Zeolites with unusual mechanical properties

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Malta & its University

Malta: **Size: 126 square miles, Population: 380,000**

The University: **Traces its origin to the founding of the *Collegium Melitense* in 1592.**

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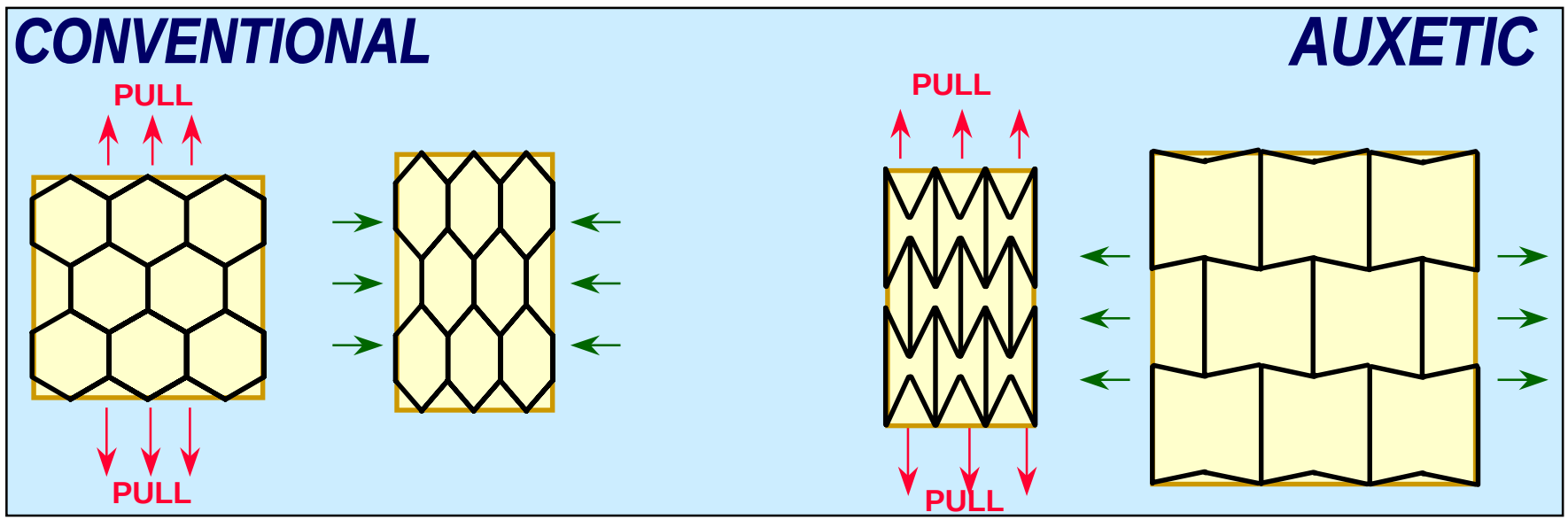
AUXETIC Materials:

Auxetic materials are materials with a **negative Poisson's Ratio**, *i.e.* materials that become fatter when stretched and thinner when squashed.

$$\text{Poisson's ratio}, \nu = -\left(\frac{\text{lateral strain}}{\text{axial strain}}\right)$$



Advantages of Auxetic Materials

When compared to conventional materials, ***auxetics*** *...*

> Are harder to indent

> Have an increased shear stiffness

> Have a natural ability to form doubly curved surfaces

> Have a higher plane fracture toughness

> Can be used as tunable filters

What gives rise to a negative Poisson's ratio?

*Auxetic behaviour is a result of **co-operation** between:*

> **Geometric features** in the macro/micro/nano structure of the material,

> The **deformation mechanisms**.

e.g. honeycomb structure

Why look at zeolites?

- **Zeolites have highly geometric nanostructures**, i.e. there is the possibility of auxetic behaviour.

- **Very little experimental data is available** on the single crystalline mechanical properties of zeolites.

- The use of zeolites as molecular sieves – the possibility of having **tunable molecular sieves**.

Initial Study(*):

(1) Using a proprietary package (Cerius^2, MSI Inc.).

(2) Initial configurations: the SiO_2 equivalents *and* the empty frameworks as supplied in the literature. No cations and water molecules were included in this initial study.

(3) Mechanical properties were calculated through force-fields supplied with Cerius^2.

Methodology was validated against published data (SOD, α-cristobalite)

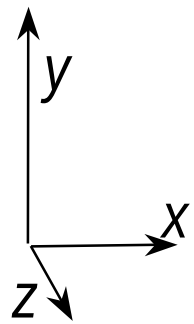
(*) J.N. Grima *et al.*, Advanced Materials (2000), p. 1912-1918
J.N. Grima, PhD Thesis, University of Exeter, UK (2000)

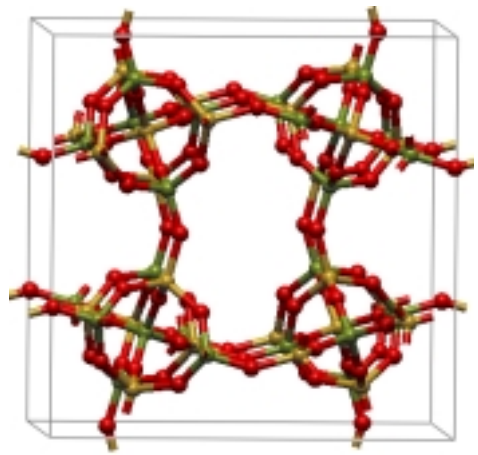
THO Thomsonite, $Na_4Ca_8[Al_{20}Si_{20}O_{80}] \cdot 24\ H_2O$

Poisson's Rations from simulations on $Si_{40}O_{80}$

Force-field:	ν_{xy}	ν_{yx}
Burchart[1]	-0.55	-0.55
BKS[2]	-0.33	-0.53
Universal[3]	-0.33	-0.40
CVFF[4]	-0.46	-0.46

(1) Burchart, PhD. Thesis, Delft. Univ. Tech, (1992)
(2) Van Beest *et. al.*, *Phys. Rev. Lett.*, **64** (1990) 1955
(3) Rappe *et al.*, *J. Am. Chem. Soc.* **114** (1992) 10046
(4) Cerius[2] User Guide, MSI Inc., San Diego, USA (1996)





