor interface was studied in a nanoconfined geometry at ambient conditions.



Figure 11. Transient experiment (a) Schematic of the experimental set-up for transient thin-film evaporation in nanochannels. (b-j) Isothermal evaporation experiments: (b-d) at 55 °C, (e-g) at 75 °C, and (h-j) at 95 °C for0.41, 0.84, and 1.24 s. No bubble formation was observed at 95 °C, which is higher than the boiling temperature of IPA. The scale bar is 50 μm.

Initially, working fluid was introduced from one micro-reservoir to completely fill the channels and the other micro-reservoir. The nanochannels were examined under an optical microscope (Nikon, ECLIPSE LV100ND) to ensure nonexistence of trapped air bubbles in the channels. The experimental set-up is placed on an isothermal platform with temperature varying between 25 and 100 °C. Since one of the micro-reservoirs was taped, the evaporation initiated from the other reservoir and continued in the nanochannel up to reaching the other reservoir. Initiation of evaporation from one side of nanochannels enabled us to precisely track the motion of the liquid–vapor interface through high-speed imaging (Phantom 711, vision research) coupled with the optical microscope. **Figure 11b** shows the isothermal evaporation in nanochannels at 55, 75, and 95 °C at different times. The liquid phase looks dark, whereas the vapor phase is the brighter stream. Interestingly, continuous evaporation was observed even at temperatures higher than the boiling temperature of IPA. That is, the liquid–vapor interface moved only in one direction and no

cavitation or bubble formation was observed inside the nanochannels. The remarkable aspect of transient evaporation is absence of any bubble in the nanochannels at temperatures more than the boiling temperature of the working liquid at ambient pressure, which is ~83 °C. Although we were expecting to move from thin-film evaporation regime to nucleate boiling at temperatures higher than boiling temperature, we did not observe any bubble formation. Note that the liquid in the nanochannels is at lower pressure than atmospheric pressure, resulting in lower boiling temperature according to the Clausius–Clapeyron equation. Formation of bubbles in channels leads to instabilities, back flow, and formation of hot spots and consequently is undesirable in thermal management devices. Two possible mechanisms could explain this phenomenon. First, in a liquid-vapor system, a nucleolus of vapor/gas should adopt a critical radius before further growth. The critical radius of spherical bubble (R_c) is written as⁹⁷

$$R_c = \frac{2 \sigma^{LV}}{P_s \exp\left(\frac{\nu_l}{RT} \left(P^L - P^s\right)\right) - P^L} \tag{1}$$

where v_L denotes specific volume of the liquid and P^s is the saturation pressure. For the given thermodynamic state of liquid in the nanochannels, the minimum critical radius of a spherical bubble is ~180 nm (See **Appendix A**, **A7**). **Equation 1** is valid for a pure and degassed fluid. However, our experiments were conducted in the ambient atmosphere. Thus, the critical radius will have the effect of dissolved gases. Accordingly, for a non-degassed fluid, the critical radius is written as⁹⁸

$$R_{C} = \frac{2\sigma^{LV}}{P_{s} \exp\left[\frac{v_{f}}{RT}(P^{L} - P_{s}) - \frac{x_{2}^{L}}{x_{1}^{L}}\right] + \frac{x_{2}^{L}P^{L}}{x_{s}} - P^{L}}$$
(2)

where x_2^L denotes concentration of air, x_1^L is concentration of solvent, and x_s is the equilibrium saturation concentration of the gas dissolved in solvent. The minimum critical nucleolus in this case is \sim 400 nm. This length scale is more than the depth of nanochannels. That is, if a vapor nucleolus forms in the nanochannels, it cannot adopt the critical radius and grow further. Thus, the minimization of energy (i.e., maximum entropy principle) requires the vapor nucleolus collapse. Although the length scale in the width dimension of nanochannels is more than the critical nucleolus dimension, formation of stable ellipsoid vapor/gas bubbles was not observed. We should add that as temperature increases, the critical radius of nucleation decreases and could lead to bubble formation. With superheat of 17 °C, we did not observe any bubble formation in the nanochannels. In several studies, scientists observed cavitation in nano structures with dimensions less than 100 nanometers. For instance, Jatukaran et al.9 reported cavitation in nano-pillared structure at the sub-10 nm scale in an isothermal condition. However, at the cavitation coordinates, the liquid pressure is undetermined (i.e. bulk fluid or liquid-vapor meniscus) and critical radius of nucleation could not be calculated through Equation 1. In another study by Duan. et al.⁹⁹, cavitation was observed in the presence of evaporation-induced negative pressure in nanofluidic channels. They suggested that entrapped bubbles act as nucleation sites for cavitation. We did not observe any entrapped bubble in our nanochannels before the experiments. Nevertheless, we conducted more than twenty experiments at temperatures higher than the boiling temperature of IPA and no bubble formation was observed. This

fact is also shown by molecular dynamic simulations of Maroo and Chung¹⁰⁰. This suggests that we can keep thin-film evaporation in nanochannels even at high temperatures.



Figure 12. Results of transient evaporation experiments (a) Coordinate of the liquid-vapor interface as a function of time (b) The average velocity and corresponding local heat flux of the liquid-vapor interface as a function of temperature for three nanochannels.

Through image analysis, we determined the transient coordinate of the liquid–vapor interface and the results are shown in **Figure 12a**. This transient coordinate for other nanochannels is shown in **Figure 35**. The corresponding velocity in these channels as a function of temperature is presented in **Figure 12b**. The uniform dimension of nanochannels and the isothermal condition provide a consistent average velocity for all studied channels. The velocity of the receding liquid–vapor interface increases monotonically with temperature and interestingly reaches a plateau at high temperatures. No further increase in temperature affects the velocity of the receding interface. Note that although the temperature of the substrate is higher than the boiling temperature, in some cases, the liquid remains at the saturation temperature during evaporation. The fundamental question is how fast an evaporating liquid–vapor interface can move in nanochannels. This phenomenon can be realized through fundamentals of thin-film evaporation and fluid

dynamics of an evaporating liquid-vapor interface. Thin-film evaporation should be viewed in the context of an evaporating meniscus, which can be divided into three regions, including the bulk meniscus, a transition region, and an adsorbed film, as shown in **Figure 13**.



Figure 13. Schematic of the liquid–vapor interface profile. High evaporation flux in the transition region leads to strong recoil pressure and change in the local contact angle.

Theories on thin-film evaporation suggest diverging evaporative flux in the transition region. This fact is shown both for diffusion-limited evaporation discussed by Hu and Larson¹⁰¹ (valid for low evaporation fluxes) and the energy approach discussed by Ranjan et al.¹⁰² and Ghasemi et al.⁷⁰. This means evaporation flux along the liquid–vapor interface is not uniform. The diverging local evaporation flux in a transition region requires liquid flow to this region from the bulk meniscus region. Otherwise, the high evaporation flux in the transition region changes the contact angle close to $\pi/_2$, which is not in agreement with the measurements. The contact angle of liquid in nanochannels is always below $\pi/_2$ and changes between 2 and 7° (see Appendix A, A5).

For the liquid flow from the bulk meniscus to the transition region for constant contact angle, the viscous dissipation should be balanced by the applied momentum on the liquid-vapor interface (see **Appendix A, A9**). Through analysis of this balance, one finds that the average velocity of liquid-vapor interface is written as

$$V = \frac{\sigma^{LV}}{6\,\mu\ln(\frac{r}{a})}\,\theta_D\,(\theta_D^2 - \theta_e^2) \tag{3}$$

where μ denotes dynamic viscosity, *a* is the thickness of adsorbed film, θ_D is the dynamic contact angle, and θ_e is the equilibrium contact angle. This velocity form has two consequences. For $\theta_D = \theta_e$, velocity of the liquid-vapor interface is zero. That is, no imposed force on the contact line (no evaporation and no induced recoil pressure). By increasing the evaporation flux and corresponding recoil force, the velocity of liquid-vapor interface increases and reaches a maximum corresponding to **Equation 3**, (i.e. $dV/d\theta_D = 0$)

$$V_m = \frac{\sigma^{LV}}{9\sqrt{3}\,\mu\ln(\frac{r}{a})}\,\theta_e^{3}.\tag{4}$$

This dynamic characteristic is discussed extensively by De Gennes et al.^{103,104}. That is, at highly sharp-edged liquid-vapor interface, viscous dissipation of liquid flow to the transition region is so high that it does not allow sufficient fluid flow to transition region for evaporation. Looking back at the experimental results suggest that at low temperatures, the contact line velocity monotonically increases with temperature. However, at high temperatures, the contact line attains a maximum velocity as discussed and any further

increase in the temperature of substrate does not affect the velocity of interface. The maximum velocity of contact line in these experiments is 160-180 µms⁻¹. If one includes this velocity range in the maximum velocity formulation, we attain an equilibrium contact angle of 4° , which is completely consistent with the measured contact angles (i.e. 2-7°, see Appendix A, A5). This suggests that the dynamic of a contact line in the nanoconfined geometries is limited by viscous dissipation of liquid flow in the meniscus. This fact has also a direct implication on the fabrication of Langmuir-Blodgett films^{105,106}. At higher velocities, a meniscus with defined contact angle cannot be kept attached to the substrate and instead a thick film of liquid will form on the surface. The evaporative heat flux for the transient experiments is shown in Figure 12b. As mentioned above, the liquid-vapor interface can attain maximum velocity up to 180 µms⁻¹ which corresponds to the evaporative heat flux of 8.4 Wcm⁻² (see Appendix A, A10). Higher limits of heat flux can be obtained for larger equilibrium contact angles. As a result, the interfacial heat flux of a moving contact line is limited by liquid flow to the transition region. However, if a stationary contact line is achieved (i.e. steady-state evaporation), this limit of fluid flow to the transition region could be omitted and high heat fluxes can be achieved. We will explore this characteristic in the next section.

Locally Heated Experiment

To reach steady-state evaporation (i.e., stationary contact line), we designed the locally heated experiment, shown in **Figure 14a**, at which the micro-reservoirs are kept at two different temperatures. In an isothermal condition, a higher evaporation rate from the open micro-reservoir (compared with the taped micro-reservoir) leads to receding of liquid

in the nanochannels from the open micro-reservoir. However, as time goes on, small evaporation in the taped micro-reservoir brings down the level of liquid in the taped micro-reservoir and the contact line starts to recede from both sides of the nanochannels; i.e., two liquid–vapor interfaces appear in the nanochannel. We could observe steady-state evaporation in an isothermal condition, but the steady-state evaporation disappeared fast. However, in the locally heated experiments, by keeping the chiller at low temperature, we can minimize liquid evaporation in one micro-reservoir and keep constant pumping of liquid to the nanochannels. In this case, we could maintain steady-state evaporation for a long time. the is 2.9%.

The motivation for conducting experiments in the locally heated setup is exploring the limit of thin-film evaporation under negative absolute pressure. All experiments were conducted at ambient pressure. The experimental set-up for the steady-state experiment is presented in **Appendix A**, **A11**. The set-up is almost the same as that of the isothermal experiments. The only difference is that a chiller was paired to a heater to induce a temperature difference across the nanochannels to obtain the stationary contact line (i.e., steady-state evaporation). The chiller was located under the cold reservoir and its temperature was kept at 16 °C, whereas the heater was located under the hot reservoir and its temperature was adjusted at three different temperatures, including 20, 40, and 60 °C, for three separate sets of experiments. An insulating layer was used to separate the chiller and heater.



Figure 14. Steady state experiment (a) Schematic of the locally heated evaporation experiment. Microscopic images of a locally heated evaporation experiment performed at 40 °C at different times are shown. Time increases from (b) to (g). The length of vapor phase (brighter area) increases as time goes on (from (b) to (f)) and reaches steady-state evaporation at (g). The scale bar is 50 µm.

Once the temperature field is imposed, evaporation initiates from the hot reservoir until the reservoir is depleted. Then, the evaporating interface moves inside the nanochannels toward the cold reservoir, and length of the liquid phase in the nanochannels decreases until it reaches a specific coordinate with no further motion (i.e., stationary contact line). At this specific coordinate, the capillary pumping of fluid by the cold reservoir is balanced by the evaporating mass flux at the liquid–vapor interface and a steady-state evaporation is achieved. Note that in steady-state experiments, the outlets of reservoirs were not taped. We should emphasize that the cold reservoir is completely filled with the working fluid and a droplet of fluid is placed on top of the cold reservoir (**Figure 35**) to ensure sufficient supply of liquid to the liquid–vapor interface for evaporation during the experiment. The fluid in the cold reservoir is at ambient pressure, whereas the liquid at the liquid–vapor interface experiences negative absolute pressure. This pressure gradient provides a high driving force for liquid flow from the cold reservoir to the liquid–vapor interface. Note that steady-state condition could not been observed in isothermal experiments. In those

experiments, despite minimizing evaporation, a small amount of evaporation took place in the taped micro-reservoir and caused evaporation of liquid in the nanochannels from the taped micro-reservoir side. This led to having two liquid–vapor interfaces in the nanochannels moving toward each other.

