Spontaneous outflow efficiency of confined liquid in hydrophobic nanopores

Yuan Gaoa,1,*, Mingzhe Li†b,1,*, Yue Zhang†, Weiyi Lu‡, and Baoxing Xua,2,*

*Department of Mechanical and Aerospace Engineering, University of Virginia, Charlottesville, VA 22904; and †Department of Civil and Environmental Engineering, Michigan State University, East Lansing, MI 48824

Edited by Alexis T. Bell, University of California, Berkeley, CA, and approved September 3, 2020 (received for review May 10, 2020)

The suspension of nanoporous particles in a nonwetting liquid provides a unique solution to the crux of superfluid, sensing, and energy conversion, yet is challenged by the incomplete outflow of intruded liquid out of nanopores for the system reusability. We report that a continuous and spontaneous liquid outflow from hydrophobic nanopores with high and stable efficiency can be achieved by regulating the confinement of solid–liquid interactions with functionalized nanopores or/and liquids. Full-scale molecular-dynamics simulations reveal that the grafted silyl chains on nanopore wall surfaces will promote the hydrophobic confinement of liquid molecules and facilitate the molecular outflow; by contrast, the introduction of ions in the liquid weakens the hydrophobic confinement and congests the molecular outflow. Both one-step and multistep well-designed quasistatic compression experiments on a series of nanopores/nonwetting liquid material systems have been performed, and the results confirm the outflow mechanism in remarkable agreement with simulations. This study offers a fundamental understanding of the outflow of confined liquid from hydrophobic nanopores, potentially useful for devising emerging nanoporous-liquid functional systems with reliable and robust reusability.

The solid–liquid interactions in hydrophobic nanopores immersed in a liquid environment lead to attractive phenomena including ultralow liquid thermodynamic fluctuation and rapid evaporations (1–5) and have yielded a wide variety of applications, from sensing (6) to nanofluid transport (7, 8) and to energy dissipation and conversion (9). For example, with high-performance liquid-hydrophobic nanopore mechanical energy absorption system has been developed (10, 11), where the external mechanical energy is dissipated to overcome the capillary energy barrier and the subsequent transport friction during the passive invasion of liquid into nanopores (12, 13). Due to the ultralarge surface area of nanoporous materials (~1,000 m²/g), such a system is capable of dissipating energy with the efficiency of ~100 J/g, ~2 orders of magnitude higher than the traditional energy dissipation materials (e.g., metal foams, textile composites, shape memory alloys) (14, 15). When the external pressure is removed, the intruded liquid may be expelled from the nanopores, making the energy absorption system reusable (16, 17). More importantly, the expulsion of confined liquid out of nanopores leads to a large amount of displacement and has been utilized in the design of actuator devices (18).

In fundamental, from the energy perspective, the spontaneous outflow of intruded liquid is favorable due to the hydrophobic nature of nanopores. However, a metastable state of outflow led by the liquid cohesion inside nanopores hinders the outflow of liquid from nanopores (19). In particular, a significant residue of confined liquid inside nanopores has been observed when the diameter of nanopores is several nanometers (20, 21). Understanding the spontaneous, stable outflow of confined liquid, which is currently lacking, is the foundation to seek novel solutions for improving either the reusability of energy dissipation system or the output mechanical strain in the actuators and help design scalable and durable pores/nonwetting liquid systems. Using molecular-dynamics simulation, we systematically study the outflow process of liquid water and electrolyte solutions out of hydrophobic nanopores decorated with the grafted silyl chains and propose nanoconfinement mechanisms of molecular repulsion/attraction and congestion to achieve the spontaneous outflow with high and stable efficiency, beyond the traditional confinements of hydrophobicity. In parallel, quasistatic compression experiments on silica-based hydrophobic nanopore/liquid systems were performed under both one-step and multistep loading conditions and confirmed the outflow mechanisms in remarkable consistency with simulations, suggesting great potentials for applications in the exploration of practical, reliable engineering nanopore–liquid systems with complete usability performance.

