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E-MRS 2022 Fall Meeting
19-22 September - Warsaw University of Technology - Poland

Thermomechanical and structural properties of {Cu_2(tebpz) MOF + water} molecular spring in a wide temperature range

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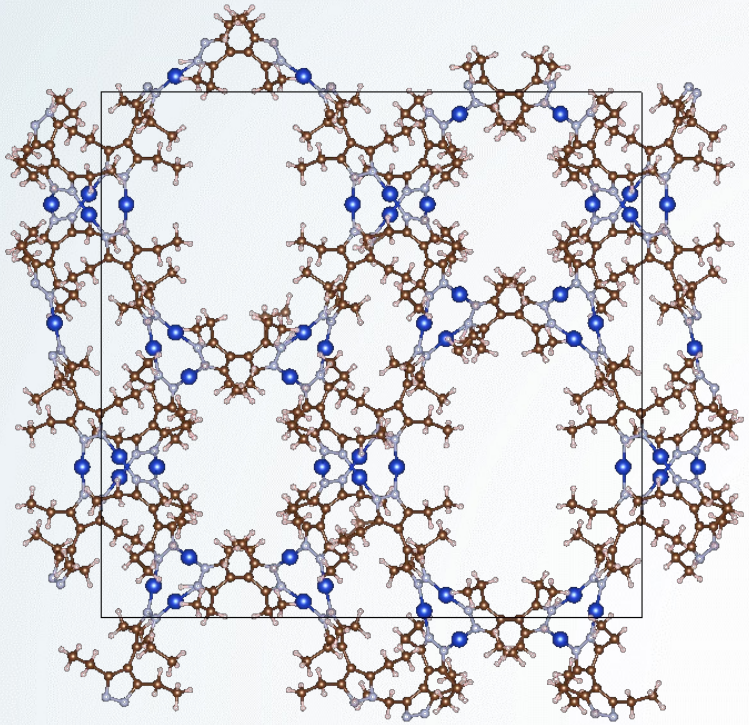
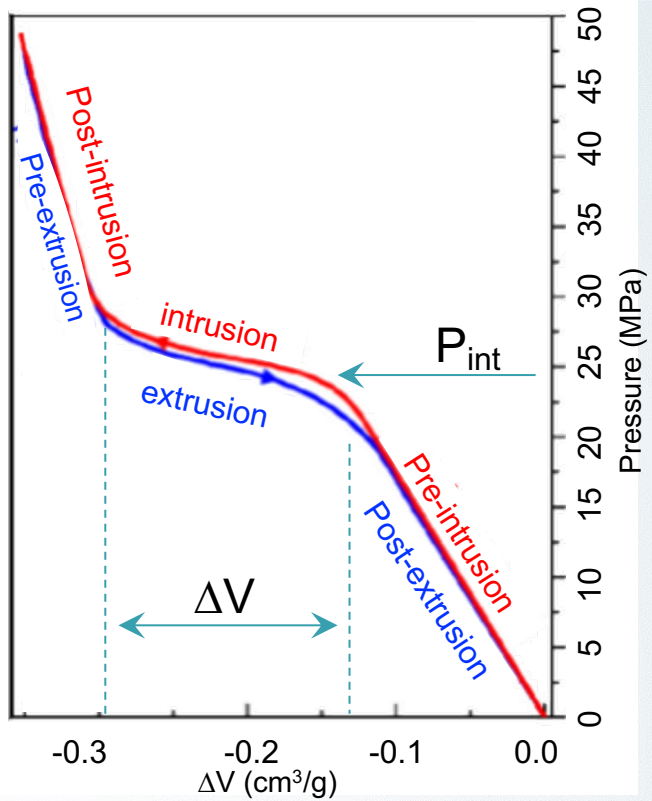


Cu_2L(L=3,3',5,5'-tetraethyl-4,4'-bipyrazolate)

$$E_{store} = P_{int}\,\Delta V$$



Porous Material	Pore topology	Liquid	P_i[MPa]	P_e[MPa]	ΔV[cm³/g]	E_i[J/g]	E_e[J/g]	Energy recovered	P hysteresis
Cu2(tebpz)	1D	H_2O	26-28	26-28	0.12	4.3	4.3	99%	0.6%

- 1 D nanoscale hydrophobic channels
- Mechanical Battery (aka Molecular Spring)
- Negative linear compressibility
- High thermal stability + structural robustness and flexibility after many intrusion-extrusion cycles