The movement of the liquid-vapor interface in the nanochannels was visualized by the optical microscope. Figure 14b-g shows the motion of a liquid-vapor interface related to the steady-state experiment performed at adjusted temperatures of 16 and 40 °C for cold and hot reservoirs, respectively. As shown in Figure 5b-f, liquid phase length decreases with time and reaches the steady-state evaporation in Figure 5g. To ensure the steady-state condition had been reached, we recorded the coordinate of the liquid-vapor interface for more than 3 min and no further motion was observed. The provided video, which is related to the experiment performed at 16 and 60 °C for cold and hot reservoirs, clearly demonstrates extreme vapor generation at the liquid-vapor interface. We should emphasize that the lifetime of the stationary contact line (i.e., steady-state evaporation) depends on the mass of the liquid provided by the cold reservoir. For instance, the approximate lifetime of a stationary contact line (i.e., steady-state evaporation) for the set of nanochannels with the highest evaporation rate (i.e., 2 µm liquid phase length) is calculated to be 16 min. This time is higher than the recorded steady-state condition (i.e., 3 min). That is, we had a sufficient supply of liquid at these high rates of evaporation.

Given the length of the liquid column in the nanochannels, the local heat flux at the interface for steady-state evaporation is written as^{107} (See Appendix A, A12)

$$\dot{q} = \frac{\rho^L h^2 \,\Delta P \,h_{fg}}{12\,\mu L} \tag{4}$$

where ρ^L denotes liquid density, *h* is the channel height, ΔP is the pressure gradient in the liquid phase, μ is the dynamic viscosity of liquid, *L* is the length of liquid in the nanochannels. irradiation. With ACSD structure, we could reach to an efficiency of 62.7% for solar desalination at solar irradiation of 1kWm⁻² (1 sun) without any clogging of the surface for prolonged operation.



Figure 15. Evaporative heat flux as a function of liquid phase length in nanochannels. At the minimum liquid phase length, and the highest evaporative heat flux, the average evaporative heat flux is 11 ± 2 kW.cm⁻².

The determined heat fluxes as a function of length of liquid in the nanochannels at three different temperatures are shown in **Figure 15**. At each hot reservoir temperature, the evaporation heat flux shows an inverse trend with the liquid phase length. The shorter length of liquid phase inside the nanochannels is associated with lower hydraulic resistance, which results in a higher flow rate to the liquid– vapor interface for evaporation. A maximum evaporation heat flux was obtained for a set of nanochannels with liquid

stream length ranging from 2 to 7 μ m length of liquid phase at 60 °C. For the nanochannels undergoing liquid–vapor phase change, we determined the average interfacial heat flux of 11 ± 2 kWcm⁻², which is extremely high among the other heat fluxes reported so far^{88,77}. Note that the accuracy of the optical microscope (500 nm) leads to large error in the heat flux measurements.

We should add that the determined heat flux is the liquid-vapor interfacial heat flux and not a device heat flux. Also, non-condensable gases could change the rate of evaporation at the interface through the accommodation coefficient¹⁰⁸. We did not use an accommodation coefficient (i.e. the Hertz-Knudsen equation) in our study to determine the evaporation flux. The negative absolute pressure of the liquid and the small length of the fluid stream resulted in this high interfacial heat flux. Once the vapor is generated, it should flow in the nanochannels and leave the structure through the hot micro-reservoir. The Peclet number of vapor (convective transport to diffusion transport) is ~ 5 (see Appendix A, A13). This suggests that vapor transport is both convection and diffusion limited. No condensation was observed in the nanochannels. At higher interfacial heat fluxes, steadystate condition could not be kept for more than 60s as the center of liquid-vapor interface entered the cold micro-reservoir. We determined the resistances in the liquid, the liquidvapor interface and in the vapor phase for mass transport (see Appendix A, A14) and found that still at high heat fluxes the momentum transport of liquid in the nanochannels is the dominant resistance. The findings suggest that higher heat fluxes are also possible by decreasing the depth of nanochannels.

IV. ON INTERFACIAL VISCOSITY IN NANOCHANNELS

The following chapter first prepared in Nanoscale 2020.

Title: On interfacial viscosity in nanochannels

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Introduction

The spontaneous filling of conduits with small volume to surface ratio with a wetting liquid is called the capillarity effect (also known as capillary motion). Capillary motion is the underlying mechanism for mass transport in many natural systems such as the capillary rise of water and nutrients through plants xylems^{109–111}, transport of water from aquifer to surface^{112,113} and the functioning of sweating glands in human body¹¹⁴. Also, capillarity plays a critical role in different microscale applications such as drug delivery¹¹⁵, chemical analysis¹¹⁶ and microfluidics and energy storage devices^{117,118}. However, capillarity in nanoscopic channels/tubes has recently gained substantial attention due to simplicity in its operation, generating reasonably high flow rates and possessing length scales comparable to ranges of intermolecular interactions. Proton-exchange membrane full cells¹¹⁹, thermal management systems of electronics/photonics^{120–123}, nanostructured material fabrication^{124,125}, shale gas/oil production, water desalination¹²⁶ and molecular separation^{127,128} are only a few examples where capillary filling in

nanochannels plays an essential role. Hence, understanding the physics of capillary motion in nanoscopic conduits is a necessity for analysis of the pertinent natural phenomena and enhancement of the related technological applications.

Lucas and Washburn are widely recognized to have proposed the first quantitative analyses of the capillarity kinetics in cylindrical capillaries. This relationship is named Lucas-Washburn (LW) equation that gives the liquid front position (x) with time (t)

$$x = K\sqrt{t} \tag{5}$$

and

$$K = \sqrt{r\gamma \cos\theta / 2\mu} \tag{6}$$

where r is the capillary radius, γ is the liquid surface tension, θ is the liquid/channel advancing contact angle and μ represents the liquid viscosity. The LW equation coefficient K can be modified for 2D channels (i.e. width much higher than the depth) with rectangular cross sections and a height of h as

$$K = \sqrt{h\gamma \cos\theta / 3\mu}.$$
 (7)

LW equation has been widely applied and verified for liquid capillary flow characterization in microchannels, but significant deviations are reported when compared against flow kinetics in nanochannels¹⁵. In fact, liquids fill nanochannels significantly slower than that predicted by LW equation, while still complying with the $x \propto \sqrt{t}$ relationship^{129–133}. Different studies have held a variety of physical phenomena responsible for the observed reduction in *K*. The electro-viscous effect^{132–134}, formation of gas nanobubbles¹³⁵, variable dynamic contact angle at the liquid/channel wall interface¹³⁶, molecular structuring and formation of a stagnant liquid layer adjacent to the walls^{137,138} and chemical selectivity of the nanochannels toward specific liquids¹³¹ are the main factors postulated to result in slowdown of the capillarity in nanoscale channels.

The electro-viscous effect in nanoscopic confined flows is caused by the presence of the electrical double layer near the liquid/wall interface. The electro-viscous effect can increase the apparent dynamic viscosity due to the electroosmotic counter flow induced by a streaming potential and lead to filling slowdown. However, it has been shown that even the maximum possible contribution of the electro-viscous effect cannot result in filling speeds as small as those observed in the experiments^{139,140}. In fact, the electro-viscous effect is not sufficiently strong to account for the observed nanoscale capillary flow slowdown. Formation of nanobubbles in front of the advancing meniscus can slow down the imbibition by increasing the viscous resistance against the liquid flow. Notwithstanding, the bubble formation effect on capillary flow rate seems negligible in sub-100 nm channels¹³⁵. Equation 6 shows that variations in the advancing contact angle between the liquid and wall can directly influence the penetration rate in nanochannels. The liquid penetration rate depends on the net force exerted on the liquid column from different existing forces including the capillary force, the inertial drag force and the viscous force. In fact, LW equation is derived based on the balance between the capillary and viscous forces. Hence, LW equation will not hold in the early stages of liquid wicking when inertial forces are dominant. Nonetheless, the inertia dominant regime has been shown to last for very limited time (less than 1 ns) and so cannot be responsible for the persistently slow capillary motion in nanochannels¹⁴¹.

Thus, current literature is still incapable of identifying the mechanism(s) responsible for the capillary flow slowdown in nanoscopic conduits. The strong liquid/wall interactions in nanochannels can lead to formation of ultra-thin stagnant liquid layers on the solid surface which can reduce the effective height of the channel and results in increased flow resistance. For example, an ice-like hydration layer can be formed by reorientation and ordering of two to three layers of water molecules due to the strong water/wall interactions in hydrophilic channels¹⁴².

Motivation and Scope

An appropriate model can be developed by assuming that the molecular interactions at the liquid/wall interface lead to physical properties of a molecularly thin liquid layer adjacent to the wall to be different from that in the bulk. Here, we elucidate the role of interfacial viscosity in capillary motion in nanochannels. We also demonstrate that by including the interfacial viscosity effect in LW equation, it can be applied to predict the kinetics of capillary motion in nanochannels.



Figure 16. The schematic of the interfacial layer developed in nanochannels with a viscosity (μ_2) greater than that of the bulk liquid (μ_1) .

Assume μ_2 to be the apparent viscosity of the thin liquid layer with a thickness l_s next to the nanochannel wall that differs from that in the bulk μ_1 , Figure 16. The liquid, hence,

moves with different velocities, i.e., u_2 and u_1 , respectively, according to Navier-Stokes equation:

$$\mu_1 \frac{\partial^2 u_1}{\partial z^2} - \frac{dp}{dx} = 0 \tag{8}$$

and

$$\mu_2 \frac{\partial^2 u_2}{\partial z^2} - \frac{dp}{dx} = 0 \tag{9}$$

where p is the liquid pressure, and x and z represent the coordinates along the flow and channel height directions, respectively. Integrating **Equation 8** and **Equation 9** and applying appropriate boundary conditions yields (see **Appendix B, B1**)

$$u_1 = \frac{1}{\mu_1} \left(\frac{dp}{dx}\right) \frac{z^2}{2} - \frac{1}{\mu_2} \left(\frac{dp}{dx}\right) \frac{h^2}{8} - \left(\frac{dp}{dx}\right) \left(\frac{1}{\mu_1} - \frac{1}{\mu_2}\right) \left(\frac{l_s^2}{2}\right)$$
(10)

and

$$u_2 = \frac{1}{\mu_2} \left(\frac{dp}{dx}\right) \frac{z^2}{2} - \frac{1}{\mu_2} \left(\frac{dp}{dx}\right) \frac{h^2}{8}$$
(11)

where h represents the channel height.

Mass flow rate \dot{m} in the channel can be obtained as

$$\dot{m} = 2\rho w \left(\int_0^{l_s} u_1 dz + \int_{l_s}^{\frac{h}{2}} u_2 dz \right)$$
(12)

where ρ is the liquid density and w is the channel width. Substituting **Equations 10** and **11** into **Equation 12** and integrating both sides yields

$$\dot{m} = 2\rho w \left(-\left(\frac{1}{\mu_1} - \frac{1}{\mu_2}\right) \left(\frac{l_s^3}{3}\right) - \frac{1}{\mu_2} \frac{h^3}{24} \right) \left(\frac{\Delta p}{x}\right)$$
(13)

where Δp represents the capillary pressure drop along the liquid-filled part of the channel, x. On the other hand, \dot{m} can be written as

$$\dot{m} = \rho w h \frac{dx}{dt}.$$
(14)

Substituting Equation 14 into Equation 13 and performing an integration on both sides yields the following relationship between the liquid front position and time:

$$x^{2} = \frac{4}{h} \Delta p \left(-\left(\frac{1}{\mu_{1}} - \frac{1}{\mu_{2}}\right) \left(\frac{l_{s}^{3}}{3}\right) - \frac{1}{\mu_{2}} \frac{h^{3}}{24} \right) t .$$
⁽¹⁵⁾

Substituting $\Delta p = -2\gamma\kappa$ for capillary pressure in Equation 15 yields

$$x = \sqrt{\left(\frac{8\gamma\kappa}{h}\right)\left(\left(\frac{1}{\mu_{1}} - \frac{1}{\mu_{2}}\right)\left(\frac{l_{s}^{3}}{3}\right) + \frac{1}{\mu_{2}}\frac{h^{3}}{24}\right)}\sqrt{t}$$
(16)

where κ denotes the mean curvature of the interface. For a 2D nanochannel with a height of *h* and a width of *w* and a liquid/wall contact angle of θ , we have $\kappa = \frac{1}{2} \left(\frac{1}{h} + \frac{1}{w} \right) \cos \theta$. It can be noticed that our governing equation for liquid displacement with time (**Equation** 16) still complies with the $x = K\sqrt{t}$ form proposed by LW equation, whereas for the nanochannels, the coefficient *K* must be replaced with K_{nc} expressed as:

$$K_{nc} = \sqrt{\left(\frac{8\gamma\kappa}{h}\right) \left(\left(\frac{1}{\mu_1} - \frac{1}{\mu_2}\right) \left(\frac{l_s^3}{3}\right) + \frac{1}{\mu_2} \frac{h^3}{24}\right)}.$$
 (17)

It can be seen that all the parameters needed to obtain K_{nc} according to Equation 17 are known except for the interfacial viscous layer thickness, l_s and the interfacial viscosity, μ_2 . These values are determined through experimental results and are compared to the developed model, Equation 16. In addition, experimental investigations of liquid flow in nanochannels with different heights as well as molecular dynamics (MD) shearing modeling confirm the applicability of the developed framework for flow in nanoscale conduits.

Experimental Section

Nanochannel Fabrication. Si nanochannels with heights of 20 nm, 40 nm and 80 nm were fabricated through a nanofabrication process discussed in the chapter 3. Each set of nanochannels includes 11 groups of channels with 9 parallel channels in each group. Channels were designed with a width of 5 μm . Each nanochannel extends between two large micro-reservoirs that are 20 μm deep. The profiles of different nanochannels were characterized via Scanning Probe Microspore (SPM) as shown in **Figure 17** and their height uniformity were confirmed (**Figure 41** in **Appendix B**). Finally, the nanochannels were sealed on top with a borosilicate glass through anodic bonding.



