European Union's Horizon 2020 research and innovation programme. grant agreement No 101017858

Retrospective and perspective of intrusion-extrusion research: experimental and technological point of view

Phase Transitions at the Nanoscale: Wetting of Nanoporous Materials, Cluster Formation, and Nanofriction Workshop, 23-26 June 2021 S. Anna in Camprena, Italy

Yaroslav GROSU

23rd June 2021

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INDEX

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Expertise, experience and scientific interests

- **Positions:**
  - Group leader at CIC energiGUNE research center, Spain
  - Research professor at University of Silesia, Poland

- **Interests:**
  - Interfacial phenomena, wettability, capillarity, corrosion, porous media
  - Energy storage, conversion, dissipation

Intrusion-extrusion process for energy applications

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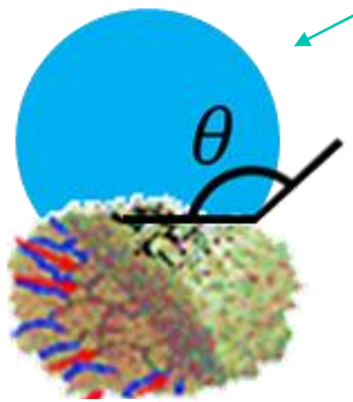
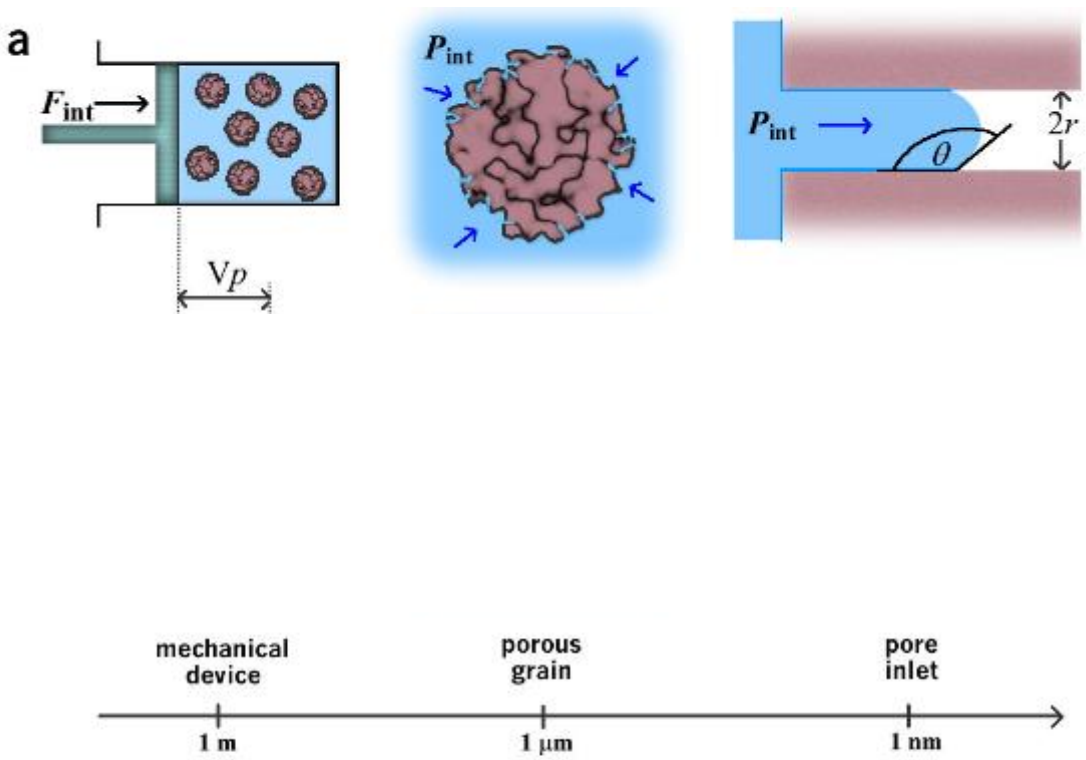
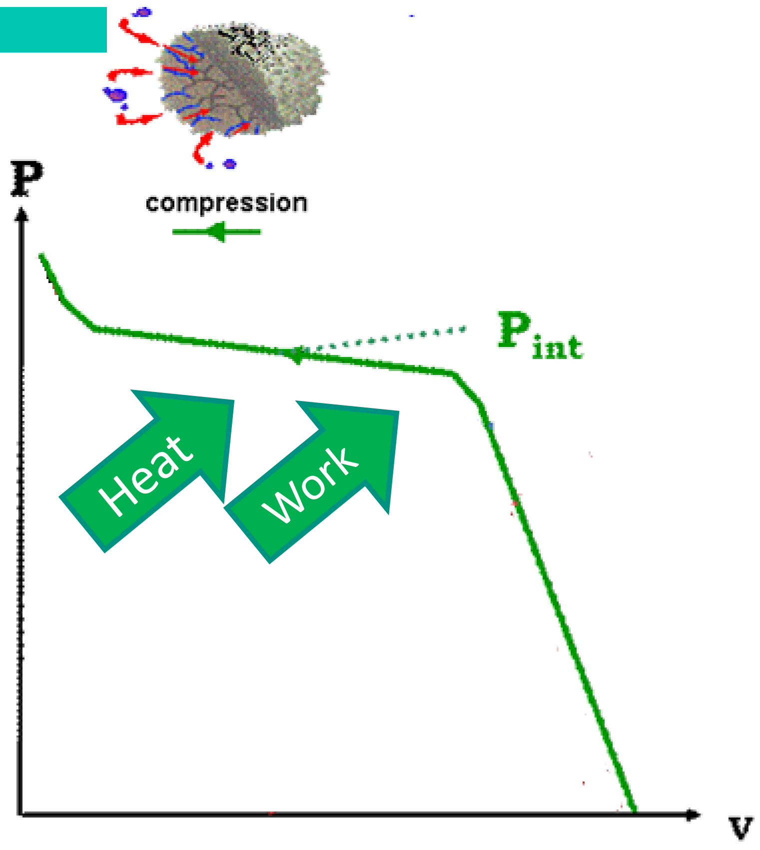


