

Anomalous solid-like necking of confined water outflow in hydrophobic nanopores

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Summary

Intrusion of liquid into hydrophobic nanopores has yielded unusual fluid and transport properties that classical theories cannot fully describe, and its extrusion yet remains largely mysterious. Here, we report that the outflow of confined water from hydrophobic nanopores exhibits an anomalous necking phenomenon followed by its breaks, similar to that of solid metal nanowires under uniaxial tension. Molecular dynamics simulations reveal that this solid-like behavior attributes to strong cohesions of water molecules and nanoporous confinements associated with hydrogen-bonding networks and dipole alignments. The extracted elastic modulus and failure strength are quantitatively described by establishing solid-like mechanics scaling laws of outflow deformation and strength. Quasistatic experiments on hydrophobic nanopores/water systems were performed and confirmed the scaling laws of both outflow deformation and strength in remarkable agreement with theoretical predictions. This study offers a facile route for probing mechanical and structural properties of nanoconfined liquid by leveraging its unprecedented solid-like outflow behavior.

Keywords: nanofluidics, hydrophobic nanopores, nanoconfinement, outflow necking, mechanical properties

Introduction

Confining liquids in a nanopore environment has yielded an overwhelming spectrum of unique fluid and thermodynamic properties that are dramatically different from those of their bulk phase.¹⁻¹⁰ Particularly, at the confinement size of nanopores smaller than 10 nm that approaches the size of liquid molecules, confined liquid shows substantially unusual behavior due to the significantly enhanced fluid interaction with solid pore walls, for example, superfast water transport,^{11,12} ultralow transport resistance,^{13,14} high proton conductivity,^{15,16} extreme phase transition temperature,¹⁷ and strongly suppressed oscillations of liquid water surface energy.² These properties have inspired numbers of practical applications in water desalination,¹⁸ contaminant filtration,¹⁹ chemical detection,²⁰ biosensing,²¹ and energy conversion.²² For example, nanoporous materials have been immersed into a non-wetting liquid to design reusable liquid porous systems for engineering applications in energy dissipation, actuation, and harvesting,²³ where a complete and high-efficiency outflow of the intruded liquid upon the removal of external stimuli is the key for reusability in design.

Unlike a continuous liquid intrusion, a metastable outflow state of confined liquid in hydrophobic nanopores is observed and leads to a significant residue of liquid inside nanopores.^{24,25} Recently we proposed a strategy for improving the spontaneous outflow stability and efficiency of intruded liquid by controlling confinements of liquids.²⁶ However, the quantitative description of the outflow of confined liquid is fundamentally lacking. Besides, the mechanical and physical properties of confined liquid that are essential to the understanding of the outflow phenomena, such as viscosity²⁷⁻²⁹ and elasticity,³⁰⁻³² have been extracted but are very controversial because of the heterogeneous structural features of confined liquid,³² especially within the molecular layers adjacent to solid walls.³³ The applied conditions in these

measurements may also change the shear rigidity of confined water.³⁴ For example, a high frequency will suppress the liquid motion and leads to the solid-like behavior of confined liquids³⁵ and yet is challenged by the findings of significant elastic behavior of water at low frequencies.³⁶ Herein, with full-atom molecular dynamics (MD) simulations, we systematically study the outflow of confined water from a hydrophobic nanotube and surprisingly find that the outflow shows a very strong similarity with the mechanical deformation of solid metal nanowires under a uniaxial tensile load, ranging from a linear increase of outflow distance with pressure gradient to gradual break with an apparent necking phenomenon. Molecular analyses reveal that this solid-like outflow behavior is led by the dynamic orientation of water dipoles and arrangement of hydrogen-bond (H-bond) networks at solid-liquid interfaces. With the analogy to the tensile response of solid metal nanowires, we propose a solid-like mechanics scaling law of outflow deformation and strength that is incorporated with the solid-liquid interfacial energy and confinement pore size and temperature of the liquid and quantitatively characterize both elastic modulus and failure strength of confined water outflow. The theoretical predictions show remarkable agreement with comprehensive MD simulation results. Outflow experiments on confined water in hydrophobic nanopores have been performed and validated the scaling law of confined water outflow for both elastic modulus and failure strength in excellent agreement. The present study provides fundamental insights on understanding outflow properties of confined liquids that can be leveraged in the engineering design of nanopore-liquid systems for broad applications.

Results and Discussion

Solid-like tensile behavior and mechanical characterization of confined water outflow

The inset of **Figure 1A** depicts the computational model. It contains a hydrophobic silica

nanotube with a length of $L_0 = 11.95$ nm and a radius r_0 immersed in a water reservoir. The water reservoir was sealed by a movable piston in 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 at the confinement temperature $T = 300$ K. More details of the atomistic model are included in the Materials and Methods section. The upper sub-plot in Figure 1A shows the history of pressure exerted on the piston, P , equivalent to the hydrostatic pressure in the hydrophobic nanopore/water system. During loading (dark blue), P initially increases with the normalized system volume change $\Delta V/V_0$ until it reaches the critical infiltration pressure P_{in} (~ 50.2 MPa, determined as the pressure of the plateau), where V_0 is the initial system volume, breaking the capillary resistance and allowing substantial invasion of water into the hydrophobic nanopore. After the complete infiltration at $\Delta V/V_0 = 0.12$, the nanopore is fully occupied by water molecules, and a confined water cylinder inside the nanotube is formed,²⁶ leading to the incompressibility of the system. Further increase in the displacement loading leads to a rapid and linear increase in P , associated with the infiltration of very few water molecules due to confinement rearrangement of molecules. In addition, the mean square displacement of confined water molecules at the full occupation shows a clear divergence, rather than converges to a constant (**Figure S1**), suggesting that the confined water remains a liquid state.³⁷