Figure 17. Uniform profiles of Si nanochannels with different heights probed with scanning probe microscopy (SPM).

Liquid Imbibition Visualization. The micro-nanofluidic chip was plasma cleaned (Harrick Plasma, PDC-001, Ithaca, NY) with Oxygen for 10 minutes before each run. The chip was then placed on an Eclipse LV100ND upright microscope stage (Nikon Metrology Inc., Brighton, MI). Afterward, the liquid was introduced to the device through the inlet of one of the reservoirs. Once the reservoir was filled, liquid started to penetrate the nanochannels due to capillarity. The liquid transport in the nanochannels was visualized through a Phantom V711 high-speed camera (Vision Research Inc., Wayne, NJ) coupled with the optical microscope system. Representative snapshots of capillary flow of IPA in nanochannels with different heights are shown in Figure 18. The liquid front (i.e., liquid/air interface) displacement in the nanochannels with respect to time was extracted by imageprocessing the captured videos using a developed MATLAB code. Experiments were carried out for two types of organic liquids, i.e., isopropanol, also known as IPA, and ethanol. These liquids provide total wetting condition in the Si nanochannels. For each set of liquid and nanochannel height, a minimum of 10 experiments were performed and the results were averaged. The ambient temperature was maintained at 20°C throughout the experiments via an active heating/cooling system.



Figure 18. Snapshots from capillary flow of IPA in nanochannels with different heights (h) all taken 1.2 seconds after flow initiation demonstrate that liquid transport is significantly faster for nanochannel with larger heights. The scale bar is equal to 50 μm.

MD Simulation. MD simulation was done by our collaborators Dezhao Huang, Tengfei Luo. In the simulations, the model consisting of 720 organic liquid molecules confined between two silica substrates, as shown in **Figure 19**, was developed. The approximate dimensions of $7 nm(x) \times 7 nm(y) \times 1.5 nm(z)$ were used for the silica substrates. Two different types of organic liquid molecules, i.e., C₃H₇OH (IPA) and C₂H₅OH (ethanol) were studied. Periodic boundary conditions were applied in the *x* and *y* directions. Since simulating channels wider than 10 nm is impractical for MD simulations due to the computational cost, the thickness of the IPA and ethanol liquid layer for the simulation was around 2 nm. We indeed performed simulations on a larger channel height (3.5 nm) at a shear velocity of 100 m/s and found the calculated viscosity (1.18 mPaS) to be similar to that from the 2 nm case (1.11 mPaS). We thus chose to use the smaller system to calculate the apparent viscosity at other shear velocities.

The amorphous silica substrate was modeled using the BKS force field^{143,144}. The popular OPLS-AA force field^{145,146} was adopted to model the organic liquids. The non-bond interactions between silica and organic liquids were simulated using the following Lennard-Jones (L-J) interaction equation

$$E = 4\varepsilon \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^6 \right]$$
(18)

where ε and σ are the energy and length constants, respectively, and r_{ij} is the distance between two atoms, i and j. A cutoff of 1 nm was chosen for the L-J interactions.

The long-range electrostatic interaction in the entire system was computed by the PPPM (particle-particle particle-mesh) approach with an accuracy of 1×10^{-5} . Simulations were performed using the large-scale atomic/molecular massively parallel simulator (LAMMPS) with a chosen time step of 1 fs.



Figure 19. An example model setup for shearing simulations, where the relaxed silica region is thermostatted at 295 K during the shearing process to dissipate the viscous heat. The top silica substrate moves at different speeds in the x-direction.

First, the system was energy-minimized and equilibrated in a canonical ensemble (NVT) at 295 K for 0.5 ns. Then, the system was optimized in an isothermal-isobaric ensemble (NPT) at 1 atm and 295 K for another 2 ns. After the structures were fully relaxed, the top part of the silica substrate was sheared by translating the top slab at constant speeds of 100, 200, 400, 600 m/s, which corresponds to shear rates on the order of 1010-1011/s, similar to those used in other non-equilibrium molecular dynamics (NEMD) simulations^{147–152}.

The viscous heat generated during the shearing simulations was dissipated using a thermostat acting on the relaxed portion of the silica substrate¹⁵³. This indirect heat dissipation method can overcome the disadvantage of directly thermostating the fluid which perturbs liquid molecular dynamics¹⁵⁴¹⁵⁵. The Navier shear viscosity was calculated as $\mu = -S_{xz}/\dot{\gamma}$ where $\dot{\gamma}$ is the shear rate, and S_{xz} is the shear component (xz) of the stress tensor, which consists of the kinetic energy contribution and the virial term¹⁵⁶.

Results and Discussion

Experimental Results

The capillary motion of IPA and ethanol inside the nanochannels of variable heights were monitored with respect to time. It was observed that liquid imbibition always follows a $x \propto \sqrt{t}$ relationship. However, the proportionality constant was significantly smaller than that predicted by LW equation (*K*). As shown in **Figure 20**, for all channel heights used in this study, significant deviations in IPA capillary flow kinetics between the experimentally obtained data and those predicted by LW equation were observed. Analogous behavior was observed in the imbibition of ethanol (see **Appendix B**, **Figure 42**).



Figure 20. Comparison between LW model prediction and the experimental results for liquid meniscus position versus square root of time in nanochannels with different heights for capillary filling of IPA.

Figure 21 shows the deviations for different channel heights that were calculated as the difference in percentage between the slope predicted from LW equation (*K*) and slope of the linear regression fitted to each data set. The divergence between the experimental observations and theoretical data based on LW equation increases for channels with smaller heights. As shown in **Figure 21** the mismatch can become as large as 45% for the nanochannels with a height of 20 nm. In addition, LW equation error was greater in experiments with IPA compared to ethanol which implies that the effect of interfacial viscous layer is more pronounced in capillary flow of IPA.


Figure 21. The deviation between the LW model and the experimental results for imbibition coefficient increases for channels with smaller heights.

Interfacial Viscous Layer Thickness Calculation

As discussed earlier, development of a several molecule-thick interfacial layer adjacent to the walls with a viscosity greater than the bulk slows the capillary filling in nanochannels. The yet unknown thickness of this layer l_s plays a critical role in determining the imbibition rate as expressed in **Equation 16**. It must be noted that the radial distribution function profiles for both organic liquids (**Figure 43** in **Appendix B**) manifest strong layering effect near the walls. Hence, in accordance with previous studies^{157,158} l_s is presumed to take on values that are multiples of the liquid molecular size i.e., $l_s = nd$, where *d* represents the liquid molecular diameter. Two different analytical methods were employed to solve for l_s .

In the first approach, an initial guess for *n* was used to calculate l_s . Then, **Equation** 16 was solved for μ_2 by substituting a datum point (x, t) from the experimental results for a 20 nm tall channel. As the interfacial layer forms owing to the liquid/wall interactions, its thickness depends on liquid and channel material properties but remains insensitive to the channel height. Hence, the obtained l_s and μ_2 were, subsequently, substituted in **Equation 17** and K_{nc} values were calculated for channels with heights of 40 and 80 nm. For both h = 40 nm and h = 80 nm, fitting of $x = K_{nc}\sqrt{t}$ to the experimental data was evaluated for the obtained K_{nc} value. This process was repeated for different input values for n. Eventually, the n value that produced the closest matches to the experimental data for all channel heights was adopted to calculate l_s .

In the second strategy, l_s was obtained by solving a system of equations for each liquid. By writing **Equation 16** for channels with 3 different heights, a system of equations was formed:

$$\begin{aligned} x &- \sqrt{\left(\frac{8\gamma\kappa_{20}}{h_{20}}\right) \left(\left(\frac{1}{\mu_{1}} - \frac{1}{\mu_{2}}\right) \left(\frac{l_{s}^{3}}{3}\right) + \frac{1}{\mu_{2}} \frac{h_{20}^{3}}{24}\right)} \sqrt{t} = 0 \\ x &- \sqrt{\left(\frac{8\gamma\kappa_{40}}{h_{40}}\right) \left(\left(\frac{1}{\mu_{1}} - \frac{1}{\mu_{2}}\right) \left(\frac{l_{s}^{3}}{3}\right) + \frac{1}{\mu_{2}} \frac{h_{40}^{3}}{24}\right)} \sqrt{t} = 0 \end{aligned}$$
(19)
$$x &- \sqrt{\left(\frac{8\gamma\kappa_{80}}{h_{80}}\right) \left(\left(\frac{1}{\mu_{1}} - \frac{1}{\mu_{2}}\right) \left(\frac{l_{s}^{3}}{3}\right) + \frac{1}{\mu_{2}} \frac{h_{80}^{3}}{24}\right)} \sqrt{t} = 0 \end{aligned}$$

where the subscripts for h and κ show the corresponding channel height. Note that to increase the reliability of the solution an overdetermined system of equations was formed

and the number of equations exceeded the number of unknowns, i.e., μ_2 and l_s . Therefore, the solution was obtained by minimizing the Frobenius norm of the residual. In addition, a constraint of $l_s = nd$ was imposed to limit the interfacial layer thickness to only take on values that are multiples of the liquid molecular size. By substituting three data points (x, t)from experiments in channels with heights of 20, 40 and 80 *nm*, respectively, the system of **Equations 19** was solved and l_s was obtained.

As expected, both methods resulted in identical solutions for l_s for both IPA and ethanol. Our results indicated that n = 4 produces the closest match to the experimental data for imbibition of IPA, whereas the best match for ethanol was obtained for n = 12. Since the molecular sizes for IPA and ethanol are $d_{IPA} = 1.6 nm$ and $d_{ethanol} = 0.44 nm$, the obtained n values correspond to $l_s = 6 nm$ and $l_s = 5 nm$ for IPA and ethanol, respectively. **Figure 22** depicts the experimental data for imbibition of IPA in a 40 nmchannel and the generated theoretical results based on **Equation 16** for several n values. Utilizing the definition of coefficient of determination (COD) the goodness of fits was evaluated and n = 4 was confirmed to yield the closest agreement with the experiment. **Figure 44** in **Appendix B** also shows the experimental data for capillary filling of ethanol in a 40 nm tall channel where n = 12 generated the closest match.



Figure 22. The COD values show that n=4 yields the closest match between our model and the experimental data for imbibition of IPA in 40 nm channel.

In addition, **as shown in Figure 22**, for both IPA and ethanol, the obtained *n* values resulted in close agreement between the model and the experimental data for all channel heights. The small deviations between the model and the experimental data for 20 nm channels are attributed to changes in the effective channel height after anodic bonding. In fact, the electrostatic interactions undergone during the anodic bonding of silicon and glass are sufficiently strong to induce small deformations and decrease the effective height of the channel compared to the 20 nm height measured prior to the bonding and cause small changes in filling rate.

The obtained l_s values also explain the difference in deviations between the experiments and LW equation observed for IPA and ethanol in **Figure 20**. In fact, the larger thickness of IPA interfacial layer compared to ethanol (6 nm versus 5 nm) results in a more significant contribution of this effect to the kinetics of the overall process. Therefore, since LW equation does not consider the interfacial layer effect, its deviations from experiments increases for flow of IPA.



Figure 23. The predicted results show close agreement with the experimental data for all channel heights for (a) IPA and (b) ethanol.

Interfacial Viscosity Calculation

As discussed earlier, the liquid viscosity within the interfacial layer adjacent to the walls, μ_2 is larger than that in the bulk, μ_1 . Either by solving the system of **Equations 19** for each liquid, or following the first approach described in previous section, μ_2 values can be obtained as one of the unknowns. **Table 1** shows the calculated μ_2 values along with the reference values of μ_1 for both IPA and ethanol. It can be seen that IPA and ethanol experience a 279% and a 276% increase in viscosity adjacent to the channel walls, respectively. This increase in viscosity can be attributed to the van der Waals and electrostatic interactions at the liquid/wall interface.

Liquid	μ_1 (mPa.s)	$\mu_2(mPa.s)$	Difference (%)
IPA	2.390	9.048	279%
Ethanol	1.173	4.405	276%

 Table 1. Comparison between the theoretically obtained interfacial viscosities of two organic liquids studied in this work and their reference bulk viscosities at 20°C and 1 atm.

Shear viscosities for both IPA and ethanol were calculated through NEMD simulations, as well. The NEMD method is chosen for shear viscosity calculation due to its robustness compared to equilibrium molecular dynamics simulations (such as Green-Kubo formula) that generally suffer from thermal fluctuation-induced noise in the auto correlation function. Several different shear velocities (V_S) ranging from 10 to 100 m/s were used, and the calculated shear viscosities are shown in **Figure 24**. It is known that shear-thinning behavior (shear viscosity decreasing with shear rate) can happen for both IPA and ethanol as reported previously¹⁵⁹. However, due to the time (~ns) and length (~nm) scales of the MD simulations, the shear rate in the simulation is much higher (1010-1011/s) than that in the experiments (~104/s). Thus, for a fair comparison with experiments, interfacial viscosity should be obtained by extrapolating the NEMD results to the low shear velocity limit. We fitted the NEMD data by applying the Carreau-Yasuda relationship^{160,161}:

$$\mu = \mu_0 \left[1 + (\lambda V_s)^a \right]^{(n-1)/a}$$
(20)

where λ is a constant with a unit of $(m/s)^{-1}$ and n and a are dimensionless constants. μ_0 (*Pa.s*) is the Newtonian viscosity, i.e., the liquid viscosity at zero shear rate. This model predicts a constant viscosity at low shear velocities that transitions to shear-thinning as the shear exceeds a certain threshold.



