Effect of breather existence on reconstructive transformations in mica muscovite

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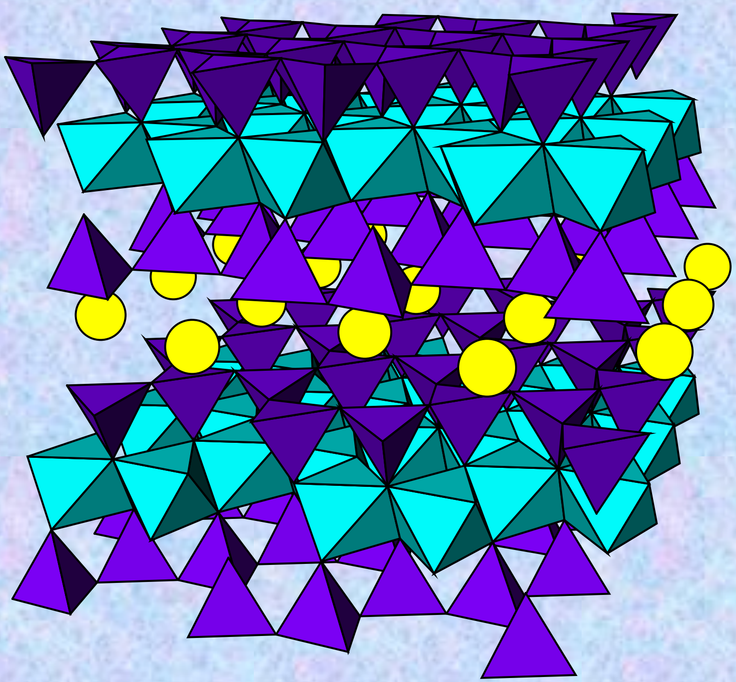
Reconstructive transformation of muscovite

Muscovite

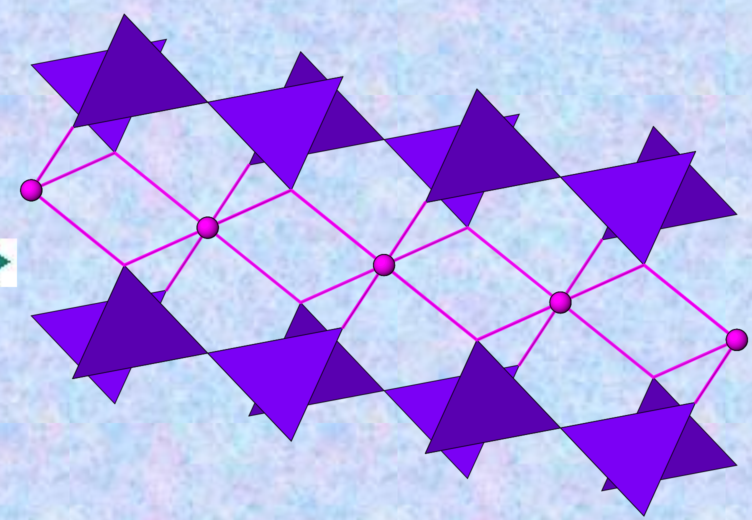
$K_2[Si_6Al_2]^{IV}[Al_4]^{VI}O_{20}(OH)_4$

