Tuning wetting-dewetting thermomechanical energy for hydrophobic nanopores: Preferential intrusion[1]

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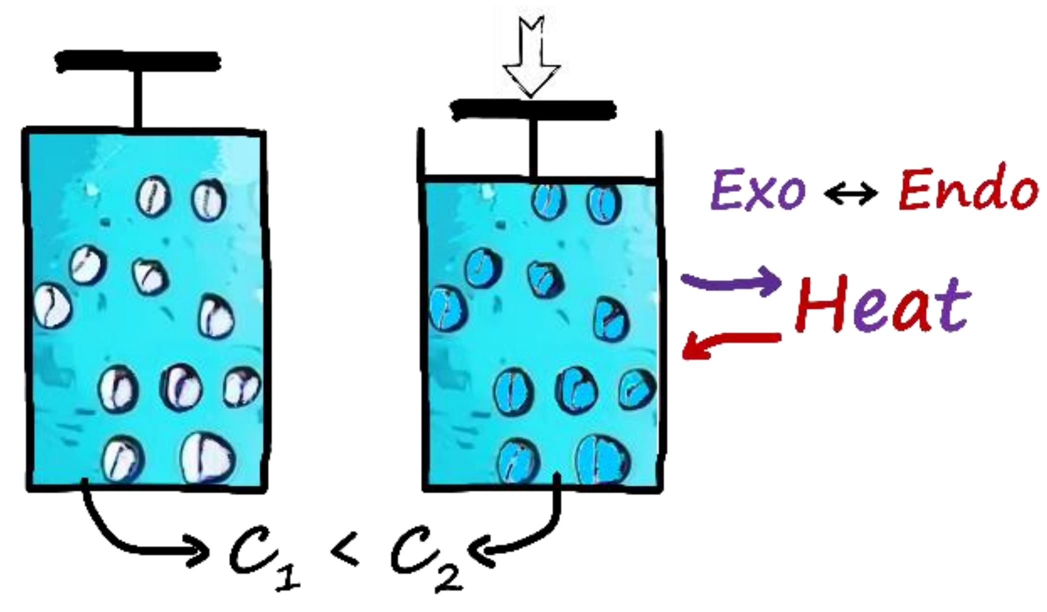
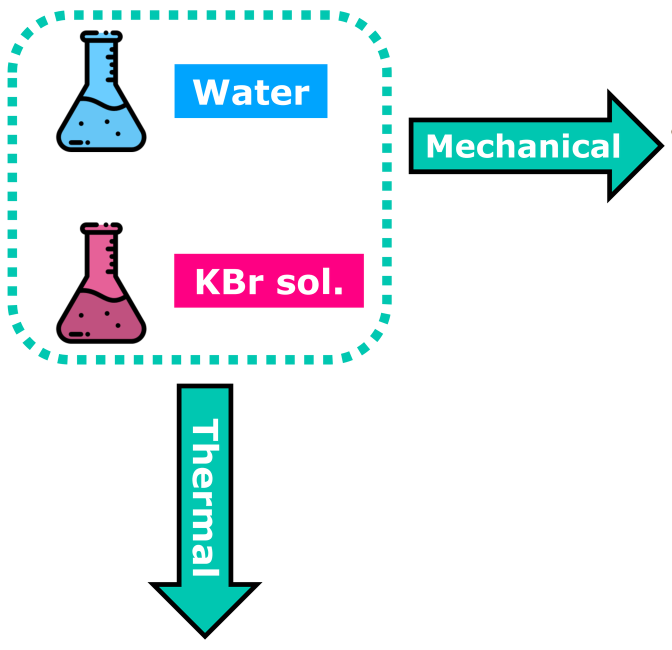
Introduction

The thermomechanical energy of compression/decompression, which is relevant to many industrial and natural processes, is a prominent property of thermodynamic systems[2]. Unfortunately, this property is challenging to tune due to fundamental limitations for simple fluids[3]. However, in this presentation, we demonstrate via direct experimental and atomistic observations that these fundamental limitations can be overcome by exploiting the preferential intrusion of water from aqueous solutions into sub-nanometer pores. We suggest this genuinely sub-nanoscale phenomenon has the potential to develop into a strategy for controlling the thermomechanical energy of microporous liquids as well as for tuning the heat of wetting/dewetting of nanopores. This effective control would be relevant to a great variety of natural and technological processes such as the separation of liquids, liquid-phase chromatography, porosimetry, energy dissipation, conversion and storage, biological and bioinspired channels and many more[4,5].