Results and Discussion


Fig. 1 depicts the computational model of the hydrophobic nanopore/liquid system. A rigid silica nanotube with 3.82 nm in diameter and 11.95 nm in length was adopted to mimic a nanopore and fully immersed into a liquid reservoir, and the reservoir was filled with water or the electrolytes of LiCl, NaCl,

Significance

The outflow of prior confined or intruded liquid from a hydrophobic pore at the nanoscale is the foundation for devising nanofluidics-enabled, reusable functional materials, structures, and devices and is fundamentally different from that at the macroscale due to nanoconfinement effects. We, in both molecular-dynamics simulations and experiments, addressed the nanoconfinement mechanism that hinders the outflow of nanoconfined various liquid by investigating both inflow and outflow processes of liquid in hydrophobic nanopores and demonstrated that a continuous and spontaneous outflow with high and stable efficiency could be achieved. The elucidated outflow mechanisms and regulation strategies will provide a rational route for exploring high-performance reusable devices in a broad scope of nanoporous materials and liquid environments by leveraging unique nanopore–liquid interactions.


The authors declare no competing interest.

This article is a PNAS Direct Submission.

Published under the PNAS license.

1Y.G. and M.L. contributed equally to this work.
2To whom correspondence may be addressed. Email: wylu@egr.msu.edu or bx4c@virginia.edu.

This article contains supporting information online at https://www.pnas.org/lookup/suppl/doi:10.1073/pnas.2009310117/*DCSupplemental.


and KCl solutions. Flexible silyl chains with different lengths ([C8: -Si(CH3)2-(CH2)7-CH3, C4: -Si(CH3)2-(CH2)3-CH3, C1: -Si(CH3)3]) uniformly grafted the inner surface of the nanopore at the density of 1 chain per nm². The liquid reservoir was sealed by a movable piston along the z direction. Periodic boundary conditions were applied to both x- and y directions. A quasistatic loading–unloading cycle with displacement control was exerted on the piston. More information about the atomistic modeling and computational methodology is given in Materials and Methods. Fig. 1B shows the history of externally applied pressure $P$ on the piston versus the number of liquid particles intruded into the nanopore $N$ during the loading and unloading processes in three different liquid–hydrophobic nanopore systems, and Fig. 1C shows representative snapshots. The light-blue curve corresponds to the system that contains a nanopore decorated with C8 silyl groups in pure water. Initially, at $P = 0$ MPa (I stage in Fig. 1C), no water molecules are intruded into nanopore, indicating the hydrophobic nature of the C8-modified nanopore wall surface. Upon moving the piston, when $P$ increases to a critical pressure $P_{\text{in}}$ (∼145 MPa, determined by the midpoint of the plateau of the curve, II stage in Fig. 1C), liquid molecules overcome the capillary resistance and start to infiltrate into the nanopore. Once the maximum occupancy volume of all nanoparticles that is determined by interactions between confined liquid and nanoparticles is fully occupied, the continuous loading will lead to a quick increase of pressure $P$ (III stage in Fig. 1C), but the infiltration of a few water molecules is associated with the adjustment of the arrangement of water molecules inside the nanopore. Upon unloading, both $P$ and $N$ decrease (IV and V stages in Fig. 1C). However, after the complete unloading with $P$ back to 0 MPa (VI in Fig. 1C), a notable number of water molecules do not flow out from and stay inside the nanopore. The same conclusion can be drawn when the nanopore is free of decoration (pink curve), or the C8-decorated nanopore is immersed in the LiCl electrolyte (dark-blue curve), although a different $P_{\text{in}}$ is required to initiate substantial intrusion of liquid in various systems. Extended simulations were conducted with different nanopore wall decorations and electrolytes, and further confirm the residency of liquid in the nanopores at the end of unloading (SI Appendix, Figs. S1–S3). Given the constant pore volumetric capacity and stable solid–liquid interactions (SI Appendix, Fig. S2), after the first loading cycle, both the maximum intruded liquid in the nanopores at the end of loading and the residual liquid in the nanopores after the complete unloading remain the same for the subsequent loading cycles, suggesting the robust intrusion and extrusion processes, independent of cyclic loading numbers (SI Appendix, Fig. S1), potentially useful for developing the systems under multiple loading conditions.