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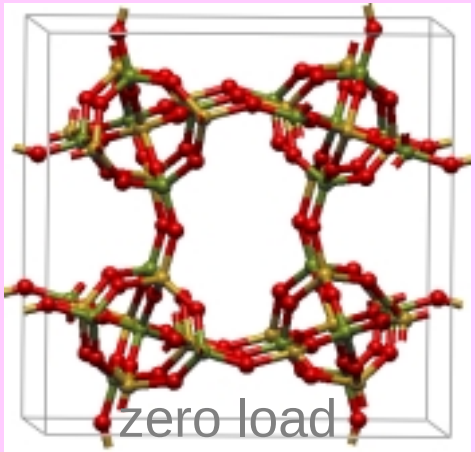
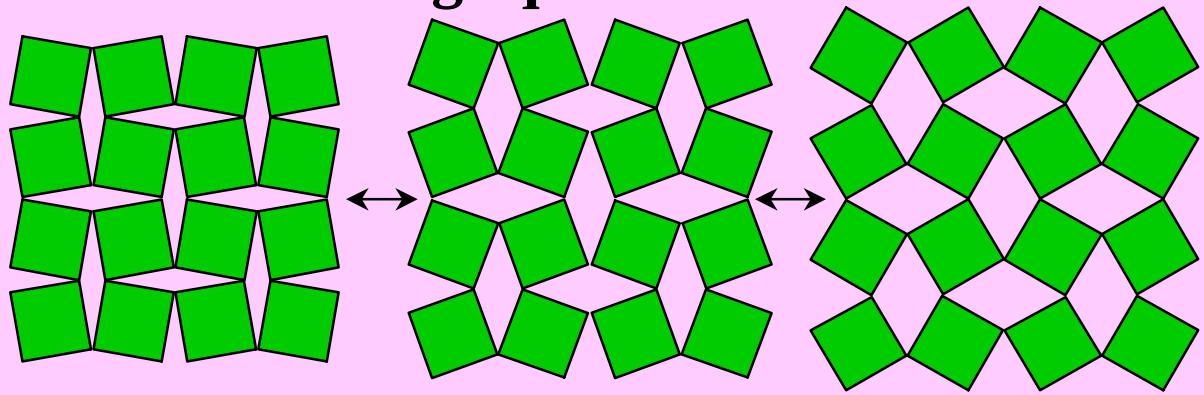
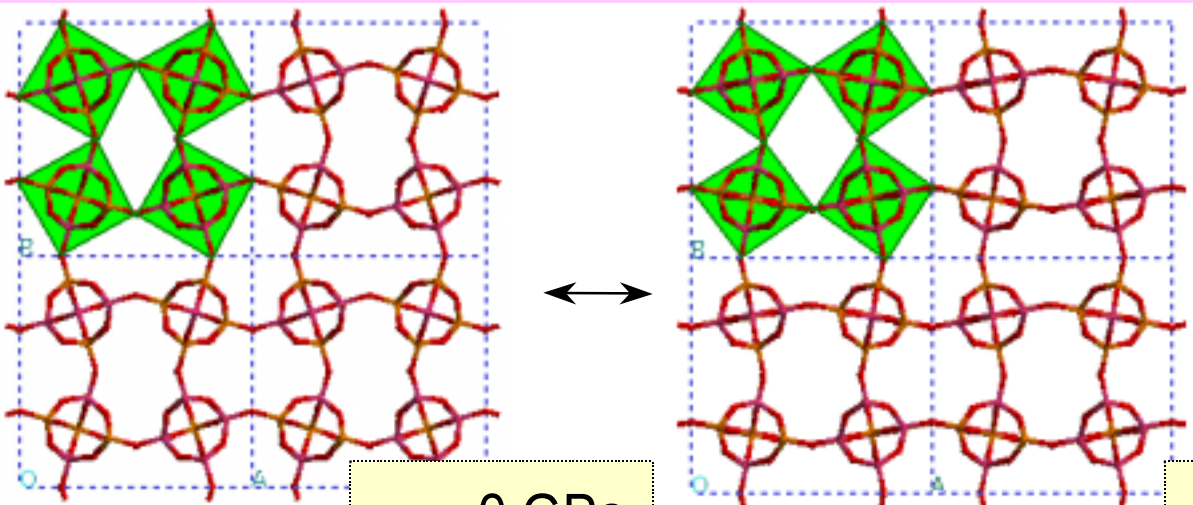
THO: Minimum energy configurations: Burchart force-field.



Idealised ‘rotating squares’: ν = -1





σ_x= 0 GPa

σ_x= 1 GPa

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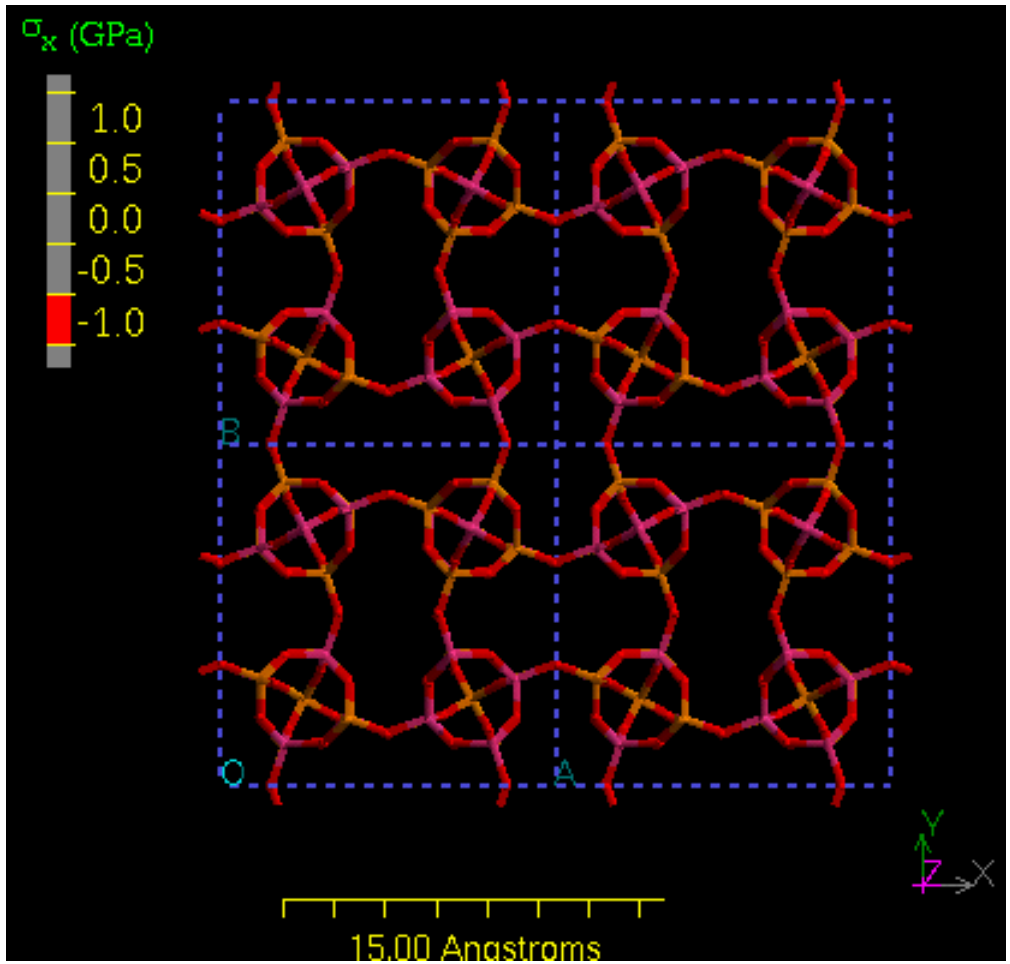
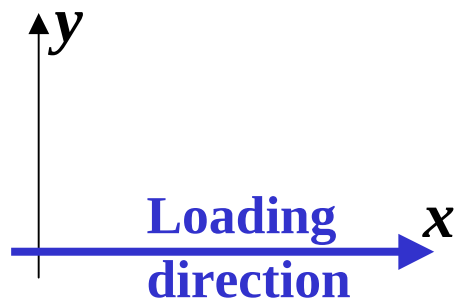
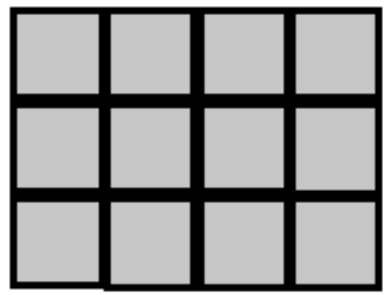
Results: THO