$$\textbf{Non} - \textbf{wetting}: \boldsymbol{\theta} > \textbf{90°}$$

> Intrusion-extrusion for energy applications

ENERGY BALANCE

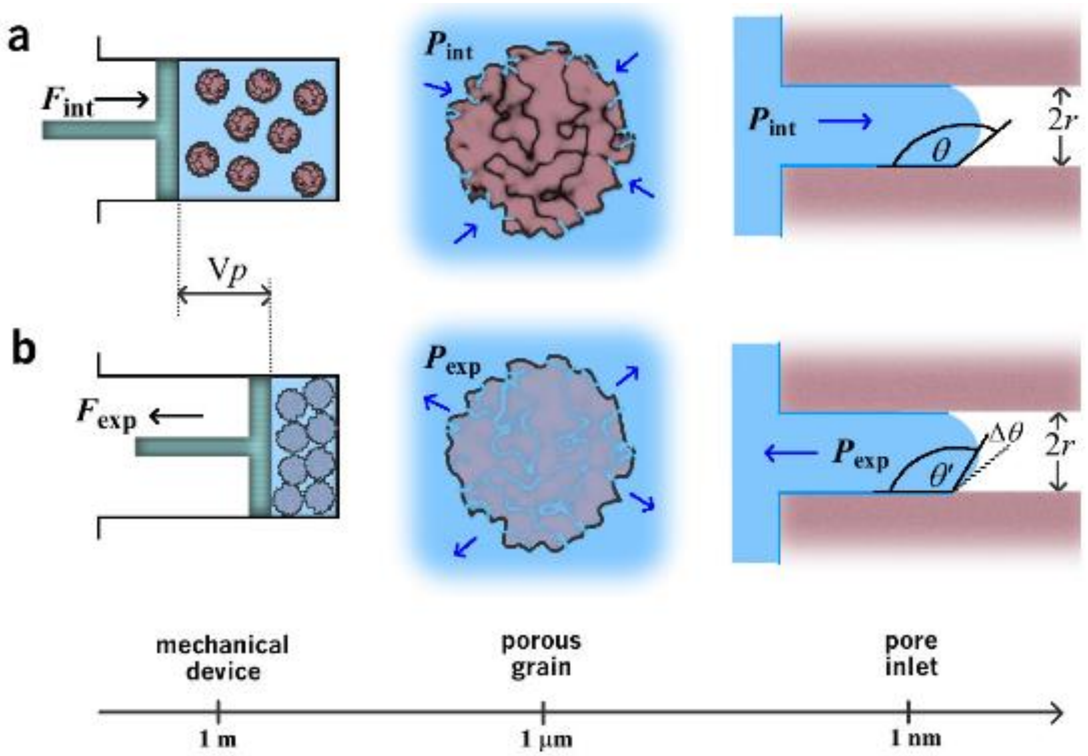


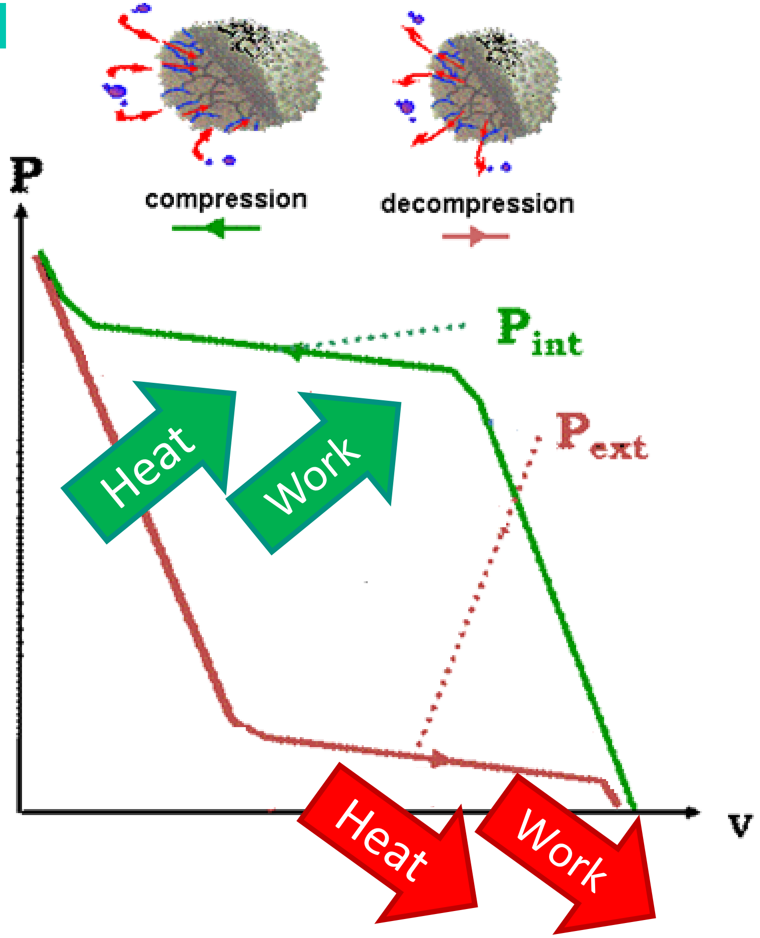


$$W_{intrusion} = P_{intrusion} \cdot \Delta V = P_{intrusion} \cdot V_{pores}$$

> Intrusion-extrusion for energy applications

ENERGY BALANCE



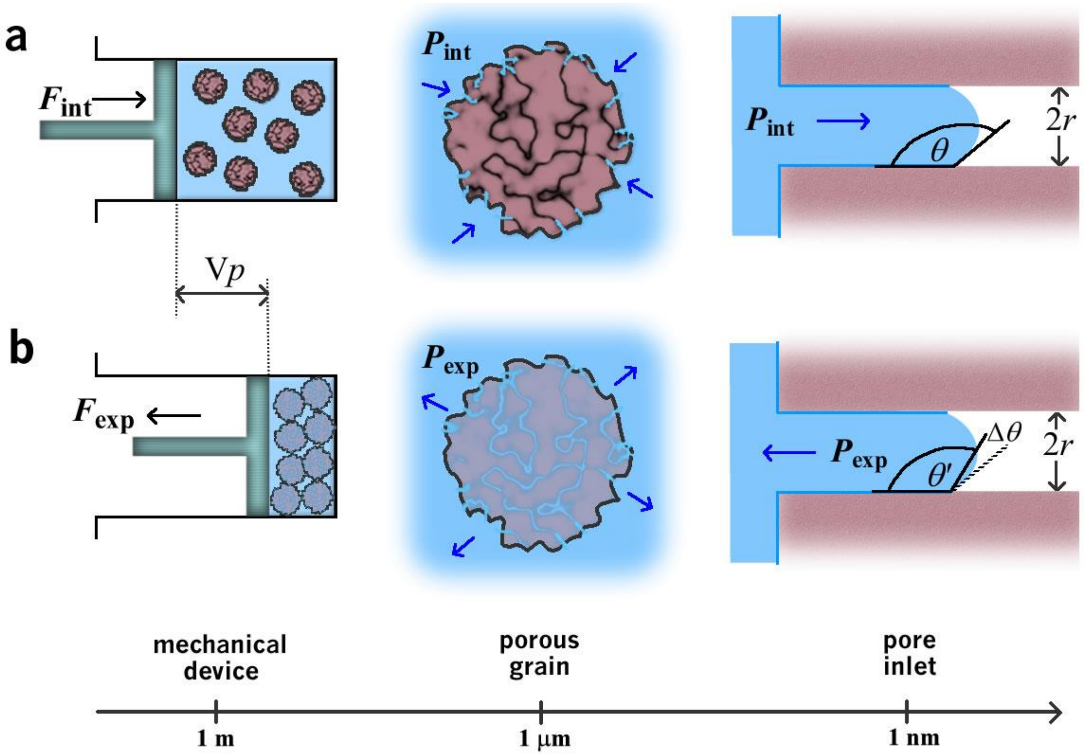


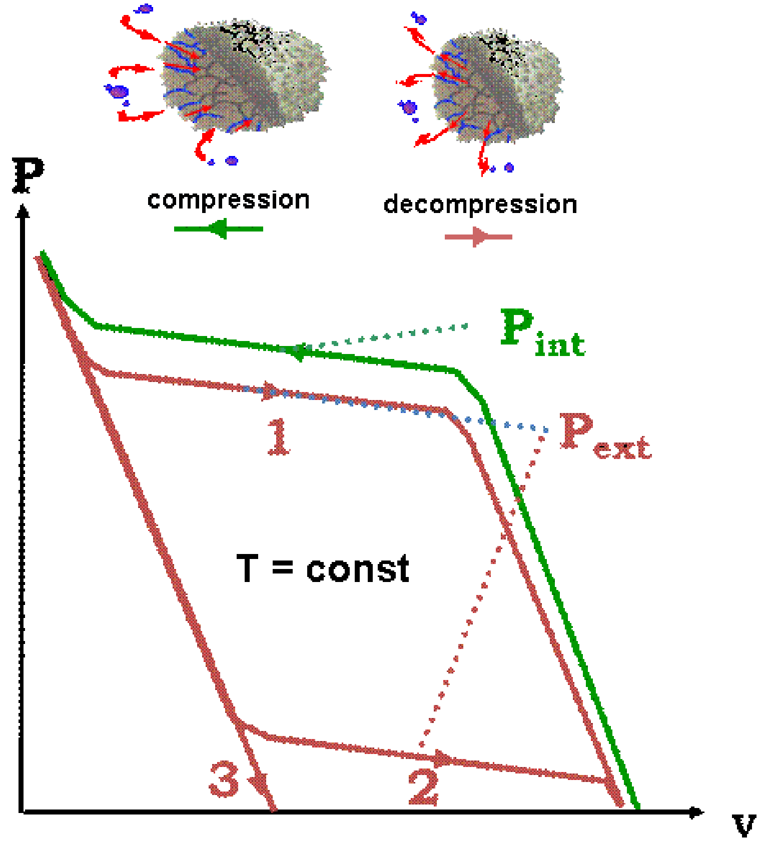
$$W_{intrusion} = P_{intrusion} \cdot \Delta V = P_{intrusion} \cdot V_{pores}$$

$$W_{extrusion} = P_{extrusion} \cdot \Delta V = P_{extrusion} \cdot V_{pores}$$

> Intrusion-extrusion for energy applications

ENERGY BALANCE





- Curve 1 – accumulation of energy
- Curve 2 – reversible dissipation of energy
- Curve 3 – irreversible dissipation of energy

Retrospective

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> Macroscopic view on the evolution of the topic

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Terminology ☹
- **Heterogeneous lyophobic systems**
- **Molecular springs**
- **Liquid springs**
- **Repulsive clathrates**

Fundamentals: int/ext pressure — heat of int/ext — mechanochemistry — electrification

1994 — 2019

Understanding crisis

Materials: oxides + alloys, grafted silica + water — salts solutions, zeolites + water — MOFs + water — stable MOFs or COFs?

2001 — 2013

Materials crisis

Valentine Eroshenko

Applications: bumpers, shock-absorbers, springs, thermal actuators — negative thermal expansion, negative compressibility, thermal energy storage, “flexible” shock-absorbers, regenerative shock-absorbers

2014 — 2021

~ 50 Classified patents

1980 idea — 1992 Partial declasification

Bumpers – retrospective

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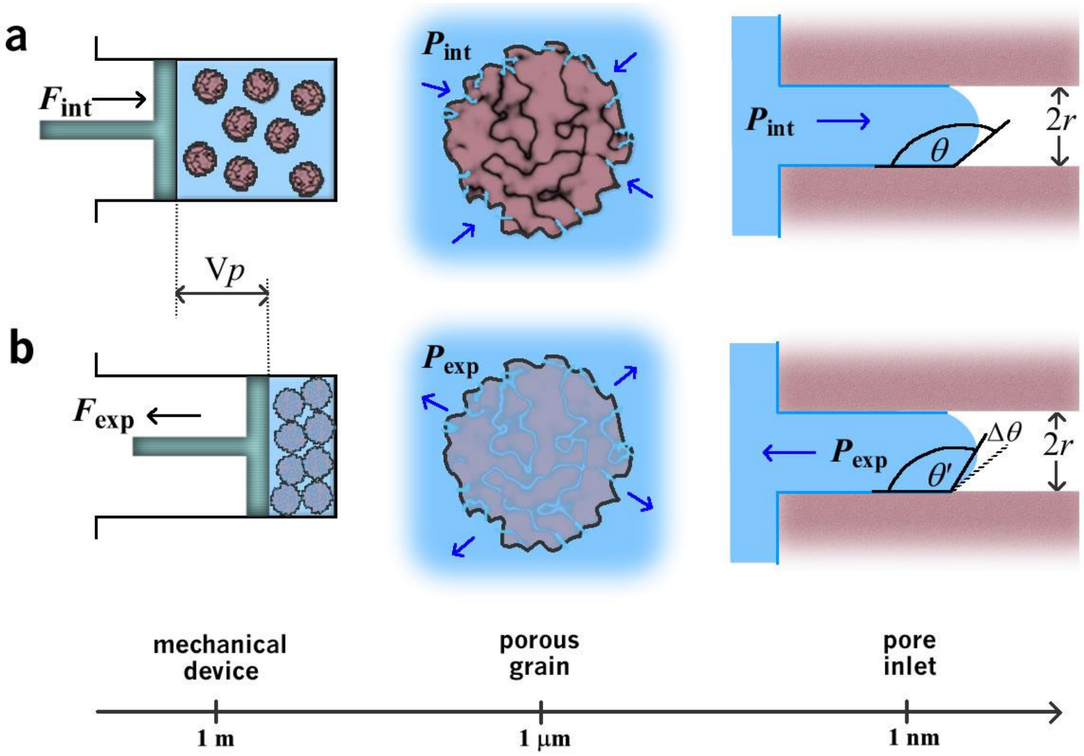
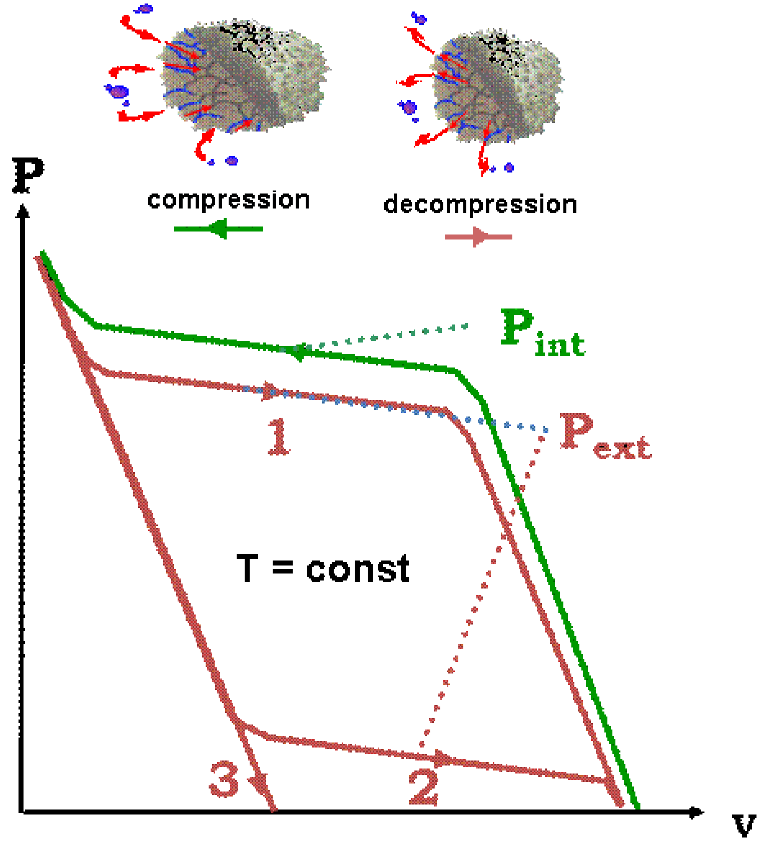
Intrusion-extrusion for energy applications

ENERGY BALANCE





- Curve 1 – accumulation of energy
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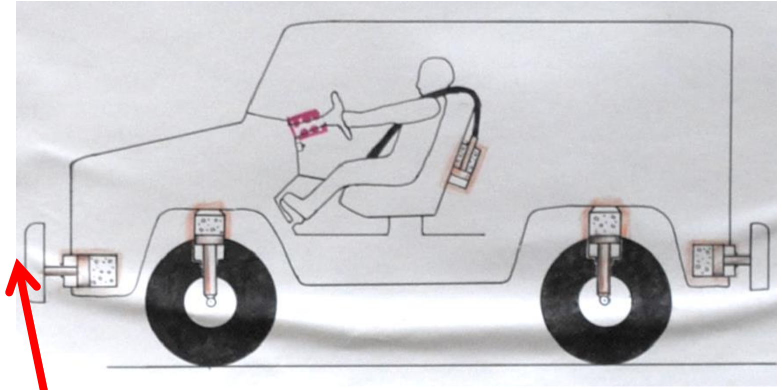
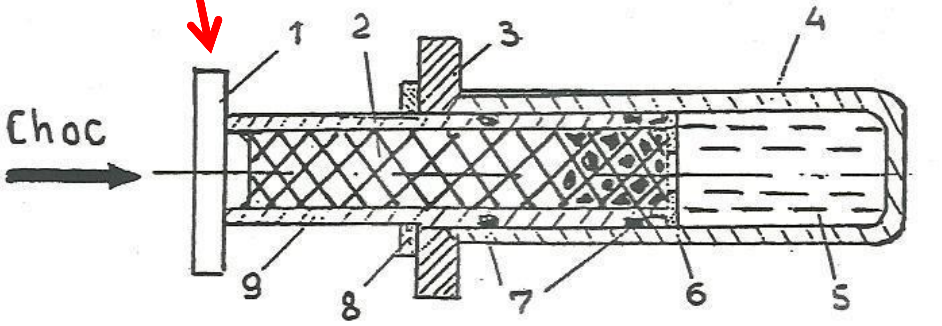
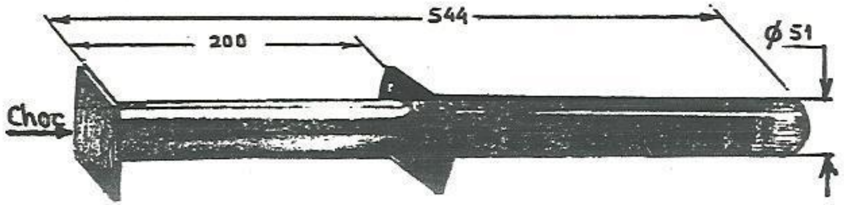
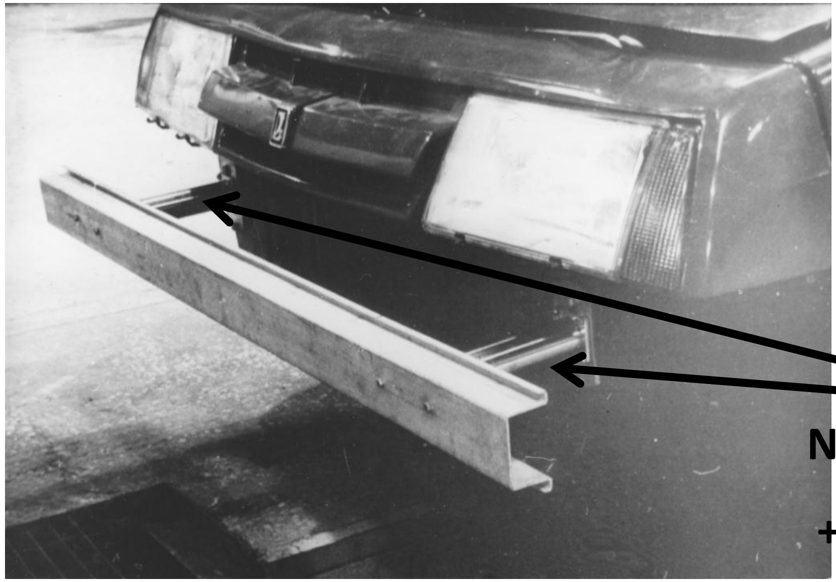
- Curve 3 – irreversible dissipation of energy