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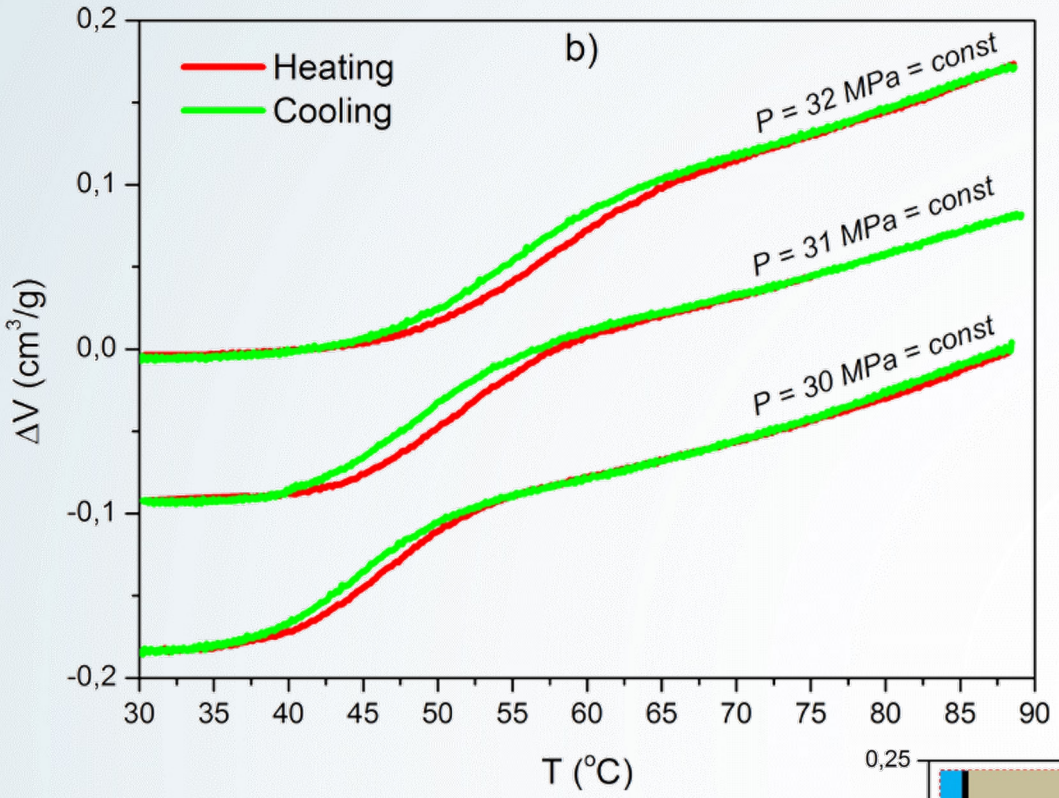
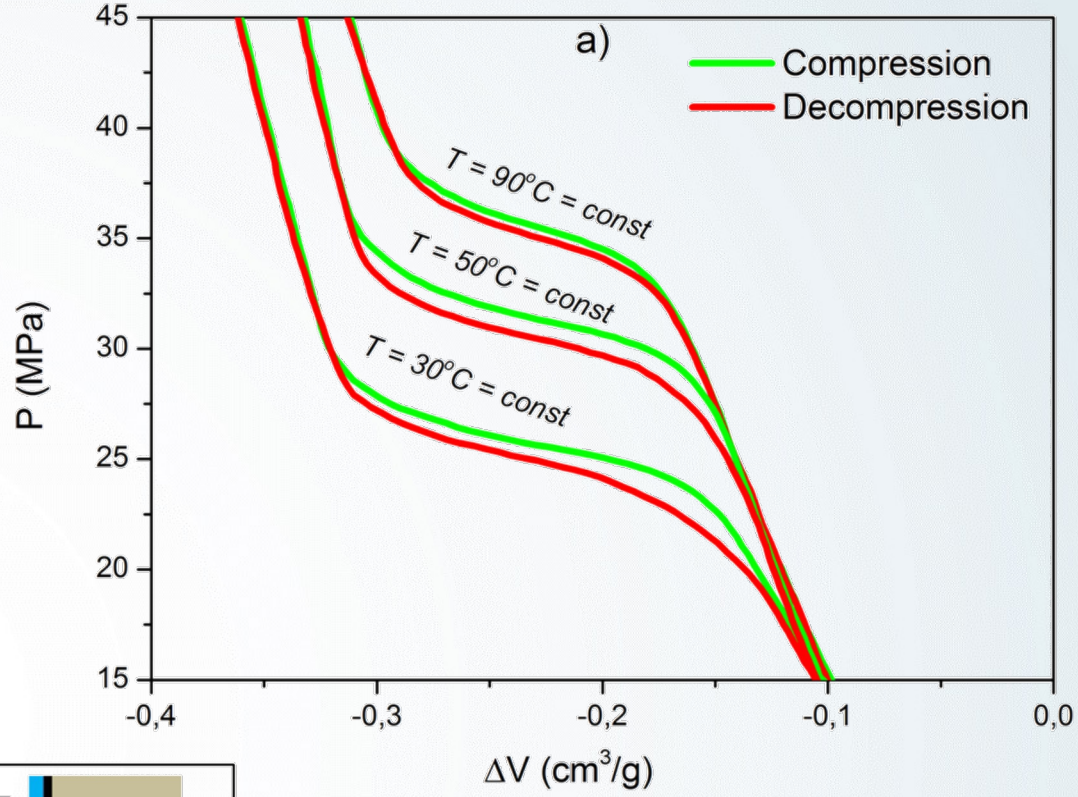
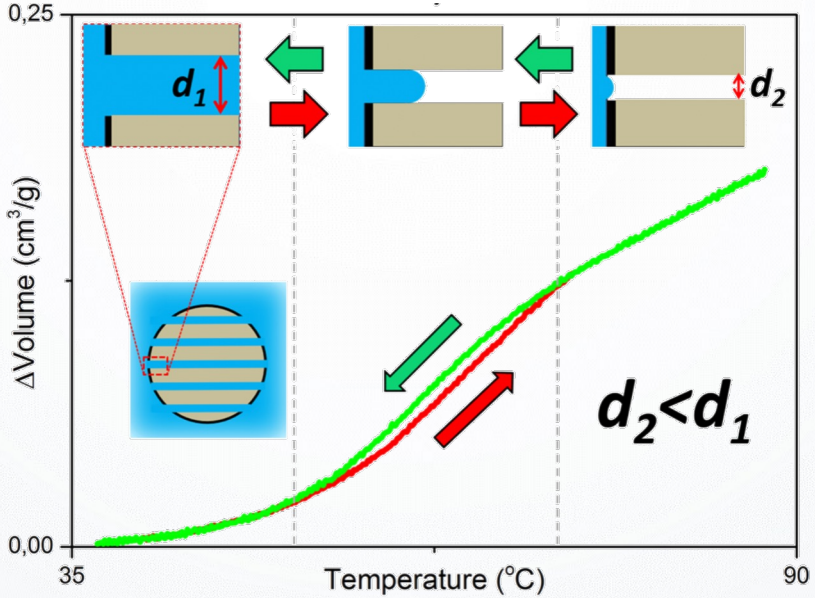
Wang J-H. et al.,Chem. Eur. J. **2014**, 20, 12004 – 12008; Grosu Y. et al., Chem. Phys. Chem **2016**, 17, 3359 –3364; Zajdel P. et al., J. Phys. Chem. Lett. **2021**, 12, 4951-4957; Lowe A. et al., Langmuir **2021**, 37, 4827-4835; Chorążewski M. et al., ACS Nano **2021**, 15, 9048-9056