Disilicate of Lutetium

$Lu_2Si_2O_7$



Lu^{3+}



300° C, 3 days

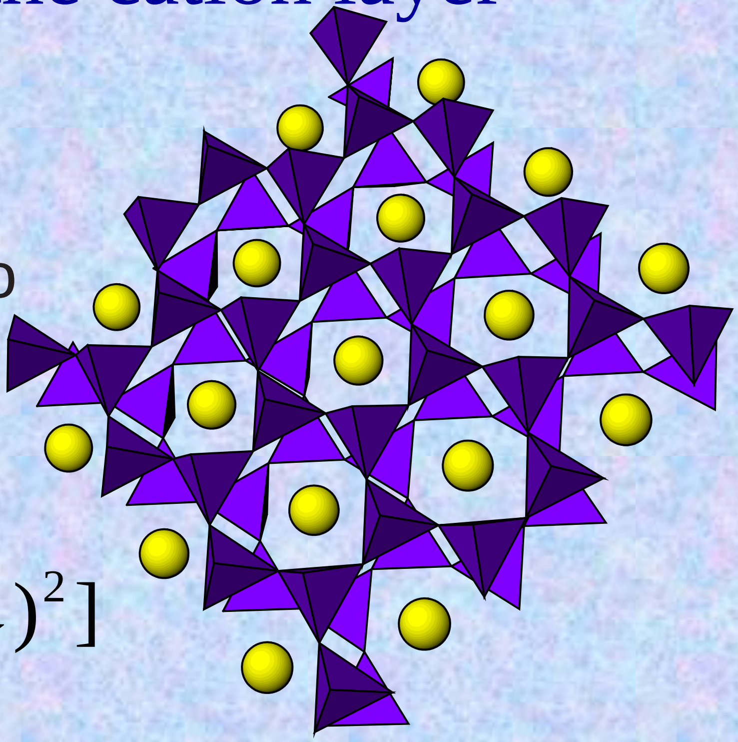
About 36% of muscovite is transformed

K^+

Reconstructive transformations in layered silicates

- In the laboratory the long times of ageing are simulated with higher temperatures
- Activation energies range typically about 200-400 kJ/mol
- They involve the breaking of the Si-O bond, stronger than that between any other element and oxygen and are observed in silicates only above 1000 C
- A condition for the transformation to take place is that sufficient atoms have enough energy to achieve a transition *activated state*.
- **Low temperature reconstructive transformations (LTRT) in layered silicates have recently been achieved at temperatures 500 C lower than the lowest temperature reported before** [Becerro et al, J. Mater. Chem **13**, (2003)]
- LTRT take place in the presence of the cation layer
- Possible application in engineered barriers for nuclear waste in deep geological repositories.

Hypothesis: 2D breathers within the cation layer



- Are their energies larger than the activation energy?
- Are there enough number of breathers to explain the increase in the reaction rate?

Hamiltonian:

$$H = \sum_{\vec{n}} \left[\frac{1}{2} m \dot{u}_{\vec{n}}^2 + V(u_{\vec{n}}) + \frac{1}{2} k \sum_{\vec{n}'} (u_{\vec{n}} - u_{\vec{n}'})^2 \right]$$

