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Compressing Liquid Nanofoam System: Liquid Infiltration or Nanopore Deformation?

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Abstract

Understanding the invasion of liquid into porous structures is the foundation of the characterization of porosity-related properties of materials and is also of fundamental importance in the design of porous solid-liquid enabled energy protection system, yet whether solid pore deforms is so far fuzzy. Here, we present a competition mechanism between liquid infiltration and cell wall buckling deformation by investigating a liquid nanofoam (LN) system subjected to quasi-static compression. The critical buckling stress of the cell wall and infiltration pressure of liquid invasion to nanopore are studied and correlated through numerical simulation and experimental validation to reveal the quantitative relation between nanopore deformation and liquid invasion. The analysis shows that the liquid infiltration occurs, independent of axial buckling stress of cell wall; in contrast, the nanopore collapses radially when the radial collapse pressure is lower than the pressure of liquid infiltration, preventing the liquid invasion. Comprehensive molecular dynamics (MD) simulations are performed and demonstrate the deformation behavior of nanopores and cell wall-liquid interactions in a broad range. Pressure-induced compression experiments on a silica-based LN system are carried out and validate these theoretical and MD results.

Keywords: Liquid nanofoam, Liquid infiltration; Nanopore deformation; Cell wall buckling; Quasi-static compression

Liquid intrusion porosimetry techniques such as mercury porosimetry have been widely used

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in the measurement of pore size distributions and pore volume in both chemical and materials science engineering¹. In particular, when the porous structures are non-wettable to the liquid, an external pressure is applied to overcome the capillary force, which leads to the subsequent transport of liquid into pores. During this process, the associated mechanical energy will be partially converted into solid-liquid interactions and partially dissipated due to the friction. Inspired by this unique phenomenon, a liquid nanofoam system has been developed to design energy protection layers and structures²⁻⁵. When the pore size is down to the nanoscale, the associated energy dissipation can be as high as 100 J/g due to the ultra-large surface area of nanopores ($\sim 100-1000 \text{ m}^2/\text{g}$), several orders of magnitude higher than that of conventional energy absorption materials^{6,7}. Besides, upon unloading, the liquid molecules flow out of the nanopores due to the hydrophobic nature of porous surfaces, making the system fully reusable⁸. In either measurement of pore distribution or design of energy dissipation structures, the underlying mechanism is the infiltration and transport of liquid molecules to pore spaces under a quasi-static pressure⁹⁻¹¹. For hydrophobic nanopores, however, whether the liquid infiltration or buckling/collapse of empty nanopores upon compression is fundamentally unanswered. The elucidation of this deformation competition mechanism will offer an immediate guidance for designing high-performance liquid-solid porous energy protective structures and for estimating porosity-related characteristics of materials via porosimetry. In addition, the understanding of this competition mechanism could provide important insights on stability assessment for other systems composed of fluid and nanoporous materials such as water transportation¹² and drug delivery system¹³.

Here, we have investigated a hydrophobic cylindrical nanopore, i.e. nanotube, suspended in a liquid environment system subjected to a quasi-static loading, and generated a quantitative model to reveal the competition mechanism between liquid infiltration and nanopore buckling/collapse. Two different deformation models of the nanopore, axial buckling and radial collapse, are identified and incorporated with liquid infiltration. The theoretical analysis shows that the liquid infiltration only depends on the critical pressure of radial collapse. When the liquid infiltration pressure is lower than the critical radial collapse pressure, liquid invades into nanopore. Otherwise, the nanopore buckles and collapses along

the radial direction, and thus, the liquid cannot be infiltrated into the nanopores. By contrast, liquid infiltration always happens, independent of axial buckling stress of the nanopore. Extensive molecular dynamics (MD) simulations have been performed on a liquid-nanotube system under a quasi-static pressure. Both surface wettability and size dimension of the nanopore are considered, and simulation results show good agreement with theoretical analysis. Further, compression experiments on a silica-based LN system have been conducted and confirm the findings.