Upon quasi-static unloading, the outflow of the invaded water driven by the solid-liquid interaction begins along with the decrease of the resultant pressure P (light blue curve in Figure 1A). Initially, as the system recovers (Stage I), the $P - \Delta V/V_0$ curve coincides with that at the overloading stage, caused by the structural adjustment of confined water molecules, similar to that of the overloading stage after the complete occupation of the nanotube. With the further

decrease of displacement loading (Stage II), surprisingly, P keeps decreasing after lower than P_{in} instead of remaining P_{in} . The $(P_{\text{in}} - P)$ is highlighted with $\Delta V/V_0$ in the lower sub-plot in Figure 1A (dark blue curve) and increases with the unloading displacement. Such deviation indicates that an internal tensile load is generated and exerted on the confined water cylinder during unloading, which is confirmed by calculating the Virial stress σ_{zz} (light blue curve in Figure 1A) in the outflow direction. Given the pressure balance within the system, a nominal stress σ is defined as $(P_{\text{in}} - P)$ to quantitatively characterize the internal tensile load. On Stage III, as the loading displacement continues to decrease, both σ and σ_{zz} reach their peaks followed by an obvious drop until stage V. On stage V, the confined water cylinder completely breaks, after which the $P - \Delta V/V_0$ relationship returns to the same with the initial loading. In addition, the outflow rate rapidly increases after the failure of the confined water cylinder, which forms a complete outflow at the end of the loading cycle (**Figure S2**). Such complete outflow is also observed in nanopores with different radii r_0 . **Figure 1B** shows the simulation snapshots at stages I-V and the number density contours (ρ_N) of the confined water during outflow. Followed upon a continuous outflow at the initial unloading stage, a clear necking associated with a rapid decrease of ρ_N in the middle of the water cylinder is observed, which corresponds well to the obvious drop of both σ and σ_{zz} in Figure 1A. A simulation animation in **Video S1** demonstrates the outflow process. This internal tension-induced necking phenomenon indicates solid-like behavior of confined water outflow and is similar to that of solid metal nanowires subjected to a uniaxial tensile load.³⁸ Further analyses of atomistic snapshots and interaction energy indicate that the necking is associated with the growth and nucleation of voids due to breaks of liquid molecular structures near the surface of the confined liquid (**Figure S3**). Similar solid-like outflows along with occurrence of necking are also observed at different r_0 and T (**Figures S4 and S5, Video S2**). In addition, when flexible SNT with different lengths is employed to mimic a deformable nanopore, similar results are

obtained, as shown in **Figures S6 and S7**. These results indicate that the effect of nanotube deformation and phonon activity on the solid-liquid interaction and the intermolecular structure of the confined liquid is negligible during the liquid outflow under a quasi-static loading/unloading condition.

Figure 1C shows the effects of confinement size r_0 and temperature T on the nominal tensile stress (σ) - strain (ε) curves, where the nominal strain ε is defined as $\Delta V_{\text{its}}/V_0 - \Delta V/V_0$, where ΔV_{its} is the volume change that corresponds to a complete intrusion of water into the nanotubes (Stage I). The initial linear relationship between σ and ε is observed, similar to the linear elastic deformation of solid metal nanowires under tension. After a critical ε , σ drops, corresponding well with the occurrence of necking in Figure 1B. This onset nominal strain of necking can also be well predicted by the Considère's criterion, as shown in **Figure S8**, featured by the presence of hydrogen bonding networks that helps maintain and stabilize the stress in the system (Figure S3). Besides, at a smaller r_0 , the same ε leads to a higher σ due to the enhanced confinement to water molecules inside nanotube. The small r_0 with the enhanced confinement also reduces the necking duration from the continuous outflow to complete break (**Figure S9**). In addition, the relationship of σ - ε shows a temperature-dependence. The confinement of liquid is weakened by an elevated temperature, leading to a lower σ at a given ε . Both size- and temperature-dependent behaviors further confirm the similarity of confined water outflow with uniaxial tensile deformation of solid metal nanowires.

Figure 1D plots the evolution of H-bond density ρ_{HB} within the confined water (Materials and Methods section) at multiple radial location r/r_0 . Subjected to an equivalent mechanical strain ε , ρ_{HB} shows a fast reduction at a higher r/r_0 (i.e. close to the solid-liquid interface at $r/r_0 = 1$) where the liquid cohesion is weak.²⁶ By contrast, ρ_{HB} at a lower r/r_0 only shows a notably

reduction right before the breaks of outflow. The snapshots (inset of Figure 1D) further show that the H-bond density begins to decrease at $\varepsilon = 4\%$, gradually forming a neck-like shape with a substantially lower H-bond density at $\varepsilon = 5.3\%$, consistent well with the σ - ε curves in Figure 1C. More extensive computations reveal that the ρ_{HB} reduction is more homogeneous in a stronger confinement environment with a smaller r_0 (**Figure S10**).