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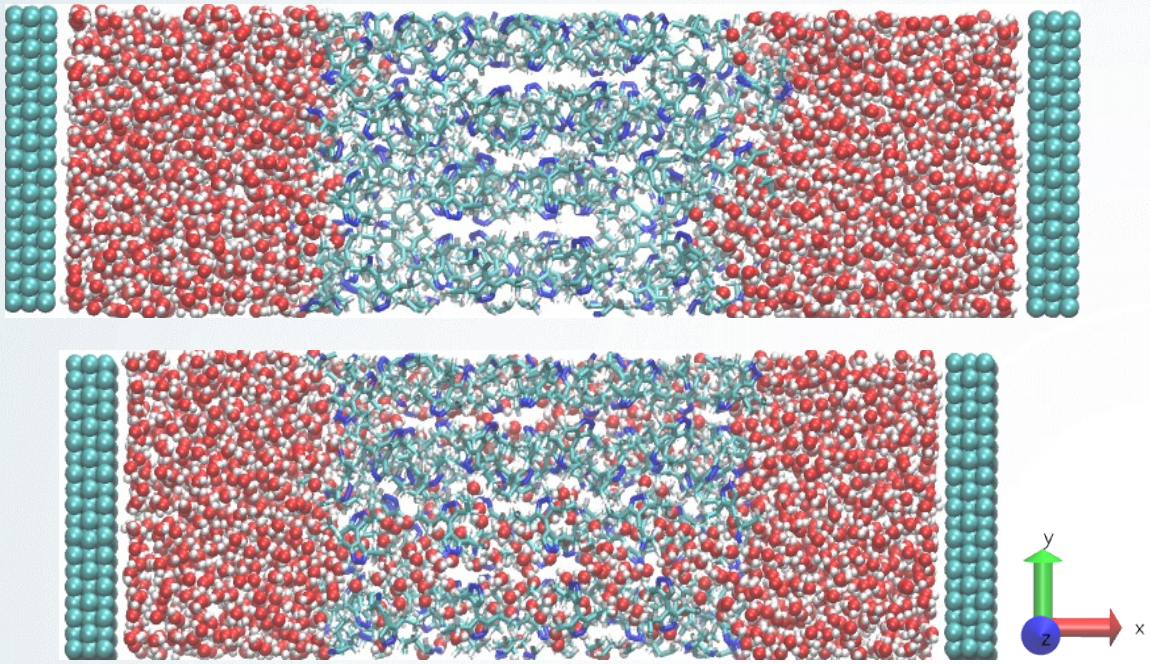
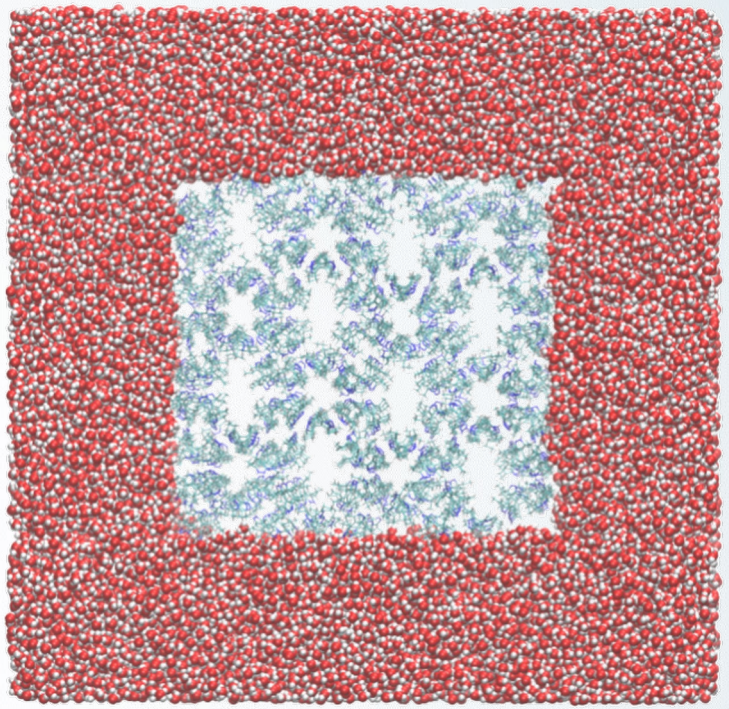
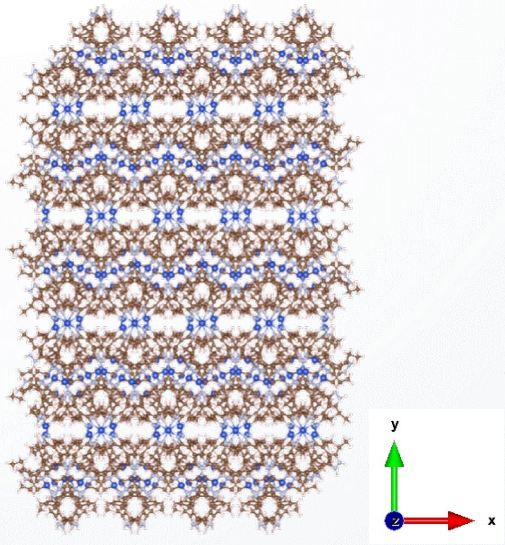
Chorążewski M. et al., ACS Nano **2021**, 15, 9048-9056; Zajdel P. et al., J. Phys. Chem. Lett. **2021**, 12, 4951-4957