**Molecular Confinement and Congestion.** To understand the effect of hydrophobic confinement on the liquid outflow, we plot the radial number density of molecules inside the fully occupied nanopore in pure water in Fig. 3A. The interface layer [also referred to as the first solvation shell (14)] is recognized by the peak near the wall of the pore. The position of the interface layer is repulsed further from the wall when the grafted silyl groups have larger lengths and molar mass (C8 > C4 > C1 > C0), leading to a larger equilibrium distance between the confined liquid and the wall of the nanopore. The larger equilibrium distance indicates enhanced hydrophobic confinement, which agrees with the larger $\eta_{\text{ext}}$ in Fig. 2B. When the liquid changes from pure water to different electrolytes, the location of the interface layer does not vary significantly (SI Appendix, Fig. S7). To extract the real-time axial transport mechanism of the liquid outflow, we obtain the mean-square displacement (MSD) of the confined liquid during the unloading process (SI Appendix, Fig. S8) and calculate the dynamic diffusion coefficient $D_w$ in the axial direction in the nanopore via $\text{MSD} = 2Dt$, where $t$ is the outflow time. Fig. 3B shows $D_w$ of the confined water molecules at different applied pressure $P$ during unloading. The increase of $D_w$ with the decrease of $P$ indicates an accelerated outflow of water molecules during unloading, which is consistent with the reduced slope of the unloading curve in Fig. 1B. Besides, the grafted chains with a larger molar mass lead to a higher $D_w$ at the same pressure due to the enhanced hydrophobic confinement effect. As a result, the spontaneous extrusion is more favorable, which agrees with a higher $\eta_{\text{ext}}$ in Fig. 2B. Given the same surface treatment with C8, a smaller ionic radius leads to a stronger liquid cohesion but weakens the hydrophobic confinement due to the liquid–solid wall interactions. Consequently, a lower $D_w$ is obtained, and leads to a smaller $\eta_{\text{ext}}$. In particular, when $P \leq 10$ MPa, a high $D_w (>4 \times 10^{-5} \text{ cm}^2/\text{s})$ (25) is obtained in comparison with the self-diffusion coefficient of water molecules confined a nanochannel at a steady-state (∼2 × 10^{-5} cm²/s, which is expected to break down the liquid cohesion and agrees with the observation on the instability of spontaneous outflow (26). Fig. 3C–F shows the radial transport during liquid outflow, where the vertical axis denotes the radial location in the tube, and the horizontal axis of the left subplot is the interaction energy at the full occupancy of the nanopore by liquid. A higher negative value indicates a stronger cohesion. The horizontal axis of the right subplot is the normalized extrusion time $t^*$, and $t^* = 0$ and 1 represent the beginning and the end of the extrusion process, respectively. The color of the contour represents the local number of particles $N$ normalized by the local maximum particle number when the nanopore is full of liquid, $N_{\text{full}}$, local. The weaker interaction energy at the interface layer suggests the local cohesion is suppressed by solid–liquid interactions. As a result, during the extrusion process, the reduction in the number of liquid molecules is more significant near the interface layer, in good consistency with a higher local outflow frequency (SI Appendix, Fig. S9). In the existence of silyl groups, the interaction energy and the cohesion are further reduced compared to the nanopore without decorations due to enhanced hydrophobic confinement, and a more significant loss of molecules is observed (Fig. 3C and D), which is consistent with a higher $\eta_{\text{ext}}$ in Fig. 2B. At given hydrophobic confinement, the existence of ions with a smaller radius in electrolyte homogeneously enhances interaction energy and liquid cohesion, and reduces molecule loss during unloading (Fig. 3E and F), which also agrees with lower $\eta_{\text{ext}}$ values in Fig. 2B. Extensive calculations considering different grafted silyl groups and liquid types further confirm both effects.
of hydrophobic confinement and solid–liquid interactions (SI Appendix, Figs. S10 and S11).

Fig. 4A demonstrates the evolution of the axial distribution of intruded particles during unloading. The vertical axis denotes the normalized axial position in the nanotube, and the horizontal axis is the normalized time $t^*$.