Molecular confinement mechanism of water outflow and response to outflow tensile deformation

Figure 2A presents the Virial Stress of the confined water cylinder during the outflow. Both the axial σ_{zz} and radial stresses $\sigma_{\rho\rho}$ show strong fluctuations, and the outermost peak close to the nanotube wall can be as high as 0.1 to 1 GPa for respective σ_{zz} and $\sigma_{\rho\rho}$. These high local stresses indicate the mechanical strength of confined liquid water cylinder is mainly contributed by the water molecules close to the nanotube wall, similar to that in metal nanowires whose tensile behavior is strongly influenced by the surface stress.^{39,40} The increase of the tensile strain mostly reduces the peak stresses near the solid-liquid interface. In particular, at a high strain $\varepsilon = 5.3\%$ where necking occurs (Figure 1D), σ_{zz} in the outermost stress peak shows an apparent decrease, corresponding well to the obvious reduction of nominal stress σ (Figure 1C). The stress contours in **Figure 2B** further confirm these variations in both σ_{zz} and $\sigma_{\rho\rho}$. Similar evolutions of these stresses are found in a stronger nanoconfinement environment with a smaller r_0 , but the magnitude of surface stress in both σ_{zz} and $\sigma_{\rho\rho}$ is amplified (**Figure 2C and D**). Especially, the peak of σ_{zz} close to the nanopore wall is largely enhanced, well consistent with an enhanced tensile failure strength at a smaller r_0 (Figure 1C). The coincidence that a larger surface stress leads to a higher failure strength in a smaller confinement nanotube size is also similar to that of tensile behavior in metal

nanowires where the surface stress dominates the strength mechanism of nanowire failure.^{39,40} Similar fluctuations of stress in circumferential direction $\sigma_{\theta\theta}$ and the reduction with ε are also observed at different r_0 ; meanwhile the nearly zero of shear stress $\sigma_{\rho\theta}$ indicates a negligible friction force exerted by nanotube wall in circumferential direction, suggesting a stable outflow along axial direction (**Figure S11**).

Figure 3A shows the radial contours of the H-bond number density ρ_{HB} and orientation $\cos(\theta_{\text{HB}-z})$ of the confined water cylinder in different nanotube sizes r_0 , where $\theta_{\text{HB}-z}$ represents the orientation of a H-bond relative to the axial outflow tensile direction. A notable densification of H-bond (light blue) is observed near the solid-liquid interface and attributes to the strong confinement of water molecules near the nanotube wall due to a high energy gradient of solid-liquid interactions (**Figure S12**), which leads to a different intermolecular structure (**Figure S13**). A smaller r_0 increases ρ_{HB} , especially ρ_{HB} near the solid-liquid interfaces. The contours of $\cos(\theta_{\text{HB}-z})$ show higher $\cos(\theta_{\text{HB}-z})$ near the solid-liquid interfaces (yellow) than those of near the center of confined water molecules (red), suggesting a better alignment of H-bonds and outflow tensile direction near the solid-liquid interfaces (yellow). Besides, similar to that of ρ_{HB} , a smaller r_0 leads to a larger $\cos(\theta_{\text{HB}-z})$. **Figure 3B** plots the probability distribution of $\cos(\theta_{\text{HB}-z})$, further confirming the strong alignment of H-bonds relative to the outflow tensile direction near the solid-liquid interfaces. Both high ρ_{HB} and $\cos(\theta_{\text{HB}-z})$ close to the solid-liquid interface are expected to promote the local molecular cohesion and interaction with nanotube wall and lead to high interfacial stresses, as observed in Figure 2A and C. Moreover, high ρ_{HB} and $\cos(\theta_{\text{HB}-z})$ at small r_0 indicate that the intensive H-bonding networks and their strong alignments relative to the outflow tensile direction promote the failure strength as obtained in upper sub-plot of Figure 1C. By contrast, the increase of

confinement temperature T will benefit the thermodynamics of confined water molecules and decreases the solid-liquid interaction, suppressing both ρ_{HB} and $\cos(\theta_{\text{HB}-z})$ (**Figure 3C and D**). Consequently, the suppressed ρ_{HB} and $\cos(\theta_{\text{HB}-z})$ will weaken the H-bonding networks and their alignments, and leads to a decreased failure strength as shown in lower sub-plot of Figure 1C. Similar results on ρ_{HB} and $\cos(\theta_{\text{HB}-z})$ have also been obtained at different r_0 and T (**Figures S14-S16**).