Figure 24. The shear viscosity values for isopropanol and ethanol at different shear velocities obtained from NEMD simulations and the analytical fit to the data.

Final shear viscosities of the liquids were obtained by evaluating μ values of the fitted regression at $V_s = 0$. The plateau shown in the inset of **Figure 24** represents the constant viscosity region at low shear rates for both liquids. We note that since the channel height of 2 nm in the simulations is smaller than the estimated interfacial layer thickness, the predicted viscosity is mainly influenced by the liquid/wall interaction and should be compared to the interfacial viscosity, μ_2 , in **Table 1**. The calculated viscosities for both liquids are in close agreement with the experimentally obtained interfacial viscosity values, as demonstrated in **Figure 25**.



Figure 25. Bulk viscosity of IPA and ethanol compared with their interfacial viscosity values obtained through numerical simulation and our theoretical model solution.

V. SURFACE TENSION NANOGATES FOR CONTROLLED ION TRANSPORT

The following chapter first prepared in ACS Applied Nano Materials, 2020.

Title: Surface tension nanogates for controlled ion transport

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Introduction

Capillary force drives liquid flow in small channels and is the critical mechanism for mass transport in nature and technology ^{114,162,163}. In the human body, brain's capillary network ^{109,164} controls blood flow and monitors neuronal activity and sweating glands function based on capillary flow to regulate body temperature; in plants, transfer of water and nutrients from soil to the root and further to the leaves is possible through this governing force ^{109–111}; on earth, transport of water from aquifer to surface is achieved through capillary wicking ^{112,165}; in energy ^{50,51,166,167} or biological systems such as proton-exchange membrane fuel cells ¹⁶⁸ and nanofluidics devices ^{1,17,53,169,170}, fluid transport in the confined channels is governed by this force ⁵; in thermal management systems of

electronics/photonics by heat pipes spontaneous liquid transfer to the hot spot is also achieved through capillary force ^{15,81,120,121,171}.

On the other side, ion channels play a pivotal role in human body through the control of ion flux across protein membrane ¹⁷² for a wide range of functions such as signal transduction, muscle development, release of neurotransmitters, hormone secretion, fever control, and brain function ^{164,173–179,}. The capillary force (f_c) is governed by interfacial energies at the solid-liquid-vapor contact line and is inversely proportional to the dimension of the channel, d, and could be expressed as $f_c = F(\sigma^{SV}, \sigma^{SL}, \sigma^{LV}, d)$, where σ is surface energy and superscripts *SV*, *SL* and *LV* denote the solid-vapor, solid-liquid and liquid-vapor, respectively ¹⁸⁰. That is, for a given set of surface energies, this force becomes dominant at small scale ^{28,124}.

Motivation and Scope

Here, we demonstrated that despite being a dominant force at small-scale, capillary force breaks down at sub-10 nm scale for some liquids and does not play any role in mass transport. In these scales, mass transport is governed through diffusion in the vapor phase, which is orders of magnitude slower transport than liquid flow. Once a liquid wets walls of a small channel and forms a liquid-vapor interface, the formed net capillary force drives the liquid flow in the channel. However, at sub-10 nm scale, the liquid-vapor interface experiences a mechanically unstable state and goes through a fracture to vapor phase. The formed vapor phase is transported through the diffusion, and the re-wetting and fracture phenomenon occurs with high frequency for mass transport. We exploited this phenomenon to introduce the concept of surface tension nanogates which are highly effective and tunable for ion transport. These channels could be activated and deactivated

through any external stimuli that actuates surface tension including temperature, electrical potential and chemical composition. The ability to control mass and ion transport across nanoconfinement plays a significant role in a broad range of application in biology, energy and water systems.

Results and Discussion

Nanochannels of Si with three selective depths of 40 nm, 20 nm and 10 nm are developed through a nanofabrication process discussed in the chapter 3. Each nanofluidic chip includes 11 groups of channels with nine channels in each group and each channel has width of 5 μm and length of 500 μm . These nanochannels connect two large micro-reservoirs with depth of 20 μm . The profile of each individual channel is probed with a Scanning Probe Microscopy (SPM) and is shown in **Figure 26a** and **Appendix C**, **Figure 46** confirming depth uniformity of the nanochannels.



Figure 26. Capillary wicking in nanochannels. (a) Uniform profile of Si nanochannels probed with SPM (b) Capillary wicking is observed in 40 nm and 20 nm channels, but the liquid front stays at quasi-static state in 10 nm channel, Temporal coordinates of (c) Isopropanol and (d) Ethanol wicking in nanochannels.

The nanochannels are sealed on top with a borosilicate glass through anodic bonding. It should be noted that to prevent channel collapse due to high electrostatic force during anodic bonding, 300 nm oxide film was thermally grown on silicon. After anodic bonding, the nanochannel survival was checked through some approaches discussed **chapter 3**. We chose isopropanol and ethanol as two working fluids with total wetting behavior on Si channels for this study. The flow of these liquids in the nanochannels is shown schematically in **Figure 26b**. For channels with depth of 40 nm and 20 nm, liquid wicks in the nanochannels, but for 10 nm channels, the liquid remains quasi-static at the

channel's entrance with no motion. The temporal motion of liquids in these channels for isopropanol and ethanol is shown in **Figure 26c-d**, As shown, for 40 nm and 20 nm channels, the liquid is driven by the capillary wicking and its velocity is governed by balance of capillary force and opposing viscous force, Washburn's equation. For these channels, the liquid motion deviates slightly from Washburn's equation^{15,29,181} due to interfacial viscosity^{182–184}, which is discussed in the **chapter 4**. However, for 10 nm channels, capillary wicking breaks down and there is no motion of liquid even after a long time.

We used three independent approaches to demonstrate capillary breakdown at sub-10 nm scale. In the first approach as shown in **Figure 27a-c**, we probed the motion of liquid in these nanochannels through a coupled high-speed imaging and an optical microscope system, **Appendix C**, **Figure 47**. One of the micro-reservoirs was filled and liquid transport was visualized in the nanochannels. Despite liquid flow in 40 and 20 nm channels, no fluid motion was observed in the 10 nm channels. To achieve high resolution imaging of liquid phase in 10 nm channels, we used wafers with 200 nm of coated Si₃N₄ through chemical vapor deposition²⁹, see **Appendix C**, **C4**. The Si₃N₄ shows a strong Fabry-Perot resonance in reflection resulting in a sharp contrast between ultrathin liquid and vapor phase ¹⁸⁵.



Figure 27. Capillary breakdown in sub-10 nm channels. (a-c) High-speed imaging of Isopropanol transport in various nanochannels. The scale bar is 50 μm. (d-f) The flow of Isopropanol in the nanochannels is visualized through florescence microscopy. The scale bar in (d-e) is 50 μm and in (f) is 80μm. (g-j) I-V curves across the nanochannels for liquids with different surface tension.

In the second approach, we used florescence microscopy to visualize liquid motion in the nanochannels, see **Appendix C**, **C5**. As shown in **Fig. 27d-f**, the liquid flow is evident in the 40 nm and 20 nm channels, but no liquid flow occurs in the 10 nm channel.

In the third approach, we used I-V curves to examine the liquid motion in the nanochannels. In these experiments, one micro-reservoir was filled, and liquid is allowed to wick to the other micro-reservoir. Then the other micro-reservoir was completely filled. For the case of 10 nm channels, both micro-reservoirs were filled with the working fluid. Two electrodes were placed in the micro-reservoirs with no contact with the walls of the micro-reservoirs and I-V curves in the channels were measured, see **Appendix C, C6**. The I-V curve for pure isopropanol is shown in **Figure 27g**, which indicates two distinct characteristics for 40 nm and 10 nm channels. The calculated electrical conductivity of

both 40 nm and 10 nm channels is $1-2.7 \times 10^{-10}$ S/m. However, for the 10nm channel, there is a threshold of electrical potential before any current in the channels could be measured. That is, an insulator phase exists in these channels. We conducted these experiments for ethanol, **Figure 26h**, and the same behavior for 40 nm and 10 nm channels were observed with electrical conductivity of $1.7-2.3 \times 10^{-10}$ S/m. One common physical property of these two liquids is their low surface tension (22.1-23 mNm⁻¹) ¹⁸⁶.

In the next set of experiments, we tuned surface tension of the working liquid to the value of 24 mNm⁻¹ through a mixture of 80% Ethanol-20% Water, **Figure 26i**. The similar characteristics were observed for the 40 nm and 10 nm channels. The surface tension of the liquid was further increased to 38 mNm⁻¹ through a mixture of 20% ethanol-80% water, **Figure 26j**. Interestingly for this working fluid, the I-V curves of 40 nm and 10 nm channels overlap with electrical conductivity of $5.7-6.2 \times 10^{-10}$ S/m. That is, the existence of electrically insulating phase in these channels is a function of surface tension of the working fluid.

To understand the threshold electrical potential in I-V curves, we designed an experimental set-up to determine electrical breakdown of ethanol and isopropanol vapor phases, see **Appendix C, C7**. These independent experiments suggest electrical break down of 2.7 kVm⁻¹ and 1.91 kVm⁻¹ for isopropanol and ethanol vapor, respectively. As nanochannels are 500 μm in length, the breakdown voltage in 10 nm nanochannels is 1.35 V for isopropanol and 0.955 V for ethanol. These voltage breakdowns are consistent with the measured breakdowns in **Figures 27g-h**. That is, the capillary wicking breaks down at these channels with only vapor phase between micro-reservoirs. Note that we just used I-

V characteristic as a precise method to explore the existence of liquid-vapor phase in the nanochannels and not to drive wetting⁴⁴ (i.e. electro-wetting). As suggested by Figure 27j, the length scale for capillary breakdown is a function of surface tension of the liquid. To further analyze this effect, we studied Deionized water flow in the nanochannels, due to its high surface tension, through florescence microscopy, Appendix C, C8. The results suggest that at 10 nm nanochannels water wicks in the channels. However, the liquid flow may not be as uniform as the other liquids due to partial wetting of the channel walls with Deionized water. Capillary wicking of water in sub-10 nm confinements has been also observed by other researcher^{1,5,133,187}. These experiments confirm that surface tension of liquid plays a critical role in capillary wicking breakdown. This fact has been also demonstrated in the study performed by Duan et al¹¹. They measured electrical conductivity of 2 nm silica nanochannels filled with ethanol and DI water, and observed that ethanol-filled nanochannels provided nearly zero conductance, while water-filled nanochannels showed quite high values. Since the electrical conductance value of bulk ethanol and DI water are in the same order of magnitude (are almost similar), and the conductance mechanism in both liquids is the same, one can conclude that the small conductance value of ethanol-filled nanochannels comes from vapor phase occupying the nanochannels.



Figure 28. Scale-dependent mass transport mechanism. (a) The liquid pressure in different nanochannels for studied fluids is shown. The experimental limit of liquid fracture as a function of surface tension (i.e. $\sim \sigma_{LV}^{3/2}$) is depicted by a dashed line. The mass flux for different length scales are shown for (b) Isopropanol and (c) Ethanol.

We determined the liquid pressure at the wicking front through Laplace equation (see Appendix C, C9) for nanochannels with different depths and for five studied types of liquids as shown in Figure 28a. As shown, the value of liquid pressure falls in the absolute negative pressure domain ^{88,99,188–190} due to high curvature of liquid-vapor interface. The state of negative liquid pressure is a thermodynamically unstable state but could be a mechanically stable state up to a spinodal decomposition limit. The limit of negative pressure for liquids is given by J. Fisher ¹⁹¹, which is proportional to $\sigma_{LV}^{3/2}$, See Appendix C, C10. Although the theoretical limit of liquid fracture is at extreme negative pressures, the measured experimental values are at moderate negative pressures. The measured experimental limit of liquid fracture for ethanol and water ^{191,192} are depicted in Figure 28a and the data are interpolated through a $\sigma_{LV}^{3/2}$ curve. This limit for liquid fracture falls above the liquid pressure in 10 nm channels for isopropanol, ethanol and 80% ethanol-20% water. That is, the liquid in these channels experience unstable mechanical state and goes through fracture to a vapor phase. In other words, no stable liquid-vapor interface could be formed for these fluids in 10 nm channels. The kinetics of wetting of these channels is governed

by interfacial energies and viscous dissipation at the meniscus region, see Appendix C, **C11**. As the liquid from micro-reservoirs wets the channels' wall, curvature of liquid-vapor interface increases, pushing the liquid pressure to lower negative values until it reaches to the fracture limit. Through the kinetics of wetting, we determined the time scale required to reach the fracture limit which is approximately 28 ns. That is the process of wetting and fracture occurs so fast. The frequency of liquid fracture is insensible to the fracture pressure and could be as low as 1 femtosecond. We could not detect this frequency with the highspeed imaging. Both wicking and diffusion have time dependence of $t^{1/2}$ The diffusion coefficient for self-vapor diffusion is in order of 10^{-9} m²/s and interestingly this coefficient for wicking process is in the same order, See Appendix C, C12 and Table 7. That is the volumetric transport by both processes is the same, but the mass transport is different by density ratio of liquid and vapor. As there is no equilibrium for the liquid wetting and fracture, this process occurs in a cyclic fashion for mass transport in these channels. We determined the mass flux in these channels for the discussed length scales as shown in Figure 28b-c, Appendix C13 for both isopropanol and Ethanol. As indicated, mass flux can be reduced by few orders of magnitudes due to capillary breakdown at sub-10 nm scales.



Figure 29. Surface tension nanogates. (a) Experimental set-up for demonstration of nanogates performance. (b-e) Transport of ions is activated and deactivated in 10 nm channels through temperature modulation.