Cu_2L slab



Cu_2L crystallite





Bulk vs Edge:

- Inner vs outer channels
- Lateral pores

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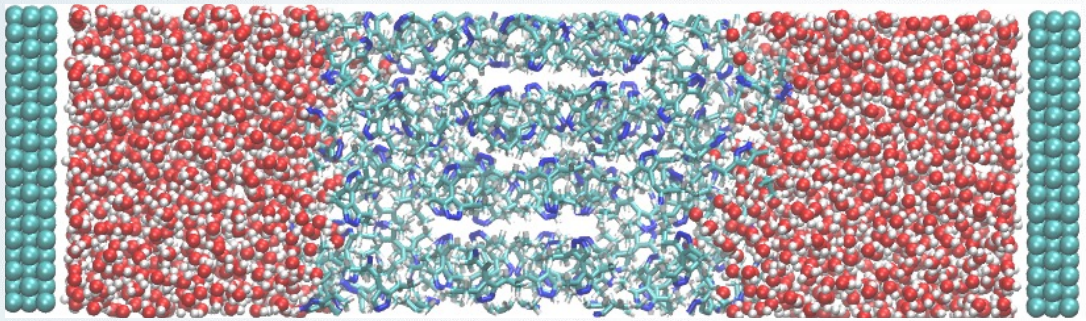
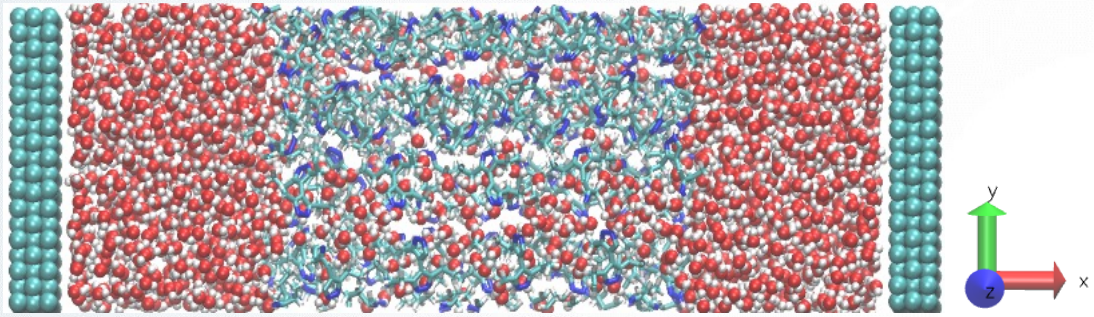
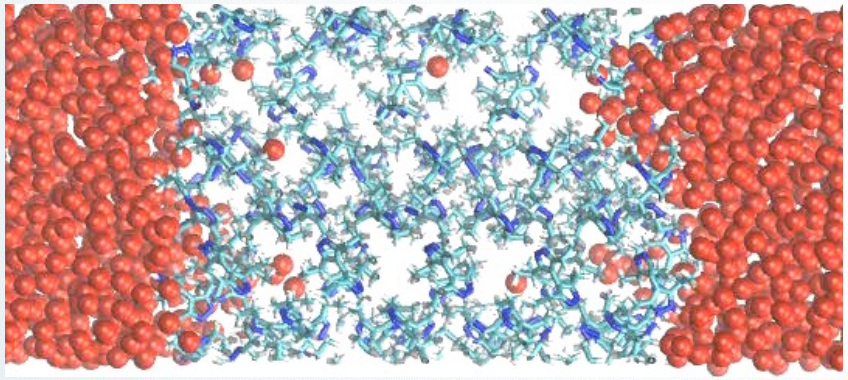
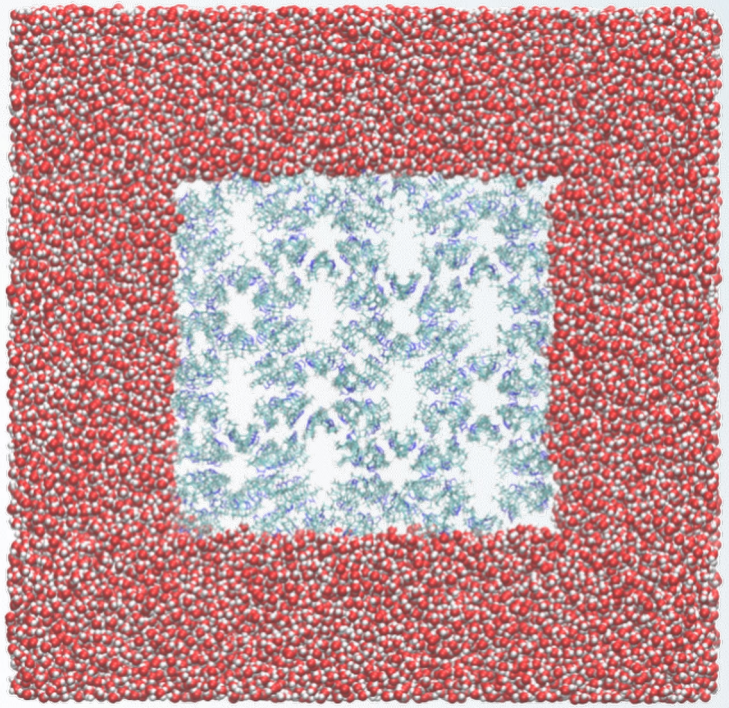
Cu_2L slab