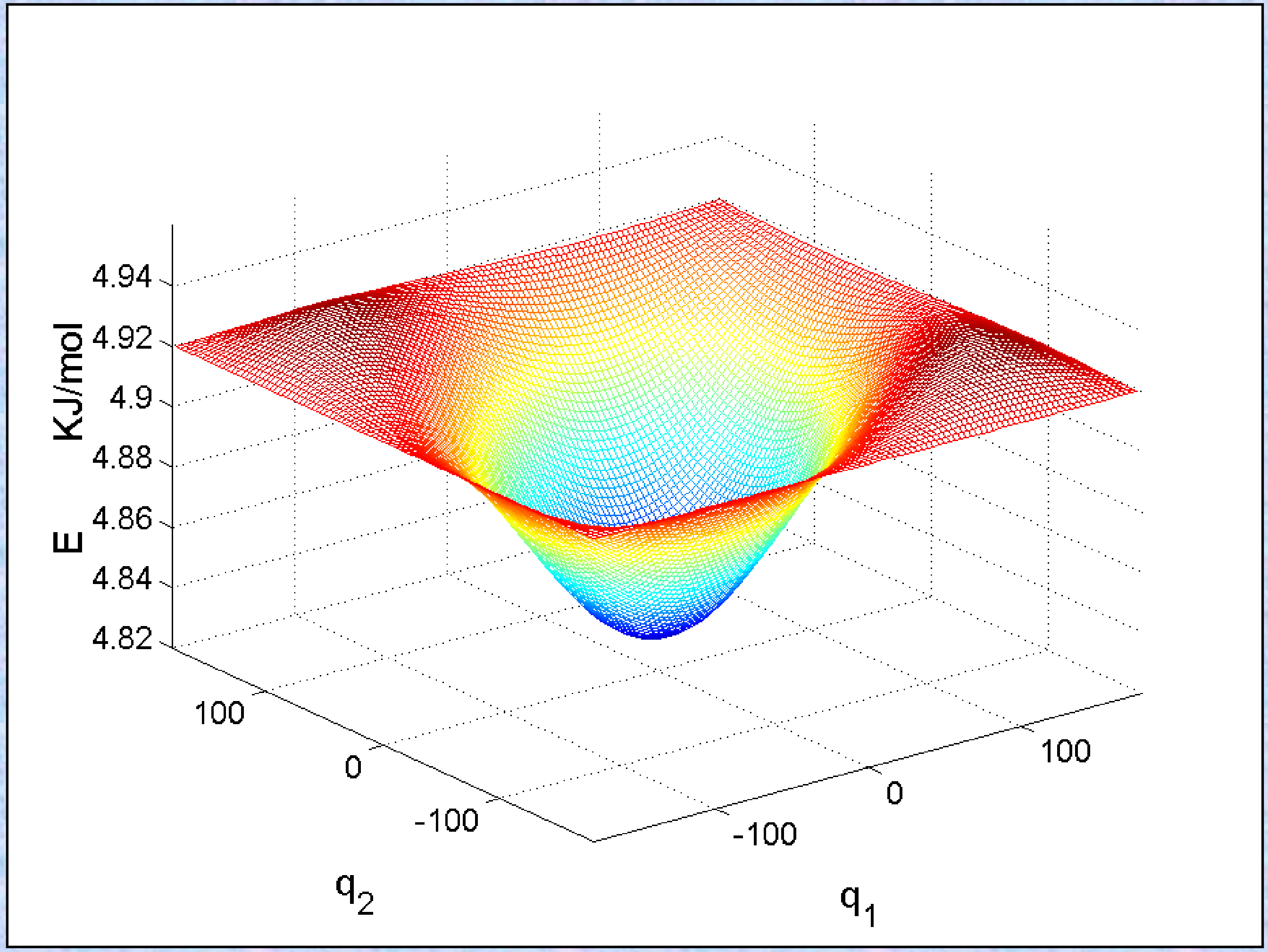
Harmonic coupling

- k=10±1 N/m (D. R. Lide Ed., *Handbook of Chemistry and Physics,* CRC press 2003-2004)

On-site potential *V*

- Linear frequency ν_0=143 cm^{-1} [Diaz et al, *Clays Clay Miner.*, **48**, 433 (2000)]