Figure 1(a) illustrates a non-wetting flexible nanotube immersed in a liquid environment, and the nanotube is empty due to the nature of the hydrophobic nanopore surface. Upon applying a pressure, the nanotube is subjected to a uniform compression, leading to either infiltration of liquid into the nanotube or deformation of the nanotube. Based on the Laplace-Young equation, the critical pressure for liquid infiltration can be determined quantitatively via $P_{in} = \frac{-4\gamma[\cos\theta]}{D}$, where γ is the surface tension between water and air/vacuum, θ is the contact angle between nanotube surface wall and water molecules and represents the surface wettability of nanotube, and D is the diameter of the nanotube. For example, take water as liquid and silica nanotube (SNT) as pore, which can be easily achieved and verified in experiments, respectively, the surface tension $\gamma = 100.75 \text{ MPa} \cdot \text{nm}$ can be obtained from a series of molecular dynamics simulations on pressure-induced infiltration of water molecules into SNT with diameter $D = 1.4 \text{ nm}$ (**Figures S1, 2 in supplementary materials**). We should note that when the size dimension and materials of tubes change, γ can also be determined by following the similar procedures. In addition to the possible mechanism of liquid infiltration, given the large aspect ratio of SNT pores, axial buckling or radial collapse might happen, leading to pore deformation. Assume the mechanical deformation energy of nanotube is $E = \lambda E_0$, where λ is the energy coefficient and reflects the deformation ability of SNTs, and E_0 is the deformation energy of a pristine SNT. According to the buckling theory, the critical pressure of axial buckling P_{axial}^{cr} for the flexible nanotube is determined quantitatively via $P_{axial}^{cr} = \frac{C_1 \lambda (D^2 + h^2)}{L^2}$,^{14, 15} where L is the length of nanotube, h is the thickness of nanotube wall, and $C_1 \lambda$ is an elastic constant of

relevance to the axial compressive stiffness of nanotubes. Similarly, the radial critical collapse pressure P_{radial}^{cr} is determined quantitatively via $P_{radial}^{cr} = \frac{C_2 \lambda}{D^3}$,^{16, 17} and is independent of length of nanotube, where $C_2 \lambda$ is an elastic constant and depends on the radial stiffness of nanotubes. For example, consider a pristine silica nanotube (SNT) with diameter of $D = 1.4nm$, $\lambda = 1$ and the simulations on uniaxial and hydrostatic compression of SNT show $C_1 = 159.16GPa$ and $C_2 = 1.93GPa \cdot nm^3$ (**Figures S3, 4, 5 in supplementary materials**).

Based on the above theoretical analysis, the quantitative relation between P_{in} , P_{axial}^{cr} and P_{radial}^{cr} can be calculated and apparently it depends on the geometry and surface wettability of nanotube. The transition between axial buckling and liquid infiltration can be determined via $P_{in} = P_{axial}^{cr}$, and it is $\cos\theta = -\frac{C_1 \lambda (D^3 + Dh^2)}{4\gamma L^2}$. Similarly, $\cos\theta = -\frac{C_2 \lambda}{4\gamma D^2}$ via $P_{in} = P_{radial}^{cr}$ which corresponds to the transition between radial collapse and liquid infiltration. As an example, take $\lambda = 0.3$ and $D = 1.4nm$ and assume a series of L and θ , **Figure 1 (b)** presents a theoretical map of the critical pressure for pore mechanical deformation and liquid infiltration. Generally, liquid is expected to invade into the nanopore when P_{in} is smaller than P_{radial}^{cr} ; otherwise, the pore is expected to collapse along the radial direction, and as a consequence, the liquid cannot be infiltrated into the nanopores. By contrast, the presence of incompressible liquid medium surrounding the nanotube provides a strong lateral constraint to the nanotube and suppresses the axial buckling of nanopores. Consequently, the liquid infiltration dominates the deformation process, independent of P_{axial}^{cr} which will be elucidated below in both molecular dynamics simulations and experiments. When D or λ changes, the similar phase diagrams can be obtained, as shown in **Figure S6 (a) (b) and (c)**. In particular, for a large λ , the nanotube will be very stiff, both P_{axial}^{cr} and P_{radial}^{cr} are far larger than P_{in} , and only the liquid infiltration will happen, independent of contact angles; for a small λ , the nanotube will become very soft, the system may be mainly dominated by the radial collapse of the nanotube.

Molecular dynamics (MD) simulations were first performed to validate the competition of liquid infiltration and cell wall buckling. **Figure 2(a)** shows MD simulation model. Water was employed as the liquid phase and silica nanotube (SNT) was adopted to model a nanopore. An SNT with the length of L and the diameter of D was immersed in a water reservoir. The initial density of water inside the reservoir was taken as that of bulk water, $\rho_0 = 998.0 \text{ kg/m}^3$. The left and right boundaries of the reservoir were bounded by two rigid wall, with the right one fixed and the left one movable to mimic a piston. A periodic boundary condition was imposed on the other four lateral planes of the computational cell. An extended simple point charge (SPC/E) model was to model water molecules¹⁸ and Tersoff potential was utilized to model the flexible SNT¹⁹. The 12-6 Lennard-Jones (L-J) potential and a Coulomb potential were used to describe the intermolecular potential between atoms²⁰.

