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Intrusion and extrusion of water in hydrophobic nanopores

Antonio Tinti[a], Alberto Giacomello[a,1], Yaroslav Grosu[b], and Carlo Massimo Casciola[a]

Author Affiliations

[a]Dipartimento di Ingegneria Meccanica e Aerospaziale, Sapienza Università di Roma, 00184 Rome, Italy;

[b]CIC Energigune, Miñano 01510, Spain

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Significance

Molecular springs, constituted by nanoporous materials immersed in a nonwetting liquid, are compact, economical, and efficient means of storing energy, owing to their enormous surface area. Surface energy is accumulated during liquid intrusion inside the pores and released by decreasing liquid pressure and thus triggering confined cavitation. State-of-the-art atomistic simulations shed light on the intrusion and extrusion of water in hydrophobic nanopores, revealing conspicuous deviations from macroscopic theories, which include accelerated cavitation, increased intrusion pressure, and reversible intrusion and extrusion processes. Understanding these nanoscale phenomena is the key to a better design of molecular springs as it allows relating the characteristics of the materials to the overall properties of the devices, e.g., their operational pressure and efficiency.

Abstract

Heterogeneous systems composed of hydrophobic nanoporous materials and water are capable, depending on their characteristics, of efficiently dissipating (dampers) or storing ("molecular springs") energy. However, it is difficult to predict their properties based on macroscopic theories—classical capillarity for intrusion and classical nucleation theory (CNT) for extrusion—because of the peculiar behavior of water in extreme confinement. Here we use advanced molecular dynamics techniques to shed light on these nonclassical effects, which are often difficult to investigate directly via experiments, owing to the reduced dimensions of the pores. The string method in collective variables is used to simulate, without artifacts, the microscopic mechanism of water intrusion and extrusion in the pores, which are thermally activated, rare events. Simulations reveal three important nonclassical effects: the nucleation free-energy barriers are reduced eightfold compared with CNT, the intrusion pressure is increased due to nanoscale confinement, and the intrusion/extrusion hysteresis is practically suppressed for pores with diameters below 1.2 nm. The frequency and size dependence of hysteresis exposed by the present simulations explains several experimental results on nanoporous materials. Understanding physical phenomena peculiar to nanoconfined water paves the way for a better design of nanoporous materials for energy applications; for instance, by decreasing the size of the nanopores alone, it is possible to change their behavior from dampers to molecular springs.

molecular springs | molecular dynamics | hysteresis | rare event methods | hydrophobic nanoporous materials