In Fig. 4A, the color describes the local number of particles normalized by the maximum number of particles $N_{\text{full}}$ that fully occupy the nanopore. The white arrows mark the outflow direction. The upper graph corresponds to the C8-decorated nanopore immersed in pure water. At $t^* = 0$, water molecules periodically concentrate at several locations due to the strong solid–liquid interaction between water molecules and silyl groups, which is not observed when grafted silyl groups are shorter (SI Appendix, Fig. S12). During unloading, a global decrease in the number of infiltrated particles can be reflected by the color change. However, in LiCl electrolyte, significant concentrations at both ends of the nanopore can be observed, which indicate molecular congestion at both exits (27). This congestion becomes less severe when the radius of alkaline ion is larger (SI Appendix, Fig. S12) and can be understood by the local accumulation of ions during intrusion associated with a higher interaction energy gradient between the ion and the nanopore at both ends of the nanopore (SI Appendix, Fig. S13). Upon unloading, the congestion gradually vanishes when 3/4 of the process is finished. To further highlight the impact of molecular congestion on the outflow, Fig. 4B shows the corresponding internal longitudinal pressure distribution evolution, and the details of calculations can be found in Materials and Methods. $\Delta P_{zz} = P_{zz} - P_{zz,\text{end}}$ reflects the pressure difference in the outflow $z$-direction, where $P_{zz}$ and $P_{zz,\text{end}}$ represent the internal pressure at axial locations inside the pore and the average pressure at both ends, respectively. When the liquid is pure water, a pressure distribution associated with the number distribution in Fig. 4A is observed during the outflow. However, the distribution contour of pressure is less continuous (with locally

![Fig. 1](https://example.com/)  
Fig. 1. The pressure-induced infiltration of liquid into a hydrophobic nanopore and subsequent spontaneous outflow of intruded liquid upon unloading. (A) Schematic of the atomistic model of liquid–hydrophobic nanopore systems, where a SiO$_2$ nanopore grafted with silyl groups is to mimic a nanopore of silica gels immersed in either pure water or aqueous solution of LiCl, NaCl, or KCl, and the diameter of bare nanotube without silyl group (i.e., C0) is $d_0 = 3.82$ nm. Both ends of the nanopore were open for allowing the intrusion and extrusion of liquid. The silyl groups are C1, C4, and C8 and their structures are -$\text{Si}$(CH$_3$)$_2$-(CH$_2$)$_3$CH$_3$, or -$\text{Si}$(CH$_3$)$_2$-(CH$_2$)$_7$CH$_3$, respectively. The chain length or molecular mass is C0.

![Fig. 2](https://example.com/)  
Fig. 2. Characterization of extrusion of liquid from hydrophobic nanopores. (A) The infiltration pressure $P_{in}$ of liquid–hydrophobic nanopore systems with different silyl groups and liquid types. (B) Spontaneous outflow efficiency $\eta_{\text{out}} (\chi = 1 - \frac{N_{\text{out}}}{N_{\text{in}}})$ in liquid–hydrophobic nanopore systems with different silyl groups and liquid types as functions of the infiltration pressure $P_{in}$ of liquid–hydrophobic nanopore systems with different silyl groups and liquid types: C0, C1, C4, and C8. For each series, from left to right is C0, C1, C4, and C8 with the molar mass C8 > C4 > C1 > C0.
alternative high and low pressure) than the number distribution, and is expected to be led by the local force interactions and thermodynamics motions of molecules. However, when the LiCl solution is intruded and confined, a significant negative $\Delta P_{zz}$ is caused by the molecular congestion and remains for 3/4 of the outflow process, impeding the outflow. For larger ions such as K+, as smaller negative pressure difference inside the nanopore is observed (SI Appendix, Fig. S14), which agrees with a larger $D_w$ and $\eta_{ext}$.

Fig. 3. Hydrophobic confinement on spontaneous outflow of the liquid from nanopores. (A) Radial distribution of the number density of the confined liquid particles in the nanopore with different surface treatments immersed in water. The dashed lines mark the locations of the outmost layers of confined molecules near the pore wall at $r/r_0 = 1$. (B) Dynamic diffusion coefficient of water molecules $D_w$ in the liquid–hydrophobic nanopore systems for nanopores treated by different silyl functional groups (molar mass $C_8 > C_4 > C_1 > C_0$) and liquid (pure water, LiCl, NaCl, and KCl solutions with a concentration of 26 wt % and the ion radius: $r_K^+ > r_Na^+ > r_Li^+$). Radial distribution of the interaction energy and number of particles during extrusion in nanopores in (C) C0-water, (D) C8-water, (E) C8-LiCl, and (F) C8-KCl liquid–hydrophobic nanopore systems.