At equilibration state, the water molecules stayed outside the SNT due to its hydrophobic nature. After that, the piston started to move to apply a quasi-static pressure to the system. All simulations were performed in NVT ensemble with Nose/Hoover thermostat²¹ at temperature 300 K. The simulations were performed using the LAMMPS package.²² More details of the MD simulation are given in the supplementary material. In simulations, to mimic the effect of surface wettability of SNTs which can be achieved through surface treatments such as the decoration of functional groups on silicon atoms²⁰, the interactive well depth between silicon atoms in SNTs and oxygen atoms in water molecules in L-J potential, ϵ_{Si-O} , was adjusted, as shown in **Figure S1**; Mechanical stiffness of SNT were tuned by adjusting the deformation energy via λ to achieve all the possible quantitative conditions among P_{in} , P_{axial}^{cr} and P_{radial}^{cr} . For example, take the geometry and strain energy tuning factor of the SNT $D = 1.4 \text{ nm}$, $L = 25 \text{ nm}$ and $\lambda = 0.3$, the critical pressure for axial buckle P_{axial}^{cr} and radial collapse P_{radial}^{cr} of SNT can be determined, and when the contact angle θ increases from 90° to 180° , the infiltration pressure P_{in} increases, as shown in **Figure 2(b)**. As a consequence, we can have three categories as $P_{in} < P_{axial}^{cr} < P_{radial}^{cr}$ at $\theta < 124^\circ$, $P_{axial}^{cr} < P_{in} < P_{radial}^{cr}$ at $124^\circ < \theta < 139^\circ$, and at $\theta > 139^\circ$, P_{in} becomes larger than both P_{axial}^{cr} and P_{radial}^{cr} .

Consider three cases with the contact angle $\theta = 103^\circ$, $\theta = 129^\circ$ and $\theta = 152^\circ$, **Figure**

2(c) shows the variation of the number of infiltrated water molecules with the applied pressure via the piston. At $\theta = 103^\circ$, based on above theoretical analysis, $P_{in} = 70$ MPa, and $P_{in} < P_{axial}^{cr} = 160$ MPa $< P_{radial}^{cr} = 215$ MPa. When the applied pressure is relatively low, only a few water molecules are oscillated near the entrance of the SNT. When the pressure is beyond the critical value of $P_{in} = 77$ MPa, the capillary resistance is overcome and water molecules burst into the SNT with an arrival of a subsequent plateau stage of pressure. At $\theta = 129^\circ$, $P_{in} = 182$ MPa, and $P_{axial}^{cr} < P_{in} < P_{radial}^{cr}$, the water molecules can still flow into the SNT, similar to that at $\theta = 103^\circ$, but with a larger infiltration pressure $P_{in} = 175$ MPa due to the higher hydrophobicity of SNT. In contrast, when the contact angle $\theta = 152^\circ$, where $P_{in} = 255$ MPa is larger than both $P_{axial}^{cr} = 160$ MPa and $P_{radial}^{cr} = 215$ MPa, the nanotube is radially collapsed when the applied pressure comes to ~ 220 MPa, smaller than P_{in} . No water molecules are able to infiltrate into the SNT. **Figure 2(d)** shows the corresponding snapshots of SNTs and invaded water molecules at different simulation times. Clearly, for $\theta = 103^\circ$, water molecules are observed in the SNT at $t=4.5$ ns and increases with the simulation time. At the same time, the SNT morphology keeps the initially straight shape during the entire simulation, indicating no axial buckling or radial collapse. Similarly, for the case of $\theta = 129^\circ$, water molecules infiltrate into the SNT but with less numbers due to a higher P_{in} at the same simulation time. More importantly, the SNT morphology remains straight, indicating that the axial buckling of SNT does not take place even with $P_{axial}^{cr} < P_{in}$. When the contact angle θ increases to 152° , the SNT collapses radially at $t=4.5$ ns and is further compressed with the increase of simulation time. As a consequence, no water molecule is observed in the SNT, indicating that the radial collapse of solid nanopore dominates the deformation progress in a liquid-nanopore system with $P_{in} > P_{radial}^{cr}$. **Figure S7** shows variation of the applied pressure with simulation time, and a sudden drop further confirms the radial collapse. These simulation results verify the theoretical assumption that the presence of liquid environment suppresses the axial buckling of nanopores and consequently, the liquid infiltration dominates the deformation process, no matter P_{axial}^{cr} is larger or smaller than P_{in} .