Results

Experiments



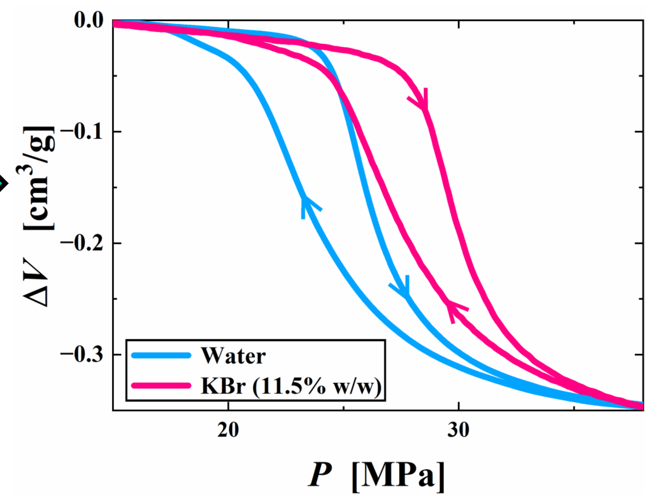


Fig. 1 Compression (intrusion)/decompression (extrusion) PV-isotherms

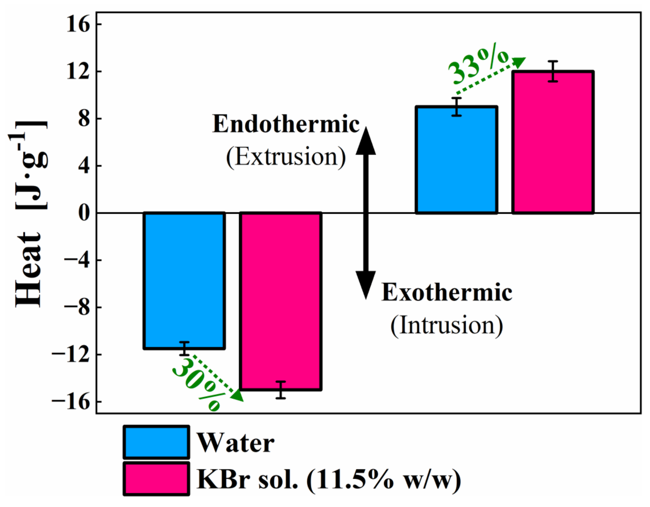


Fig. 2 Intrusion and extrusion heats where exothermic in negative and endothermic in positive.

Thermal & mechanical performances affected

Simulations

MD simulation of intrusion

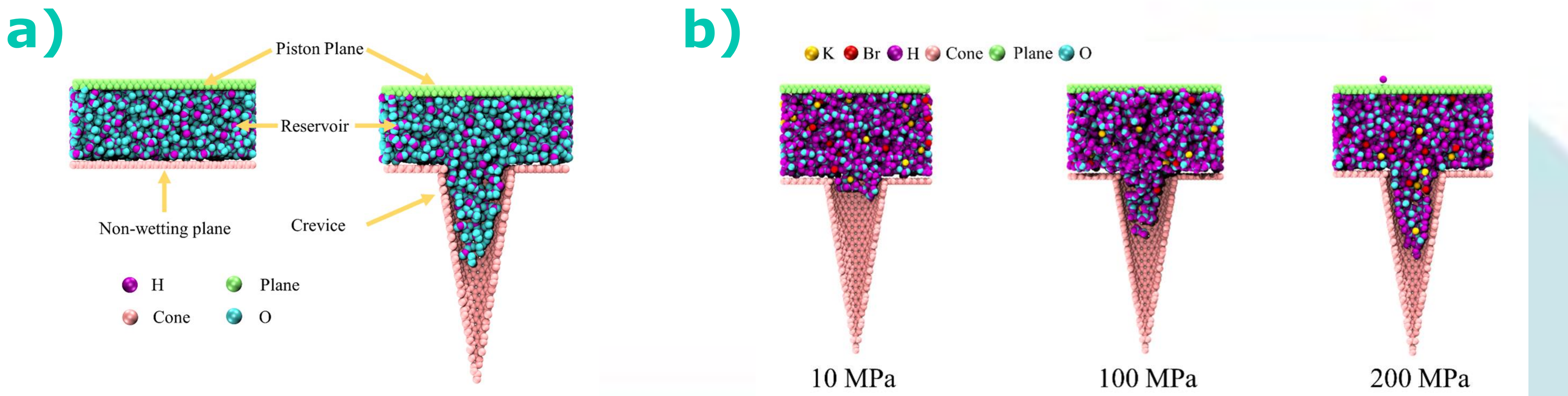


Fig. 3 a) Configurations to simulate intrusion where the first system consists of a liquid reservoir situated between two flat planes and the second system where a flat plane is transformed into a plane featuring a 2 nm diameter hole with a crevice (nano-cone). **b)** Snapshots of the Visual Modelucar Dynamics (VMD) for the intrusion of the KBr solution at 10, 100 and 200 Mpa.