Mean energy of each phonon mode



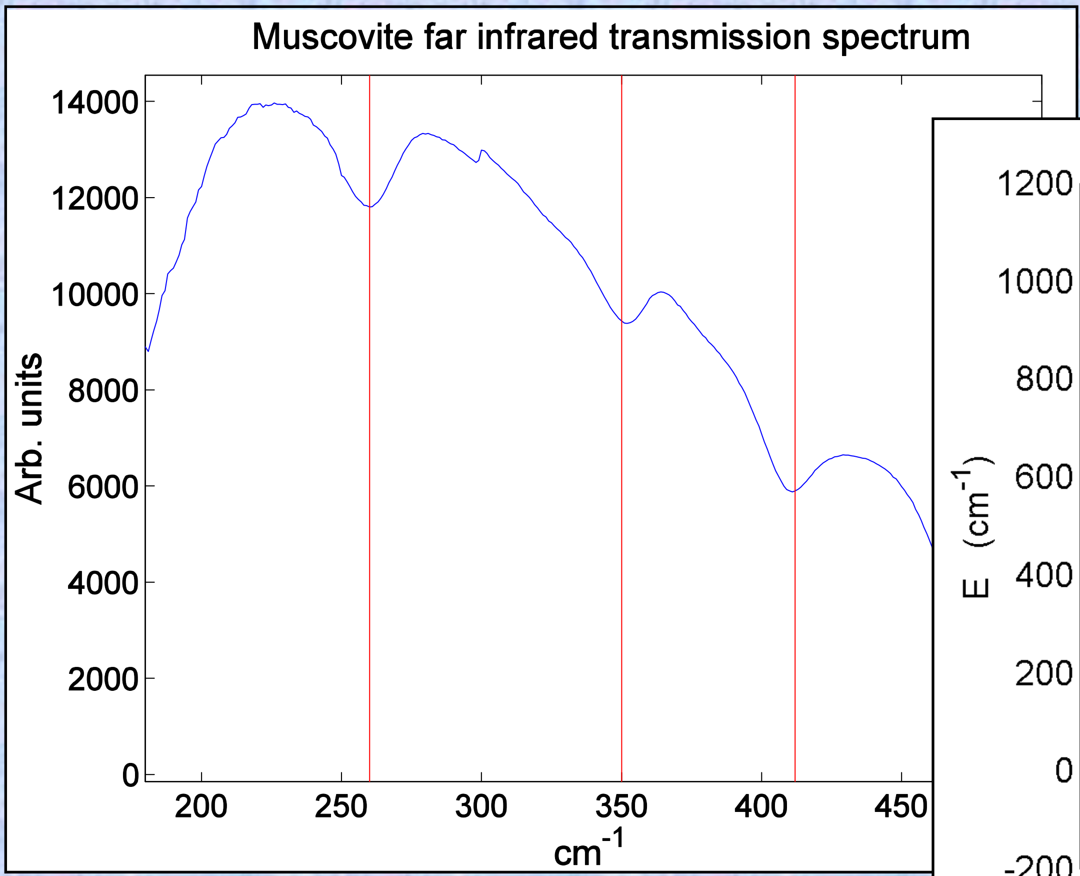
$<E_{ph}>=(n+0.5)\ h\nu$

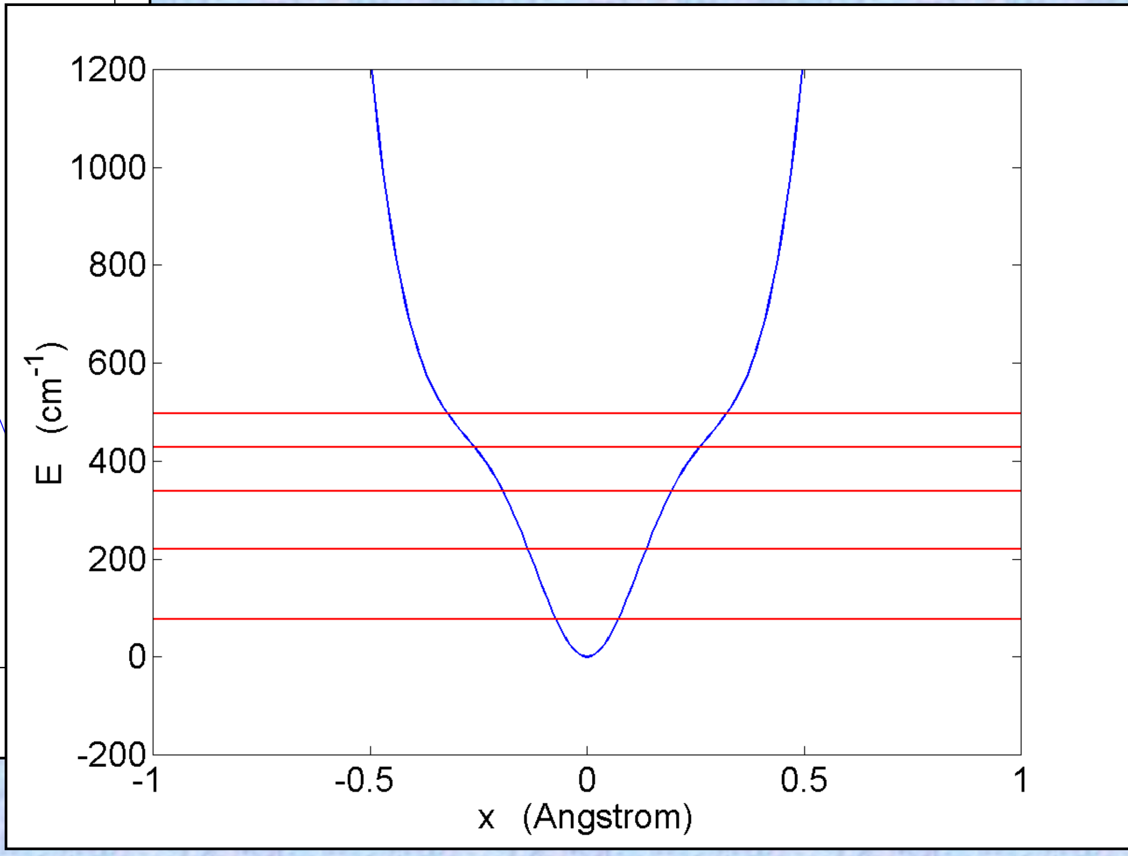
$n=1/(e^{\beta h\nu}-1)$

T=573 K

Mean phonon energy of about 5 kJ/mol, much smaller than the activation energy