To further validate the competition between liquid infiltration and solid nanotube

buckling, we considered a short SNT with $L=20$ nm, and accordingly the axial buckle pressure P_{axial}^{cr} increases to 260 MPa while $P_{radial}^{cr} = 215$ MPa does not change, leading to $P_{axial}^{cr} > P_{radial}^{cr}$. Following the similar simulation procedures, further MD simulations were performed. **Figure 3(a)** shows that the water molecules can infiltrate into the SNT at $\theta = 129^\circ$, where P_{in} is smaller than both P_{axial}^{cr} and P_{radial}^{cr} . When the contact angle θ increases to 152° , where P_{in} is larger than P_{radial}^{cr} but smaller than P_{axial}^{cr} , the SNT collapses in the radial direction when the applied pressure exceeds $P_{radial}^{cr} = 220$ MPa, yet is smaller than P_{in} . There is no infiltration of water molecules into the SNT. **Figure 3(b)** shows the corresponding simulation snapshots of SNTs and infiltrated water molecules. Similar to those observations in **Figure 2(d)**, no axial buckling or radial collapse of the SNT is observed when $P_{in} < P_{radial}^{cr}$, and water molecules successfully invade into the SNTs; while the radial collapse of nanopore occurs once $P_{radial}^{cr} < P_{in}$. **Figure S8** shows the density profile of water inside the SNTs along the radial direction of SNT with different SNT length and wettability after the water molecules have intruded into the nanopore. The fluctuation of these density profiles represents the liquid-solid interaction in the confined nanotube and becomes larger for a smaller contact angle.²³ However, given the same contact angle, the same configuration of confined water molecules is obtained once water molecules are invaded into the SNT, and independent of P_{axial}^{cr} , further confirming that there is no mechanical deformation of the SNTs even at $P_{axial}^{cr} < P_{in}$ when the length of SNT increases from 20 nm to 25nm. These simulation results further verify the theoretical assumption that when P_{in} is smaller than P_{radial}^{cr} , liquid is expected to invade into the nanopore; when P_{in} becomes larger than P_{radial}^{cr} , the pore is expected to collapse along the radial direction.

To qualitatively validate the theoretical model and simulation results, we further performed quasi-static compression experiments on the silica-based LN system. The silica nanoporous particles (Perform-O-Sil 668, Nottingham Corp.) were hydrophobic and the average pore diameter was 115 nm. This LN consisting of 0.2 g of the nanoporous silica and 2 g of saturated lithium chloride (LiCl) aqueous solution (46 wt%) was sealed in a stainless-steel cylinder by two pistons with O-rings and compressed by a universal tester (Model 5982,

Instron, Inc.) at a constant rate of 1 mm/min, as illustrated in **Figure 4(a)**. Once the desired peak force was reached, the crosshead of the Instron was moved back at the same velocity. The specific volume change of the LN samples was defined as $\Delta V = A \cdot \delta / m$, where A was the cross-sectional area of the pistons of 126 mm², δ was the displacement of the piston, and m was the mass of the silica gel.

Same experimental setup was adopted for dry pre-compression on silica nanoporous particles without the presence of liquid. Different peak forces applied on three silica gel samples were 0.25 kN, 0.50 kN and 0.75 kN, respectively to induce different levels of pore damage. The applied pressure was calculated as $P = F/A$, where F was the force applied on the piston. Thus, the applied peak stress, σ_{max} , were 2 MPa, 4 MPa, and 6 MPa accordingly. More details of the material preparation and the testing setup are given in the supplementary material. **Figure 4(b)** shows the stress-strain curves of dry pre-compression tests. The observed hysteresis behavior indicates that permanent mechanical deformation including buckling and collapse of nanopores occurred even at the peak stress, σ_{max} , as low as of 2 MPa. With the increase of the peak stress, the associated loop area of hysteresis in stress-strain curve increases, and the deformation of nanopores become more severe as more nanopores are permanently deformed. Besides, due to relatively wide pore size distribution in the silica gel (**Figures S9** in supplementary materials), no clear elastic to plastic transition was observed in this dry pre-compression tests.