To further understand the molecular confinement mechanisms, **Figure 4A** presents the probability of water dipole orientation distributions along the confinement radial direction r/r_0 , where $\theta_{\text{dp}-z}$ is the angle between a water dipole and the outflow tensile z -direction. It demonstrates two distinct regions with a white dashed line marked at the boundary, referred to as the interface region close to the nanotube wall and the bulk region close to the radial center of nanotube, respectively. Note that the location of the white dashed line also agrees with that of the density peak closest to the nanopore wall (Figure S12A) and depends on the confinement nanotube size and temperature. For example, the white dashed line locates $r/r_0 = 0.7$ at $r_0 = 1.91$ nm at 300K and $r/r_0 = 0.4$ at $r_0 = 1.10$ nm at 300K. Within the interface layer, two preferences of $\theta_{\text{dp}-z}$ marked as I and II are found near $\theta_{\text{dp}-z} = 45$ and 135 degrees. The fraction of water dipoles with $\theta_{\text{dp}-z} = 45$ or 135 degrees increases with the decrease of r_0 . By contrast, within the bulk region, the dominance of $\theta_{\text{dp}-z} = 90$ degrees is observed. **Figure 4B** illustrates the schematics of a single water molecule near the nanotube solid wall. Apparently, water dipoles with $\theta_{\text{dp}-z} = 45$ or 135 degrees will facilitate the formation of H-bonds in alignment with the outflow tensile z -direction, in a good consistency with the strong alignments of H-bond orientation in Figure 3B. The upper plot in **Figure 4C** shows the free energy G (Materials and Methods) versus $\theta_{\text{dp}-z}$ for various confinement sizes r_0 . Two free

energy barriers that help stabilize the dipole orientations are found near $\theta_{\text{dp-z}} = 45$ and 135 degrees (I and II) within the interface regions. Moreover, with stronger confinements at smaller r_0 , the free energy wells are deeper, in good agreement with the probability distributions of both dipole (Figure 4A) and H-bond orientations (Figure 3B). In the bulk region at $r/r_0 < 0.4$, G shows a low energy state at 90 degrees, and the energy well barely changes with r_0 , which corresponds to the transition of $\theta_{\text{dp-z}}$ from the interface region to the bulk region (Figure 4A). These behavior in G can be further understood with the solid-liquid interactive potentials demonstrated in **Figure S17**. Upon being subjected to a tensile strain during outflow, rotations of water molecules are expected and lead to redistributions of water dipoles. For example, for the water cylinder confined in the nanotube of $r_0 = 1.91$ nm at $\varepsilon = 5.3\%$, **Figure 4D** shows a strong shift of $\theta_{\text{dp-z}}$ in the bulk region (highlighted in dashed black box) where the severe necking appears in comparison with that at $\varepsilon = 0$ (Figure 4A). Correspondingly, the energy well in the bulk region shows an apparent derivation from $\theta_{\text{dp-z}} = 90$ degrees toward a smaller $\theta_{\text{dp-z}}$, as presented in the lower subplot of Figure 4C. **Figure 4E** plots the time-averaged dipole vector of water molecules. A shorter arrow represents a dipole orientation that changes significantly and randomly with time; A longer one indicates a stable local dipole orientation that is less time-dependent. At $\varepsilon = 0$, the stable local dipole orientation of ~ 45 or 135 degrees associated with longer arrows near the tube wall is observed, while the dipole orientation is more random in the bulk region, consistent with the probability plot in Figure 4A. At $\varepsilon = 5.3\%$, a significant neck that initially nucleates at the interface region with dipole orientation of 45 degrees occurs, and consequently, the dipole orientations at the neck tend to shift toward 45 degrees, which confirms the shift of $\theta_{\text{dp-z}}$ distribution in Figure 4C and D.

Quasistatic compression experiments on outflow of confined water in nanopores

To verify the solid-like outflow response of the confined water, we performed quasistatic compression experiments on Kiesel gel nanopores/water systems. The schematic of the experimental setup is given in the inset of **Figure 5A**. The Kiesel gel nanoporous materials were first treated by silyl functional groups C8, C12, and C18 to achieve hydrophobic wall surfaces of nanopores with a target radius r_0 (**Figure S18**) and then were immersed in water. These treatments with high-molecular-weight functional groups also ensure a complete outflow of intruded water after unloading.²⁶ The treated Kiesel gel nanopores/water system was placed into a testing cell for conducting quasistatic compression experiments under a cyclic loading condition. More information can be found in the Materials and Methods section. **Figure 5A** presents the evolution of applied pressure P with $\Delta V/V_0$ under three consecutive quasi-static loading cycles. $\Delta V/V_0$ is the normalized system volume change and V_0 is the initial system volume. The identical cyclic behavior demonstrates the complete outflow of infiltrated water after each unloading. For each loading/unloading cycle, upon loading, water overcame the capillary resistance and infiltrated the nanopore when the applied pressure P reached the infiltration pressure P_{in} , where P_{in} was determined as the midpoint of the pressure plateau, the same as in simulations. Upon unloading, followed by an initially rapid decrease of P with the decrease of $\Delta V/V_0$, similar to that at the loading stage, a pressure plateau was obtained but with a lower pressure level, also in good agreement with simulations (**Figure 1A**), confirming the generation of an internal tensile load and its exerting on the infiltrated water. Similar results are also founded at different T and r_0 in **Figure S19**. **Figure 5B** further shows the dependence of $P - \Delta V/V_0$ on r_0 . P_{in} shows an increase with the decrease of r_0 , suggesting an increased capillary resistance and enhanced confinement to infiltrated water molecules, consistent well with simulations (**Figure 1A**). Besides, at a smaller r_0 , the P at the unloading-induced pressure plateau is lower, leading to a high nominal stress exerted on the confined water and thus a faster outflow. The further experiments show an elevated T lowered the P_{in} but enhanced the

unloading-induced pressure plateau (**Figure S20**) and led to a slow outflow of confined water. These both size and temperature dependences agree well with the simulation findings (Figure 1C).