First intrusion-extrusion Bumper







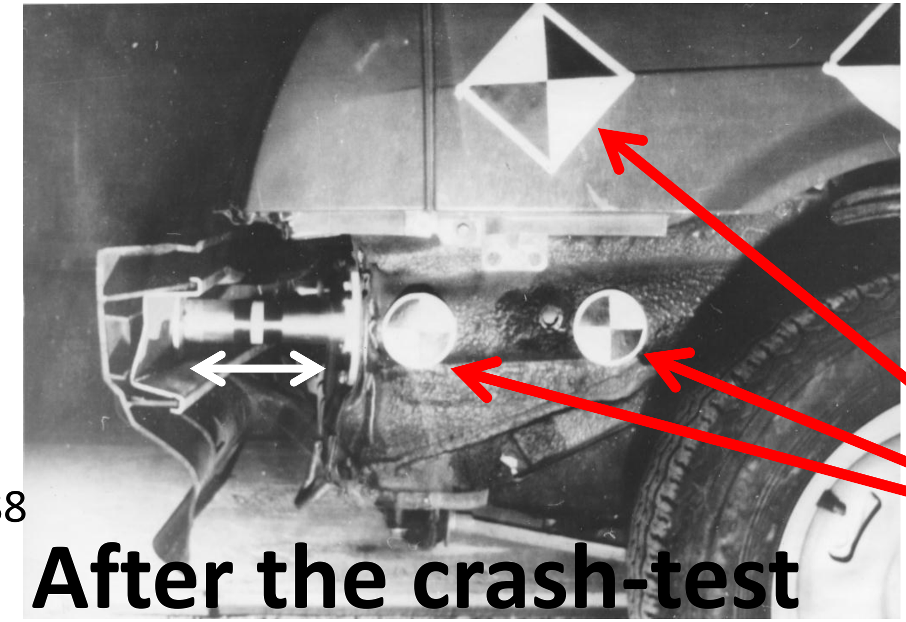


Nanoporous material

+ non-wetting liquid

Eroshenko ~1988

First intrusion-extrusion. *Crash-test*

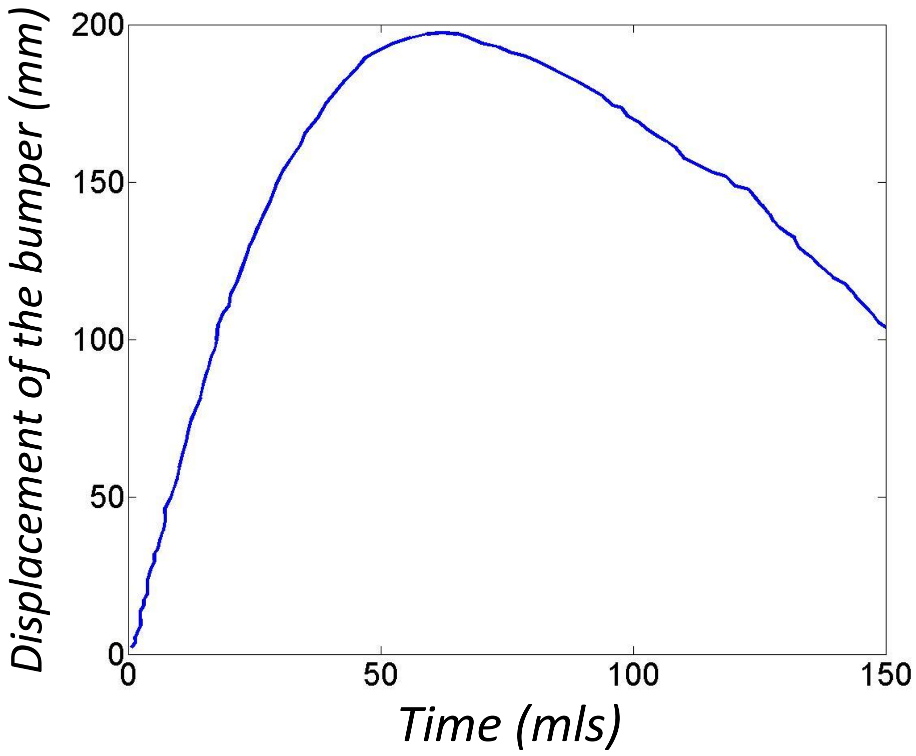


Eroshenko ~1988

Conditions:

Speed: 35-40 km/h

Mass of the car: 915 kg



No damage after the crash!

Bumpers – perspective

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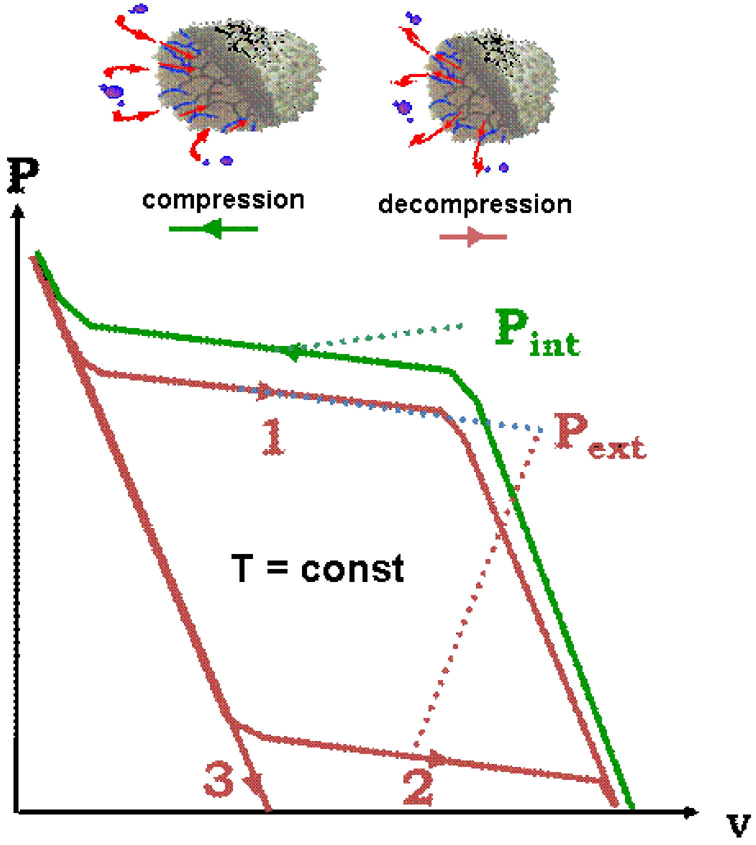
> Intrusion-extrusion for energy applications

ENERGY BALANCE

- Increase porosity
- Tune intrusion pressure
- Stability of porous material is not an issue
- Environmental characteristics are less important



- Curve 1 – accumulation of energy
- Curve 2 – reversible dissipation of energy
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Shock-absorbers – retrospective

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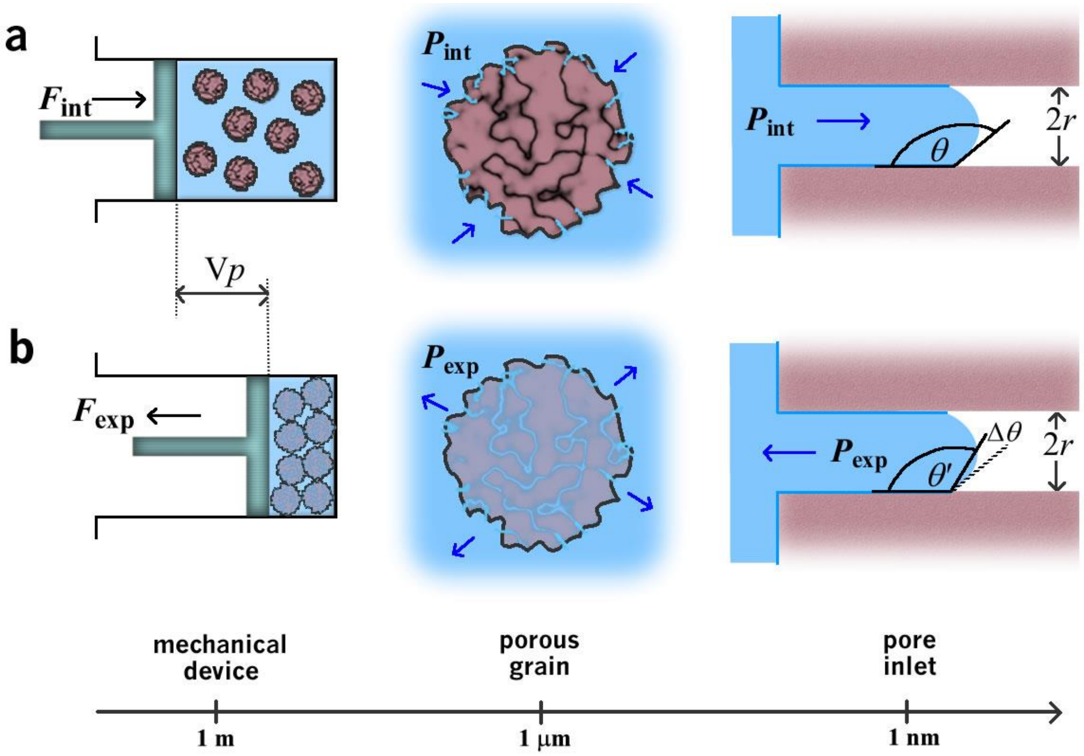
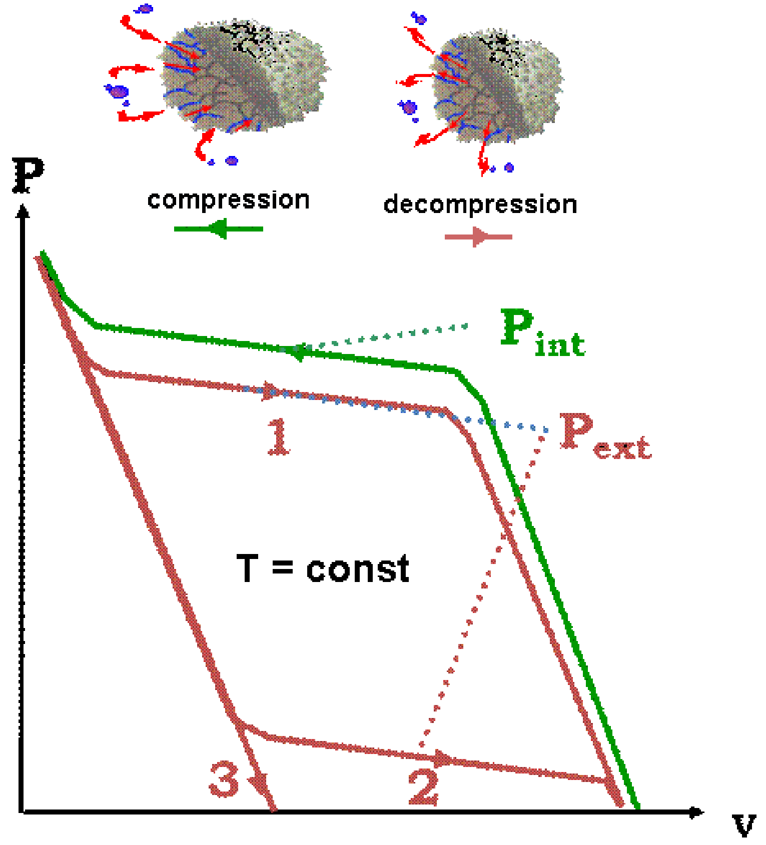
Intrusion-extrusion for energy applications

ENERGY BALANCE





- Curve 1 – accumulation of energy
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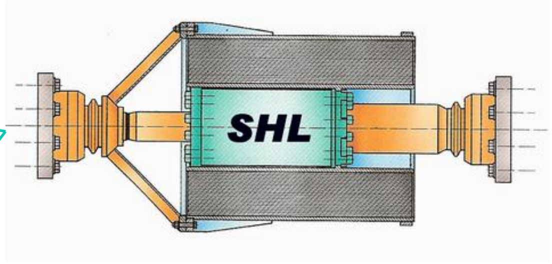
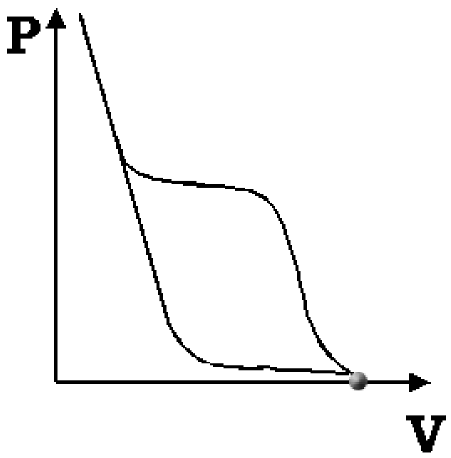
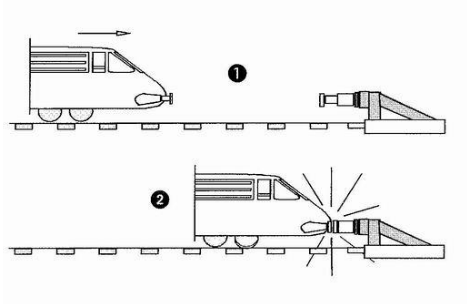
Shock-absorbers



