Pressure driven wetting of a model nanopore

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European Research Council
Established by the European Commission

Heterogeneous lyophobic systems

Recent attention has been given to **liquid springs**, lyophobic nanoporous materials that can act as **springs**[1] or **energy dissipators**[2] when pressure is applied to them.

Liquid springs consist of a container with some kind of **non-wetting liquid**, like water, and a **lyophobic nanoporous material**. When pressure is applied to the liquid it will start intruding into the nanoporous material. When the pressure is decreased the liquid can extrude and the container returns to the original volume.

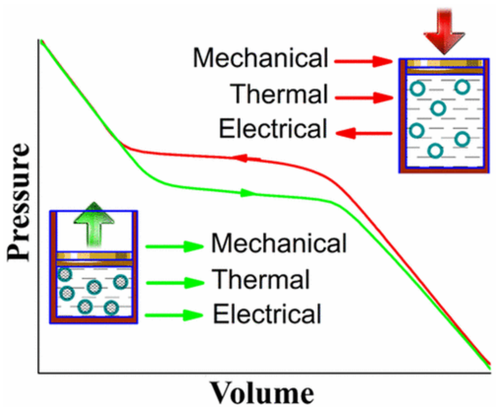
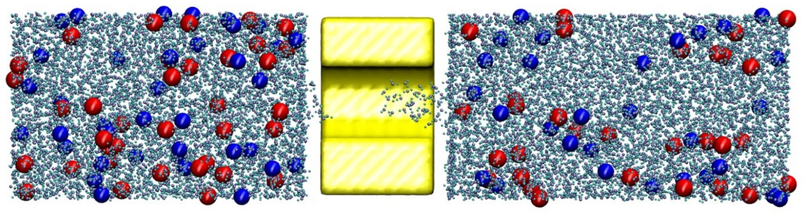


Figure taken from [2]

If this process has no **hysteresis**, it can be used as a **mechanical energy accumulation device**. When the intrusion and extrusion pressure are different one observes an **hysteresis loop** which is associated with a **dissipation of energy** like which can be used in **shock absorbers** or **bumpers**.



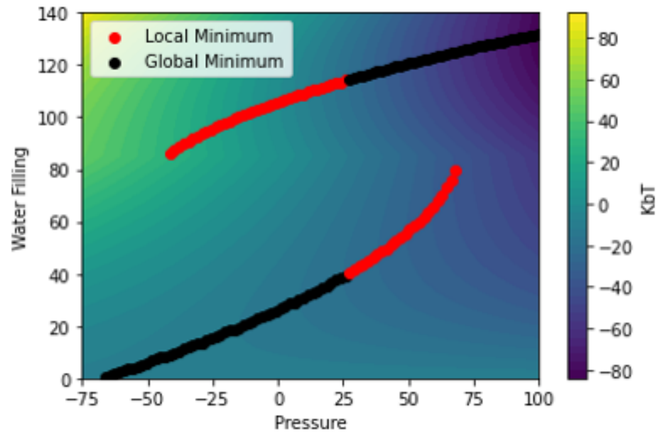
Molecular dynamics simulations of **nanoporous materials** have been used to study **intrusion** and **extrusion** processes which cause the spring behaviour but it is not able to reach **experimental timescales**[3].

Free energy of a model nanopore

We used **restrained molecular dynamics** (RMD) to compute **the free energy** as a function of the **liquid filling** inside of the porous material providing knowledge of the stable or metastable states at a given **pressure**.

We computed the stable and metastable states from -70 to 100 MPa

to **model** the behaviour that would be observed when performing pressure cycles in **molecular dynamics** (MD).



The **filled(wet) state** is only favoured at pressures larger than 25MPa.

The **empty(dry) state** is still stable to pressures of around 60Mpa.

References

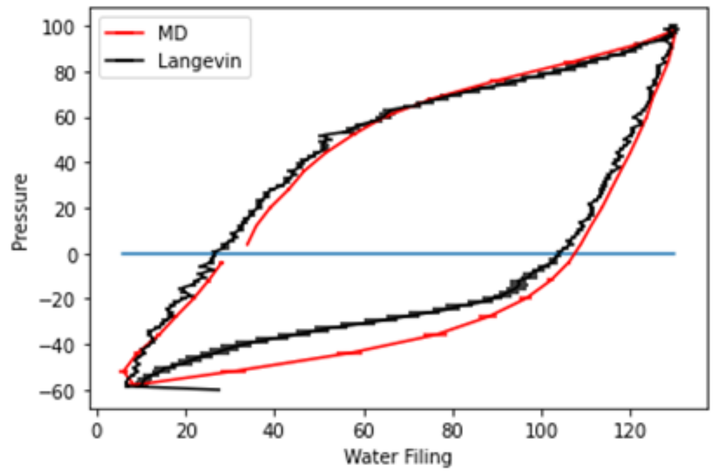
1 - Eroshenko, V. (2000), US Patent # 6,052,992
2 - Y. Grosu, et al., ACS Appl. Mater. Interfaces
3 - A. Tinti et al., PNAS
4 - S. Plimpton, J Comp Phys

This work was supported by the ERC Grant No. 803213

Dynamical methods

We used **LAMMPS**[4] to **simulate** the effect of a **piston compressing** and **decompressing** the system at a given rate and measured the filling level of the pore and the volume of the system.

Using the results obtained by RMD we performed **overdamped Langevin Dynamics** (LD) using the free energy as a **potential of mean force**(PMF), with a **reaction coordinate dependent diffusivity** and compared the pressure loops with the ones obtained in MD.



Both the **intrusion pressure** and the level of filling where **well captured** with the **extrusion pressure** being **understimated** by 10-20 MPa

An **histeresys loop** was observed as **expected** from the free energy calculations. This is the kind of loop observed in **dissipative systems.**

The transition between the **empty (high volume)** and **filled (low volume)** states happens only when the pressure is suficient for the **barrier of transition is small enough.**