Fig. 4. Molecular congestion during unloading. (A) Evolution of particle distribution in the nanopore during unloading process. The outflow liquid is water and LiCl. The normalized outflow time $t^* = 0$ and 1 represent the beginning and the end of unloading process, respectively. White arrows denote the outflow direction. (B) Evolution of the distribution of the axial pressure difference $\Delta P_{zz}$ inside the nanopore during outflow, where $\Delta P_{zz} = P_{zz} - P_{zz,end}$, and $P_{zz}$ and $P_{zz,end}$ represent the pressure at the axial locations inside the pore and the averaged pressure at both ends, respectively. White arrows denote the outflow direction.
Molecular Repulsion and Attraction. To further understand the regulation mechanism to the outflow by the molecular confinement and congestion, Fig. 5A depicts the occupation probability of water molecules in the interface layer. When the water molecules are confined in the pristine nanopore without surface functional groups, a repeating pattern whose periods coordinate well with the atomic lattice structures of the nanopore is obtained in both angular and axial directions (Fig. 5A, Top Left Inset), and is determined by the distribution of the interaction energy between the wall of silica nanopore and water molecules (SI Appendix, Fig. S15A). When short silyl chains C1 are grafted to the pore surface, the repulsion of the hydrophobic silyl groups drives local molecules further from the pore wall, and the occupation probability shows a more significant periodic ribbon pattern that corresponds to the locations of the grafted chains (SI Appendix, Fig. S15B), suggesting enhanced hydrophobic confinements. As the molar mass and the degree of freedom of silyl chains increase, the mobility and radial extension of the chains are enhanced (SI Appendix, Fig. S17), which decreases the periodicity of the occupation pattern in the interface layer. In addition, the occupation probability that shows a notable discontinuity with the connection between different locations is further weakened by the stronger repulsion from the hydrophobic functional groups, indicating enhanced hydrophobic confinement. This enhanced solid–liquid interaction leads to the degradation of the hydrogen bond network and the cohesion of liquid in the interface layer (SI Appendix, Fig. S17), and facilitates the molecular extrusion with a high \( \eta_{\text{ext}} \). Similar results are obtained when the confined liquid changes to electrolyte solutions (SI Appendix, Fig. S18). Fig. 5B further shows the averaged atomic interaction energy per molecule (both ion and water molecule) \( E_{\text{int}} \). It increases as the ion size increases, suggesting the strengthened attraction between liquid particles in the presence of ions with a smaller radius. Correspondingly, \( D_w \) decreases in the existence of ions and the decrease of the ionic radius (Fig. 3B), impeding the outflow of the confined liquid. In addition, the attraction in solvation shells can be obtained by examining the difference between \( E_{\text{int}} \) and the interaction energy in pure water \( E_{\text{int,w}} \) (Fig. 5B, Inset). The radius of the solvation shells of water–ion clusters can be estimated from the radial distribution functions (SI Appendix, Fig. S19), and \( \text{Li}^+ \)-water: 0.21 nm, \( \text{Na}^+ \)-water: 0.24 nm, \( \text{K}^+ \)-water: 0.29 nm. \( E_{\text{int}} - E_{\text{int,w}} \) increases as the ion size decreases. As a result, the strong attraction leads to the stable water–ion clusters with severe molecular congestion during extrusion of confined liquid and thus decreases \( \eta_{\text{ext}} \).