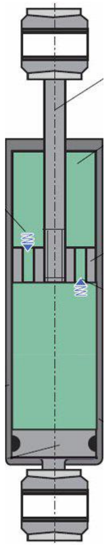
Frequency independent dissipation



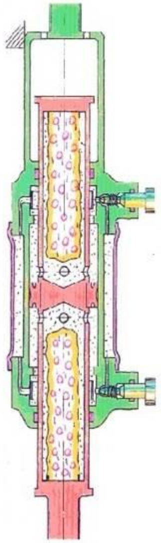


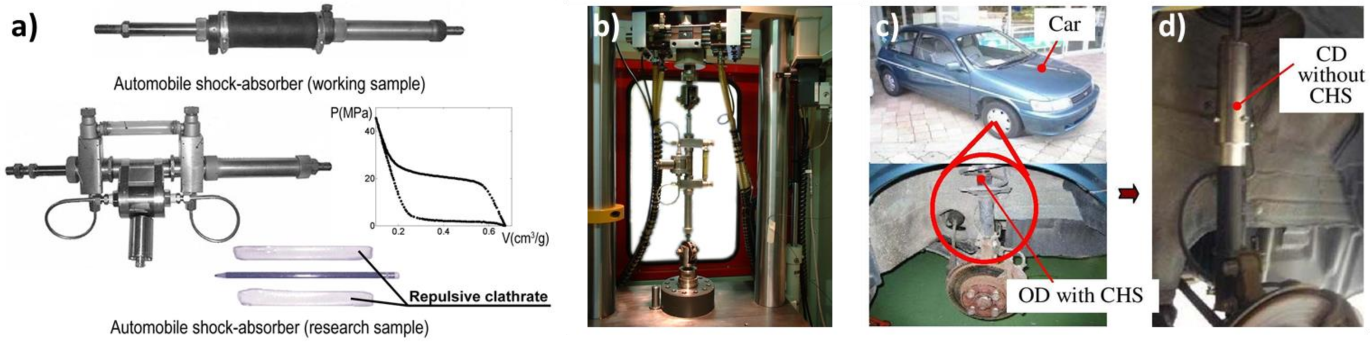
Works of
- Eroshenko
- Suciu

Conventional shock-absorber



Intrusion-extrusion shock-absorber





e)

	Frontal suspension		Rear suspension	
	Photo, mass and outer diameter		Photo, mass and outer diameter	
Actual suspension	Oil damper in parallel with spring 	5.9 kg 135 mm	Oil damper in parallel with spring 	2.8 kg 105 mm
Proposed suspension	Colloidal damper in parallel with spring 	6.2 kg 135 mm	Colloidal damper in parallel with spring 	3.4 kg 105 mm
Proposed suspension	Colloidal damper without spring 	4.6 kg 55 mm	Colloidal damper without spring 	1.9 kg 40 mm

Shock-absorbers – perspective

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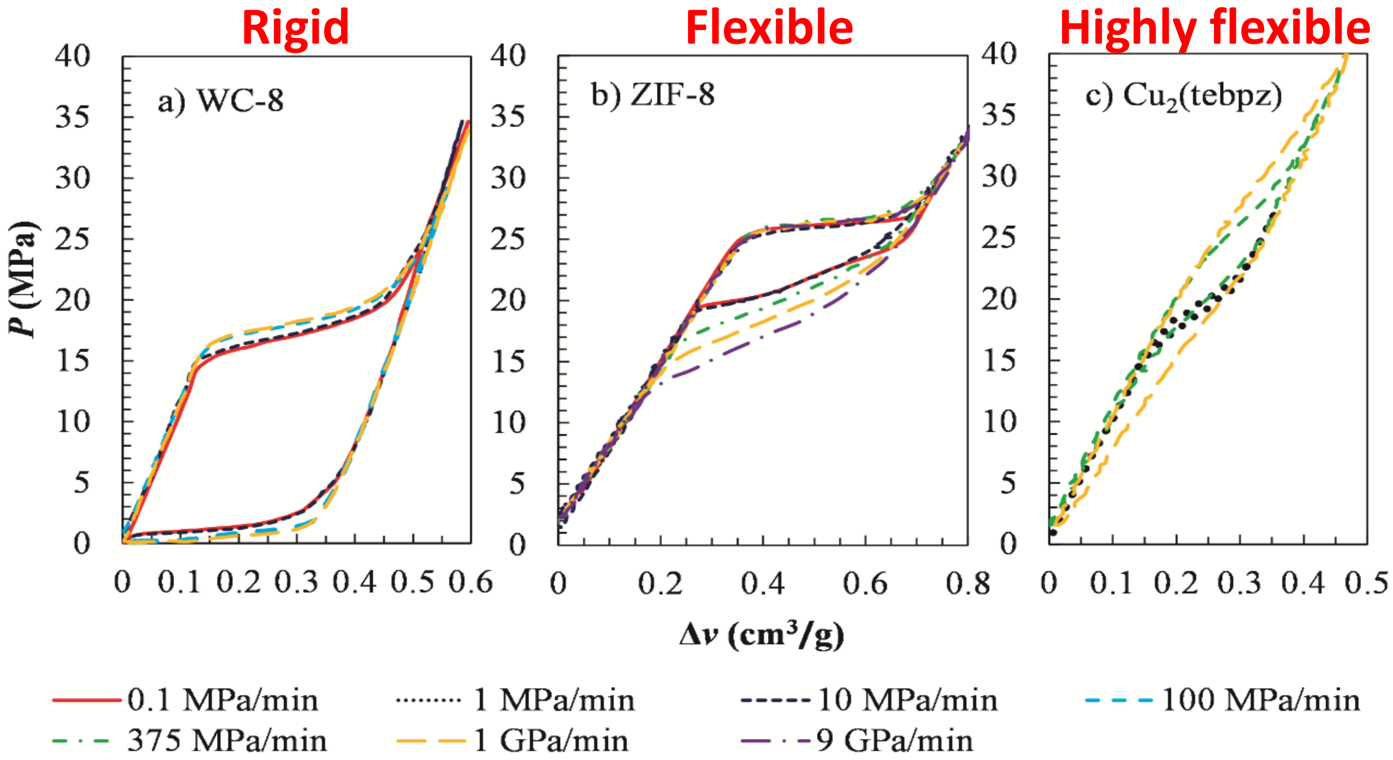
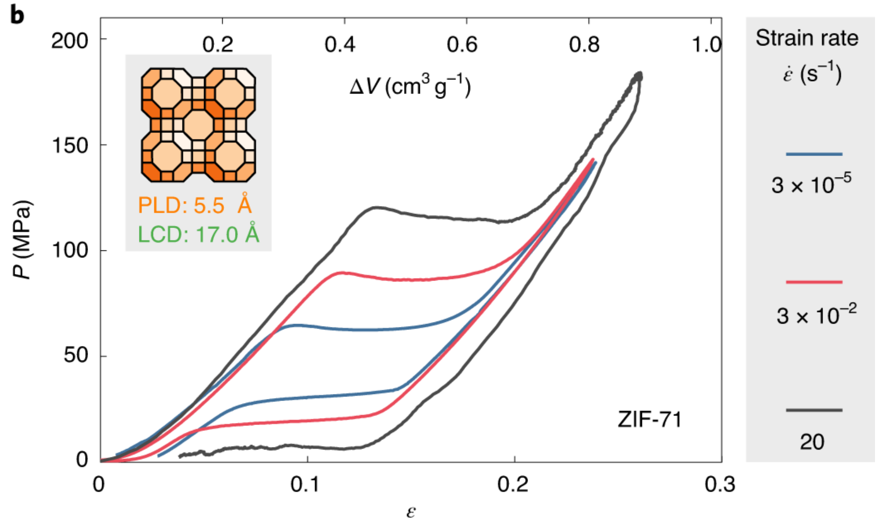
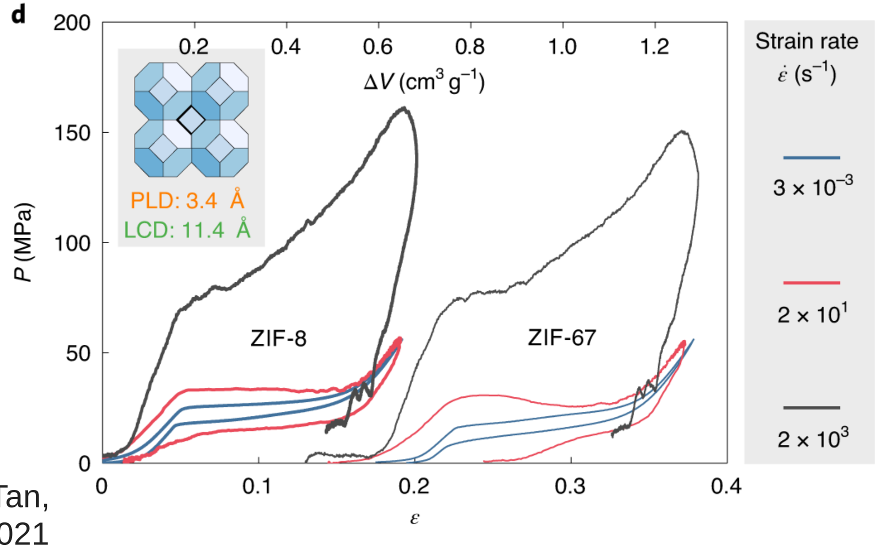
> Flexibility of porous material on the hysteresis of int-ext process



Lowe A., Tsyrin N., Chorążewski M., Zajdel P., Mierzwa M., Leão J.B., Bleuel M., Feng T., Luo D., Li M., Li D., Stoudenets V., Pawlus S., Faik A., Grosu Y. Effect of Flexibility and Nanotriboelectrification on the Dynamic Reversibility of Water Intrusion into Nanopores: Pressure-Transmitting Fluid with Frequency-Dependent Dissipation Capability. *ACS Applied Materials & Interfaces* 2019





Sun Y., Rogge S.M., Lamaire A., Vandenbrande S., Wieme J., Siviour C.R., Van Speybroeck V. and Tan, J.C. High-rate nanofluidic energy absorption in porous zeolitic frameworks. *Nature Materials* 2021

Emerging application – Regenerative shock-absorbers

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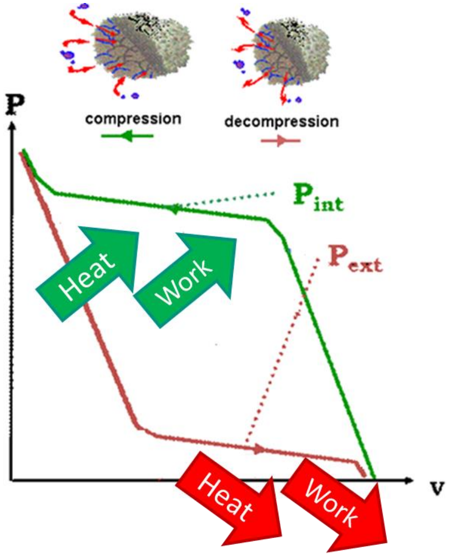
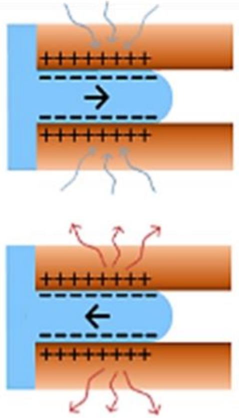
Regenerative shock-absorbers

ELECTRO-INTRUSION

$$\text{Work}_{intrusion} + \text{Heat}_{intrusion} >> \text{Work}_{extrusion} + \text{Heat}_{extrusion}$$

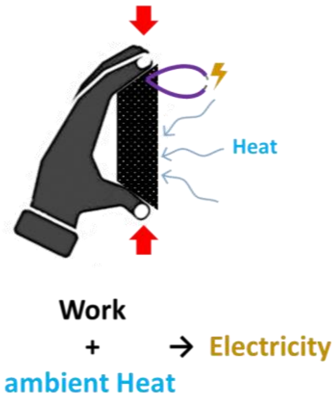


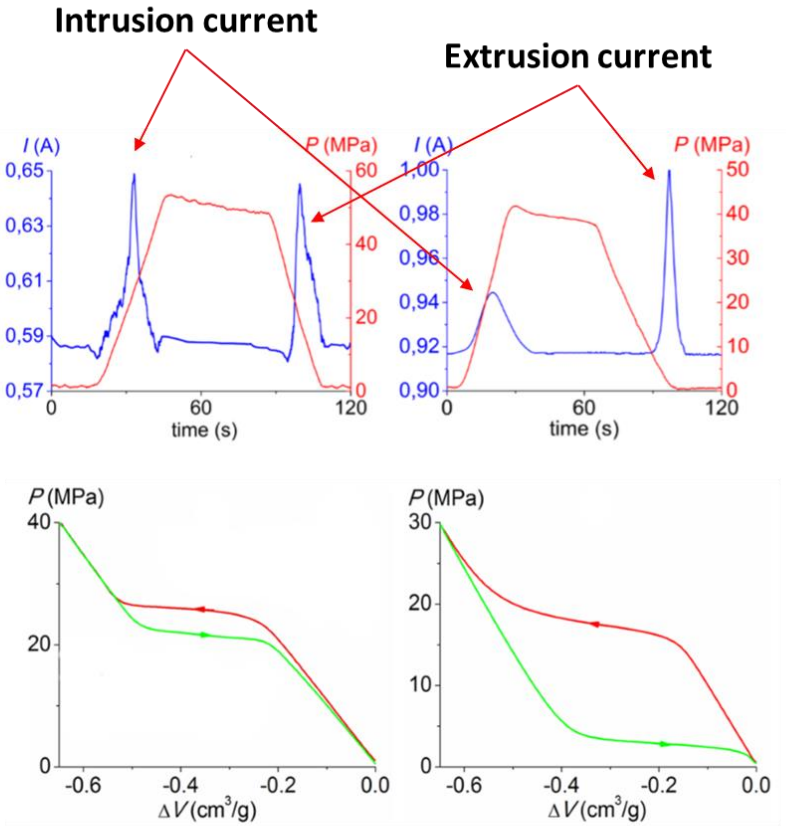


2 + 2 = 1

$$\frac{E}{W} > 1$$

Intrusion-extrusion
Triboelectric generator





ZIF-8 MOF + H_2O | Grafted silica + H_2O

1. Grosu Y et al. 2017. ACS Applied Materials & Interfaces
2. Lowe A et al. 2019. ACS Applied Materials & Interfaces
3. Electro-intrusion FET-proactive project: https://www.electro-intrusion.eu