Pressure-induced liquid infiltration tests on LN systems were conducted on all the silica gel particles with or without dry pre-compression. **Figures 4(c-f)** show the P - ΔV curves of various LN samples. Initially, the liquid did not enter the nanopores due to the surface hydrophobicity of the silica gel, and the porous particles may experience compression or/and bending deformation. As the external pressure reached a critical value, the capillary effect was overcome and the liquid was driven into the nanopores. Consequently, a stress plateau was observed, similar to simulation results in **Figures 2 and 3**. Once all nanopores were filled, the system became incompressible. The width of the stress plateau reflected the specific nanopore volume of the silica gel specimens, ΔV_{sp} . The liquid infiltration pressure,

P_{in} , was defined as the pressure at the mid-point of the stress plateau. For LN system without pre-compression (i.e. $\sigma_{max} = 0$), P_{in} was about 2.6 MPa, high enough to deform nanopores in comparison with the dry pre-compression on particles, yet the liquid was successfully invaded, in consistency with theoretical analysis and MD simulations, and ΔV_{sp} was around $1.60 \text{ cm}^3/\text{g}$. As the pre-compression peak stress σ_{max} increased from 0 to 6 MPa, P_{in} increased from 2.6 MPa to 4.2 MPa, and ΔV_{sp} of corresponding LN decreased from $1.6 \text{ cm}^3/\text{g}$ to $1.10 \text{ cm}^3/\text{g}$. The results of all liquid infiltration tests were summarized in **Table 1**. The increased P_{in} is in consistency with the liquid infiltration into small pores as the large pores collapsed prior by the dry pre-compression. The decreased ΔV_{sp} also agrees well with the increased collapse volume of nanoporous particles by the applied dry pre-compression in **Figure 4(b)**. P_{in} is smaller than that in simulations due to the larger pores used in experiments.

To further confirm the whole process was dominated by liquid infiltration rather than permanent mechanical deformation of nanopores under compression on LN systems, the silica nanoporous particles were collected by filtering out the liquid, then thoroughly rinsed by ethanol and warm DI water to remove the residual electrolytes in the nanopores followed by drying in the air (the details of the recycling process can be found in the supplementary material). The recycled silica nanoporous particles were mixed with same amount of saturated LiCl solution and tested under quasi-static compression. The P - ΔV curves are plotted as the second loading-unloading cycles in **Figure 4(b-d)**. The liquid infiltration performance of all silica gel samples with different levels of dry pre-compression remained the same, indicating that the nanoporous structures was not further deformed in the first loading-unloading cycle with the presence of the non-wettable liquid. Please note that the silica nanoporous particles have 3-D porous structures, as shown in **Figure S10**. When suspended in a liquid solution, upon compression, liquid invades in a spatial dimension and no radial collapse deformation is expected.

In summary, we have investigated both liquid infiltration and cell wall buckling of a liquid nanofoam system under compression and presented a theoretical map for understanding the fundamental competition of these two deformation mechanisms. The

molecular dynamics simulations were performed and the results show that the liquid suppresses the axial buckling deformation of nanopore and invades into nanopores. In contrast, when the radial collapse pressure of nanopore is smaller than the liquid infiltration pressure, the radial collapse deformation leads to failure of the nanopore before the infiltration of liquid, and thus, liquid infiltration is interrupted. These findings have been further confirmed by pressure-induced infiltration compression experiment on a silica-based LN system. The present study not only addresses the long-standing and puzzling question between liquid infiltration and nanopore buckling in the measurement of properties of relevance to porous structures in a broad range of materials, but also provides a quantitative guidance for designing a high-performance liquid nanofoam energy absorption system and nanofluidics enabled devices.

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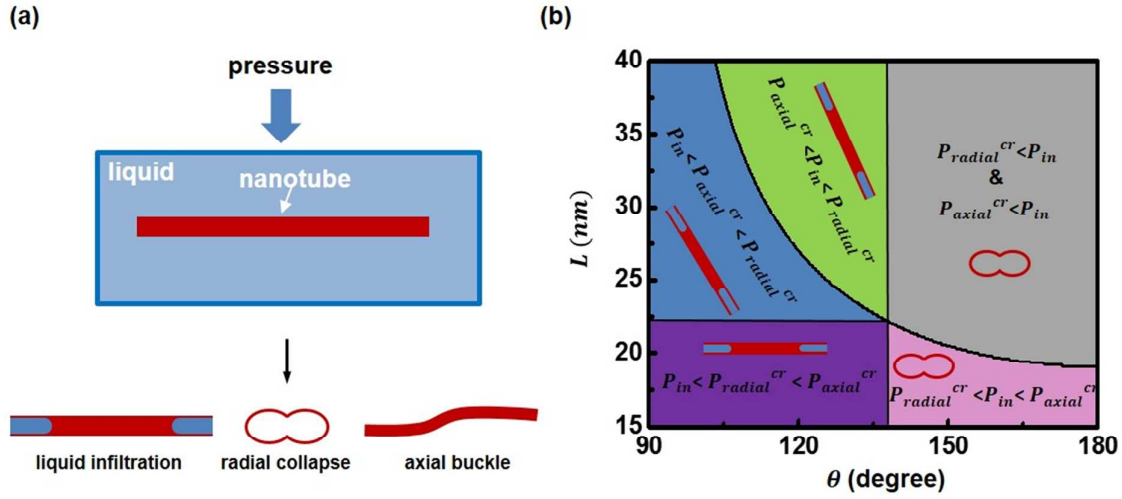