As the capillary breakdown leads to change of mass transport mechanism from liquid wicking to vapor diffusion, we explored this physical concept to develop a new generation of ion channels. The current known ion channels are ligand-gated, mechanically-gated and voltage-gated^{52,193,194}. The ion transfer through liquid phase could be significantly faster than that of the vapor phase. To demonstrate these novel ion channels, we chose temperature as the external stimulus to actuate surface tension. A fluid mixture of 50%Ethanol-50%Water was chosen for these nanogates as transition between liquid fracture and wicking could occur by small surface tension change, **Appendix C**, **C14**. A set of Si nanochannels with the depth of 10 nm was chosen for these nanogates. Micro-reservoir (1) was filled with a solution of 0.1 M NaCl and micro-reservoir (2) was filled with a pure liquid. We used ionic conductance measurements in micro-reservoir (2)

to demonstrate performance of these surface tension nanogates, Figure 29a. At room temperature, nanogates are closed as the vapor phase exists in these nanochannels. We incrementally decreased temperature of the nanochannels from room temperature to 11 °C, as shown in Figure 29b-c. There is a minimal change in conductance of micro-reservoir (2), but no ion transport is detected. As the temperature of nanochannels was decreased to 8 °C, there is a sharp boost in the conductance of the micro reservoir (2) indicating the open nanogates and transport of ions by diffusion. Once the temperature of nanochannels was increased again, the conductance becomes approximately constant with no further change indicating closed nanogates. The further slight increase in conductance is due to temperature effect as shown in Appendix C, C14 and Figure 54. These ion nanogates could be activated and deactivated by any means that could tune surface tension. To further show these nanogates, we showed transport of K⁺ and Cl⁻ across these ion gates in Figure **29d-e**. Similar to Na⁺ ions, the gating characteristics could be achieved by temperature modulations. The activation of nanogates also demonstrated through florescence microscopy in Appendix C, Figure 55.

CONCLUSION

The fundamental study of fluid behavior at the nanoscale, which have been enabled by rapid development of nanofabrication and measurement techniques, carries the hope that new emerging phenomena happening at this scale will lead to innovative solutions for existing challenges in science and engineering. This dissertation presented experimental study of thin film evaporation (phase change), liquid capillary flow and mass transport at sub-10 nm scale (fluid transport) within 2-D planner silicon nanochannels made by MEMS fabrication approach.

With regard to phase change investigation at nanoscale, we utilized the concept of negative absolute liquid pressure in nanochannels to achieve unprecedented evaporative heat fluxes. This negative pressure provides a high driving force for liquid flow to the interface for evaporation. The findings suggest that there is no bubble formation in the channels at temperatures higher than the boiling temperature as the depth of nanochannels is smaller than the critical nucleolus dimension. This shows high reliability and stability of this mode of thermal management for electronics. For a moving contact line in nanochannels, there is a plateau in heat flux at which viscous dissipation in the thin-film evaporation region dictates the motion of the contact line. However, in the steady-state evaporative condition (i.e., no moving contact line), the concept of negative pressure allowed the exploration of unprecedented limits of evaporative fluxes. We demonstrated average heat fluxes of 11 ± 2 kW cm-2 in these nanochannels through a thin-film evaporation approach. By tuning the depth of nanochannels, higher heat fluxes could be

achieved. The presented rational method to achieve high heat fluxes paves the path for design of advanced thermal management devices for electronic/photonic systems.

With regard to liquid transport at nanoconfinements, we proposed a theoretical model for capillary flow in nanoscale conduits as the well-known Lucas-Washburn equation has been confirmed to be incapable of predicting the liquid flow kinetics in channels with nanoscopic heights. Our model incorporated the interfacial viscosity effect on the kinetics of liquid imbibition in nanochannels and was able to successfully predict the capillary flow rates for different liquids in channels with different heights as compared against experimental observations. In fact, we illustrated that the increased viscosity in a several molecule-thick layer adjacent to the walls is the primary reason for the lower rates of capillary motion observed in nanoscopic channels. With assistance of our collaborators, MD simulations were also conducted, and shear viscosities of the liquids studied in this work were obtained through NEMD, which matched the experimental results very well. The close agreement between the results from the experimental data based on our model and the numerical simulations underscores the role of interfacial viscosity in capillarity slowdown in nanochannels and clarifies the underlying physical phenomena responsible for the slow filling in nanochannels.

With regard to exploring mass transport mechanism at ultra-small scale, we demonstrated that, despite being the dominant force at small scale, capillary wicking breaks down at sub-10 nm scale and plays no role in the mass transport. The breakdown length depends on the interfacial tensions at the solid-liquid-vapor contact line. As the liquid contact line advances in sub-10 nm channels to wet the surface, the liquid could experience unstable

state of negative pressure due to high curvature of liquid-vapor interface and fracture to vapor phase. The liquid-vapor interface adopts a state of quasi-static in which process of wetting and fracture occur in a cyclic fashion. The mass flux at these scales is governed by vapor diffusion which is orders of magnitudes slower than capillary wicking. This breakdown leads to the concept of surface tension nanogates. These gates could be turned on/off by any means that actuate surface tension. The transport of Na⁺ and K⁺ ions across these gates was demonstrated. This new type of efficient and tunable ion gate offers a new avenue for controlled mass transport and promises extensive implementation in drug delivery, molecular separation, energy conversion, power generation, and sea water desalination.

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Appendix A

A1 - Governing physics in thin film evaporation at nanostructures

Thermal As discussed, the thin film evaporation phenomenon in micro/nano structures is a coupled multi-physics momentum transport, energy transport, and gas kinetics problem. On the momentum transport aspect, miniaturization of the electronic devices and consequent cooling systems increases hydraulic resistance of the fluid flow. As the radius of confinement for the fluid flow decreases, the fluid transport to the liquidvapor interface becomes limited. This limit imposed by the momentum transport on thin film evaporative heat flux may be written as

$$\dot{q}_m = \left(\rho_L \, h_{fg} \, \Delta P \, \kappa\right) / (\mu \, L) \tag{21}$$

where ρ_L denotes the liquid density, h_{fg} is the enthalpy of the liquid-vapor phase change, ΔP is the driving pressure, κ is the permeability of the micro/nano structure (which is a function of pore geometries), μ is the viscosity of the liquid, and *L* is the length scale of the fluid flow in the structure. Here, we focus on capillary-driven flow without any external pumping source. In the capillary-driven system, the driving pressure is correlated to the surface tension of the liquid, σ , radius of confinements (pores) in the micro/nano structure, *r*, and the apparent contact angle, θ , $\Delta P = (2\sigma \cos \theta)/r$. Thus, for a given liquid, the limit imposed by the momentum transport is a function of pore radius, the length scale of the fluid flow in the structure and contact angle or $\dot{q}_m = \dot{q}_m (r, L, \theta)$. On the energy transport aspect, the energy transport to the liquid-vapor interface is a function of solid-liquid thermal conductance, liquid-vapor thermal conductance and thermal diffusivity of the thin film of liquid. The critical dimension of nanostructures is defined as $L_c = C_L k_L/(G C_s)$, where C_L denotes the heat capacity of liquid, k_L is the liquid thermal conductivity, *G* is the thermal conductance of liquid-vapor interface and C_s is the heat capacity of solid. For metal-water interfaces, G is in order of 100 MWm⁻²K⁻¹ and L_c is in order of 30 nm. Thus, if the length scale of solid structures falls below this critical length scale, the role of interfacial energy transport becomes important and appears in thermal management picture.

On the gas kinetics aspect, thin film evaporative mass flux is limited by the net flux of molecules from the liquid-vapor interface to the vapor phase. Currently, there are three main theories on the evaporation phenomenon; Hertz-Knudsen model^{66,67} (HK), Statistical rate Theory (SRT)^{68–71} and Non-equilibrium thermodynamics (NET)^{72–75}. The Hertz-Knudsen model for the rate of evaporation was derived from the concept of the maximum evaporation rate under equilibrium condition. In this theory, the molecules move from the liquid surface of the Knudsen layer (several molecular mean free path lengths thick) according to a half-Maxwellian distribution function and their flux depends on thermodynamic properties of interfacial liquid. On the other side, the flux of impinging vapor molecules from the vapor phase to the liquid surface depends on thermodynamic properties of interfacial liquid. In this for evaporation and consequent heat flux is written as⁶⁶

$$\dot{q}_k = h_{fg} \sqrt{\frac{M}{2 \pi R}} \left(\sigma_e \frac{P_l}{\sqrt{T_l}} - \sigma_c \frac{P_v}{\sqrt{T_v}} \right)$$
(22)

where *M* denotes the molar mass of liquid, *R* is the gas constant, σ_e and σ_c are empirical evaporation and condensation accommodation coefficients, P_l is the liquid pressure, T_l is liquid temperature, P_v is the vapor pressure and T_v is the vapor temperature at the boundary of the Knudsen layer. The accommodation coefficients are defined as the probability of crossing the interface by a molecule impinging on the surface, defined by Knudsen¹⁹⁵ to explain the experimental findings.

As discussed, this theory does not provide predictions consistent with the measurements. Although, there is still ongoing research to determine the accommodation coefficients, we think the measured values of these coefficients are complex functions of liquid and vapor temperature, heat flux and geometry. The evaporation and condensation coefficients should not be used synonymously as they have different definitions. The main problem, as pointed out by Barret and Clement¹⁹⁶, is that the KTG equation does not satisfy momentum and energy conservations. As the energy supply to the interface drives the evaporation, the coupled nature of heat and mass transfer should be considered to provide a sound theory of evaporation.

The second theory, called statistical rate theory (SRT)^{68–71} is based on the transition probability concept defined in quantum mechanics and the Boltzmann definition of

entropy. This theory predicts the rate of molecular transport across the boundary of macroscopic phases given by

$$\dot{m} = 2 K_e Sinh \left(\Delta s^{LV}\right) \approx 2 \sqrt{\frac{M}{2 \pi R T_l}} \left(P^s \left(T_l\right) - P^v\right)$$
(23)

where \dot{m} denotes the mass flux, K_e is the equilibrium molecular exchange rate, Δs^{LV} is the entropy change associated with the transport of a liquid molecule to the vapor phase, and P^s is the saturation pressure of the vapor. The linear approximation of the evaporation flux by the SRT is similar to the KTG expression with the evaporation coefficient of unity. The nonlinear form of SRT has received some validations with the experimental data^{69,197,198}. The main drawback of this theory is similar to KTG in that both theories do not satisfy the momentum and energy conservation during the transport of liquid molecules to the vapor phase.

The third theory is derived from the non-equilibrium thermodynamics (NET)^{72–75}. In this theory, the continuity and momentum equations are integrated over a control volume at the interface. The momentum equation represents the mechanical equilibrium at the free surface. As the evaporation process is accompanied by the heat transport, the energy equation therefore must be integrated into these equations as well. The energy equation can be written in the Stefan condition form for a stationary interface with a mass transport¹⁹⁹. The system of equations is not closed and entropy production correlation from thermodynamics should be included with the system of equations to solve for the evaporation across the liquid-vapor interface. The entropy production rate is defined as the

sum of all thermodynamic forces multiplied with their respective fluxes⁷². The final form of the evaporation flux without neglecting the cross-effect Onsager coefficients is written as

$$\dot{m} = -C_{mm} \frac{R T^{L}}{M} \ln[\frac{P^{V}}{P^{s} (T^{L})}] - C_{mq} \frac{T^{V} - T^{L}}{T^{L}}$$

$$\dot{q} = -C_{qm} \frac{R T^{L}}{M} \ln[\frac{P^{V}}{P^{s} (T^{L})}] - C_{qq} \frac{T^{V} - T^{L}}{T^{L}}.$$
(24)

The Onsager reciprocal principal suggests that the cross-effect coefficients must be equal and therefore the coefficient matrix is symmetric. The cross-effect coefficient, C_{qm} , couples the heat and mass evaporation fluxes. This coefficient is one of the missing puzzle pieces in NET. The experimental results by Badam et al.⁷⁵ and Fang and Ward²⁰⁰ suggest that the value of C_{qq} is consistent among all of the experiments. The main difficulty is to determine the value of C_{mm} and C_{mq} . The reported values of C_{mm} differ by three orders of magnitude, due to inaccuracy in the pressure measurements⁷⁵. The current deficiency in our knowledge of evaporation comes from the inability to probe the thermodynamic properties at the liquid-vapor interface. This inability has resulted in unjustified assumptions and precluded rational development of the phase-change technologies. The ability to probe the interfacial thermodynamic properties provides a route to determine the exact Onsager coefficients in the NET and establish a predictive theory for evaporation in the nanoscale.

A2 – Fabrication of nanofluidic device



Figure 30. Fabrication process of Nanofluidic device.



Figure 31. An example of collapsed nanochannels due to high electrostatic force during anodic bonding.



A4 – Characterization of nanofluidic system

The geometry of the developed nano-channels is studied with Scanning Electron Microscopy (SEM) and is shown in **Figure 23**. The structure is made up of nine sets of nano-channels and two micro-reservoirs located perpendicularly along the two ends of the nano-channels, as shown in **Figure 23a**. The reservoirs are 2 mm in width, 4 mm in length and 25 μ m in depth. **Figure 23b** shows one set of nanochannels. Each set of nano-channels consists of 11 separate channels. Two individual channels are shown in **Figure 23c** at higher magnification.