Springs – retrospective

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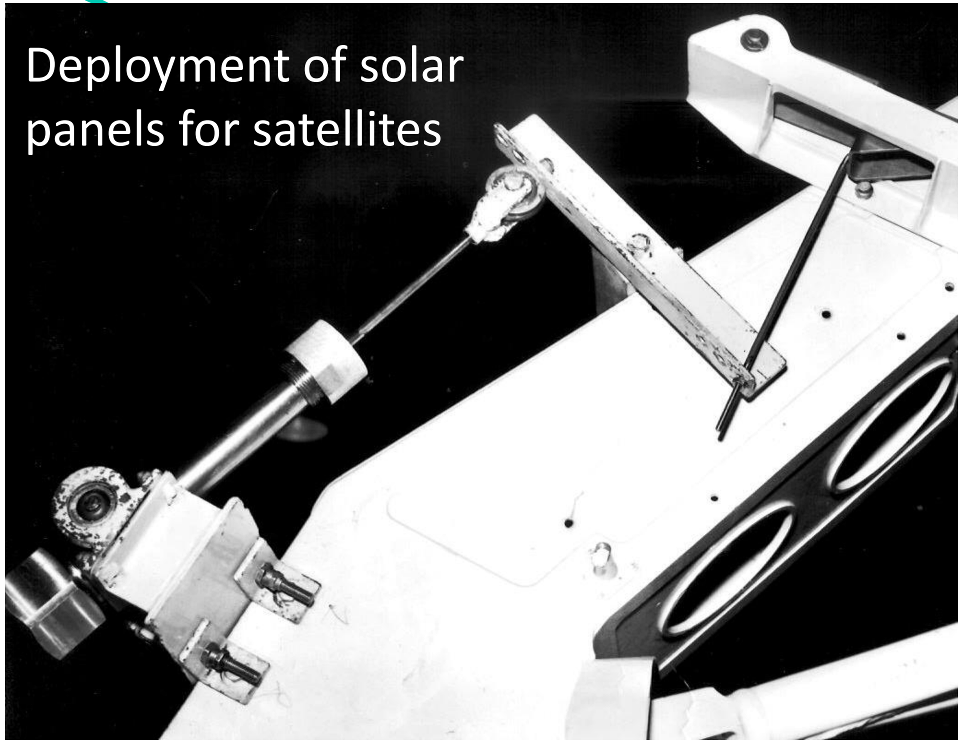
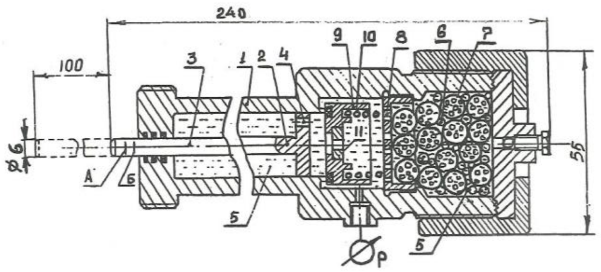
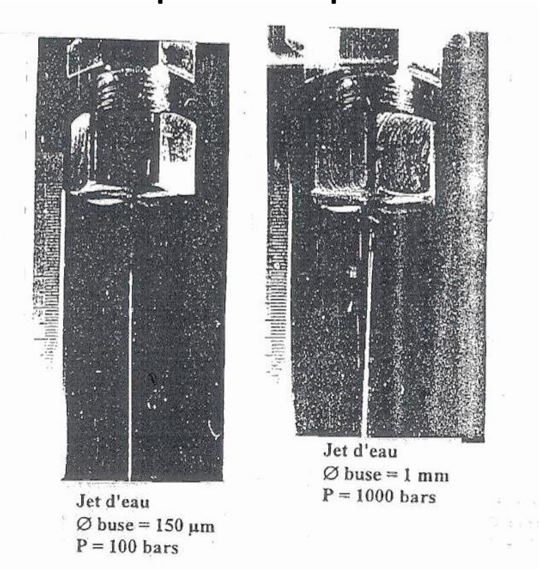
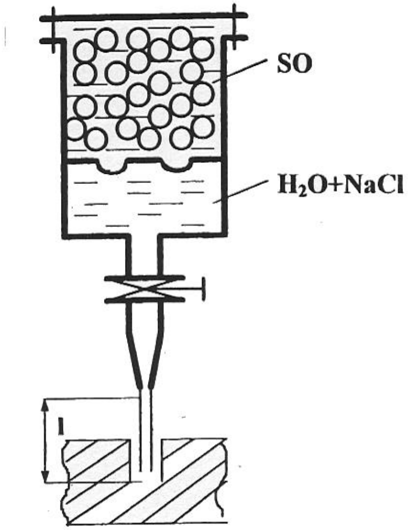


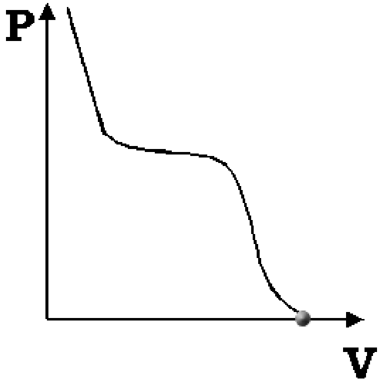
- Accumulates 2 kWh/m^3
- Constant force of 800 H
- Displacement of 10 cm
- Smooth discharge



Liquid scalpel







Materials crisis:

- Mesoporous – hysteretic
- Microporous (zeolites) – not stable

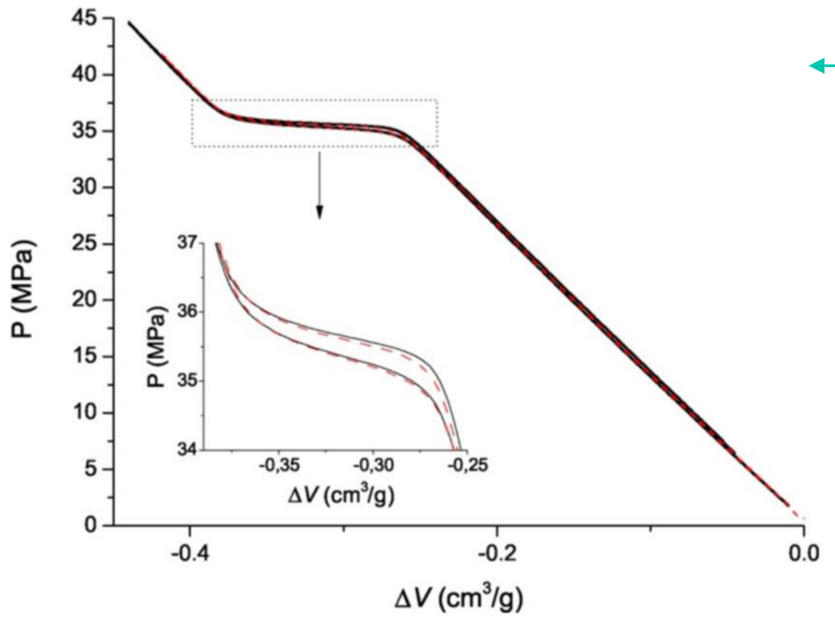
Knowledge crisis:

- Hysteresis control - ?

Early Eroshenko´s works

Springs – perspective

Cu_2(tebpz) + water



Grosu at al 2016 ChemPhysChem

Where we are:

- It is possible!
- Stable up to 170ºC

What we need:

- Higher porosity
- Hysteresis understanding
- Intrusion/extrusion pressure tuning

Thermal actuation – retrospective

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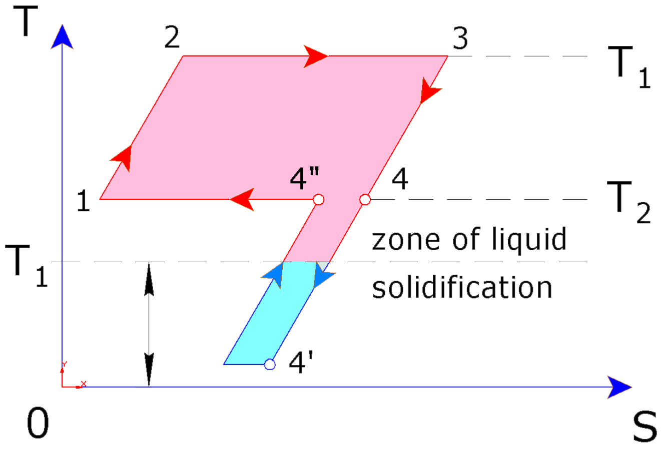
> Thermal actuation

RETROSPECTIVE- "THERMAL LOCK"



- Length of device is 13 cm
- Constant force of 2000 H
- Smooth discharge
- Rechargeable

Applications:

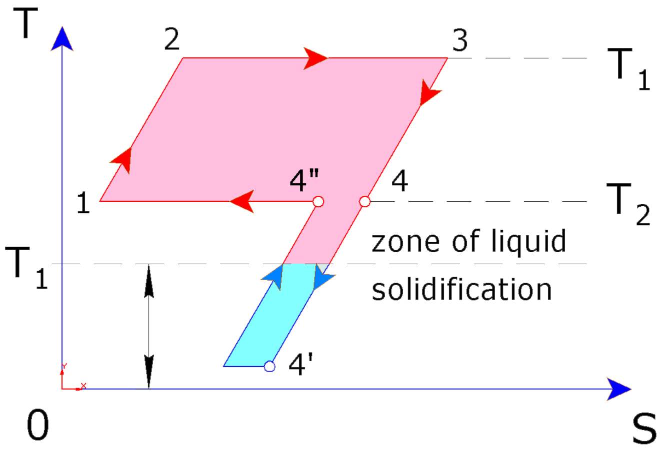
1. Fire protection – emergency valve
2. Protection of nuclear reactors from overheating:

Egorov VS, Portyanoy AG, Sorokin AP, Maltsev V.G., V. R. M. I. A.
Thermal Sensitivity of the Starting Device. Ru Patent 2138086, 1996.

Early Eroshenko´s works

Thermal actuation

RETROSPECTIVE- "THERMAL LOCK"



- Length of device is 13 cm
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Applications

1. Fire protec
2. Protection

Egorov VS, Po
Thermal Sensit

Thermal actuation – perspective

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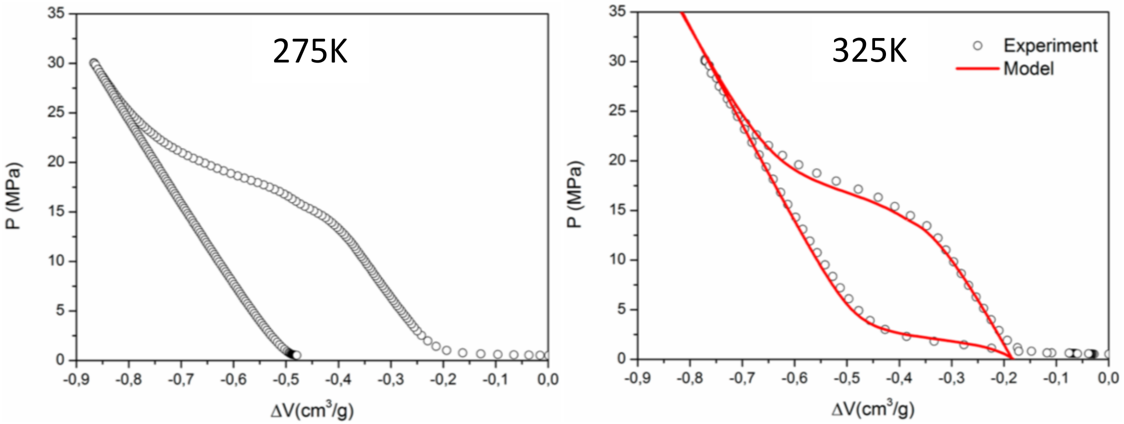
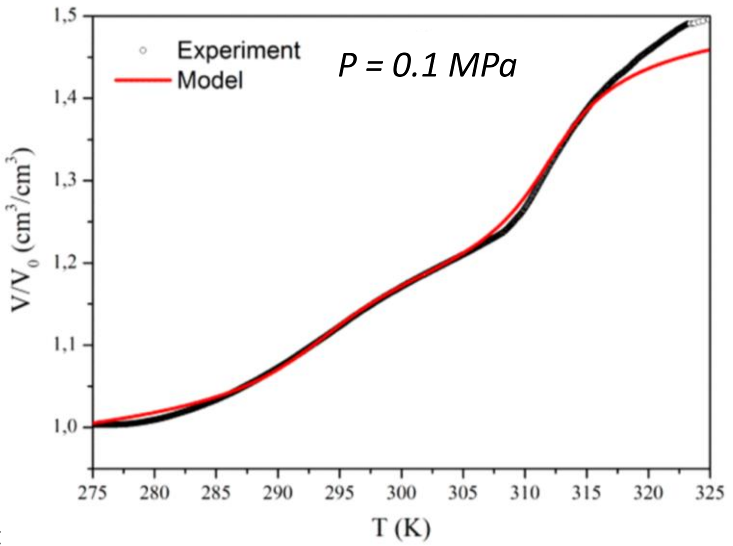
Thermal actuation