Figure 1: Theoretical analysis of liquid infiltration and nanopore deformation for a liquid nanofoam system subjected to a quasi-static pressure. (a) Schematics of non-wetting liquid-nanotube composite system under compression, and three deformation mechanisms: liquid infiltration, radial collapse and axial buckling of nanopore. **(b)** Quantitative relation among critical pressure for liquid infiltration P_{in} , axial buckle P_{axial}^{cr} and radial collapse P_{radial}^{cr} , with variation of surface wettability represented by contact angle θ and tube length L . The tube diameter $D = 1.4\text{nm}$ and the deformation energy factor $\lambda = 0.3$.

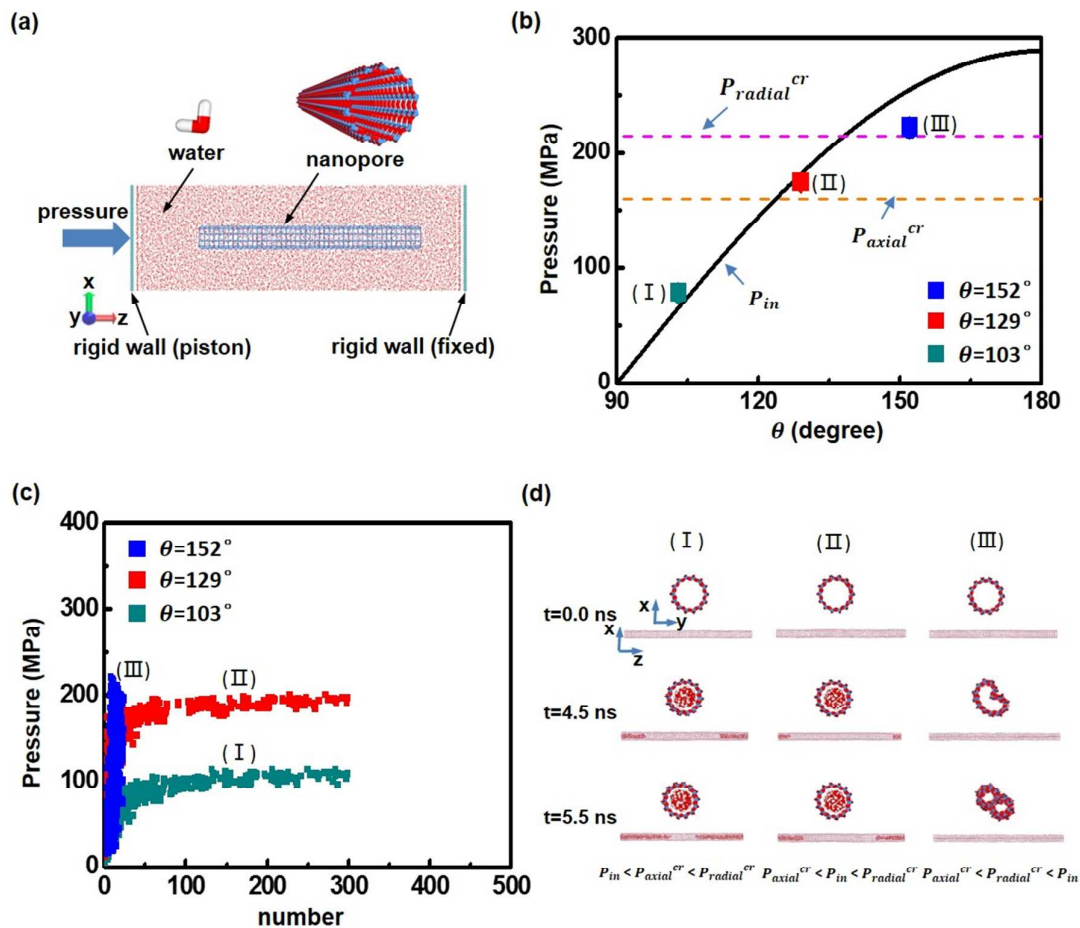


Figure 2: Molecular dynamics simulations of pressure-induced liquid infiltration into a long nanopore. (a) Computational model of water-nanopore system under compression. (White: hydrogen atom, red: oxygen atom, blue: silicon atom) (b) Critical axial buckle pressure and radial collapse