- The rotating squares deformation mechanism in action







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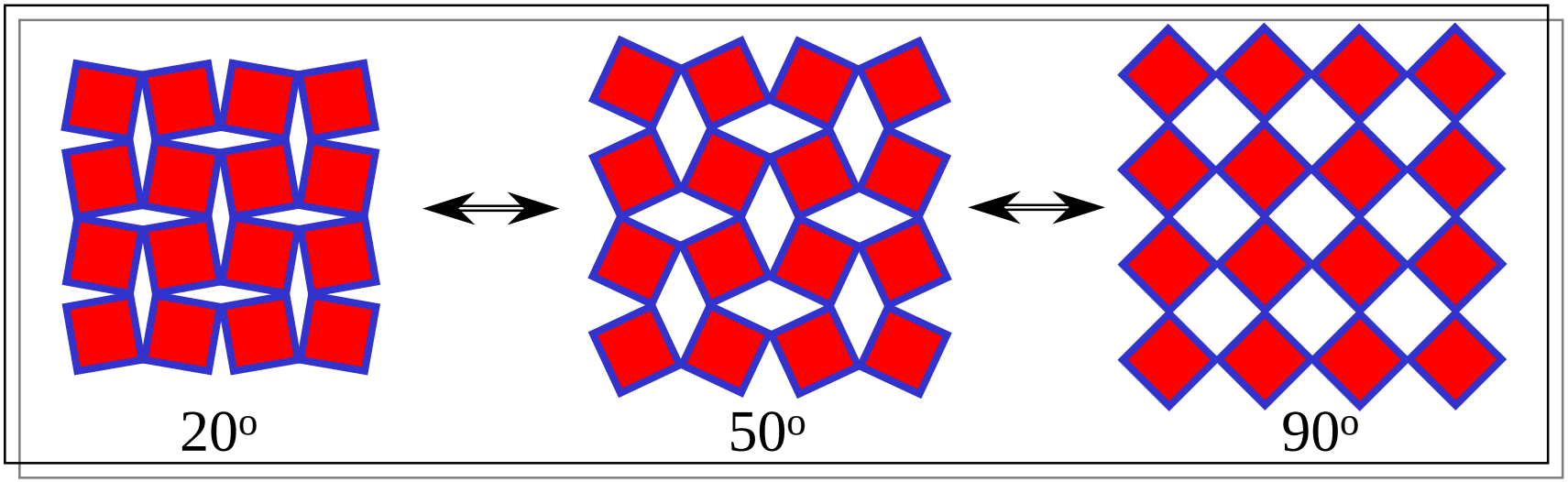
The ‘Rotating Squares’ mechanism:

Idealised *‘RS’* model*:

Poisson's ratio = -1



(*) J.N. Grima & K.E. Evans, *J.Mat.Sci.Lett*, **19** (2000) 1563

Requirements:

(1) rigid square-like unit

(2) flexible hinges

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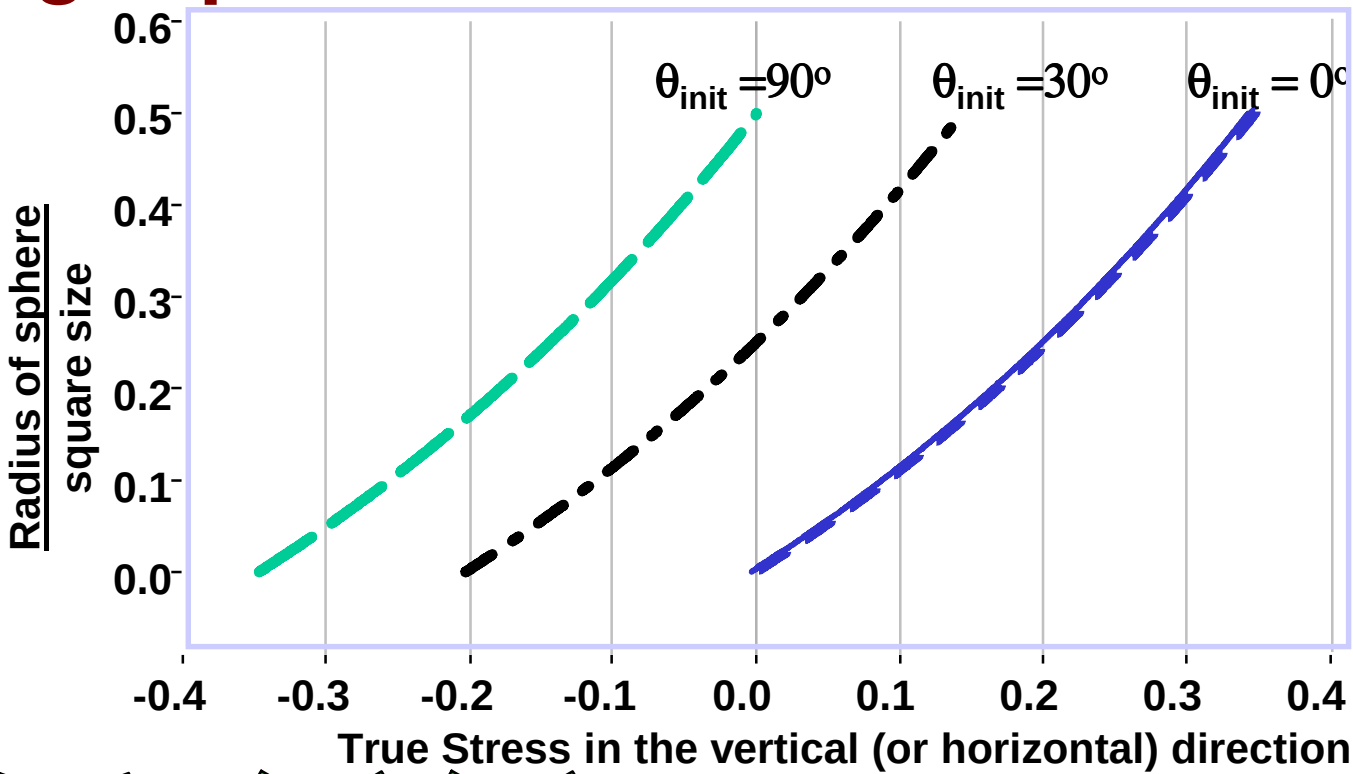
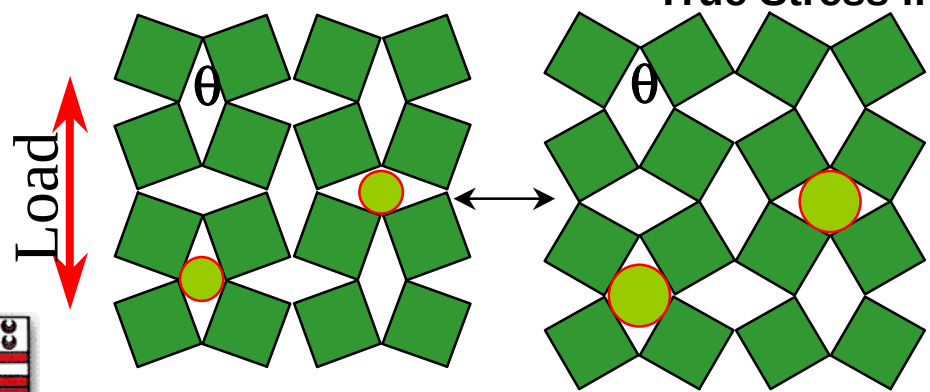
The ‘Rotating Squares’ mechanism: Filters





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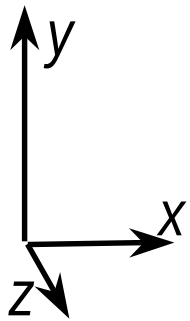
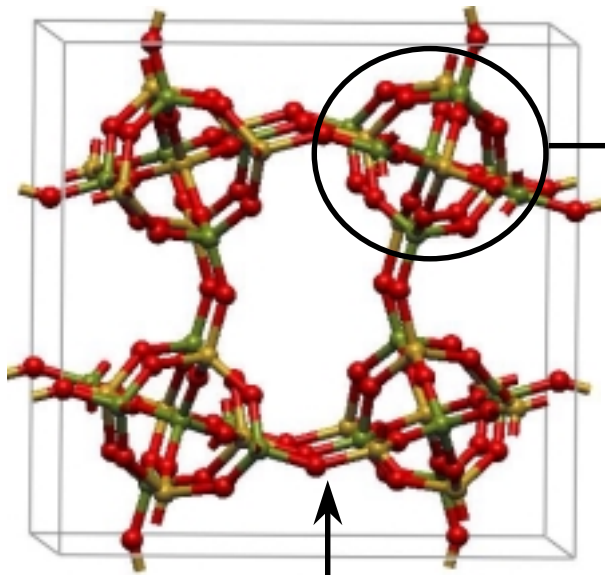
The ‘Rotating Squares’ mechanism in THO:

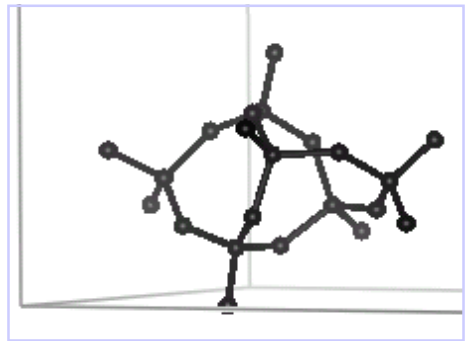




RIGID ‘SQUARE’

… cage-like structure

=



FLEXIBLE ‘HINGE’

… Si-O-Al groups

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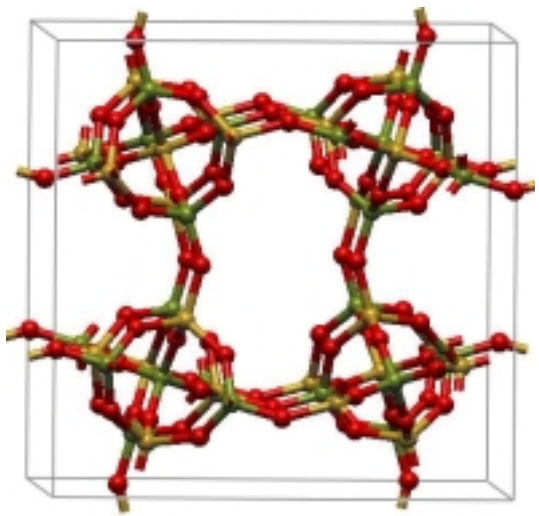
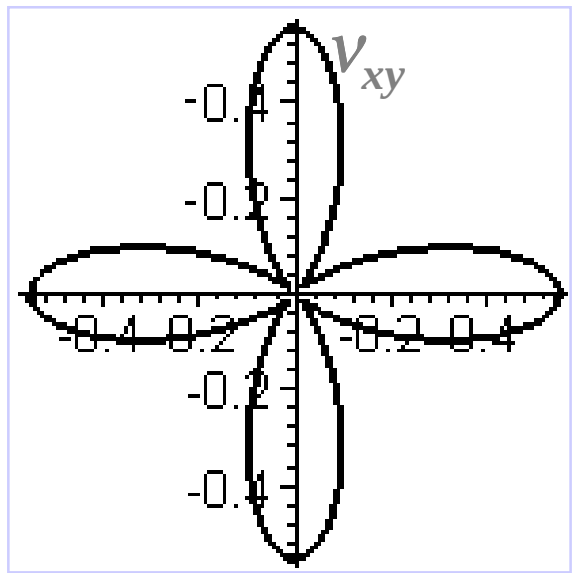
Deviations from the idealised *RS* behaviour

Idealised Rotating Squares Model: Poisson's ratio for loading in any direction in the plane is **-1** (i.e. ν is independent of loading direction).

Molecular Modelling on THO ($Si_{40}O_{80}$): Poisson's ratio in the xy plane for loading in x-direction is only c. –0.40, and this depends on loading direction (becomes less auxetic on axis rotation).





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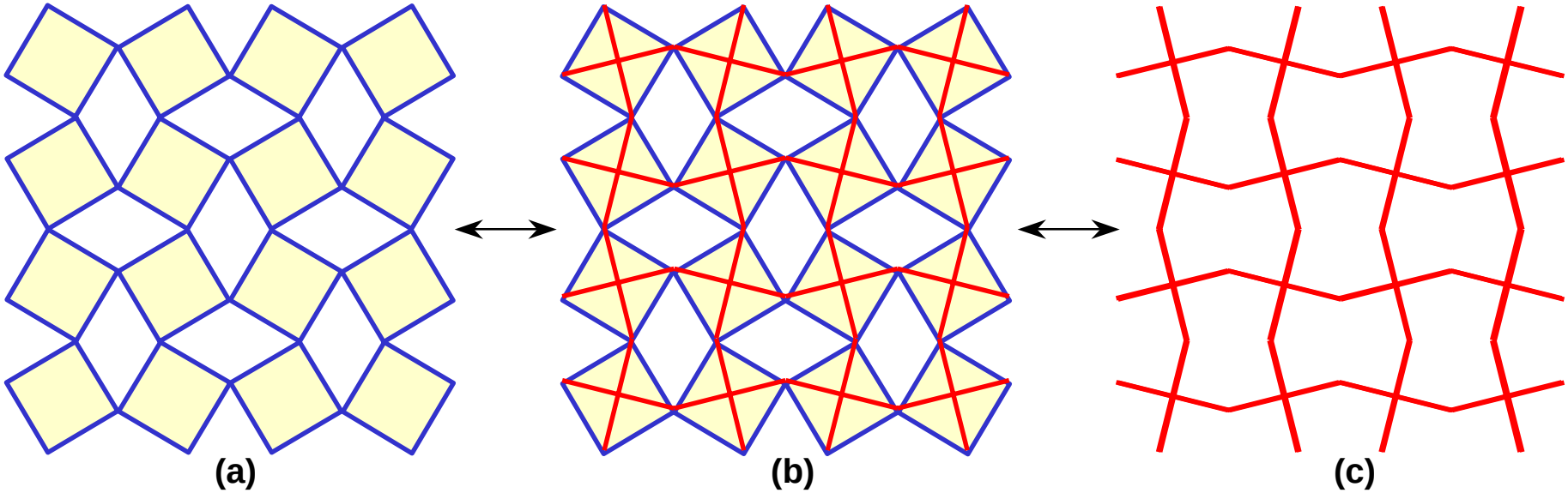
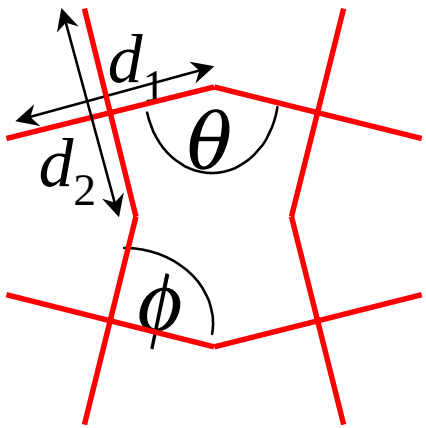
Improved ‘RS’ analytical model:





Variables:

d_1, d_2, ϕ and θ

(+ associated stiffness constants)