Size-dependent deformation and strength scaling law of confined water outflow

Given the strong similarity of both overall mechanical deformation and existence of local surface stress between confined water outflow and solid metal nanowires, we have extracted the elastic modulus E and failure strength σ_f of confined water cylinder from the nominal stress-strain curves in Figure 2C. Both of them exhibit a strong dependence on confinement nanotube size and temperature (**Figure S21**), further confirming a similarity between the confined water outflow and mechanical deformation of solid nanowires under tension.⁴¹ To quantitatively characterize the size- and temperature-dependent outflow behavior, we propose a solid-like mechanics model of confined liquid outflow. **Figure 6A** illustrates the schematics of a confined water nanowire (the confinement nanotube is not shown). The applied uniaxial tensile load is equivalent to the nominal stress σ ($= P_{in} - P$) during the outflow as defined in Figure 1A, and the surface stress results from the interfacial interaction of the nanotube wall to the most adjacent liquid water molecules. As a result, the E of the confined water cylinder under the outflow-induced equivalent uniaxial tension can be described by a deformation scaling law incorporating the solid-liquid interactions at the nanoscale confinements⁴² via $E = E_b + C_e \frac{\gamma_{SL}}{r_0}$, ($r_0 < r_c$), where r_c is the critical confined size of nanopore radius, E_b is the elastic modulus of bulk water without confinement and is zero,⁴³ and C_e is the elastic deformation constant of the system. γ_{SL} is the solid-liquid interfacial energy density and depends on both confinement temperature and size of nanopores (**Figure S22**). $\frac{1}{r_0}$ represents the size effect due to the nanoconfinement, similar to the deformation scaling law of solid metal

nanowires,⁴¹ which decreases with the increase of confinement size. When the nanoconfinement effect vanishes at $r_0 \geq r_c$, E will reduce to E_b . **Figure 6B** shows the comparison of elastic moduli between MD simulations and theoretical predictions. Their remarkable agreement confirms the robustness of the deformation scaling law (light blue line). Further, in the absence of confinement effect at $r_0 \geq r_c$, γ_{SL} is taken as the counterpart of liquid water on a flat silica substrate, $\gamma_{SL,\infty}$, and the critical pore size $r_c \sim 160$ nm at $T = 300$ K can be obtained, well consistent with the critical length scale (~ 100 nm) on fluid behavior in nanopores.^{4,44} A similar scaling law (black line) is also established to describe the failure stress σ_f , and it is $\sigma_f = \sigma_{f,b} + C_f \frac{\gamma_{SL}}{r_0}$, ($r_0 < r_c$), where $\sigma_{f,b}$ is failure strength of bulk water without confinement subjected to uniaxial tension and is zero,⁴³ and C_f is the failure strength constant of the system. The remarkable agreement between simulations and theoretical prediction is also obtained, as shown in Figure 6B. Unlike the elastic modulus that depends on the overall cohesion of confined water at the early stage of outflow, the failure strength of confined water is largely determined by the local liquid cohesion near the necking region that requires strong confinements (Figure 1D and Figure 5E) and leads to a small r_c of ~ 11 nm in comparison with that of E . In parallel, with experimental measurements of $P-\Delta V/V_0$ (Figure 5A and B and Figure S20), we can convert them into nominal stress (σ)-strain (ε) curves (**Figure S23**) and extract both E and σ_f of confined water cylinders in Kiesel gel nanopores (**Figure S24**). Both E and σ_f are also plotted in Figure 6B. With the experimental determinations of γ_{SL} and $\gamma_{SL,\infty}$ (**Figure S25**), theoretical results from both the deformation and strength scaling laws can be also obtained and show great consistencies with corresponding experimental measurements of E and σ_f . Besides, the resultant critical confinement radius of r_c is ~ 160 nm and ~ 15 nm for respective E and σ_f , highly consistent with simulations. We should note that several practical challenges of settings between MD simulation and experiment, including system size, pore

uniformity, and surface structures make their one-to-one comparison difficult. These factors cause unsynchronized confinement and outflow of water, where small pores enhanced confinement effects and promoted the outflow. The pore size distribution is expected to lead to lower E and σ_f in experiments compared with simulations. Nevertheless, the excellent consistencies of E and σ_f in both simulations and experiments with counterpart theoretical predictions connect them for quantitative evaluations and confirm the proposed solid-like mechanics model and size- and temperature-dependent outflow deformation and strength scaling laws of confined liquid in nanopores.