PERSPECTIVE

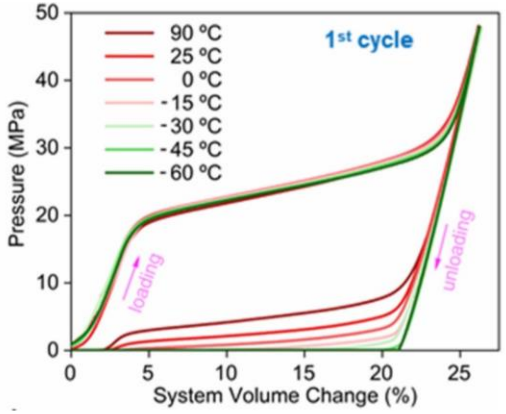
Grafted silica + water



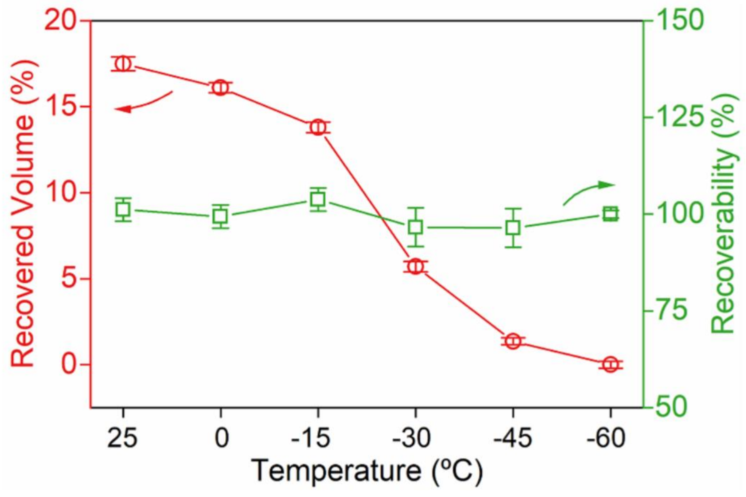
Grosu Y et al *J Phys Chem C* 2017



Grafted silica + LiCl solution

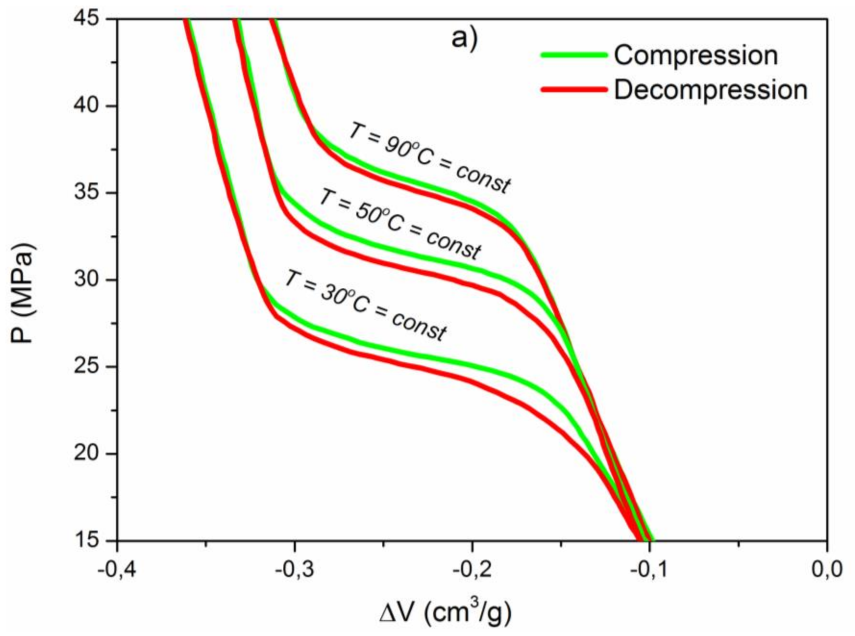


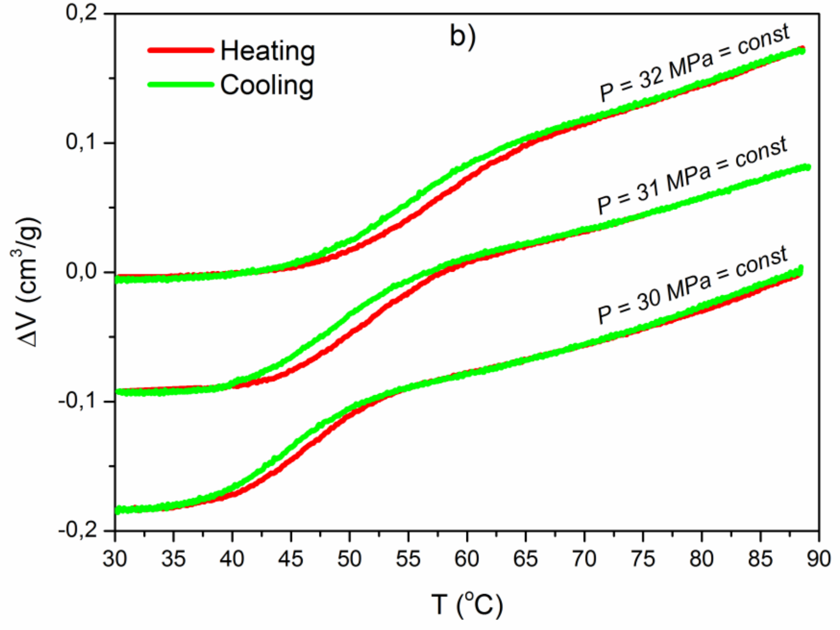
Li et al *Smart Mater Struct* 2021



> “Flexible” Thermal actuation

CU2(TEBPZ) + WATER

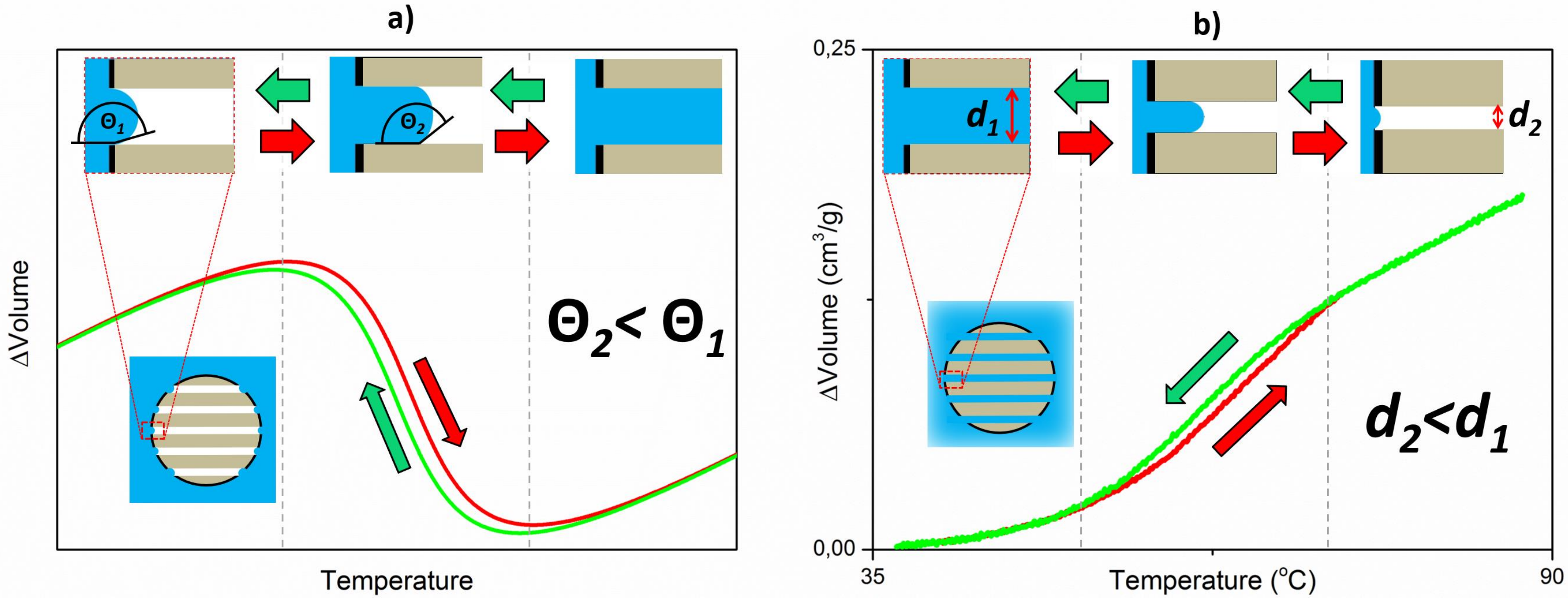




ACS Nano 2021

Thermal actuation

CU2(TEBPZ) + WATER



$$E_{heating} = \frac{W_{ext} - W_{exp}}{C_P \cdot \Delta T + Q_{ext}} \cdot 100\%$$

$$E_{heating} = \frac{W_{ext} + W_{exp}}{C_P \cdot \Delta T - Q_{ext}} \cdot 100\%$$

$$E_{cooling} = \frac{W_{int} - W_{con}}{C_P \cdot \Delta T + Q_{int}} \cdot 100\%$$

$$E_{cooling} = \frac{W_{int} + W_{con}}{C_P \cdot \Delta T - Q_{int}} \cdot 100\%$$

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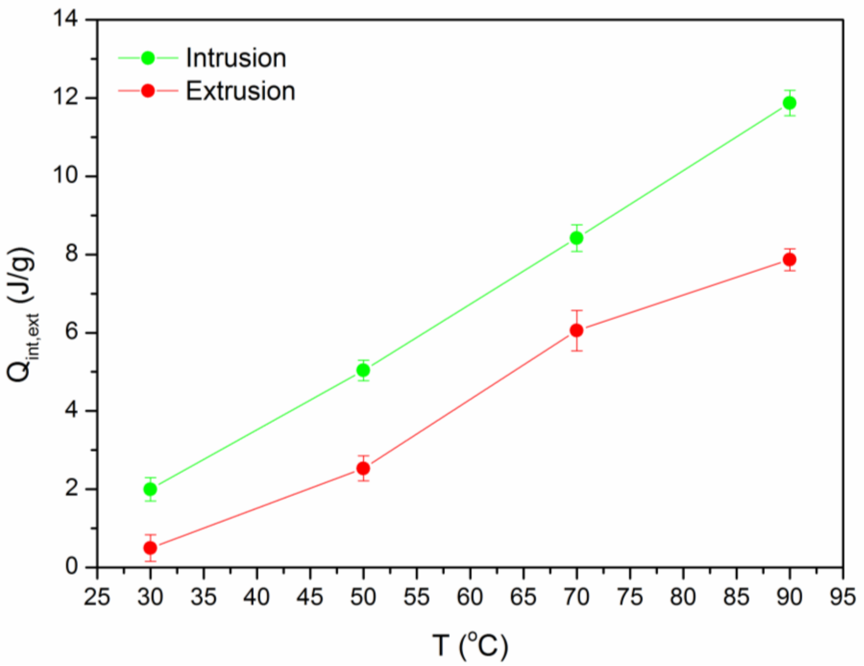
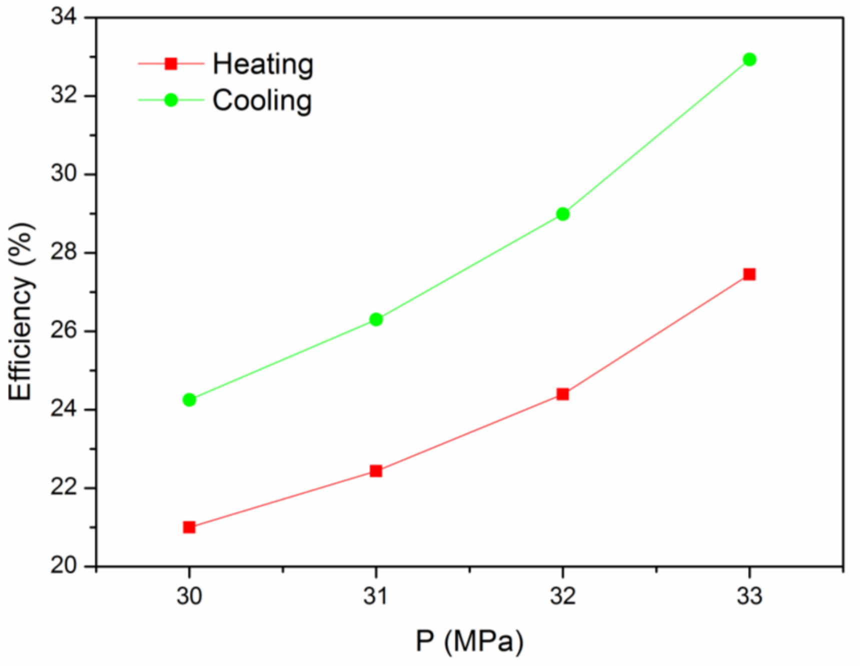
Thermal actuation