pressure of nanopore and variation of critical infiltration pressure with different surface wettability (characterized via θ). (c) Variation of the number of infiltrated water molecules into nanotube with different surface wettability. (d) Snapshots of MD simulation at different simulation times (bottom: side view; Top: axial view). The pore dimensions: $D = 1.4nm$, and $L = 25nm$ and the deformation energy factor: $\lambda = 0.3$

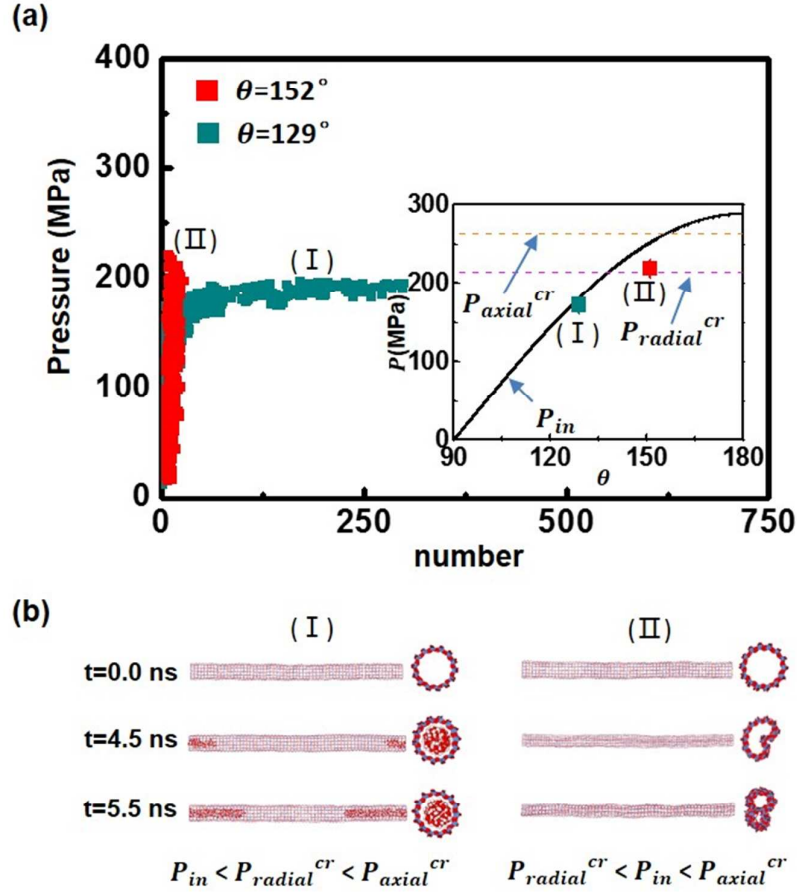


Figure 3: Molecular dynamics simulations of pressure-induced liquid infiltration into a short nanopore. (a) Variation of the number of infiltrated water molecules into nanotube with different surface wettability. The inset shows the critical axial buckle pressure is large than the radial collapse pressure of SNT. (b) Snapshots of MD simulation at different simulation times (left: side view; right: axial view). The pore dimension: $D = 1.4nm$, and $L = 20nm$ and the deformation energy factor: $\lambda = 0.3$