Figure 32. SEM image of the developed structure. (a) The entire structure including micro-reservoirs and nano-channels. (b) One set of nanochannels consisting of 11 individual channels. (c) Two individual nanochannels at higher magnification.

A5 - Contact angle analysis

Th schematic of an evaporating interface inside a 2D nanochannel is shown in **Figure 33**. As shown, $\cos \theta = \frac{r}{R}$ and $\sin \theta = 1 - \frac{h}{R}$, one can find $\frac{h}{r} = \frac{1 - \sin \theta}{\cos \theta}$. Therefore, by measurement of $\frac{h}{r}$, contact angle is determined. The contact angle in the depth direction could not be measured by the optical approaches. We considered the same contact angle in

the depth direction as that of the width direction. Note that IPA is a highly wetting fluid for silicon and glass substrates.



Figure 33. Schematic of liquid-vapor interface inside a 2D nanochannels. θ denotes a contact angle, r is the dimension of nanochannels, h is the centerline depth, and L is the liquid phase length.

The liquid-vapor interface for one set of nanochannels during transient evaporation captured at 54°C is shown in **Figure 34**. The values of h and r were measured through image processing (ImageJ) and the values of contact angles in the nanochannels are presented in **Table 2**.



Figure 34. One set of nanochannels used to measure contact angle. Channel 1 is the first channel from the top. The scale bar is 20 μm.

nanochannel	r (µm)	h (μm)	h/r	θ (°)
1	2.25	2	0.888	7
2	2.3	2.2	0.956	2
3	2.3	2.1	0.913	5
4	2.4	2.2	0.916	5
5	2.4	2.2	0.916	5
6	2.35	2.3	0.978	1
7	2.4	2.3	0.958	2
8	2.5	2.3	0.920	5
9	2.5	2.4	0.960	2
10	2.45	2.2	0.897	6
11	2.4	2.3	0.958	2

Table 2. Contact angle for one set of nanochannels

A6 - Calculation of liquid pressure at the liquid-vapor interface

The liquid pressure at the liquid-vapor interface is calculated through the Young-Laplace equation, $\Delta P = \sigma C$, where $\Delta P = P_v - P_l$ is a pressure discontinuity across the liquid vapor interface. P_v denotes the vapor pressure and is equal to $P_{atm} \cong 10^5 Pa$, P_l is the liquid pressure, σ is the surface tension of the liquid and C is the curvature of the liquidvapor interface which can be expressed as $C = \cos \theta \left(\frac{1}{R_1} + \frac{1}{R_2}\right)$, where $\theta = 4^o$ is the average measured contact angle in S4, $R_1 = 90 nm$ is half of the channel's height and $R_2 = 3 \mu m$ is half of the channel's width. Taking the dependence of surface tension on temperature, liquid pressure at different temperatures is determined and tabulated in **Table 3**.

Temperature	σ^{LV} ($\frac{mN}{m}$)	$P_l(kPa)$	$R_{c}(nm)$	$R_{C}(nm)$
(°C)	" " <i>m</i> "		(Degassed	(Gas
			liquid)	dissolved
25	22.6	-158.5	275	7499
38	21.6	-146.9	268	3037
55	20.2	-130.7	250	1322
70	19	-116.6	214	628
75	18.7	-113.7	198	501
80	18.3	-108.6	183	400

Table 3. Surface tension, liquid pressure and critical radius of bubble nucleation at various temperatures.

The complete form of the Young-Laplace equation is written as

$$P^{V} + \dot{m}^{2} \left(\frac{1}{\rho^{V}} - \frac{1}{\rho^{L}}\right) - P^{L} = \sigma^{LV} (C_{1} + C_{2}) + \Pi$$
(25)

where \dot{m} is the evaporation mass flux, and ρ_1 and ρ_v are densities in the liquid and vapor phases, respectively. The term $\dot{m}^2(\frac{1}{\rho^L} - \frac{1}{\rho^V})$ stands for recoil pressure on the liquid-vapor interface. For the maximum mass flux, the recoil pressure term is an order of magnitude smaller than the curvature term and could be neglected. However, it may appear in Laplace equation at higher heat fluxes.

A7 - Critical radius (R_C) of a vapor nucleus

The calculated values of the critical radius for bubble nucleation at different temperatures are tabulated in **Table 2**.

A8 - Motion of contact line in nanochannels

Transient coordinates of the liquid-vapor interface for two other nanochannels are shown in **Figure 35**. Consistent with the other nanochannels, there is a plateau in the velocity of the contact line in these nanochannels.



Figure 35. (a) and (b) Coordinate of liquid-vapor interface as a function of time for two representative channels at different temperatures ranging from 25 to 100°C. The velocity increases monotonically with temperature and reaches a plateau at higher temperatures.

A9 - Viscous dissipation at sharp-edged interfaces

Let's consider a liquid-vapor interface in the nano-channel with equilibrium contact angle of $\theta_e \leq \frac{\pi}{2}$. During a transient phase change (i.e. moving contact line), evaporation occurs dominantly in the transition region close to the walls. That means, the evaporation flux along the liquid-vapor interface is not uniform and is diverging in the transition region. The local evaporation flux leads to a vapor recoil pressure, which pushes the liquid-vapor interface toward the liquid in the normal direction. The induced vapor recoil force per unit area is written as

$$P_r = j_{ev}^{2} \left(\rho_V^{-1} - \rho_L^{-1} \right) \tag{26}$$

where j_{ev} denotes local evaporation flux, ρ_v is the vapor density and ρ_L is the liquid density. This force leads to a change in *local* contact angle to θ_D , (dynamic contact angle) which is different from θ_e (equilibrium contact angle). This difference causes a net driving force in the x < 0 direction corresponds to

$$P_r = j_{ev}^{2} \left(\rho_V^{-1} - \rho_L^{-1} \right) \tag{27}$$

where σ^{LV} denotes the surface tension of liquid-vapor interface. For a transient evaporation condition, this driving force causes motion of triple line in the x < 0 direction as it evaporates. Once $\theta_D = \theta_e$, the liquid-vapor interface becomes stationary (i.e. no evaporation).



Figure 36. For liquid-vapor interfaces, a wedge assumption is used to determine the fluid flow to the transition region.

Note that at equilibrium contact angle, the pressure across the interface is balanced by interface curvature and disjoining pressure. The velocity profile of the liquid near the contact line is shown in **Figure 36**. For liquid-vapor interfaces, the motion of the contact line can be treated as a wedge problem¹⁰⁴. The gradient of liquid velocity is written as $\frac{dv}{dz} = \frac{dv}{dx} \frac{dx}{dz} = \frac{V}{x\theta_D}$, where V denotes the velocity averaged over the thickness of the wedge. The liquid flow in the transition region is dominated by viscous flow and is governed through Poiseuille's equation written as

$$-\frac{dp}{dx} = \mu \frac{d^2v}{dz^2}$$
(28)

and by integration

$$p^{L}(x) - p^{\nu} = \int_{x}^{\infty} \mu \, \frac{d^{2}\nu}{dz^{2}} \, dx \, \approx \, - \frac{\mu V}{x\theta_{D}^{2}} \,. \tag{29}$$

Note that the pressure merge with vapor pressure as x approach infinity. Now, we determine the viscous dissipation of fluid flow to the transition region written as

$$I = \int_0^\infty dx \, \int_0^{r/2} \mu \, (\frac{dv}{dz})^2 \, dz \, \approx \frac{\mu V^2}{\theta_D} \int_0^\infty \frac{dx}{x} \tag{30}$$

where r denotes height of the nanochannel. The integral at both limits diverges. To avoid this, we truncate the integral on the upper limit by L, the length of the transition region and in the lower limit by a, the molecular dimension

$$I = \frac{3\,\mu V^2}{\theta_D} \ln(\frac{L}{a}) \,. \tag{31}$$

By equating viscous dissipation and *FV*, one finds the average velocity of the meniscus. By small contact angle approximation in the transition region, one finds ($\cos \theta \approx 1 - \theta^2/2$)

$$I = FV = \sigma^{LV} \left(\theta_D^2 - \theta_e^2\right) V \tag{32}$$

and

$$V = \frac{\sigma^{LV} (\theta_D^2 - \theta_e^2)}{\mu} \left[\frac{\theta_D}{\ln \left(\frac{L}{a}\right)} \right].$$
(33)

The outcome of **Equation 33** is quite remarkable. It suggests that once $\theta_D = \theta_e$, the velocity of the liquid-vapor interface becomes zero. That means the meniscus is stationary with no imposed force. Furthermore, if θ_D goes to zero, the velocity becomes zero. That is, viscous dissipation in a sharp meniscus is extremely strong and impedes any fluid transport to the transition area for evaporation. In this case, although heat transport to the transition region is adequate, the slow fluid flow to this region mitigates phase-change and only small evaporation occurs in the meniscus region. Between these two limits, the velocity of fluid goes through a maximum, which correspond to maximum evaporative heat flux at the interface (i.e. $dV/d\theta_D = 0$),

$$V_m = \frac{\sigma^{LV}}{9\sqrt{3}\,\mu\ln(\frac{L}{a})} \,\,\theta_e^{\,3}\,. \tag{34}$$

That is a moving contact line on a hot substrate attains a maximum velocity. The maximum heat flux is then written as

$$\dot{q}_m = \rho_L h_{fg} \frac{\sigma^{LV}}{9\sqrt{3}\,\mu\ln(\frac{L}{a})} \,\theta_e^{\,3} \,. \tag{35}$$

The above mathematical formula plays an important role in rational design of nanostructures for thin film evaporation.

A10. Heat flux calculations: transient experiments

In the transient experiments (i.e. isothermal experiments), the measured average velocity of the liquid-vapor interface, *V*, was used to determine local heat flux written as

$$\dot{q} = \dot{m}h_{fg} = \rho V h_{fg} \tag{36}$$

where h_{fg} is the latent heat of the liquid (737.7 kJ kg⁻¹, at 25°C), \dot{m} is the mass flux, ρ is the fluid density (781 kg/m³, at 25 °C). Note that the temperature dependence of the thermophysical properties is taken into account in all calculations.

A11 - Experimental set-up for steady-state experiments

The schematic of the experimental set-up in steady-state evaporative conditions is shown in **Figure 37**. A droplet of liquid is placed on top of the cold reservoir to continuously supply liquid for the phase change.



Figure 37. Schematic of the experimental setup for steady-state experiments.

A12 - Heat flux calculations: steady-state experiments

In steady-state condition, the heat flux is determined through Equation S18 except fluid velocity is determined through Poiseuille flow analysis. The liquid flow in the nanochannels is laminar (Re \sim 0.1) and the liquid velocity is written as ¹⁰⁷

$$V = \frac{\mathrm{H}^2 \,\Delta\mathrm{P}}{12\mu\mathrm{L}} \tag{37}$$

where H denotes the height of the channel, μ is the fluid viscosity, L is the length of liquid in the nanochannels after reaching the steady-state evaporation. Thus, interfacial heat flux for steady-state evaporation in the nanochannels at 60 °C is written as

$$\dot{q} = \frac{\rho h_{fg} \mathrm{H}^2 \Delta P}{12\mu L} = \frac{748 \times 737.7 \times 10^3 \times (180 \times 10^{-9})^2 \times 2.3 \times 10^5}{12 \times 8 \times 10^{-4} \times 2 \times 10^{-6}}$$
(38)
= 21416.7 W cm⁻².

Furthermore, the corresponding length of liquid-vapor interface at these high heat fluxes is shown in **Figure 38**.



Figure 38. The liquid is evaporating in steady-state condition in the nanochannels. The minimum length of liquid corresponds to $2 \pm 0.5 \mu m$. The scale bar is 20 μm .

A13 - Vapor transport in the nanochannels

For the vapor outward flow, we should initially determine which mechanism (advection or diffusion) is the dominant transport phenomena. The Knudsen number is written as

$$K_n = \frac{\lambda}{r} = \frac{k_B T}{\sqrt{2\pi}d^2 P h} \tag{39}$$

where λ denotes the molecular mean free path, r is the physical length scale (in our case it is considered to be channel's height), k_b is the Boltzmann constant, T is the temperature, d is the diameter of vapor molecules and P is pressure. For isopropyl alcohol, λ is 24 nm and d is 6.5×10^{-10} m and consequently Knudsen number is 0.135, which is in the range of 0.01 to 10. This indicates that the diffusion process is between the Knudsen diffusion regime and the molecular diffusion regime, and the diffusion coefficient inside the nanochannel is calculated from the Knudsen $(D_{kn} = \frac{h}{3} \sqrt{\frac{8RT}{\pi M_v}} = 0.204 \ cm^2/s)$ and the molecular $(D_M = \frac{h}{3} \sqrt{\frac{8RT}{\pi M_v}} = 0.028 \ cm^2/s)$ diffusion coefficient⁸:

$$\frac{1}{\overline{D}} = \frac{1}{D_{Kn}} + \frac{1}{D_M}.$$
(40)

Thus, the diffusion coefficient in the studied nanochannels is $0.024 \ cm^2/_S$. The relative ratio of advective transport to diffusive transport is written as

$$Pe = \frac{LV_{\nu}}{\overline{D}} \tag{41}$$

where L denotes the length scale, V_{ν} is the vapor phase velocity. The velocity of the vapor phase is determined through conservation of mass at the liquid-vapor interface $\rho_L V_L = \rho_V V_V$. At the maximum evaporation flux, the velocity of vapor molecules is 140.25 ms⁻¹ considering $\rho_L = 748 \ kgm^{-3}$, $v_l = 0.39 \ ms^{-1}$ and $\rho_{\nu} = 2.08 \ kgm^{-3}$. Thus, the Peclet number is ~ 5 indicating that vapor removal is governed by both advection and diffusion..