MD results

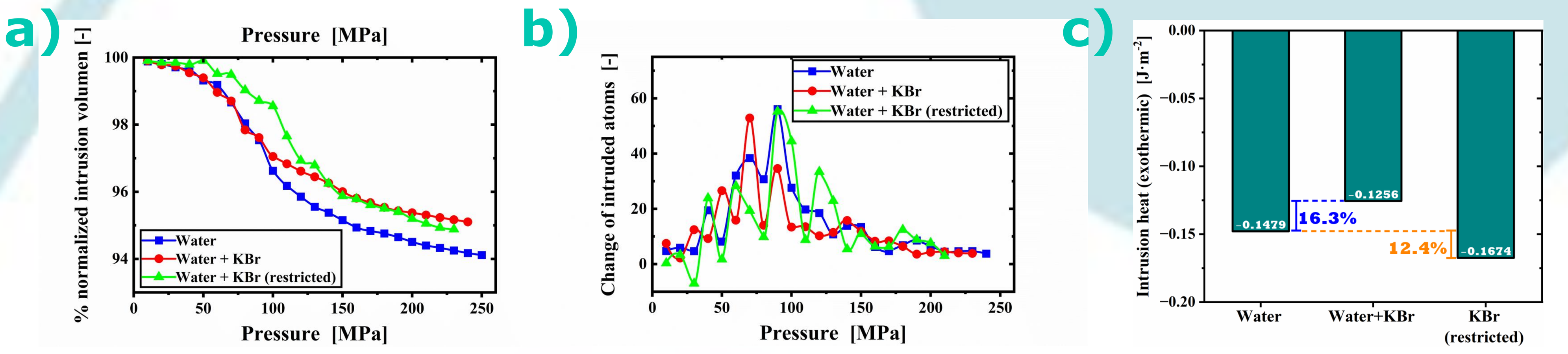


Fig. 4 a) Percentage of water not intruding into the crevice as a function of pressure. Data are normalized with respect to the system at atmospheric pressure. Atomistic counterpart of the experimental variation of volume *vs* pressure remarking that cannot be expressed in volume variation per gram of porous material like in experiments, because the ratio between the volume of cavities and mass of the solid differs from that of ZIF-8. Three simulated alternatives, i.e., water (blue), KBr solution with salt allowed to enter the cavity (red) and KBr solution with salt prevented from entering the cavity (green). **b)** The change in the number of intruded atoms with respect to the previous pressure point depending on the pressure for the three simulated alternatives. **c)** The intrusion heat for the three simulated alternatives i.e., water, free-KBr and restricted-KBr atoms.