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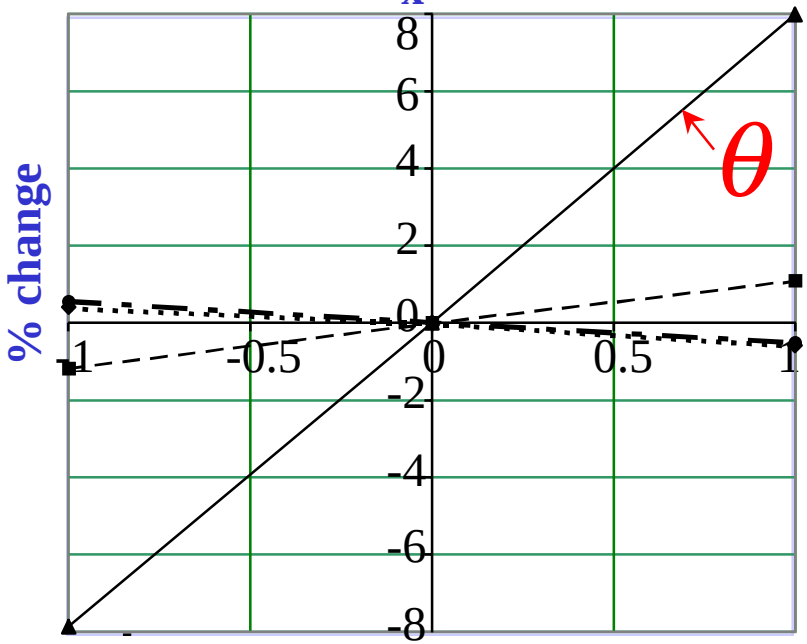
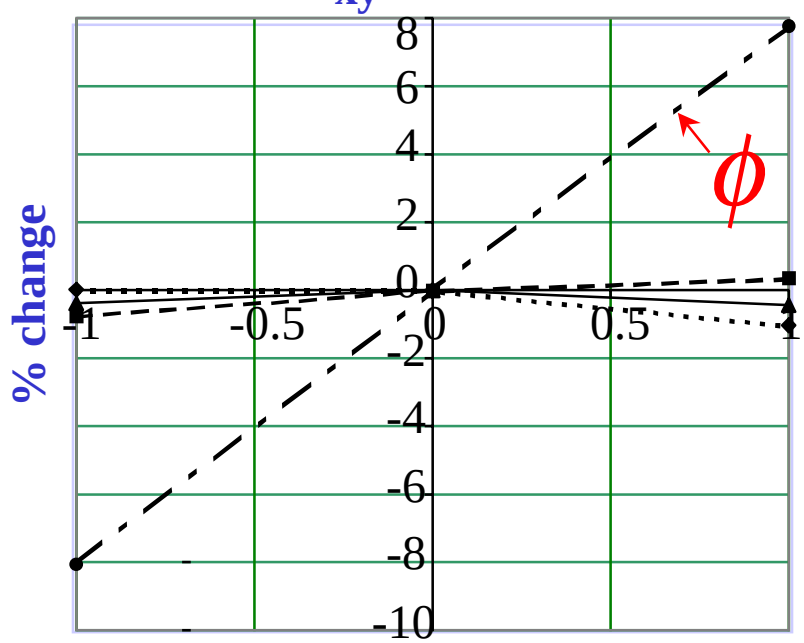
Development of the model:

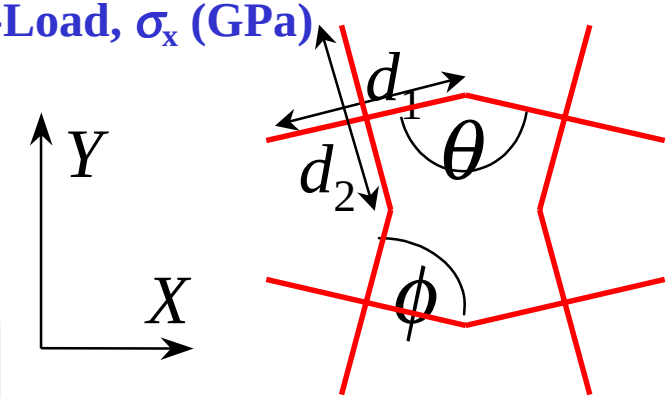
Tensile load (σ_x)



Shear load (τ_{xy})



Key: d_1 d_2 θ ϕ



$$\nu_{XY} = \nu_{YX} = -\left[1 + 4\left(\frac{k_\theta}{k_\phi}\right)\right]^{-1}$$

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Comparison of AM with molecular modelling data:

Molecular Modelling:

$E^* = 23.9\text{GPa}$

$G^* = 8.02\text{GPa}$

$\theta = 148.6^o$

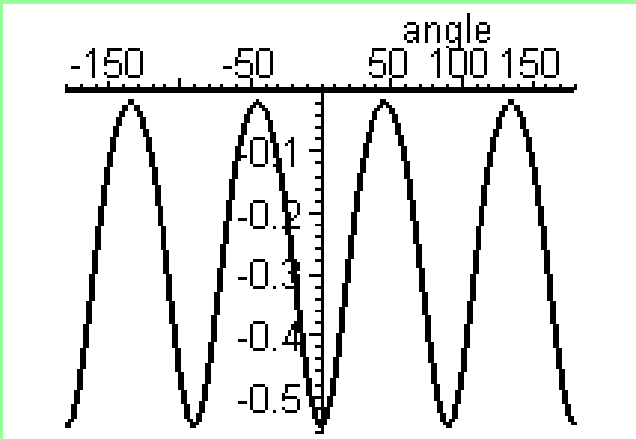
(*on-axis)

Compute the stiffness constants:

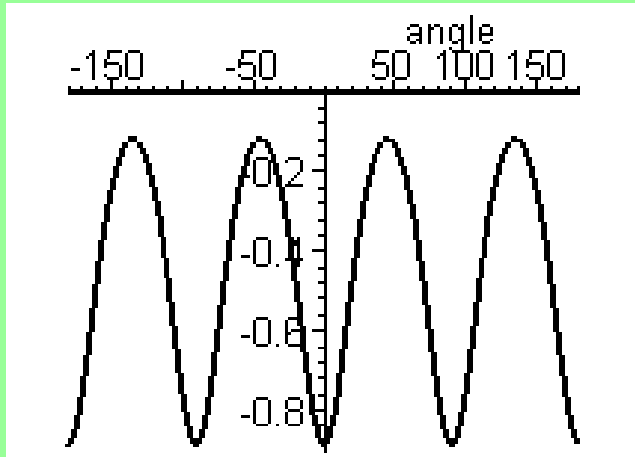
$k_\theta = 0.23$

$k_\phi = 7.43$

Compare Poisson's ratios:



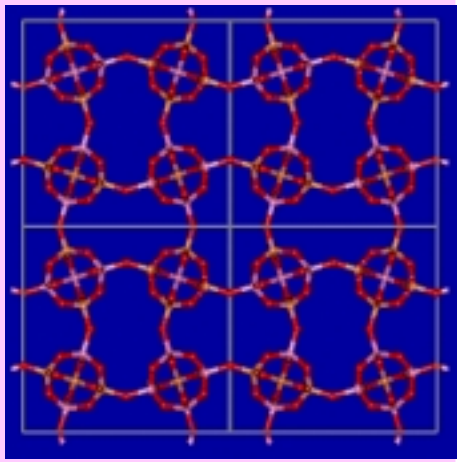
Molecular Model

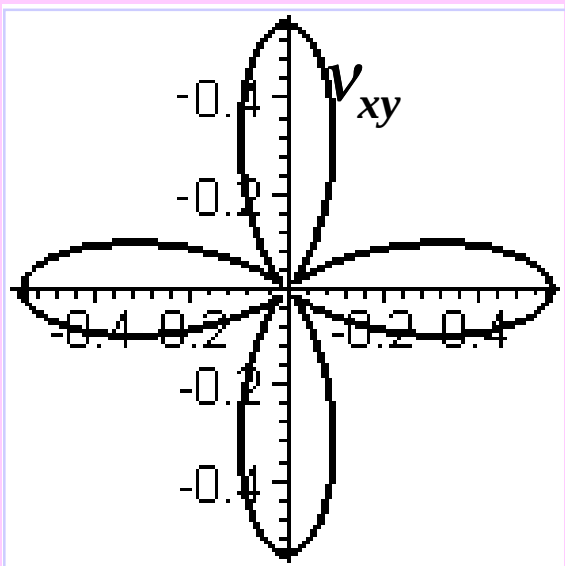


Analytical Model

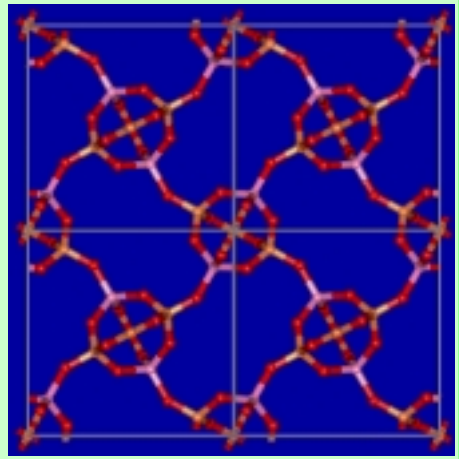
Other auxetic zeolites with a similar nanostructure:

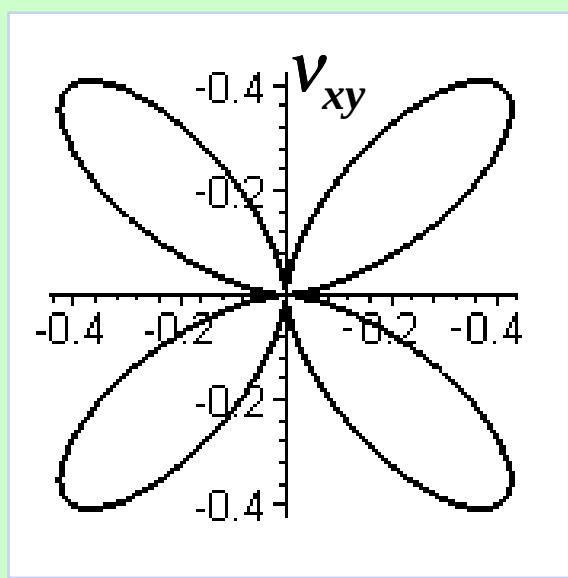
THO



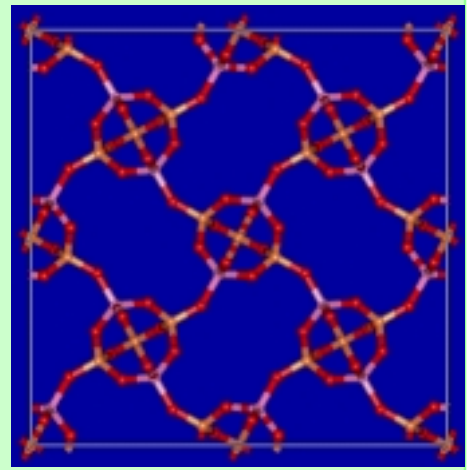


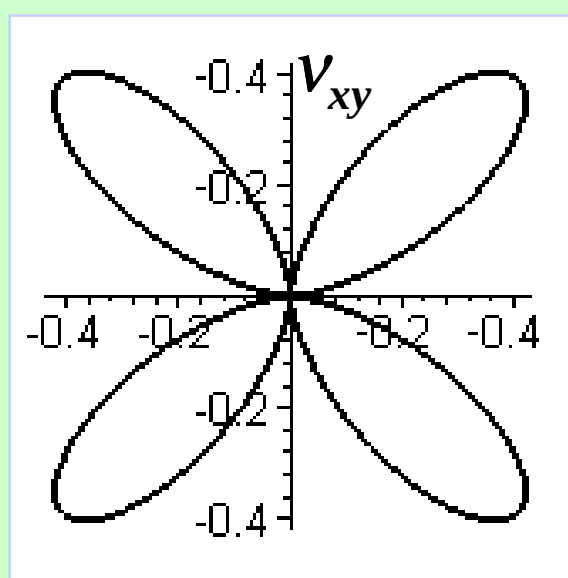
EDI

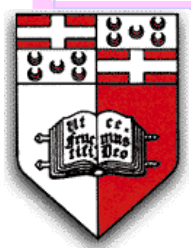




NAT







similar properties … more confidence in results.

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Problem:

Real zeolites have interstitial cations (and water).

What is their effect?

Methodology[(i)]:

(1) Software = Cerius^2

(2) Force-field based simulations using force-fields supplied with Cerius^2 and modifications of them.

(3) Modelling concentrated on the following zeolites with a RS nanostructure:

> NAT > EDI,

modelled as (a) dehydrated zeolites (b) hydrated. In both cases the cations were added[(ii)]. Results were compared to those obtained on the SiO_2 equivalents and the empty frameworks.

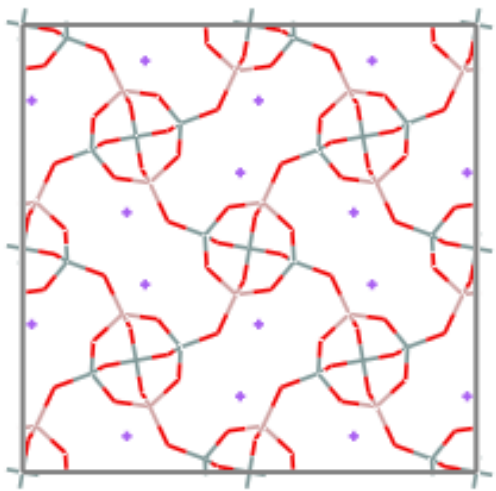
(i) Methodology was validated against the published data of SOD.
(ii)The coordinates for the water molecules and cations were obtained from Treacy and Higgins, 2001

Results: NAT

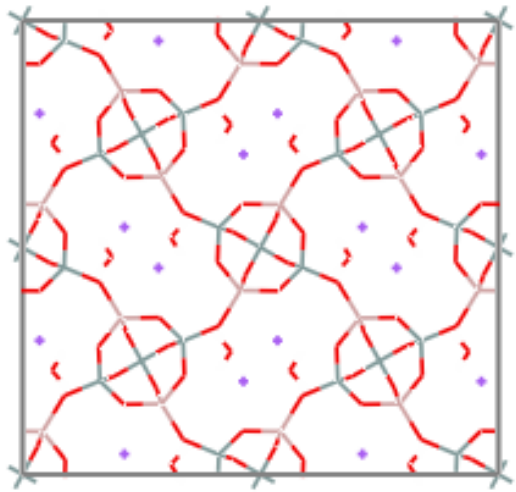
- Auxetic behaviour was retained with the addition of cations and water, but to a lesser degree:

Empty NAT framework > **NAT framework with cations** > **NAT framework with cations + water**

- Properties could still be explained in terms of the **'Rotating Squares' deformation mechanism**.



NAT with cations



NAT with cations + water

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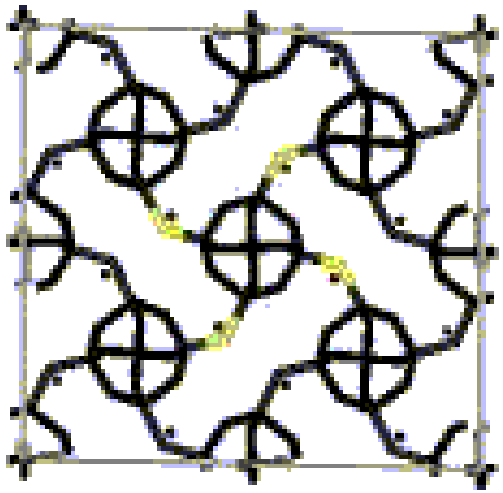
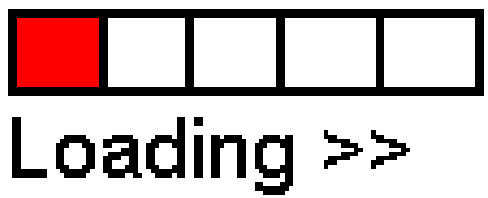
Results: NAT

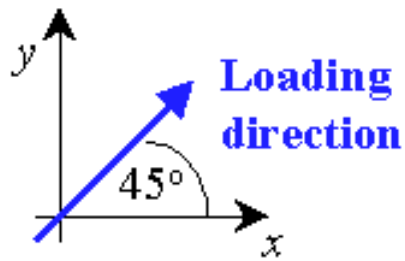
- The rotating squares deformation mechanism in action

NAT Framework + cations

(dehydrated)