A14- Resistances of mass transport in steady-state evaporation

Three transport phenomena are involved in evaporation at nanochannels including liquid transport to the liquid-vapor interface (capillary-driven transport), interfacial phasechange of liquid to vapor phase (gas kinetics transport), and vapor outward transport (advection and diffusion). Here, we compare the role of these transport phenomena in evaporation through comparing resistance of each transport phenomena. The corresponding resistance model is shown in **Figure 39**.



Figure 39. Resistance model for steady state evaporation.

As it is shown, there are three major resistances in series inside the nanochannel. (i) the resistance of liquid flow in the nanochannel can be written as $R_{Ca} = \frac{12\mu_l L_l}{\rho_l h^2}$, where μ_l is the liquid viscosity, L_l is the length of the liquid in the nanochannel, ρ_l is the density of liquid and h is the height of the nanochannels. (ii) the resistance of a phase change at the liquid-vapor interface is expressed as $R_k = \frac{1}{\sigma} \sqrt{\frac{2\pi RT}{M}}$, where σ represents an accommodation coefficient (assumed to be 1), R is a universal gas constant and M is the molar mass of the fluid, and (iii) the resistance of the vapor outward flow. As discussed in S10, the vapor removal is a combination of advection and diffusion phenomena. As a result, the resistance of the vapor flow inside the nanochannel is considered as the combination of two parallel resistance: a) the resistance induced by the advection is written as $R_{ad} = \frac{12\mu_g L_g}{\rho_g h^2}$, where μ_g is the vapor viscosity, L_g is the length of the vapor phase and ρ_g is the vapor density; and b) the resistance induced by diffusion is written as $R_D = \frac{RTL}{D}$, where L is the diffusion length and D is the diffusion coefficient which is calculated in A13. Therefore, the vapor

outward resistance is written as $R_v = \frac{R_{ad} R_D}{R_{ad} + R_D}$. The contribution of each resistance in the mass transport phenomena at steady state evaporation is demonstrated as percentage of the total resistance in **Figure 40**. The total resistance is equal to $R_{TOT} = R_{Ca} + R_k + R_v$. The results indicate that the capillary flow resistance is the dominant resistance to mass transport at all temperatures.



Figure 40. Contribution of different mass transport resistances is plotted at 20°C, 40°C and 60°C for the smallest length of liquid phase at each temperature. R_V, R_k and R_{Ca} denote the vapor removal resistance, phase change resistance and capillary flow resistance, respectively.

Appendix B

B1 - Applying Boundary Condition for the Governing Equations of Capillary Flow

Applying Navier-Stokes equation to both bulk liquid and the interfacial layer yields

$$\mu_1 \frac{\partial^2 u_1}{\partial z^2} - \frac{dp}{dx} = 0 \tag{42}$$

and

$$\mu_2 \frac{\partial^2 u_2}{\partial z^2} - \frac{dp}{dx} = 0 \tag{43}$$

where subscripts 1 and 2 represent the bulk and the interfacial layer properties, respectively. The following boundary conditions must be satisfied:

$$\left(\frac{\partial u_1}{\partial z}\right)_{z=0} = 0$$

$$(u_2)_{z=\frac{h}{2}} = 0$$

$$(u_1)_{z=l_s} = (u_2)_{z=l_s}$$

$$(\tau_1)_{z=l_s} = (\tau_2)_{z=l_s}$$
(44)

where z = 0 marks the middle of the channel and, z = h/2 is the location of the nanochannel wall. Also, τ is the shear stress in the liquid. Integrating both sides of **Equations 42** and **43** twice and applying boundary conditions (44), yields the flow velocities in bulk liquid u_1 , and within the interfacial layer u_2 :

$$u_{1} = \frac{1}{\mu_{1}} \left(\frac{dp}{dx}\right) \frac{z^{2}}{2} - \frac{1}{\mu_{2}} \left(\frac{dp}{dx}\right) \frac{h^{2}}{8} - \left(\frac{dp}{dx}\right) \left(\frac{1}{\mu_{1}} - \frac{1}{\mu_{2}}\right) \left(\frac{l_{s}^{2}}{2}\right)$$
(45)

and

$$u_2 = \frac{1}{\mu_2} \left(\frac{dp}{dx}\right) \frac{z^2}{2} - \frac{1}{\mu_2} \left(\frac{dp}{dx}\right) \frac{h^2}{8}.$$
(46)



Figure 41. Height profile analysis of nanochannels obtained by Scanning Probe Microscopy. Height uniformity across the nanochannels with heights of (a) 20 nm, (b) 40 nm and (c) 80 nm is confirmed.

B2- Deviation of LW



Figure 42. The deviation of the LW model prediction from the experimental observation for imbibition of ethanol in nanochannels with heights of 80 nm, 40 nm, and 20 nm.

B3- Radial distribution of oxygen atoms



Figure 43. Radial distribution function of the oxygen atoms in the hydroxyl groups of ethanol and IPA molecules with respect to silicon atoms of the wall.

B4 - Comparison between model and experimental results



Figure 44. The COD values show that n=12 yields the closest match between our model and the experimental data for imbibition of ethanol in 40 nm channel.

B5- Velocity profile



Figure 45. Velocity profiles of (a) ethanol and (b) IPA confined in silicon nanochannels under different shear velocities.
Appendix C

C1 - Characterization of nanochannels

After fabrication of nanochannels through photolithography and reactive ion etching, we used scanning probe microscopy to explore the channels topography and find the precise depth of channels. **Figure 46** shows the height profile of 40 nm, 20 nm and 10 nm channels. The surface roughness of nanochannels is around 4 Å.



Figure 46. Height profile analysis of nanochannels obtained by Scanning Probe Microscopy. (a) 40 nm nanochannels, (b) 20 nm nanochannels, (c) 10 nm nanochannels.

C2 - Capillary wicking experimental set-up

The schematic of capillary filling experimental set-up is shown in **Figure 47.** The micro-nanofluidic device was cleaned via plasma cleaner for 10 minutes before each run. Afterward, the liquid was introduced to the device through the inlet of one reservoir. Once it fills the reservoir, capillary wicking initiates in the nanochannels from the filled reservoir side. We used high-speed camera (Phantom V711) coupled with optical microscope (Nikon) to track motion of the liquid-vapor interface as a function of time.



Figure 47. Schematic of the capillary filling experimental set-up. The liquid is introduced through the access hole on top of the left reservoir. The red arrow shows the direction of liquid motion inside the nanochannels.

C3 - Washburn's equation

The dynamic of liquid capillary wicking (filling) in nanochannels with rectangular cross section is described by Washburn's equation,

$$x = \sqrt{\frac{\sigma^{LV} \cos \theta \,\mathrm{h}\,\mathrm{t}}{3\mu}} \tag{47}$$

where, x is a meniscus location (liquid length inside a channel), σ^{LV} is a surface tension of the liquid, θ is the contact angle, h is the channel height, μ is the liquid viscosity and t is filling time. In different studies, the capillary filling experiments have confirmed the validation of this equation. We also performed capillary filling experiments in our fabricated micro-nanofluidic device. The location of a meniscus as a function of time was monitored by a high-speed camera mounted on an optical microscope and analyzed with a MATLAB image processing code. **Figure 48 a-d** presents the experimental results for channels with 500 nm, 80 nm, 40 nm and 20 nm height, respectively. We should add that each graph contains the results of four individual channels in order to demonstrate the consistency of our capillary wicking results. The Washburn's equation corresponding to each channel height is also plotted in all graphs. As demonstrated, capillary wicking in all the channels (regardless of their height) qualitatively follows the Washburn equation (i.e. $x \propto \sqrt{t}$). However, the wicking dynamic deviates quantitatively from Washburn equation as the channel height decreases. This behavior has been reported by various studies and is attributed to interfacial viscosity effect in very small conduits.



Figure 48. Capillary filling results for (a) 500 nm nanochannels, (b) 80 nm nanochannels, (c) 40 nm nanochannels, (d) 20 nm nanochannels filled with Isopropanol. The Washburn equation for each channel height is plotted in order to make a comparison with experimental data.

C4 - Silicon Nitride nanochannel

Figure 49 shows the optical microscopy image of one set of Silicon Nitride nanochannels with depth of 10 nm. We repeated capillary filling experiments in these nanochannels, but no liquid motion was distinguished even after using optical enhancement layer.



Figure 49. Optical microscopy image of one set of 10 nm Silicon Nitride nanochannels during capillary filling experiment. As it is shown, no liquid flow can be observed in these channels. The scale bar is 50 µm.

C5 - Fluorescence (confocal) microscopy

To further explore the capillary breakdown of liquids with low surface tension (like Isopropanol) at 10 nm scale, we utilized fluorescence microscopy approach. In this method, the SYTO9 diluted in Isopropanol with a concentration of 5 x 10^{-5} mol/L was used as a florescent dye solution. First, 40 nm, 20 nm and 10 nm nanochannels were completely filled with this solution and then, confocal microscope (Nikon- Eclipse Ti-s) was used to reveal the existence of the solution in these nanochannels.

C6 - Electrical conductance measurement set-up

We measured electrical conductance of four solutions including Isopropanol, Ethanol, 80% Ethanol- 20% Water and 20% Ethanol- 80% Water in 10 nm and 40 nm nanofluidic devices. **Figure 50** shows the measurement set-up of this experiment. First, the device was filled with a solution. Afterward, a pair of electrodes (anode and cathode) were immersed into the solution through the access holes on each reservoir. We should add that there was a specific distance between electrodes and all walls of the reservoir. In fact, electrodes had contact neither to the reservoir nor to the glass. A high-resolution source meter (Keithley 2602B) was connected to the electrodes in order to measure electrical conductance of the solution. We plotted I-V (current-voltage) curves and calculated electrical conductance for all the solutions as presented in **Table 4**.



Figure 50. Schematic of the experimental set-up for electrical conductance measurement in nanochannels. As it is demonstrated electrodes do not have any contact with the reservoir and glass.

Nanochannel's	Electrical conductance (S×10 ⁻¹⁰)					
height	Isopropanol	Ethanol	80%Ethanol 20% Water	20%Ethanol 80% Water	Air	
10 nm	2.9	2.3	1.88	5.29	13.02	
40 nm	0.97	1.67	2.46	6.19	13.02	

Table 4. Electrical conductance values of different liquids measured in 10 nm and 40 nm nanochannels.

C7 - Electrical breakdown measurement set-up

An electrical insulator can become electrically conductive when sufficient electric field is applied across it. This phenomenon is known as an electrical breakdown and can take place within solid, liquid and gas phases. Electrical breakdown in gases is characterized by Paschen's law which describes the dependence of the breakdown voltage on the gas pressure and electrodes distance. **Figure 51a** shows the experimental set-up designed to determine the breakdown voltage of Isopropanol vapor and Ethanol vapor. As indicated, the container was half filled with the liquid and sealed perfectly. Therefore, significant amount of vapor is confined in the headspace of the container. Two electrodes with a distance of 1 mm were used to apply electric field to the gas molecules confined in the sealed container. The typical I-V results from the DC measurement is presented in **Figure 51b**.



Figure 51. Electrical conductance measurement of vapor. (a) Schematic of the experimental set-up to measure the electrical conductance of vapor. (b)Electrical conductance measurement of Ethanol and Isopropanol vapors. Two electrodes are distanced at 1 mm in these measurements.

C8- Fluorescence microscopy- water flow

The same fluorescent dye with the same concentration but diluted in water (higher surface tension) was used to demonstrate the effect of liquid surface tension on the capillary breakdown. **Figure 52** indicates the confocal microscopy images of 40 nm, 20 nm and 10 nm nanochannels filled with this solution. It is shown that water can flow even in 10 nm nanochannels due to its higher surface tension.



Figure 52. Confocal microscopy images of nanochannels filled with fluorescent dye solution diluted in water (a) 40 nm channels, (b) 20 nm channel, (c) 10 nm channel. The scale bar is 50 μm.

C9- Calculation of liquid pressure through Young-Laplace equation

To determine the liquid pressure at the liquid-vapor interface, we used Young-Laplace equation which is expressed as:

$$p_{l} = p_{v} - \sigma^{LV} \cos \theta \left(\frac{1}{R_{1}} + \frac{1}{R_{2}}\right)$$
(48)

where, p_l denotes a liquid pressure at the liquid-vapor interface, $p_v \cong 101$ kPa is a gas pressure, σ^{LV} is a surface tension of the liquid, R₁ is half of the channel height, R₂ is half of the channel width and θ is the contact angle. Although our geometry composed of three silica walls and one borosilicate glass, the roughness and surface energy for both materials are very similar, yielding approximately the same contact angle. The value of contact angle and surface tension used in the calculation is presented in **Table 5**.

liquid	Surface tension (mN/m)	Contact angle (°)	
IPA	23	~ 0	
Ethanol	22.1	~ 0	
80% ethanol- 20% water	24	~ 0	
20% ethanol- 80% water	38	~ 2-3	
water	72	~ 2-5	

Table 5. Value of surface tension and contact angle used to calculate the liquid pressure.