Quasistatic Compression Experiments. To confirm these computational findings, we have performed quasistatic compression experiments on liquid/MCM-41 silica gel nanoporous material systems. The schematic of the experimental setup and the SEM photo of MCM-41 silica gel nanoporous materials can be found in SI Appendix and SI Appendix, Fig. S20. The MCM-41 silica gel nanoporous materials were treated by silyl groups (C1, C4, or C8) and immersed in pure water or LiCl, NaCl, KCl electrolytes with a concentration of 26 wt %, the same as in simulations. The average diameter of nanopores was \( 3.2 \pm 0.3 \) nm. More information is included in Materials and Methods. In each loading step, two loading–unloading cycles were performed. Fig. 6A shows \( P - \Delta V \) curves under two consecutive loading cycles in a single-step testing on the C8-LiCl nanopores system, and the design of loading history is highlighted in the inset, which contains two pairs of consecutive loading and unloading cycles from zero to the maximum displacement at quasistatic loading rates. In each loading cycle, the liquid was intruded into nanopores after the \( P \) reached a critical infiltration pressure \( P_{\text{in}} \), where \( P_{\text{in}} \) was determined as the midpoint of the infiltration pressure plateau width. The nanopores were eventually filled up with liquid and became incompressible with a sharp increase of \( P \) after the pressure plateau. Upon unloading, similar to molecular-dynamics (MD) simulations, \( P \) dropped quickly and \( \Delta V \) decreased (Fig. 1B). Besides, the \( P - \Delta V \) curves of the first and the second loading cycles are different, and the significant reduction in the width of the pressure plateau \( (\Delta V_1 < \Delta V_2) \) suggests that the partial liquid was confined inside the nanopores after the completion of the first loading–unloading cycle, which led to the reduction in the effective vacant specific pore volume of the nanopores. However, after the second loading cycle, multiple loading cycles will lead to the same \( P - \Delta V \) curves, indicating the same intrusion and extrusion processes (SI Appendix, Fig. S21). Similar results are observed in other liquid–nanoporous material systems (SI Appendix, Fig. S21), and agree well with the MD simulations (SI Appendix, Figs. S22 and S1 E and F). The extrusion outflow efficiency \( \eta_{\text{ext}} \) is estimated in experiment by \( V_2/V_1 \). Fig. 6B shows that \( \eta_{\text{ext}} \) increases with the length and molar mass of the grafted silyl group (C1 < C4 < C8), which also agrees well with MD simulations. Generally, the liquid first would invade the large nanopores during the loading process because of a low infiltration pressure, and the slope of pressure

![Fig. 5. Morphology and interactive energy of confined liquid particles. (A) Occupation probability of outmost layers of water molecules in interaction with the nanopore wall in angular and axial directions. The color denotes the probability for a molecule to show up at a location. In the inset of C0, green and blue dots mark the positions of silicon and oxygen atoms, respectively. The blue squares mark the repeating square lattices of the silica nanotube. (B) Averaged interaction energy of each liquid particle (both ion and water molecule) \( E_{\text{int}} \) in different liquids. The distribution of attraction energy within the water–ion cluster, whose radii (\( \text{Li}^+ \)-water: 0.21 nm; \( \text{Na}^+ \)-water: 0.24 nm; \( \text{K}^+ \)-water: 0.29 nm) are estimated by the radial distribution functions. The attraction energy is described by the difference between \( E_{\text{int}} \) and the interaction energy in pure water \( E_{\text{int,w}} \).](https://www.pnas.org/content/117/25/11775/fig/fig5)
plateau in \(P - \Delta V\) curves in Fig. 6B reflects the specific ratio of pore-size distribution in nanoporous materials. Besides, large nanopores prohibit the outflow of confined liquid due to the low infiltration pressure, as we demonstrated in MD simulations. To further decouple the effect of pore sizes on outflow in experiments, a three-step loading condition with increasing peak loading pressure in each step was employed. Fig. 6C shows the \(P - \Delta V\) curves of the three-step loading experiment on C8-LiCl system, and the inset illustrates the loading history, where the third peak loading pressure was set to match that in the one-step experiment. Because of the same total pore volumetric capacity, Fig. 6A and C shows the same total infiltration plateau widths of the one-step and three-step experiments. However, in three-step loading tests, the nanopores with larger diameters in the samples are invaded first by the loading cycle with a lower applied pressure \(P\) due to the negative dependence of the infiltration pressure \(P_{\text{in}}\) (Fig. 2A) while the nanopores with smaller diameters remain empty and are intruded by the following loading cycles with a higher \(P\). Fig. 6D shows the variation of \(\eta_{\text{ext}}\) as \(P_{\text{in}}\) and pore size \(d\) (estimated via Young’s equation) in each loading step. A higher \(\eta_{\text{ext}}\) is obtained with the increase of loading steps, further confirming the small nanopores with strong nanoconfinement promote the outflow of confined liquid. Similar results are also obtained on other alkaline ion solutions, strong nanoconfinement promote the outflow of confined liquid. The parallel pressure-induced experiments on the cyclic inflow–outflow behavior of various nanopore–liquid systems have provided qualitative observations to MD results and verified the regulation mechanism to the spontaneous outflow of liquid in hydrophobic nanopores. These reported results lay the foundation for controlling the outflow of liquid from hydrophobic nanopores via the adjustment of intrinsic solid–liquid interactions in the nanoconfined environments, and unlock a vast array of potential applications in the design of nanofluidics-enabled, reusible, sustainable functional materials, structures, and devices by leveraging the outflow efficiency of prior confined or intruded liquid in nonwetting liquid–nanoporous systems.