Conclusion

We have presented an unexpected solid-like outflow of confined water in a hydrophobic nanopore and demonstrated its strong similarity with that of mechanical deformation of solid metal nanowires subjected to a uniaxial tensile load from the initial continuous outflow response to the gradual break along with a formation of an apparent neck-like shape. Extensive molecular dynamics simulations reveal that this similarity is underpinned by the cohesion mechanism of confined water molecules near the nanotube walls and can further attribute to the hydrogen-bond networks and alignments relative to the outflow direction. Further studies show that the confinement to the layer of water molecules near the nanotube walls leads to significant stresses at the solid-liquid interface and dominates the temperature and confinement size-dependent outflow of confined water. The parallel quasistatic outflow experiments on hydrophobic Kiesel gel nanopores/water systems with different pore sizes confirmed the solid-like outflow behavior of intruded water at various temperatures. A solid-like mechanics model of confined liquid is proposed to quantitatively characterize the solid-like outflow behavior by defining an equivalent deformation stress and strain to the respective outflow pressure gradient and systematic volume reduction. The scaling laws for both elastic modulus and the failure

strength of confined water outflow are established and confirmed with comprehensive MD simulations and experimental measurements in remarkable agreement. This work provides fundamental understandings for the quantitative descriptions of confined liquid outflow in hydrophobic nanopores and also offers valuable insights of characterizing liquid properties in a nanoconfined environment, potentially useful to devise nanofluidics-enabled devices and functional structures with a fast responsibility and reliable reusability to external mechanical stimuli for broad applications.

Experimental Procedures

Resource availability

Lead contact

Further information and requests for resources and materials should be directed to and will be fulfilled by the Lead Contact, Prof. Baoxing Xu (bx4c@virginia.edu).

Materials availability

This study did not generate new unique reagents.

Data and code availability

All computational and experimental data and simulation code in the paper are available upon reasonable request to the lead contact.

Atomistic modeling of water-hydrophobic nanopore systems for MD simulations

A rigid silica nanotube with two open ends was adopted to model a hydrophobic nanopore immersed in the water. The radius of the silica nanotube ranges from 1.10 to 1.91 nm, which ensures at least ~740 water molecules with multiple layers confined in nanopores (Figure S12A). The water reservoir possessed a dimension of 9 nm (x -direction) $\times$ 9 nm (y -direction).

In the z -direction, the water reservoir was sandwiched by a rigid wall and a rigid piston initially separated by 18.5 nm. The upper and lower ends of the nanotube were respectively separated by ~ 2.5 and ~ 3.5 nm from the wall and the piston. The water molecules were modeled by the TIP3P model⁴⁵ that is frequently employed in the study of water transport⁴⁶ and confinement effect.⁴⁷ The interactions between non-bonded atoms were modeled by the Lennard-Jones potential.²⁶ Specifically, the equilibrium distance and potential well depth for the solid-liquid interactions were set respectively as $\sigma_{\text{O(water)}-\text{O(nanopore)}} = 0.333$ nm, $\sigma_{\text{O(water)}-\text{Si(nanopore)}} = 0.333$ nm, $\epsilon_{\text{O(water)}-\text{Si(nanopore)}} = 0.1153$ kcal/mol, and $\epsilon_{\text{O(water)}-\text{O(nanopore)}} = 0.0369$ kcal/mol to mimic the hydrophobicity of the nanopore.^{26,48} The particle-particle-particle-mesh (PPPM) method with a root mean of 0.0001 was applied to evaluate the Coulombic interactions between all charged atoms.

Molecular dynamics (MD) simulation and calculation methods

All MD simulations were performed with LAMMPS.⁴⁹ The time step was set as 1 fs. The system was first relaxed in the canonical (NVT) ensemble at the target temperature for 1 ns. In the following 1 ns, the piston was slightly adjusted in the z -direction to ensure a zero pressure P . Next, a quasistatic displacement load was applied on the piston in the negative z -direction, which forced the infiltration of water molecules into nanotube. After the system became incompressible due to the complete infiltration, a quasistatic displacement in the positive z -direction was applied to perform unloading to the system.

The Virial stress was calculated via $\sigma_{ij} = \frac{1}{V_{\text{slab}}} \sum_k^{N_{\text{slab}}} \left(\frac{m_k v_{k,i} v_{k,j}}{V_{\text{slab}}} + \frac{r_{k,i} f_{k,j}}{V_{\text{slab}}} \right)$, where V_{slab} is the volume of the slab, subscript k denotes the k^{th} atom in the slab, m_k is the atomic mass, $v_{k,i}$

and $v_{k,j}$ are the atomic velocity vector components in i and j -directions, respectively, $r_{k,i}$ is the position vector component in the i -direction, and $f_{k,j}$ is the force vector component in the j -direction. The radial stress under cylindrical coordinate $\sigma_{\rho\rho}$ was obtained by transformation $\sigma_{\rho\rho} = \sigma_{xx} \cos^2 \theta + \sigma_{yy} \sin^2 \theta + \sigma_{xy} \sin(2\theta)$, where θ is the angular coordinate of a single particle. For the Virial stress of the whole water cylinder, V_{slab} is considered as $\pi r_0^2 l$. To calculate stress distribution, the volume inside the nanopore was divided into 40 slabs, two thousand adjacent frames with a sampling rate of 0.25 ps were adopted to calculate averaged values in simulation.