C10- Calculation of liquid pressure through Young-Laplace equation

In the nanochannels, the liquid is under absolute negative pressure due to high curvature of a liquid-vapor interface. There is a minimum negative pressure that a given liquid can stand and below this pressure spontaneous formation of vapor occurs in the stressed liquid. In order to determine the fracture pressure (i.e. the minimum negative pressure), the net-work associated with formation of a vapor bubble with radius of r should be considered first:

$$W = \sigma^{LV}A + pV - p_r V \tag{49}$$

where, $\sigma^{LV}A$ is work associated with a formation of liquid-vapor interface bounding the bubble, pV is work related to a formation of cavity with volume V, and p_rV is work required to fill the bubble reversibly with vapor of pressure p_r . Equation 49 can be rewritten as $W = 4\pi r^2 \sigma^{LV} + \frac{4}{3}\pi r^3(p-p_r)$. For large values of liquid negative pressure, P_r is negligible in comparison with p. If W is plotted as a function of r, the maximum work corresponding to bubble formation with radius of $r^* = -2\sigma^{LV}/p$ is found to be $W_{max} = 16\pi\sigma^{LV^3}/3p^2$. Based on the nucleation theory, bubble formation rate is proportional to $\exp(\frac{-W_{max}}{kT})$ and the fracture pressure of a liquid is expressed as:

$$p_{l} = -\left(\frac{16\pi}{3k_{B}T} \frac{\sigma^{LV^{3}}}{\ln\frac{Nk_{B}T}{h}}\right)^{1/2}$$
(50)

where, k_B is the Boltzmann constant, T is a temperature, N is the Avogadro number, and h is the Planck's constant. As demonstrated in **Equation 50**, the fracture pressure of a

liquid depends on its surface tension, and liquids with higher surface tension can stand higher negative pressure.

C11- Kinetics of wetting in nanochannels

Consider a flow of a liquid with a contact angle of $\theta_D > \theta_E$ inside the nanochannel. The driving force for the liquid movement is $F = \sigma^{LV} (\cos \theta_E - \cos \theta_D)$, where θ_E is an equilibrium contact angle and θ_D is a dynamic contact angle. As indicated in **Figure 53a**, for the liquid wedge, there is no-slip boundary condition at the walls, and velocity reaches a maximum at z (i.e. half of the channel depth). We define the velocity V of the liquid wedge as the average velocity over the thickness of the wedge (i.e. z). By considering $z = \tan \theta_D x$, a velocity gradient over z is expressed as:

$$\frac{dv}{dz} \approx \frac{V}{\tan \theta_D x}.$$
(51)

The opposing force for the liquid flow is viscous friction. We determine the energy TS corresponding to viscous dissipation through general expression of:

$$T\dot{S} = \int_0^\infty dx \int_0^e \mu \left(\frac{d\nu}{dz}\right)^2 dz$$
(52)

where e denotes a length scale in z direction. Note that Equation 52 is written per unit length of the line in the y-direction. By considering Equation 51, we find

$$T\dot{S} \cong \int_0^\infty dx \,.\, \mu \frac{V^2}{e^2} e \tag{53}$$

and

$$T\dot{S} = \frac{3\mu V^2}{\tan\theta_D} \int_0^\infty \frac{dx}{x}.$$
(54)

Since the integral in **Equation 54** diverges at both limits, we consider x = L (length of the channel) on the upper limit and x = a (the molecular size) on the lower limit side. Therefore, one finds

$$\int_{a}^{l} \frac{dx}{x} = \ln\left(\frac{L}{a}\right) \equiv l \tag{55}$$

where, *l* is a dimensionless coefficient changing from 15 to 20.

Through balance of energy added (FV) by liquid motion and viscous dissipation,

$$\int_{a}^{l} \frac{dx}{x} = ln \left(\frac{L}{a}\right) \equiv l$$

$$\frac{3\eta l}{\tan \theta_{D}} V^{2} = \sigma \left(\cos \theta_{E} - \cos \theta_{D}\right) V.$$
(56)

By considering $\theta_E = 0$ for liquids with total wetting, V is expressed as

$$V = \frac{\sigma \left(1 - \cos \theta_D\right) \tan \theta_D}{3\eta l}$$

$$V = \frac{\sigma \left(\tan \theta_D - \sin \theta_D\right)}{3\eta l}.$$
(57)

Once the liquid touches the walls of nanochannels, it has contact angle of approximately $\frac{\pi}{2}$, Figure 53b. We need to find wetting time, τ , for the contact angle to reach equilibrium condition (i.e. θ_E)

$$v = \frac{dx}{dt}$$

$$dt = \frac{dx}{v}$$
(58)

and

$$\tau = \int \frac{dx}{V} = \int_0^{d/2} \frac{3\eta l}{\sigma \left(\tan \theta_D - \sin \theta_D\right)} dx$$
(59)

where

$$\sin \theta_D = 1 - \frac{x}{R}$$

$$x = R \left(1 - \sin \theta_D \right),$$
(60)

$$\cos\theta_D = \frac{\left(\frac{d}{2}\right)}{R},\tag{61}$$

$$x = \left(\frac{d}{2}\right) \frac{\left(1 - \sin \theta_D\right)}{\cos \theta_D}$$

$$dx = \frac{d}{2} \left(\frac{\sin \theta_D - 1}{\cos^2 \theta_D}\right) d\theta ,$$
(62)

$$dx = \frac{d}{2} \left(\frac{\sin \theta_D - 1}{\cos^2 \theta_D} \right) d\theta, \tag{63}$$

$$\tau = \int_{\frac{\pi}{2}}^{0} \frac{3\mu l}{\sigma \left(\tan \theta_D - \sin \theta_D\right)} \frac{d}{2} \left(\frac{\sin \theta_D - 1}{\cos^2 \theta_D}\right) d\theta \,. \tag{64}$$

We solved this equation through Mathematica to find the wetting time scale in nanochannels.



Figure 53. The kinetics of capillary wetting in the nanochannels. (a) velocity profile of a liquid wedge. (b) Once the liquid touches the nanochannel wall, it has contact angle of $\sim \frac{\pi}{2}$. The liquid wedge is driven in the nanochannels to reach the equilibrium contact angle of $\theta_E \sim 0$.

C12- Coefficient of wicking process and determination of mass flux

As discussed in C3, $x \propto \sqrt{t}$ describes the dynamic of liquid wicking in nanochannels. This dependence is similar to vapor diffusion process. Therefore, we can define a coefficient for liquid wicking, and compare it with vapor diffusion coefficient. Based on Washburn's equation:

$$x^2 = D_{Wt}t \tag{65}$$

and

and

$$D_{Wt} = \frac{\sigma^{LV} \cos \theta h}{3\eta} \tag{66}$$

where, D_{Wt} denotes the theoretical wicking coefficient of a liquid. However, this theoretical coefficient is higher than the coefficient (D_{We}) obtained from our experimental data. This difference is attributed to interfacial viscosity effect at very small scales. All the theoretical and experimental values of wicking coefficient are presented in **Table 6**.

Nanochannel's height	Isopropanol		Ethanol		
	D_{Wt} (m ² s ⁻¹)	$D_{We} (m^2 s^{-1})$	$D_{Wt} (m^2 s^{-1})$	$D_{We}(m^2 s^{-1})$	
20 nm	6.4×10^{-8}	1.72×10^{-8}	12.64×10^{-8}	4.6×10^{-8}	
40 nm	12.8×10^{-8}	5.95×10^{-8}	25.3×10^{-8}	10.5×10^{-8}	

Table 6. Theoretical and experimental values of capillary wicking coefficient.

We also determine mass flux caused by capillary wicking (J_l) in nanochannels through $J_l = \rho v$, where ρ is the liquid density and v is the liquid velocity. To calculate the liquid velocity, we take derivative from **Equation 66**,

$$2x \, dx = D_{We} \, dt$$

$$\frac{dx}{dt} = v = \frac{D_{We}}{2x} = \frac{1}{2} \sqrt{\frac{D_{We}}{t}}$$
(67)

and

$$D_{Wt} = \frac{\sigma^{LV} \cos \theta h}{3\eta}.$$
 (68)

Equation 68 is used to obtain the mass flux of liquid wicking in 40 nm and 20 nm nanochannels. However, this equation is not valid for 10 nm nanochannels since mass flux in these nanochannels is governed by vapor transport, discussed in **C13**.

C13- Vapor transport in 10 nm nanochannel and its mass flux calculations

Mass transport in 10 nm channels is governed by vapor diffusion process rather than liquid capillary wicking. To determine mass flux caused by vapor diffusion, we should consider Fick's first law:

$$j = -D_{Tot}\nabla C \tag{69}$$

where, j is mass flux, D_{Tot} is the vapor diffusion coefficient and ∇C is concentration gradient of vapor across the nanochannel's length. Note that there are two primary diffusive regimes governing the vapor diffusion, including molecular diffusion regime and Knudsen diffusion regime. Knudsen number, which is known as the ratio of mean free path of vapor molecules to the length scale (channel's height), determines which diffusion regime is dominant. To find Knudsen number, we should first obtain the mean free path of the vapor molecules which is expressed as:

$$\lambda = \frac{k_B T}{\sqrt{2\pi} d^2 p} \tag{70}$$

where T is temperature, d is a diameter of gas molecules and p is pressure. The calculated values of mean free path and Knudsen number for Ethanol and Isopropanol vapors are presented in **Table 7**. Since the Knudson number for both liquids are within the range of 0.01-10, vapor diffusion is in the transition regime where the total diffusion coefficient is:

$$\frac{1}{D_{Tot}} = \frac{1}{D_{Kn}} + \frac{1}{D_m}.$$
(71)

 $D_{Kn} = \frac{h}{3} \sqrt{\frac{8RT}{\pi M_v}}$ is the Knudsen diffusion coefficient, and $D_m = \frac{\lambda}{3} \sqrt{\frac{8RT}{\pi M_v}}$ is the molecular diffusion coefficient where, h is the channel's height, and M_v is a molecular weight of the vapor. We considered that the vapor concentration is linearly decreased across the nanochannel's length. As a result, $\frac{dc}{dx} = \frac{C_2 - C_1}{L}$ where $C_2 = \frac{p_{sat}}{RT}$ is the saturated vapor concentration at the entrance of the nanochannel connected to the filled reservoir, C₁ ~ 0 is the vapor concentration at the end of the nanochannel connected to the empty reservoir, and L= 500 µm is the nanochannel's length. We should add that p_{sat} denotes the saturation vapor pressure. By putting all the calculated values in **Equation 71**, the vapor diffusion mass flux of Ethanol and Isopropanol in 10 nm nanochannel are obtained 0.005 kg/m²s and 0.00097 kg/m²s, respectively.

 Table 7. Mean free path, Knudsen number and diffusion coefficients values of Ethanol and Isopropanol vapor in 10 nm nanochannel.

Vapor type	λ (nm)	K _n	$\mathbf{D}_{\mathrm{Kn}}\left(\mathbf{cm}^{2}\mathbf{s}^{-1}\right)$	$D_{m}\left(cm^{2}s^{-1}\right)$	$D_{Tot}(cm^2s^{-1})$
Ethanol	47.05	4.705	0.01224	0.0575	0.01023
Isopropanol	3.53	0.353	0.01072	0.00378	0.00279

C14- Surface tension nanogates

As discussed, surface tension plays a central role in capillary breakdown at sub 10nm scale. We introduced a gating mechanism for 10 nm channels based on the dependence of liquid surface tension on temperature. In these nanogates, we aimed to turn on/off liquid wicking based on the temperature actuation. We chose a mixture of 50%Ethanol50%Water as the parent liquid in these 10 nm channels. For this composition of liquid at room temperature, capillary breakdown occurs in the nanochannels, **Figure 54a**. However, as temperature decreases and consequently surface tension increases, the system moves from capillary breakdown regime to capillary wicking regime. To demonstrate performance of these nanogates, discussed in chapter 5. In these experiments, ionic solution of 0.1 M NaCl or KCl in 50%Ethanol-50%Water was introduced in one micro-reservoir and pure solvent of 50%Ethanol-50%Water was introduced in the other micro-reservoir. We measured the electrical conductivity in the reservoir containing pure solvent. The constant voltage was applied and the current was measured at different temperatures. We started measurements at room temperature and continued down to 8°C. At each temperature, the device was kept for 40 mins to provide sufficient time for ionic diffusion process.



Figure 54. (a) The I-V curves at room temperature for fluid of 50%Ethanol-50%Water filled in two depths of nanochannels is shown. (b) The dependence of electrical conductivity on temperature in the micro-reservoir. The solution in the micro-reservoir is 0.1 M NaCl with 50% Ethanol-50%Water as the solvent.

The electrical conductivity of the pure solvent increased sharply once the device temperature reached 8 °C. This jump of electrical conductivity is caused by opening the

nanogate (i.e. liquid flow) leading to fast ionic diffusion through liquid inside the nanochannels. In order to confirm that this sharp increase is caused by gating characteristic of the nanochannels, we measured the ionic conductivity of the reservoir filled with 0.1 M NaCl solution in 50% Ethanol-50% Water as a function of temperature, **Figure 54b**. The results indicate that the electrical conductivity reduces as temperature decreases. In fact, lower temperature of electrolyte leads to increase in viscosity and consequently decrease in mobility of ions in the solution. To further confirm these gating characteristics, we conducted florescence microscopy in the nanochannels as a function of temperature shown in **Figure 55**. As shown at room temperature, the nanogates are closed with no liquid in the channels. However, at temperature of 8 °C, the nanogates are open with liquid flow in these channels.



Figure 55. The characteristics of flow in the 10 nm channels for the fluid of 0.1 M NaCl solution in 50% Ethanol-50% Water. (a) and (b) at temperatures higher than 8 °C, capillary breakdown occurs, and only vapor phase is present in the channels. (c) At temperature of 8 °C, the liquid starts to move in the nanochannels as shown from left to right.