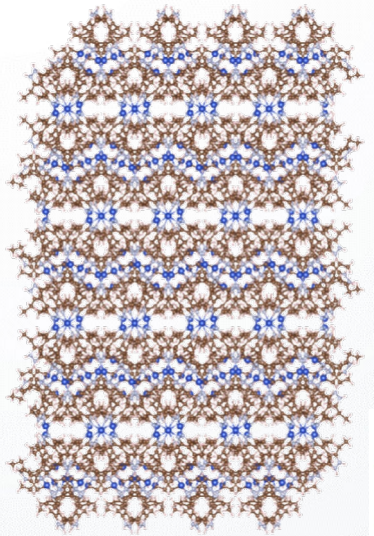


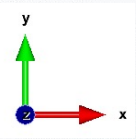




Cu_2L crystallite







Bulk vs Edge:

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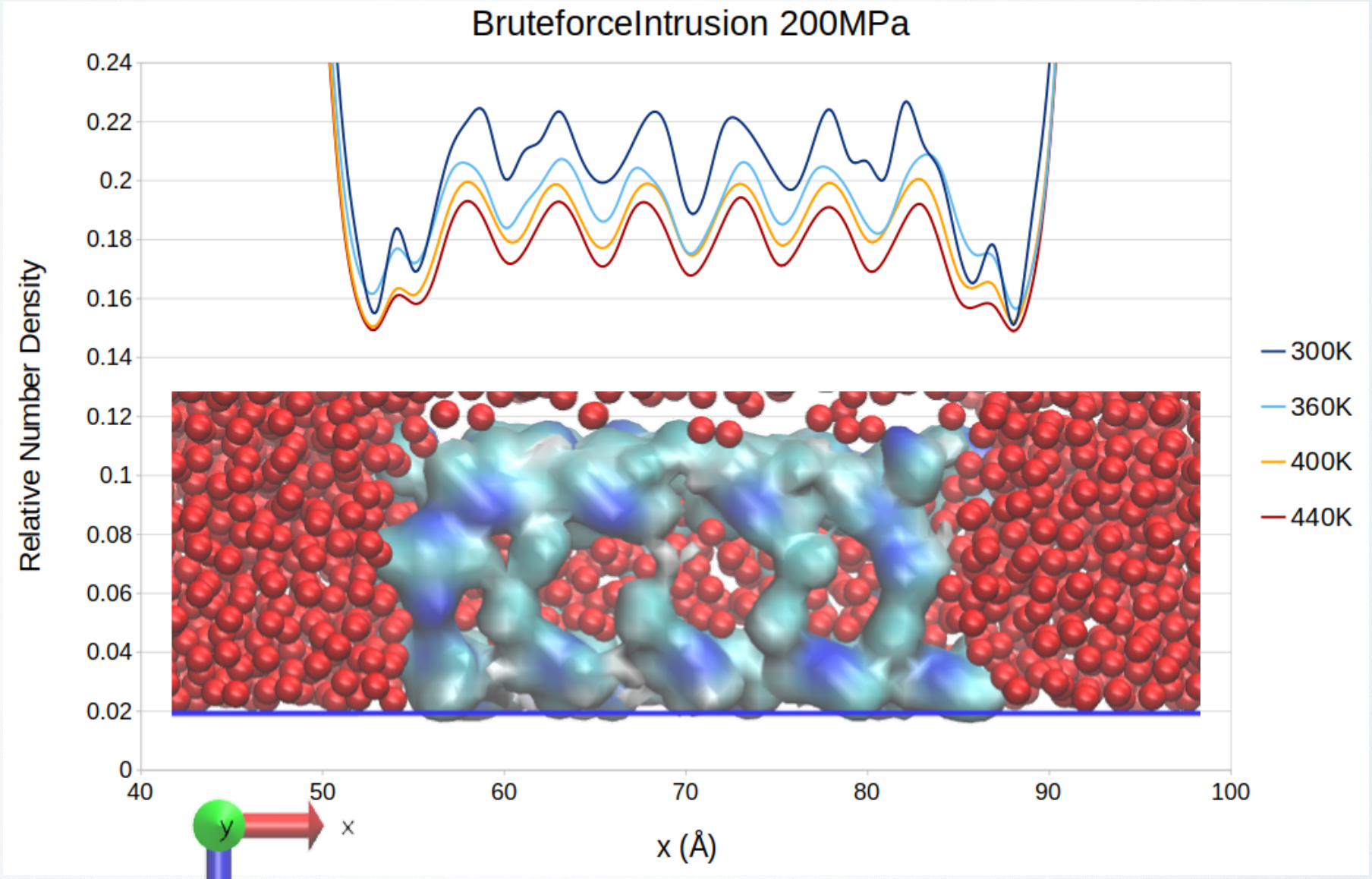
$$\Delta\rho^{int} \approx 16\%$$
$$\Delta\rho^{bulk} \approx 9\%$$