An H-bond between a pair of water molecules at a specific moment in simulations was identified by two criteria of atomistic geometry:⁵⁰ (i) the distance between two oxygen atoms should be smaller than 0.35 nm, and (ii) the angle between oxygen-hydrogen covalent bond and the oxygen-oxygen direction should be less than 30 degrees. The location of an H-bond is considered as the averaged coordinate of the donor and acceptor. To calculate the 2-D H-bond density and orientation, the volume inside the nanopore was divided into 40×40 slabs, five thousand adjacent frames with a sampling rate of 0.1 ps were adopted to calculate averaged values in simulation.

The free energy G profile at different dipole angles θ_{dp-z} was obtained according to $G = -k_B T \ln(< \text{Prob}(\theta_{dp-z}) >)$, where k_B is the Boltzmann constant, $\text{Prob}(\theta_{dp-z})$ denotes the probability of a specific θ_{dp-z} at a certain location, and the bracket $<>$ represents the time average.

The elastic modulus E was determined by taking the linear stage of nominal stress (σ)-strain (ϵ) curve within ϵ range of 0-3% (Figure 1C). The fracture strength σ_f was taken as the stress at the fracture point of the confined water cylinder that corresponds to complete break of confined water outflow.

Material preparation

The nanoporous material investigated in current study was a hydrophilic nanoporous silica (53698 Kiesel gel, Sigma-Aldrich, Inc.). The as-received material was in a powder form, with particle size ranging from 40 to 75 μm . The hydrophilic nanopore surface was converted to hydrophobic by anchoring a thin layer of silyl groups on the nanopore wall.⁵¹ The surface reagents including n-Octyldimethylchlorosilane (C8), Dodecyldimethylchlorosilane (C12), and n-Octadecyldimethylchlorosilane (C18) were purchased from Gelest, Inc. Briefly, 1 g of Kiesel gel was mixed with 40 mL of anhydrous toluene for 3 h. 10 mL of surface reagent and 1 mL of pyridine were then injected into the mixture, after which the mixture was stirred at 95 $^{\circ}\text{C}$ for 24 h. Finally, the treated Kiesel gel was filtered, washed, and dried. The nanopore size of the treated Kiesel gel (Figure S18) was characterized by porosimetry method.⁵²

To prepare the water-Kiesel gel sample, 0.1 g of treated Kiesel gel and 0.58 g of water were placed in vacuum ($< 3 \text{ kPa}$) for at least 1 h to minimize the air in the nanopores and water, after which the Kiesel gel and water were quickly mixed and sealed in a stainless-steel testing cell. The length of the samples, l , were $5.9 \pm 0.1 \text{ mm}$.

Quasi-static compression test

The sealed water-Kiesel gel samples were compressed by a universal tester (5982, Instron, Inc.) at a constant speed of 2 mm/min. This loading speed was selected to ensure the system equilibrium during the water outflow process (**Figure S26**).^{53,54} As the compression progressed, the piston displacement δ and the resultant force, F , gradually increased. A peak force, at which all nanopores are filled with water, was set to control the loading-unloading process. Once the peak force was reached, the Instron platen was moved back at the same speed. A single test was triplicated for each sample with three consecutive quasi-static loading cycles. The pressure built in the Kiesel gel nanopores/water system was calculated as $P = F/A$, where A was the cross-sectional area of the piston. The volume change of the system was calculated as $\Delta V/V_0 = \delta/l$, where l is the sample length in the loading direction. The nominal stress σ was defined as $(P_{\text{in}} - P)$, and the nominal strain ε was determined as $\Delta V_{\text{in}}/V_0 - \Delta V/V_0$, where ΔV_{in} is the volume change at which $P = P_{\text{in}}$, similar to that in MD simulations. For self-comparison purpose, all elastic moduli were calculated from the linear stage of $\sigma - \varepsilon$ curves in the strain range of 0-3% (Figure S23), same as simulations. The failure stress was calculated from $\sigma_f = P_{\text{in}} - P_{\text{out}}$, where P_{in} and P_{out} are the midpoints of the pressure plateau in the loading and unloading curves, respectively.

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Author Contributions

Conceptualization, Y.G., M.L., W.L., and B.X.; Methodology, Y.G., M.L., W.L., and B.X.; Investigation, Y.G., M.L., H.Z., and Y.Z.; Resources, W.L. and B.X.; Writing-Original Draft, Y.G., M.L., H.Z., Y.Z., W.L., and B.X.; Writing-Review & Editing, Y.G., M.L., W.L., and B.X.; Funding Acquisition, W.L. and B.X.; Supervision, W.L. and B.X.

Declaration of Interests

The authors declare no competing interests.