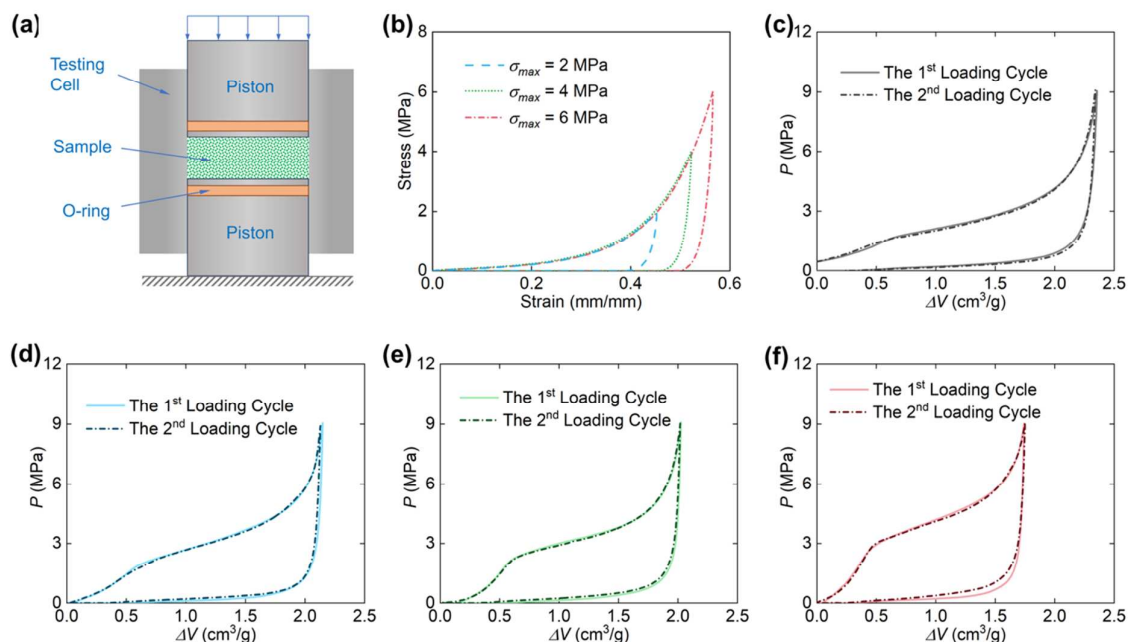
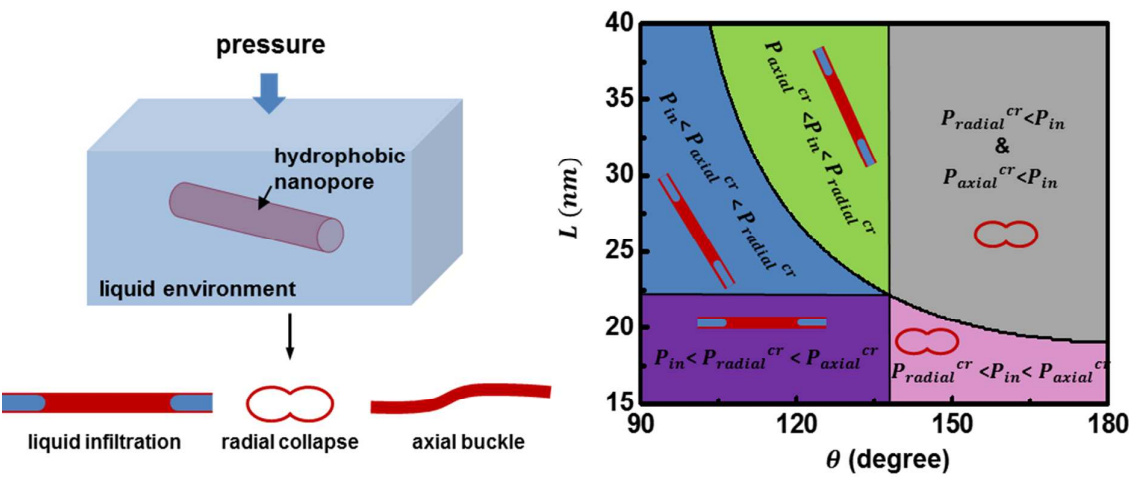


Figure 4: Experiments of pressure-induced liquid infiltration on porous silica-lithium chloride (LiCl) aqueous solutions. (a) The schematic of the experimental setup. **(b)** Loading history of the dry pre-compression on empty silica gels under various peak stress σ_{max} . **(c)** Sorption isotherm curves of LN system without dry pre-compression. **(d)** Sorption isotherm curves of LN system with dry pre-compression at $\sigma_{\text{max}} = 2$ MPa. **(e)** Sorption isotherm curves of LN system with dry pre-compression at $\sigma_{\text{max}} = 4$ MPa. **(f)** Sorption isotherm curves of LN system with dry pre-compression at $\sigma_{\text{max}} = 6$ MPa. The loading rate for all experiments was 1 mm/min.

Table 1. ΔV_{sp} and P_{in} of various LN samples

σ_{max} (MPa)	ΔV_{sp} (cm ³ /g)	P_{in} (MPa)
0	1.60	2.6
2	1.45	3.2
4	1.30	3.4
6	1.10	4.2

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The competing mechanisms between solid nanopore deformation and liquid invasion for non-wetting liquid/nanopores systems under compression are addressed.