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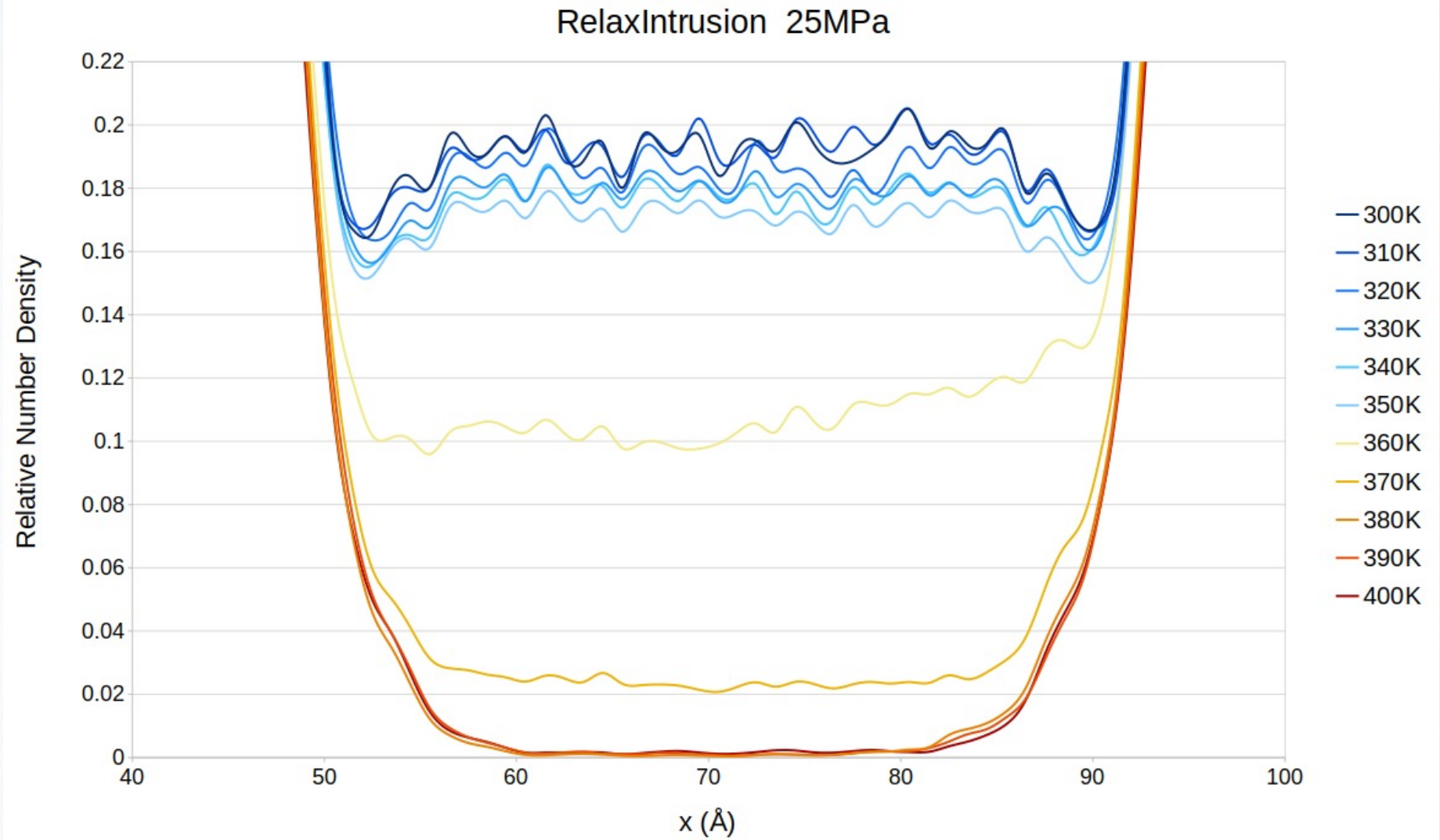
Consistent with experimental observations - Increasing temperature under a costant pressure results in a non-wetting liquid extrusion from the pores