CU2(TEBPZ) + WATER





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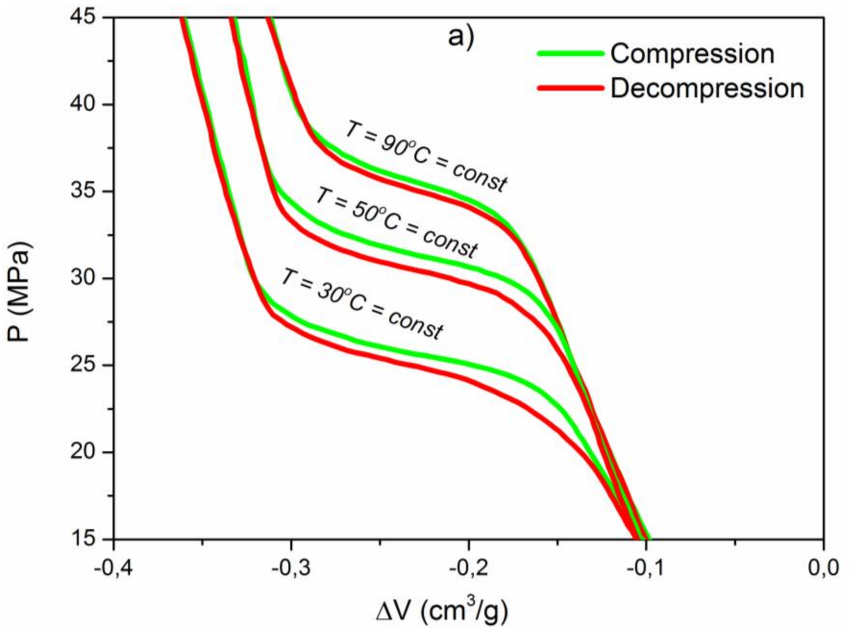
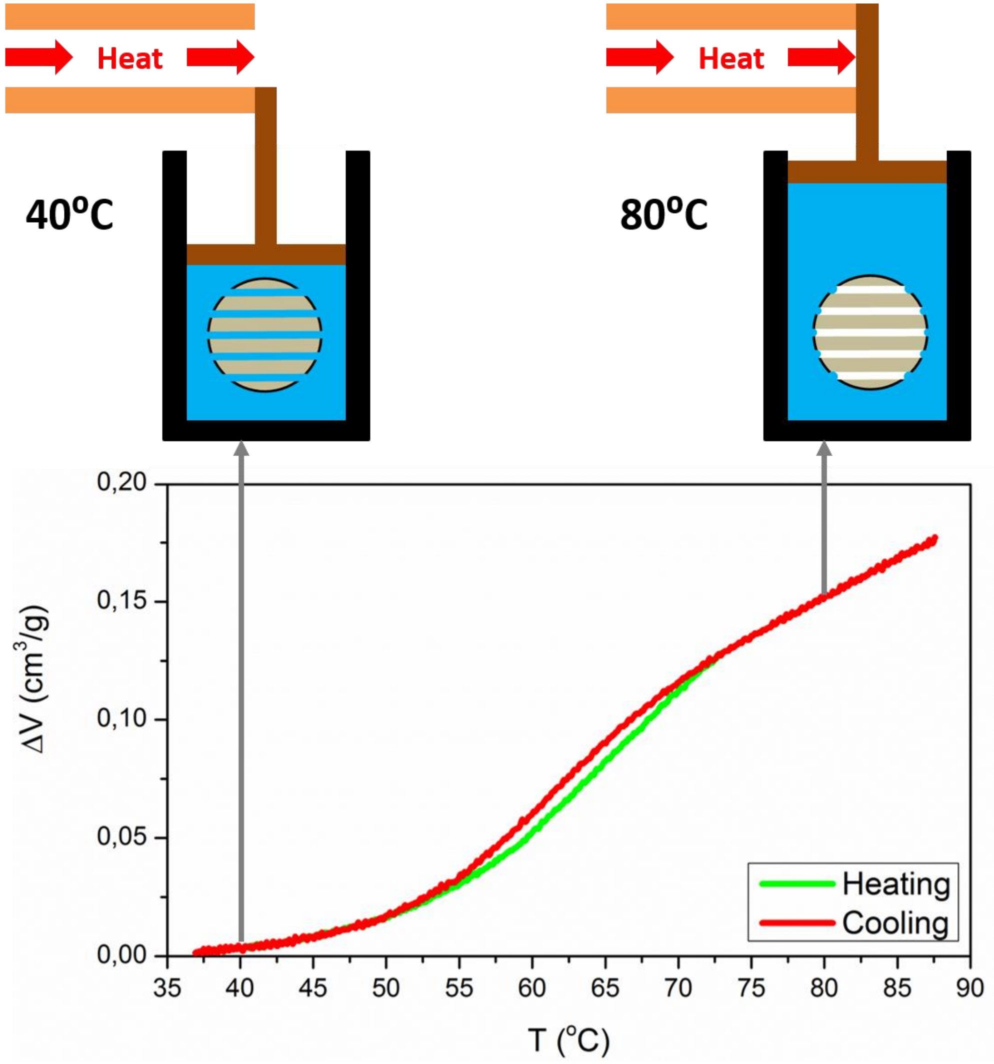
Thermal actuation

CU2(TEBPZ) + WATER

Temperature regulating valve-actuator





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Emerging application – negative compressibility

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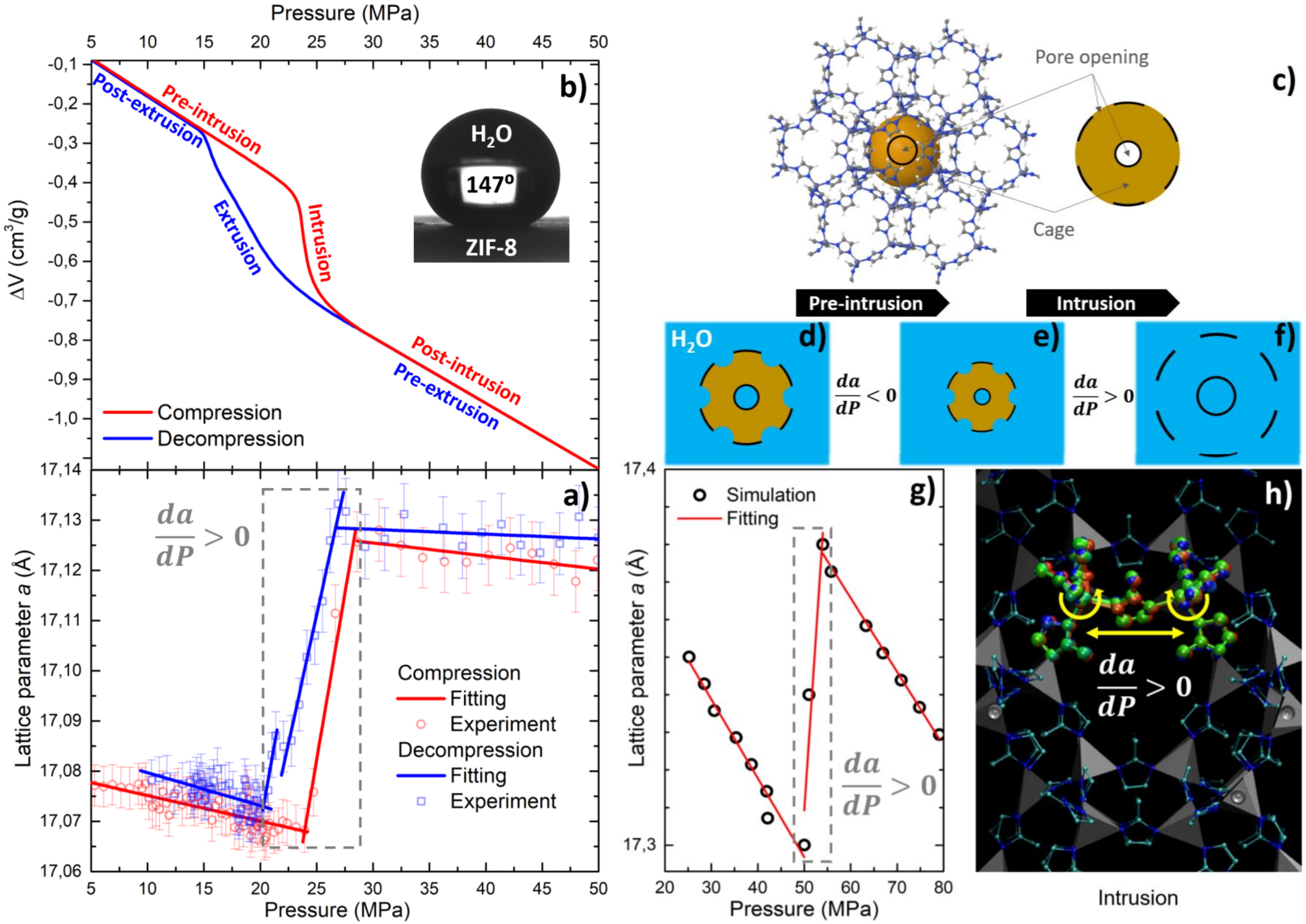
Negative compressibility

ZIF-8 + WATER



Nano letters 2021

Simone Meloni
University
of Ferrara

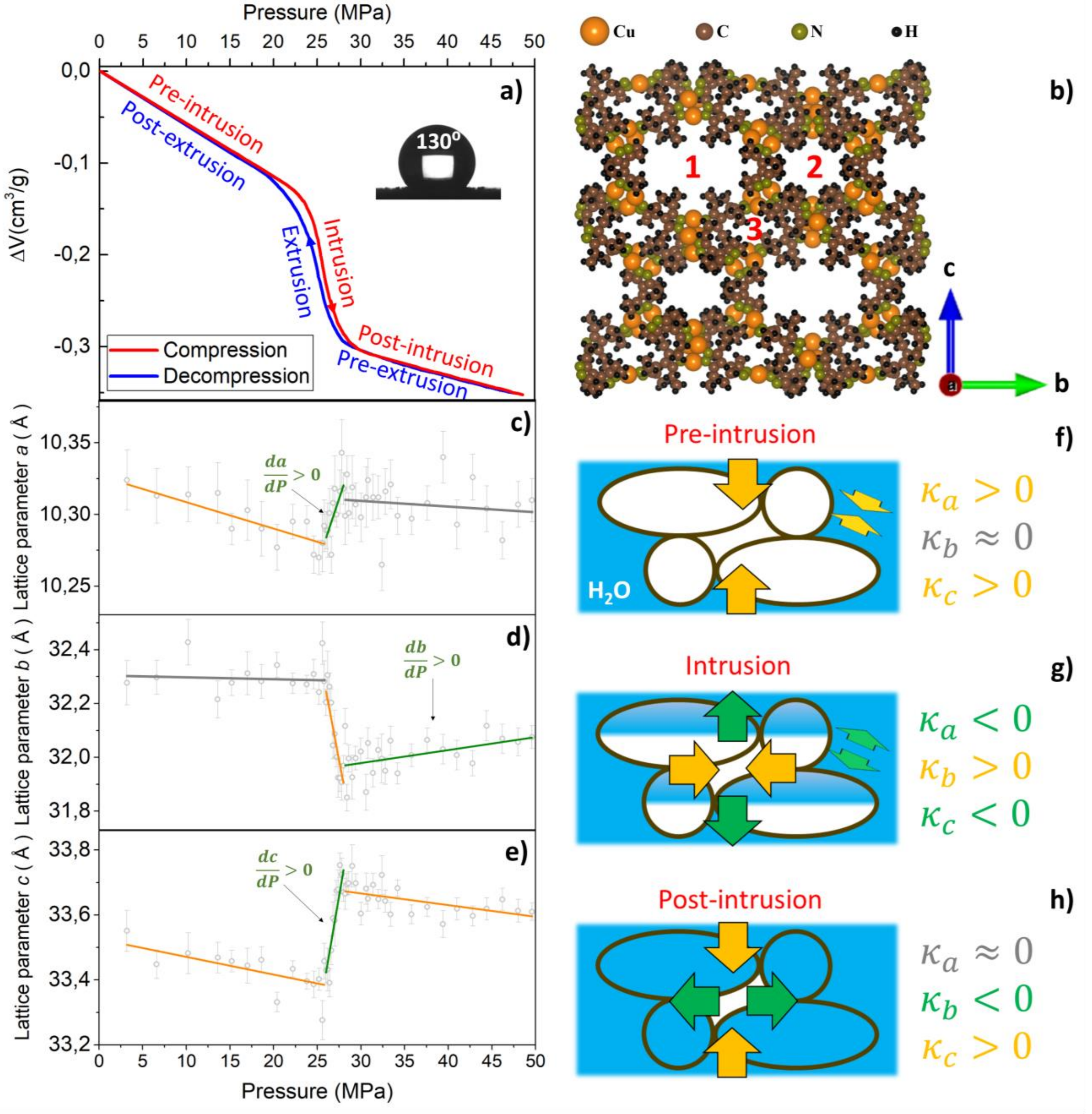
Marco Tortora
Sapienza
University
of Rome

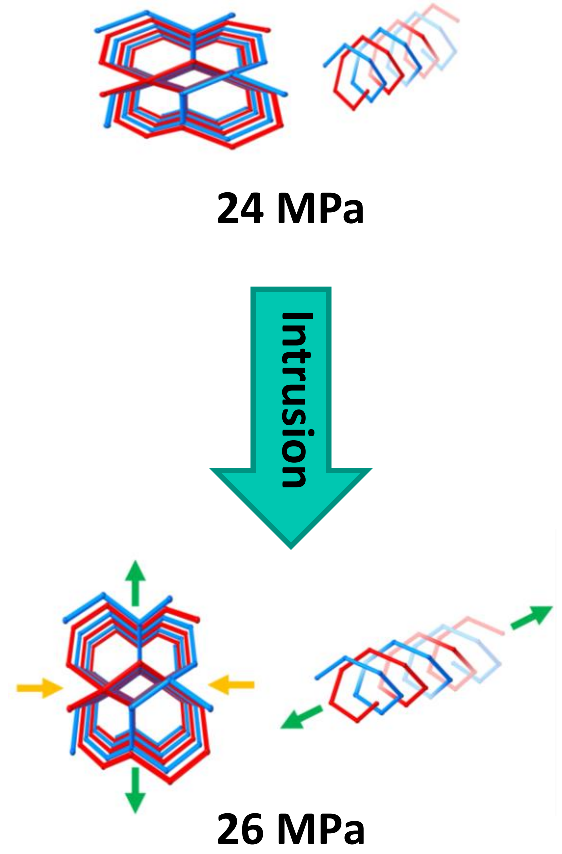
Alberto Giacomello
Sapienza
University
of Rome