Int/ext heats at different concentrations

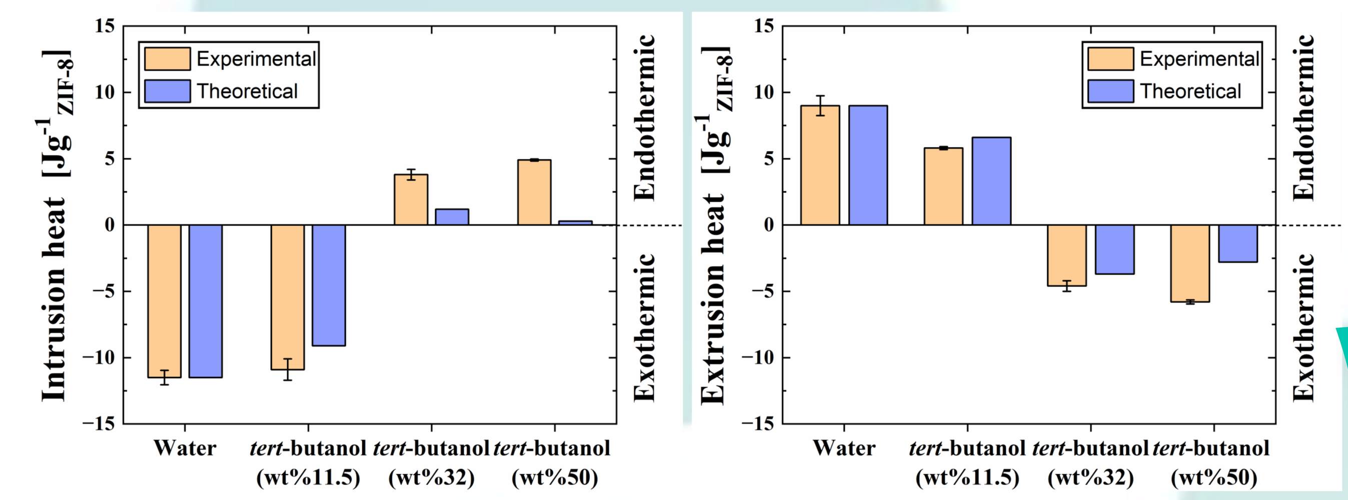
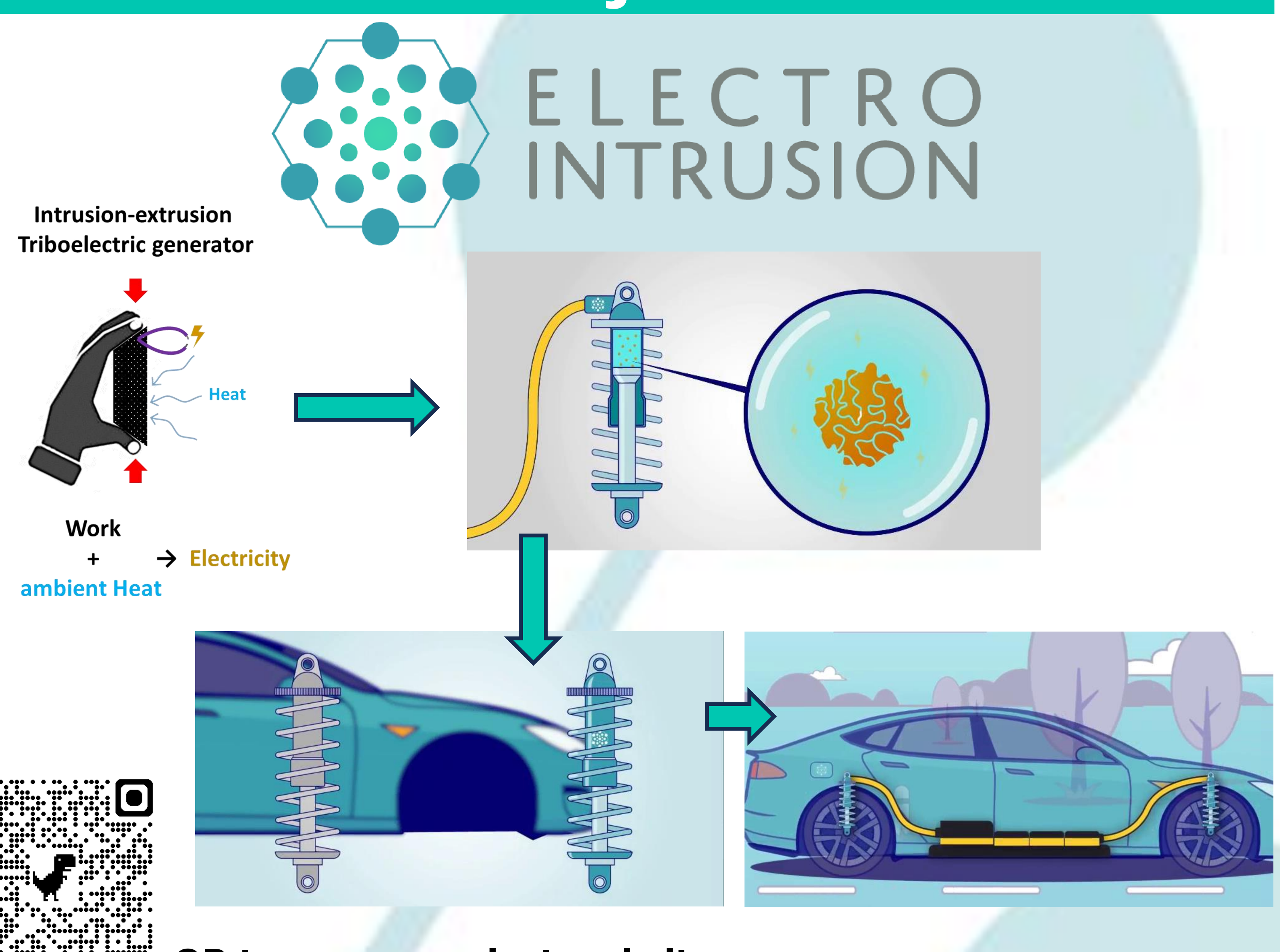


Fig. 5 Thermal performance for {ZIF-8+ tert-butanol solution}.

Thermal performance tunning

Project



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Conclusions

- Thermomechanical energetics of microporous liquids can be tuned.
- Experimental and theoretical results show that both mechanical and thermal energies of the intrusion-extrusion process can be tuned via preferential intrusion.
- By varying the concentration of solution, one can achieve an endothermic or exothermic compression/decompression process.
- With further development, results suggest that preferential intrusion of species from a solution into sub-nanoporous materials can become a strategy for tuning the heat of the intrusion-extrusion process relevant to technological and natural systems.

Acknowledgments

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