Materials and Methods

Atomistic Modeling of Liquid–Hydrophobic Nanopore for MD Simulation. A rigid silica nanotube with both ends opened was adopted. Silyl functional groups C1, C4, and C8 with a simple chain structure and strong hydrophobicity were selected for the surface treatment on the oxygen atoms of the silica gel. The surface energies of C1, C4, and C8 silyl groups are 23.0, 24.2, and 25.0 mJ/m², respectively (22–24). The locations of decorated oxygen atoms were evenly distributed in both the angular and axial directions of the nanotube. The behavior of silyl groups was described by the Transferable Potentials for Phase Equilibria (TraPPE) force field (28–30). The nanotube was
immersed in an electrolyte reservoir comprising Li^+, Na^+, or K^+ cations with the same single-atom structure and valence, Cl^− ions, and water molecules. The solvent pore was created by a Briscoer-Emmett-Teller (BET) analyzer (ASAP 2000, Micromeritics Instrument Corp.). The measured average pore diameter was 3.2 ± 0.3 nm, and the pore volume of the raw MCM-41 material was 0.56 cm^3/g. A thin layer of silyl groups was anchored on the nanopore wall surface to convert the hydrophilic surface to hydrophobic. About 1 g of raw MCM-41 was mixed with 40 mL of anhydrous toluene. Then, 10 mL of surface reagent and 1 mL of pyridine was added into the mixture, after which the mixture was heated to 95 °C and stirred for 24 h. The treated MCM-41 was filtered, washed, and dried before use. The surface reagents, including n-Octyldimethylchlorosilane (C8), n-Butyldimethylchlorosilane (C4), and Octamethyltrichlorosilane (C0), were obtained from Gelest, Inc. The liquids used in quasistatic compression tests were deionized (DI) water, Laci aqueous solution (26 wt %), and KCl aqueous solution (26 wt %). The liquid/MCM-41 samples were prepared by mixing 0.1 g of surface-treated MCM-41 with 1 mL of liquid in a stainless-steel testing cell (SI Appendix, Fig. S20). The sealed samples were compressed by a universal tester (5982, Instron, Inc.) at a speed of 2 mm/min, which corresponded to a deformation speed of 10−3 cm/s (35), and could be deemed as a quasistatic loading (∼0.1 s). Besides, a peak force was set to control the infiltration process. With the increase of displacement, the resultant load, F, gradually increased to the peak force, after which the Instron cross-head was moved back at the same speed. The loading–unloading cycle was repeated at least three times for each sample. The developed pressure in the system was calculated as P = F/A, where A was the inner cross-sectional area of the testing cell. The specific volume change was calculated as ∆V = A · d/m, where d and m were the displacement and mass of MCM-41, respectively. For each liquid/MCM-41 material system, at least two samples were tested; the highly consistent plateaus in P−∆V curves were obtained to prove negligible effects of the variations of MCM-41 porous structures. The peak loading pressure was set as a constant in each loading cycle, and was determined based on the critical infiltration pressure of nanofluids–liquid systems to ensure a full occupancy of all nanopores by liquid after the completion of loading.

Data Availability. All study data are included in the article and SI Appendix.

ACKNOWLEDGMENTS. Y.G. acknowledges the support from the John Bell McLaughry Fellowship at the University of Virginia; B.X. acknowledges the start-up funds at the University of Virginia and National Science Foundation Directorate for Engineering Division of Chemical, Bioengineering, Environmental and Transport Systems (Grant #1805451); and W.L. acknowledges the start-up funds at Michigan State University and National Science Foundation Directorate for Engineering Division of Chemical, Bioengineering, Environmental and Transport Systems (Grant #1803695).


25252 | www.pnas.org/cgi/doi/10.1073/pnas.2009310117
Gao et al.