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Figure 1. Mechanical response and characterization of a water-hydrophobic nanopore system

(A) (top) Applied pressure P on the piston as a function of the normalized displacement loading $\Delta V/V_0$ during the loading and unloading. Inset: schematic of the atomistic model of the water-hydrophobic nanopore system, where L denotes loading and UL denotes unloading. (bottom) Variations in Virial stress σ_{zz} and nominal tensile stress σ , defined as $P_{\text{in}} - P$ with $\Delta V/V_0$ upon unloading P , where P_{in} is the infiltration pressure and is defined as the pressure of the plateau. (B) (left) Simulation snapshots of confined water cylinder corresponding to I to V stages during unloading. (right) Evolution of water molecular number density ρ_N during unloading at different axial (z) direction, where t^* denotes the start ($t^* = 0$) and the end ($t^* = 1$) of the unloading. (C) Nominal stress-strain ($\sigma - \varepsilon$) curves of the confined water cylinder confined in nanopores with multiple radii r_0 (top) and at different temperature T (bottom), where the nominal strain ε is defined as $\Delta V_{\text{its}}/V_0 - \Delta V/V_0$, and ΔV_{its} is the critical system volume change that corresponds to a complete intrusion of liquid into the nanotubes (Stage I). (D) H-bond density ρ_{HB} in response to nominal strain ε at different radial locations (r/r_0). Inset: simulation snapshots of H-bonds at different strains ε .

Figure 2. Surface stress in confined water under a hydrophobic nanopore

Axial distributions of axial σ_{zz} (top) and radial $\sigma_{\rho\rho}$ (bottom) Virial stresses in confined water cylinders at different nominal tensile strain ε in nanopores with radii of (A) 1.91 nm, and (C) 1.10 nm. Axial σ_{zz} (top) and radial $\sigma_{\rho\rho}$ (bottom) Virial stresses contours in the cross-sectional ($x - y$) plane at different nominal tensile strain ε in nanopores with radii of (B) 1.91 nm, and (D) 1.10 nm.

Figure 3. H-bond properties of water in hydrophobic nanoconfinement

(A) Cross-sectional ($x - y$) plane distributions of H-bond density ρ_{HB} and orientation $\cos(\theta_{\text{HB}-z})$ in water cylinders confined at the same temperature $T = 300$ K but different radii r_0 of nanopores. (B) Probability distribution of $\cos(\theta_{\text{HB}-z})$ at the same temperature $T = 300$ K but different radii r_0 of nanopores. (C) Cross-sectional ($x - y$) plane distributions of H-bond density ρ_{HB} and orientation $\cos(\theta_{\text{HB}-z})$ in water cylinders confined at the same temperature r_0 but different temperatures T . (D) Probability distribution of $\cos(\theta_{\text{HB}-z})$ at the same temperature r_0 but different temperatures T .

Figure 4. Water dipole orientations in hydrophobic nanoconfinement

(A) Radial probability distributions of water dipole orientations $\theta_{\text{dp}-z}$ in nanopores with different radii r_0 . (B) Schematics of preferred dipole orientations at solid-liquid interfaces. (C) Free energy G profiles versus specific dipole orientations $\theta_{\text{dp}-z}$ at different radial locations r_0/r in nanopore. (D) Radial probability distributions of water dipole orientations $\theta_{\text{dp}-z}$ in nanopore with $r_0 = 1.91$ nm subjected to strain $\varepsilon = 5.3\%$. (E) Vector plots of water dipole orientations in a nanopore with $r_0 = 1.91$ nm without and with strain $\varepsilon = 5.3\%$.

Figure 5. Quasistatic compression experiments on hydrophobic Kiesel gel nanopores/water systems

(A) Evolutions of the applied pressure P with the normalized system volume change $\Delta V/V_0$ in three consecutive unloading-unloading cycles in single tests at a confinement temperature $T = 350$ K. The Kiesel gel nanopores were grafted by C12 functional groups, and the averaged pore size was $r_0 = 3.46$ nm. The infiltration pressure P_{in} is determined as the midpoint of the pressure plateau. Inset: schematic of experimental setup. (B) $P - \Delta V/V_0$ relationships at different averaged pore sizes achieved with various surface treatments. The confinement temperature $T = 350$ K.

Figure 6. Mechanics model of confined water outflow and scaling laws of outflow deformation and strength

(A) (left) Configuration of water molecules under the confinement of a hydrophobic nanotube, where red dots represent oxygen atoms of confined water molecules, cyan surface marks the profile of the water cylinder, and the nanotube is not shown here, and (right) its equivalent solid-like mechanics model of confined water nanowire with surface stress subjected to uniaxial tensile loading. Dash lines illustrate the surface stress that results from interfacial interaction of the nanotube wall to the most adjacent liquid water molecules, and the applied tensile load to both ends is equivalent to the nominal stress $\sigma (= P_{in} - P)$ during the outflow of confined water. (B) Comparison of elastic moduli E (top) and failure stress σ_f (bottom) of confined water outflow among simulations, experiments, and theoretical predictions. The errors in experiment were obtained with triplicated tests and are less than 2%.

Video S1. Water outflow process in a nanopore with $r_0 = 1.91$ nm

The silica nanotube and water molecules confined inside are shown. In the confined liquid, the blue color indicates the surface mesh constructed with a probing radius of 0.35 nm while the red and white particles respectively represent oxygen and hydrogen atoms. A clear necking phenomenon can be observed.

Video S2. Water outflow process in a nanopore with $r_0 = 1.10$ nm

The silica nanotube and water molecules confined inside are shown. In the confined liquid, the blue color indicates the surface mesh constructed with a probing radius of 0.35 nm while the red and white particles respectively represent oxygen and hydrogen atoms. The necking phenomenon is less significant compared to that at $r_0 = 1.91$ nm.