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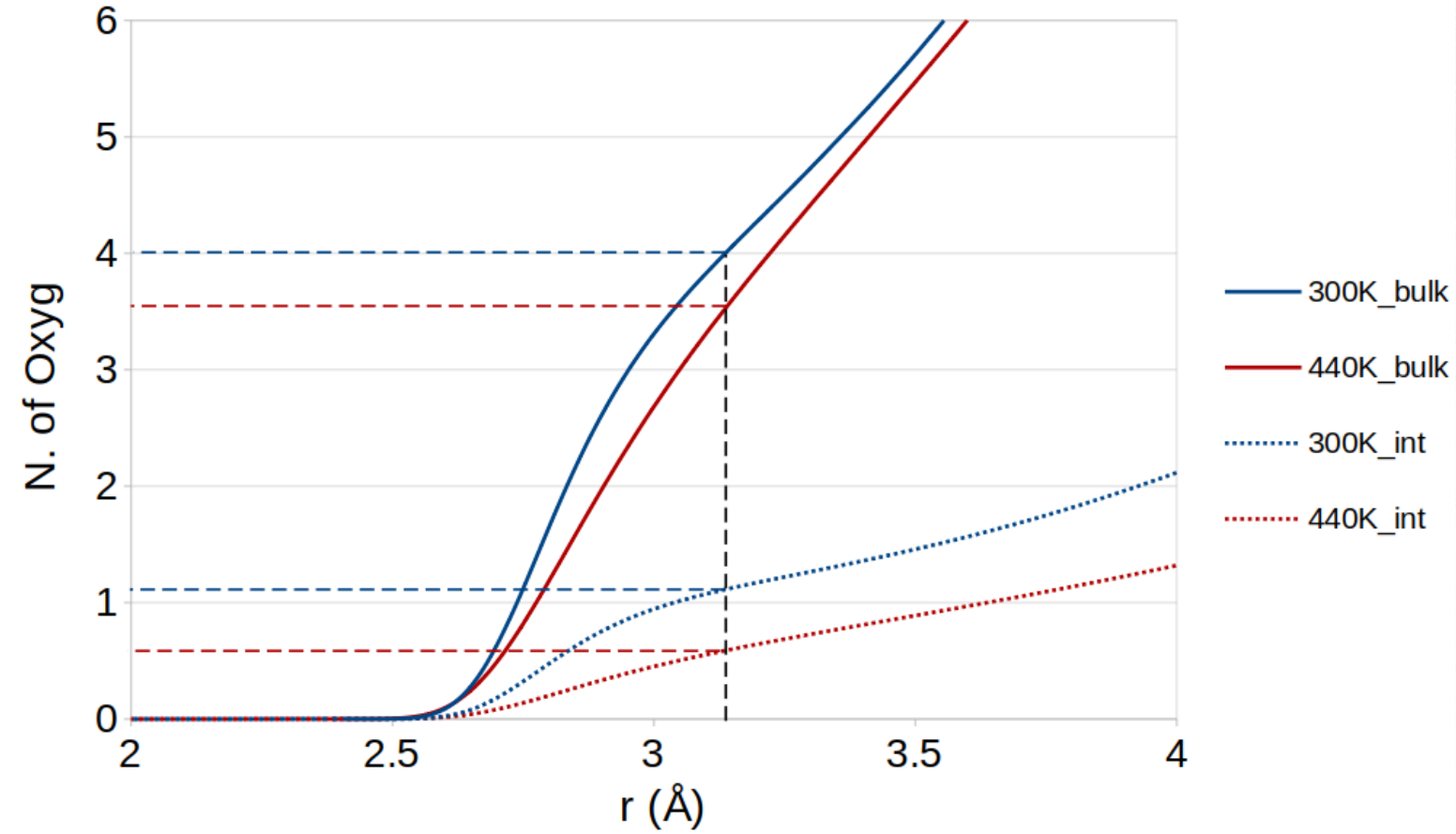
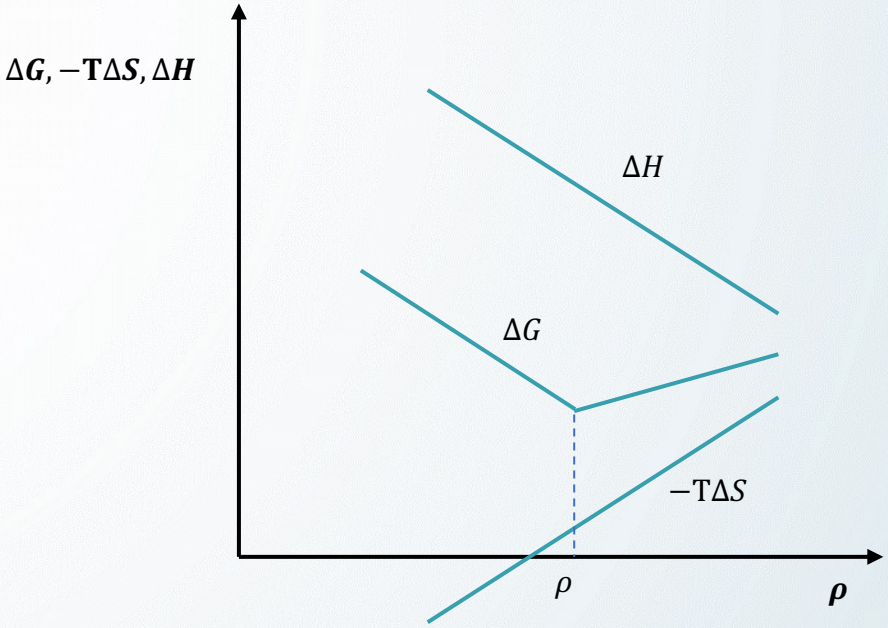
Intg g(r)