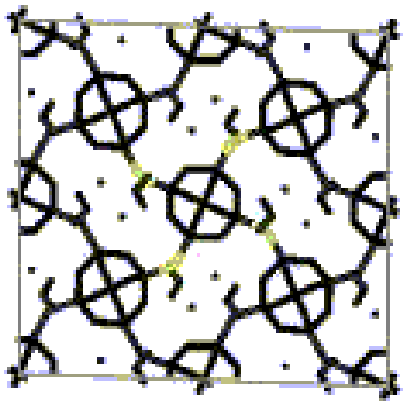


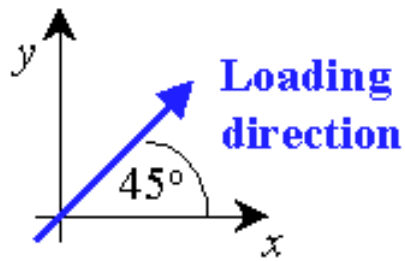


Results: NAT

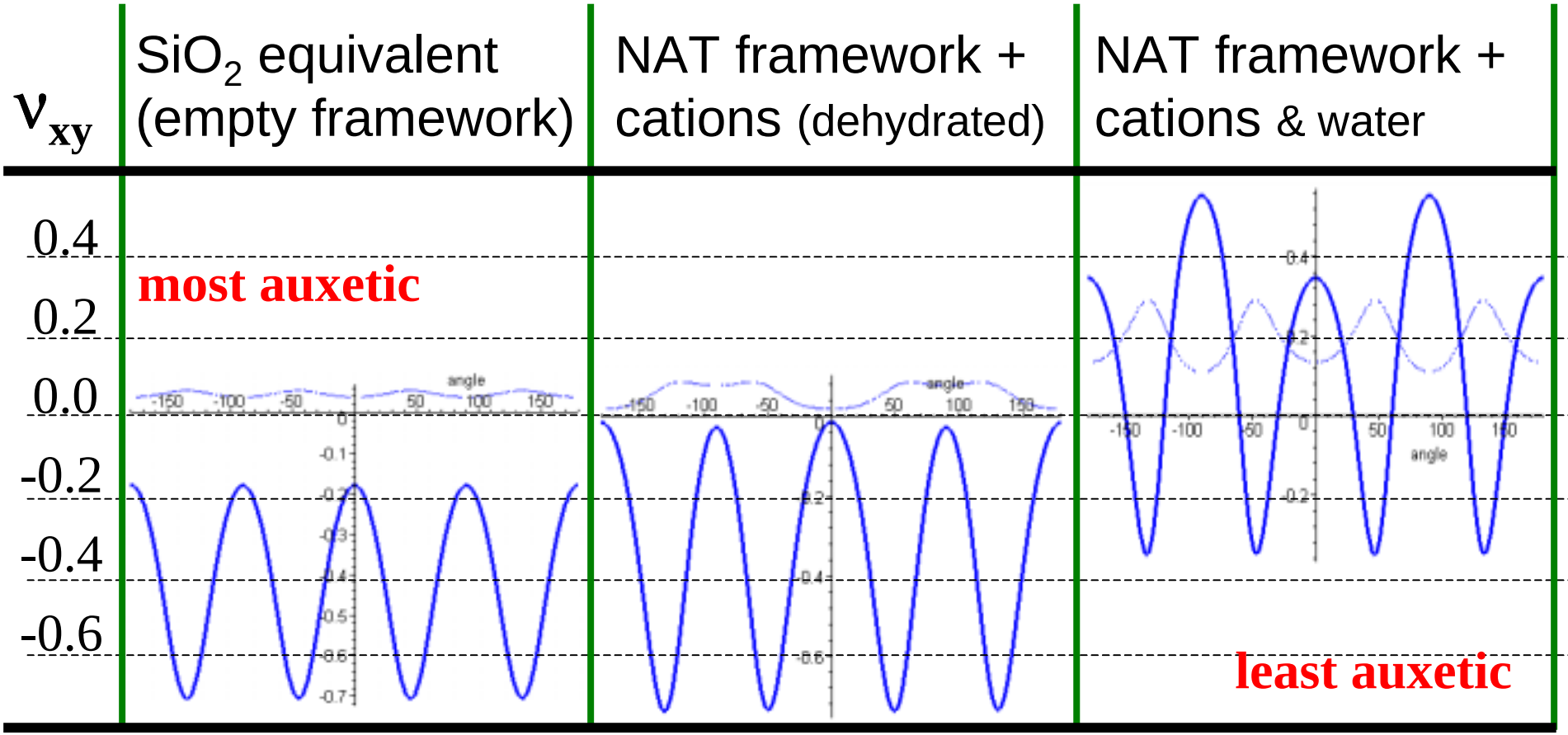
- The rotating squares deformation mechanism in action

NAT Framework + cations + water





Results: NAT - The Poisson's ratio in the XY plane



… similar behavior: maximum ν_{xy} auxeticity at 45^0 to main axes.

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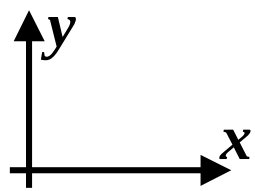
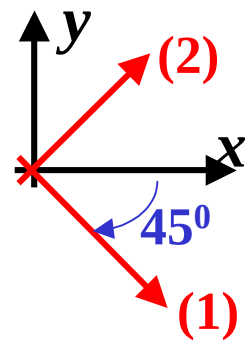
Results: NAT - The mech. properties in the XY plane

	On-Axes			45° to main axes	
	E_x	ν_{xy}	ν_{yx}	ν_{12}	ν_{21}
SiO_2 equivalent	23.98	-0.24	-0.24	-0.7	-0.7
Empty framework	19.29	-0.24	-0.14	-0.8	-0.8
Framework + Cations	20.18	-0.11	-0.08	-0.7	-0.7
framework + cations + water	31.16	0.53	0.33	-0.3	-0.3





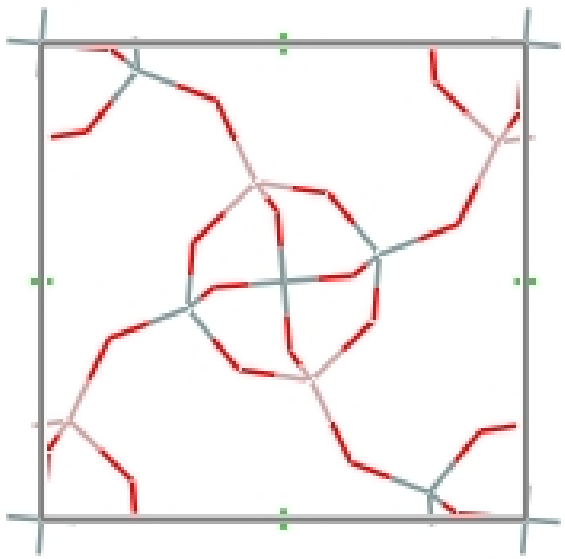
Explanation of Results: NAT

1. Auxeticity present in all cases because ‘rotating squares’ deformation mechanism is operational in all cases. This confirms the important relationship between the framework nanostructure and the mechanical properties.

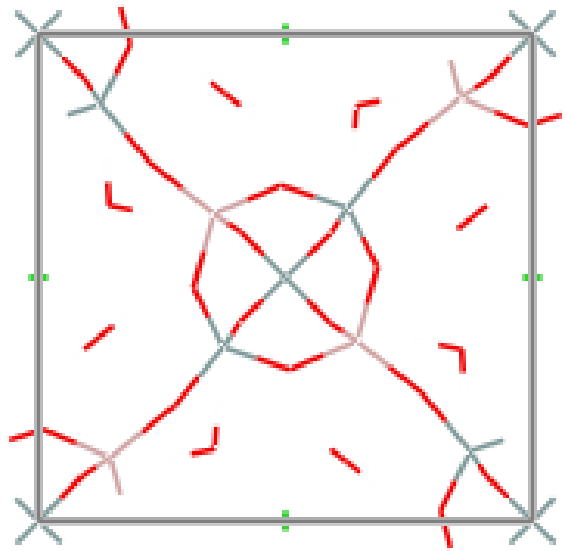
2. Reduced auxeticity is probably due to interactions between the interstitial molecules and cations and the zeolite framework, effectively limiting the framework’s flexibility and therefore making the structures more stiff.