Carlo Massimo Casciola
Sapienza University
of Rome

Negative compressibility

CU2(TEBPZ) + WATER





J Phys Chem Lett 2021

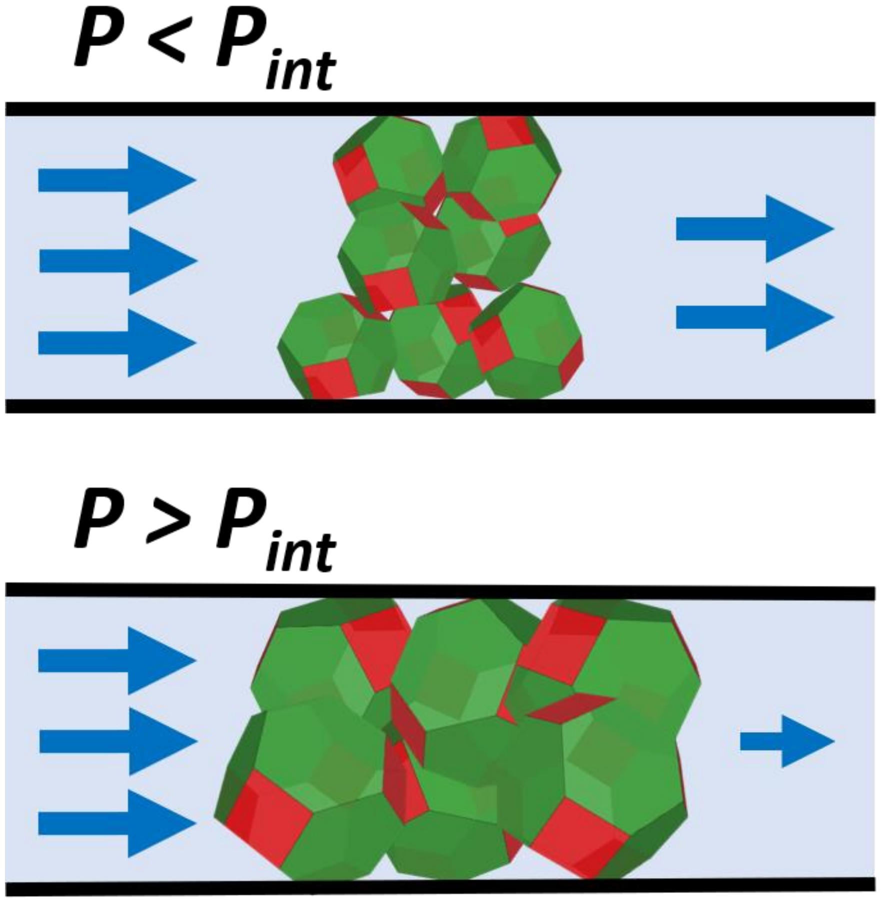
Negative compressibility

ZIF-8 + WATER

Table 1. Experimental Linear Compressibility Coefficients for Materials with a Pronounced NLC Effect

Material	κ_l, TPa^{-1}	ref
BiB_3O_6 (0–5 GPa)	−6.7(3)	1
BiB_3O_6 ($P \rightarrow 0$)	−12.5	1
MIL-53 MOF	−28	20
$[Ag(en)]NO_3$	−28.4(18)	25
$Zn[Au(CN)_2]_2$	−42(5)	26
MCF-34 MOF	−47.3	22
$InH(BDC)_2$	−62.4	27
$[Zn(L)_2(OH)_2]_n$	−72[a]	23
$Ag_3[Co(CN)_6]$	−76.9	28
ZIF-8 MOF	−37.2[b]	19
ZIF-8 MOF (intrusion)	−1020(130)[b]	this work
ZIF-8 MOF (extrusion 1)	−770(120)[b]	this work
ZIF-8 MOF (extrusion 2)	−610(40)[b]	this work

[a]Negative area compressibility was reported. [b]Negative volumetric compressibility was reported



Negative compressibiloty of more than 1 order of magnitude higher compared to the state – of – the – art

Nano letters 2021

Emerging application –
Thermal energy storage

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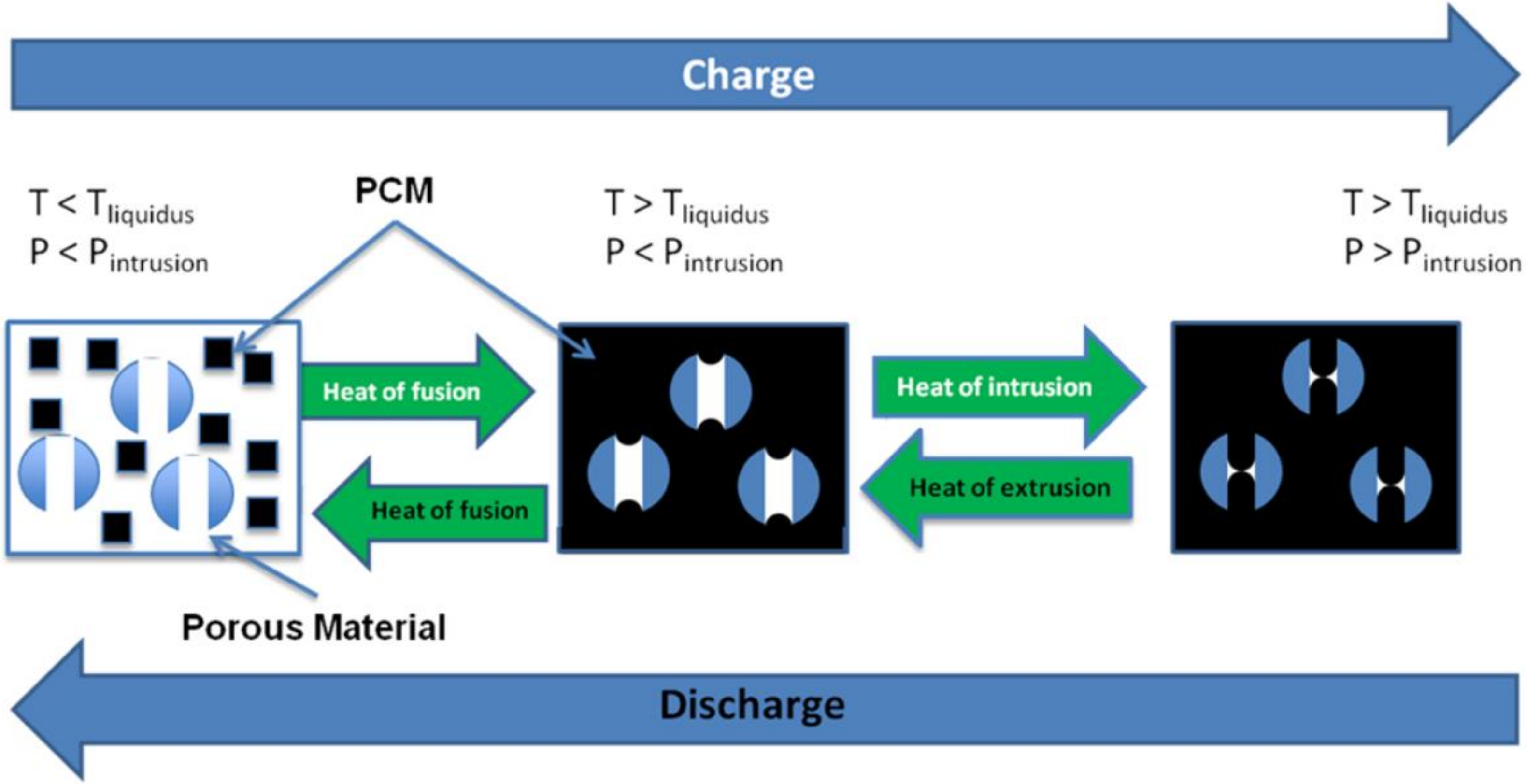
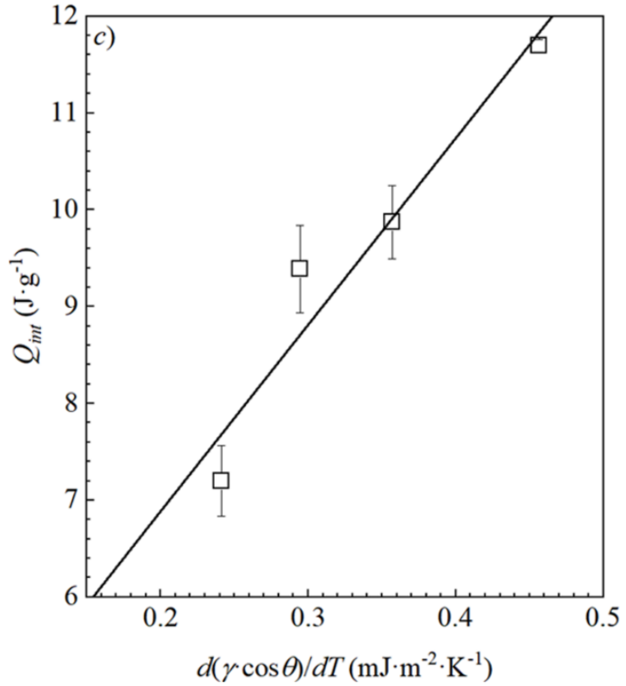
> Thermal energy storage





Langmuir 2021

Summary

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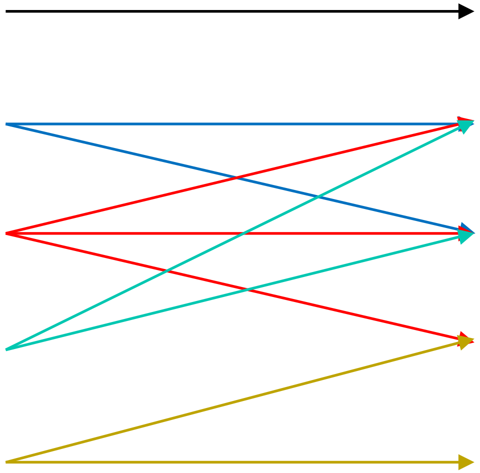
Summary

Promising applications:

- Regenerative shock-absorbers
- “Flexible” shock-absorbers
- “Flexible” thermal actuators
- Negative compressibility
- Thermal energy storage



Challenges:

- Understand intrusion-extrusion electrification
- Stable MOFs and COFs
- Understand intrusion-extrusion into-from flexible pores
- Understanding heat of intrusion-extrusion
- Lyophobic materials + non-aqueous solutions

More information

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> Additional information

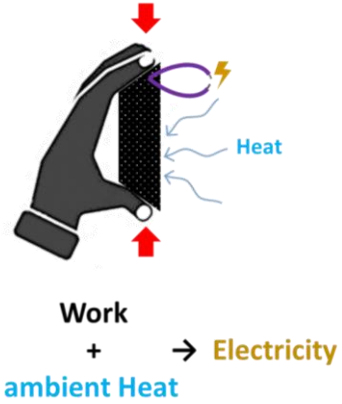
PAPERS AND PROJECTS

Recent papers

- M. Chorążewski, P. Zajdel, T. Feng, D. Luo, A. R. Lowe, C. M. Brown, J. B. Leão, M. Li, M. Bleuel, G. Jensen, D. Li, A. Faik, Y. Grosu. Compact Thermal Actuation by Water and Flexible Hydrophobic Nanopore. *ACS Nano*. **2021**. DOI: 10.1021/acsnano.1c02175.
- Tortora M., Zajdel P., Lowe A.R., Chorążewski M., Leão J.B., Jensen G.V., Bleuel M., Giacomello A., Casciola C.M., Meloni S., Grosu, Y. Giant Negative Compressibility by Liquid Intrusion into Superhydrophobic Flexible Nanoporous Frameworks. *Nano Letters*, **2021**, 21(7), pp.2848-2853.
- P Zajdel, M Chorążewski, J B Leão, G V Jensen, M Bleuel, H-F Zhang, T Feng, D Luo, M Li, A Lowe, M Geppert-Rybczynska, D Li, Y Grosu. Inflation Negative Compressibility during Intrusion-Extrusion of a Non-Wetting Liquid into a Flexible Nanoporous Framework. *J. Phys. Chem. Lett.* **2021**.
- Lowe A., Tsyrin N., Chorążewski M., Zajdel P., Mierzwa M., Leão J.B., Bleuel M., Feng T., Luo D., Li M., Li D., Stoudenets V., Pawlus S., Faik A., Grosu Y. Effect of flexibility and nanotriboelectrification on the dynamic reversibility of water intrusion into nanopores: Pressure-transmitting fluid with frequency-dependent dissipation capability. *ACS Appl. Mater. & Interf.* **2019**. 11(43), pp.40842-40849.
- Lowe, A.R., Wong, W.S., Tsyrin, N., Chorążewski, M.A., Zaki, A., Geppert-Rybczyńska, M., Stoudenets, V., Tricoli, A., Faik, A. and Grosu, Y. The Effect of Surface Entropy on the Heat of Non-Wetting Liquid Intrusion into Nanopores. *Langmuir*. **2021**

Electro-intrusion Horizon 2020 FET-proactive project

https://www.electro-intrusion.eu



GRACIAS · THANK YOU · ESKERRIK ASKO

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