$$\Delta S \propto nRTln\frac{\rho_A}{\rho_B}$$

$$\Delta G = \Delta H - T\Delta S$$



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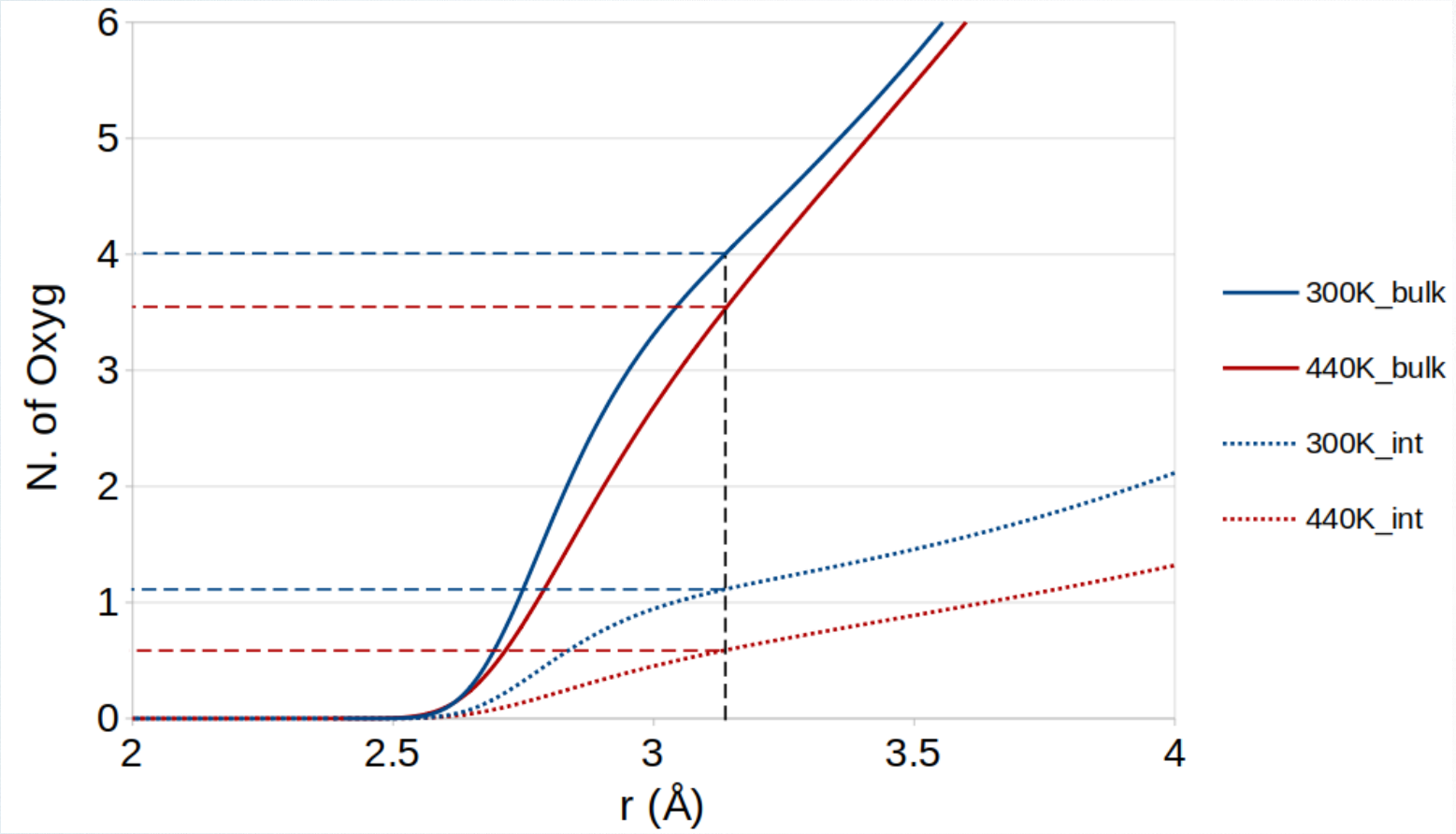
Intg g(r)



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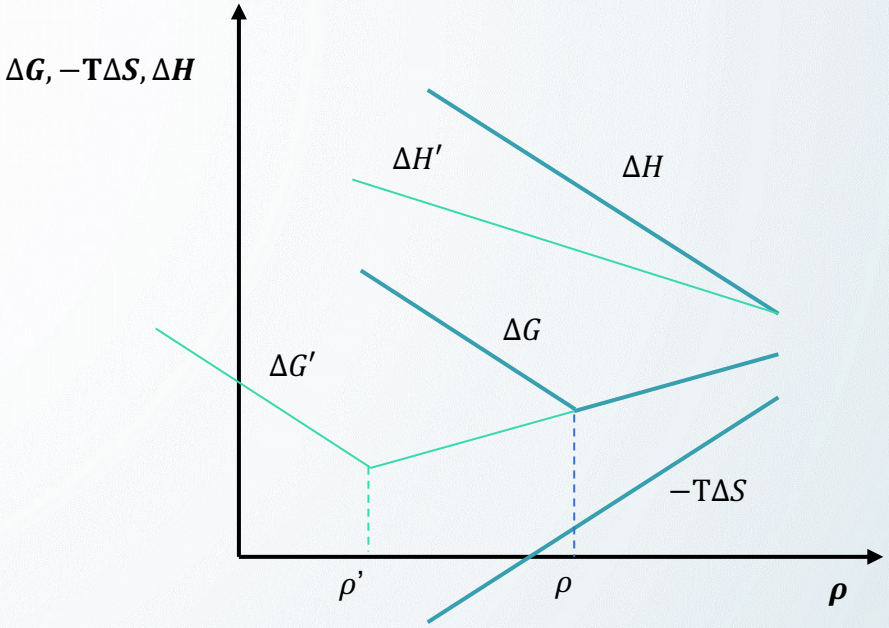

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Conclusions

- We investigated the phenomenon of intrusion/extrusion driven by both pressure and temperature in Cu2L, a MOF suitable for energy storage and conversion

- Consistently with experiments, and against simplistic models, we have shown that temperature increase can drive extrusion

- We presented preliminary results of the investigation of the origin of this phenomenon: in Cu2L temperature increase brings to a large reduction of confined water density and a contemporary increase of vapor density

Thanks for your attention!

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