Results: EDI

- Similar trends were observed for EDI. However, the structure was observed to be stiffer and less auxetic than the NAT structure.



EDI with cations



EDI with cations and water

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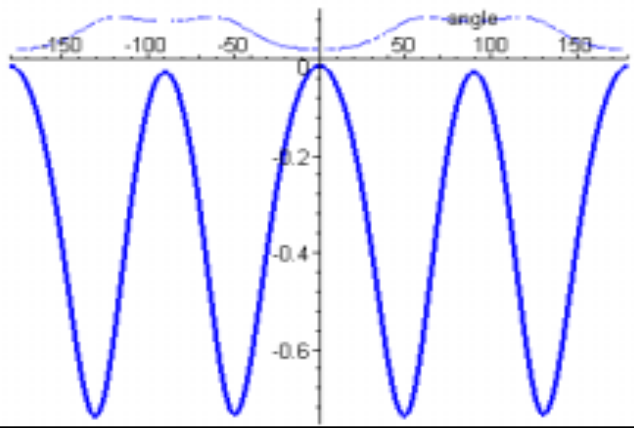
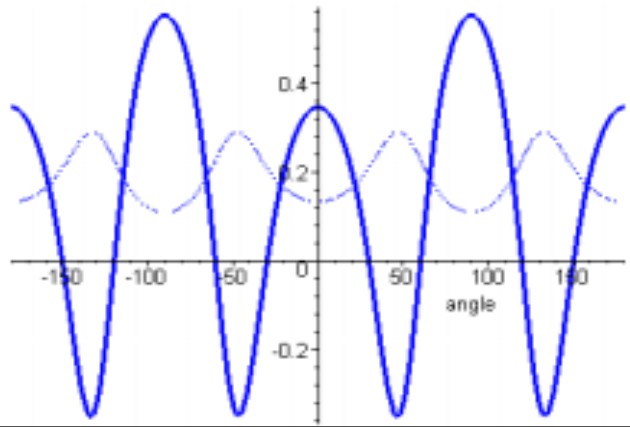
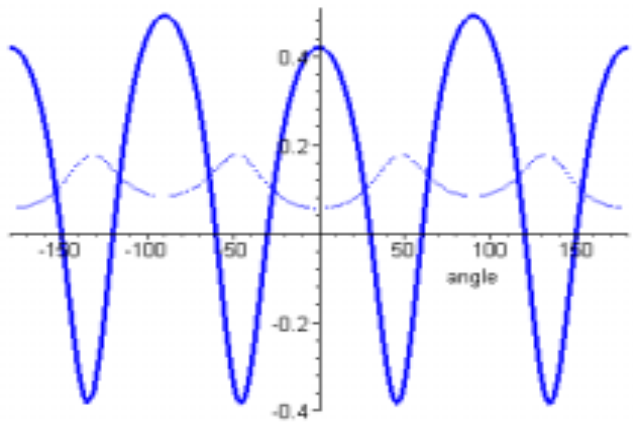
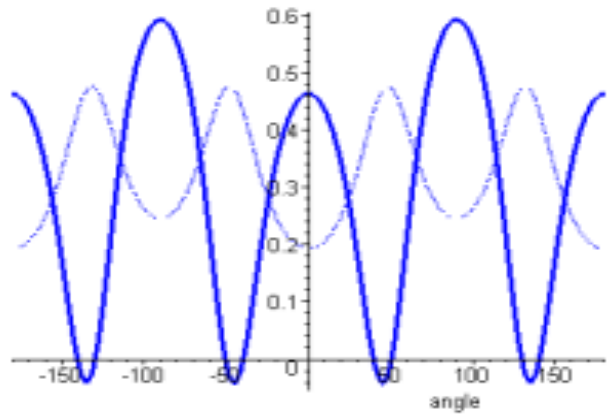
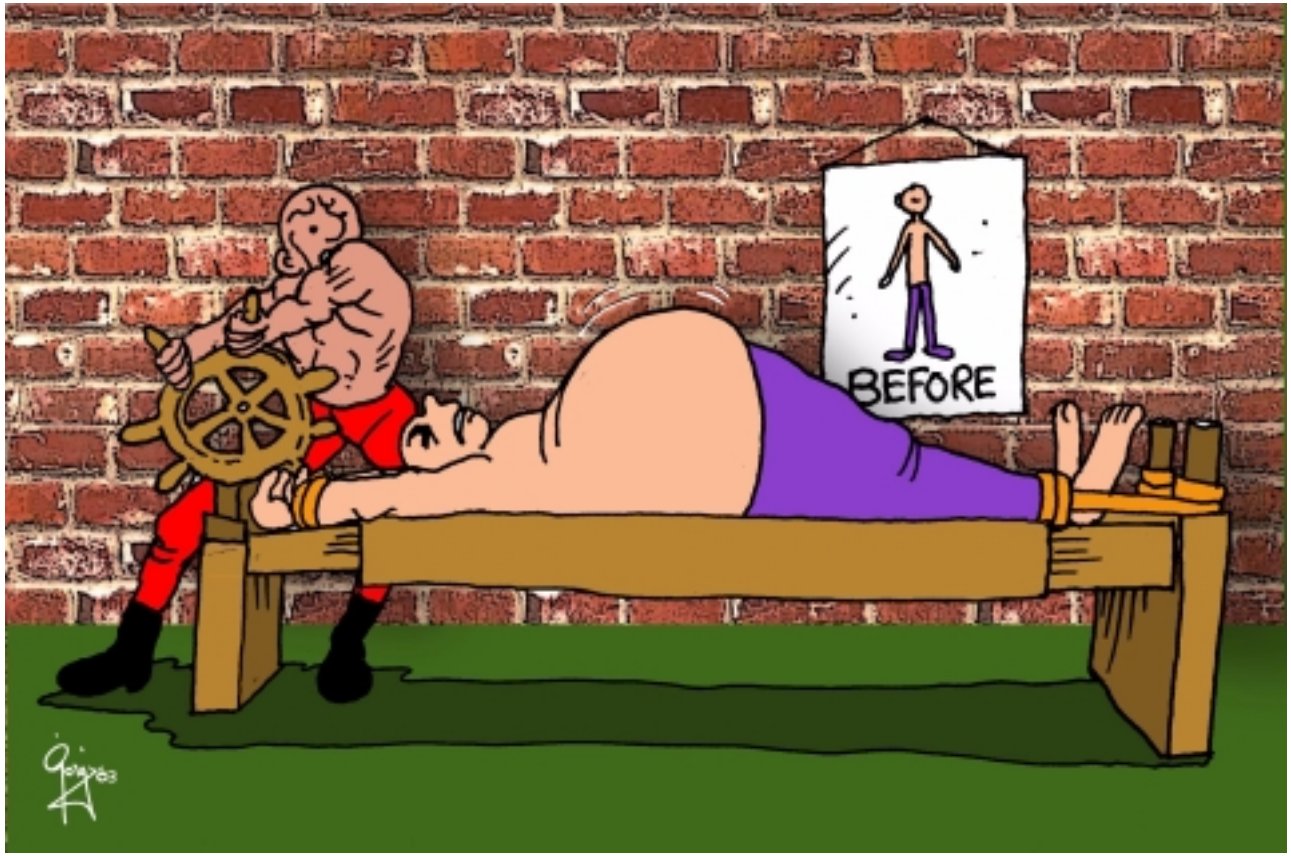
	(dehydrated)	(hydrated)
NAT		
EDI		

Conclusions:

- A number of auxetic zeolites have been identified.
- In THO, NAT and EDI, this unusual behavior was explained in terms of a simple ‘rotating squares’ model.
- Auxeticity is maximum in the empty frameworks. However, some auxetic behavior is retained in the presence of cations and water molecules as ‘RS’ deformation mechanism is still operational.



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