On-site potential obtained from infrared spectrum

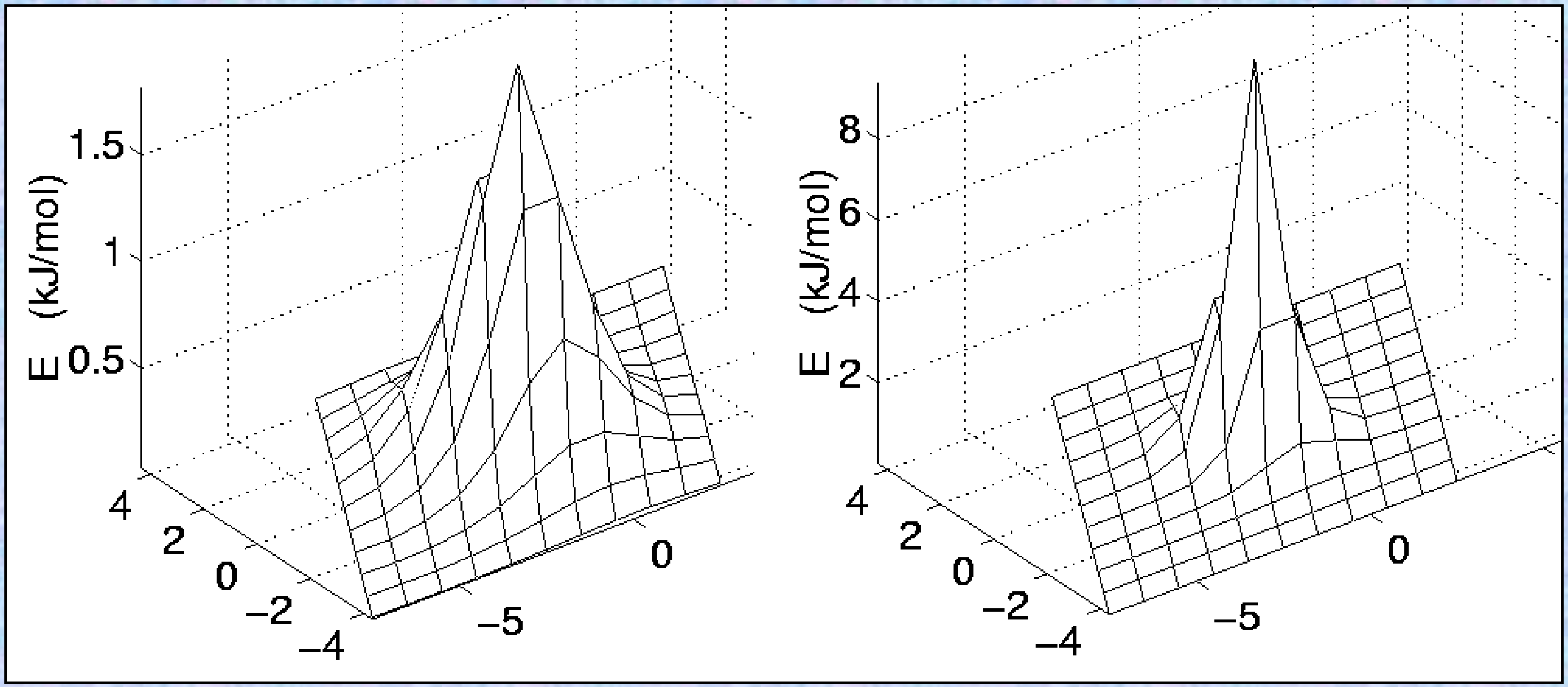




Fitting the potential: $V(x) = D\,(\,[1-\exp(-\,b^2 x^2)\,]+\gamma\, x^6)$

$D = 453$ cm^{-1} $b^2 = 36$ Å^{-2} $\gamma = 49884$ cm^{-1} Å^{-6}

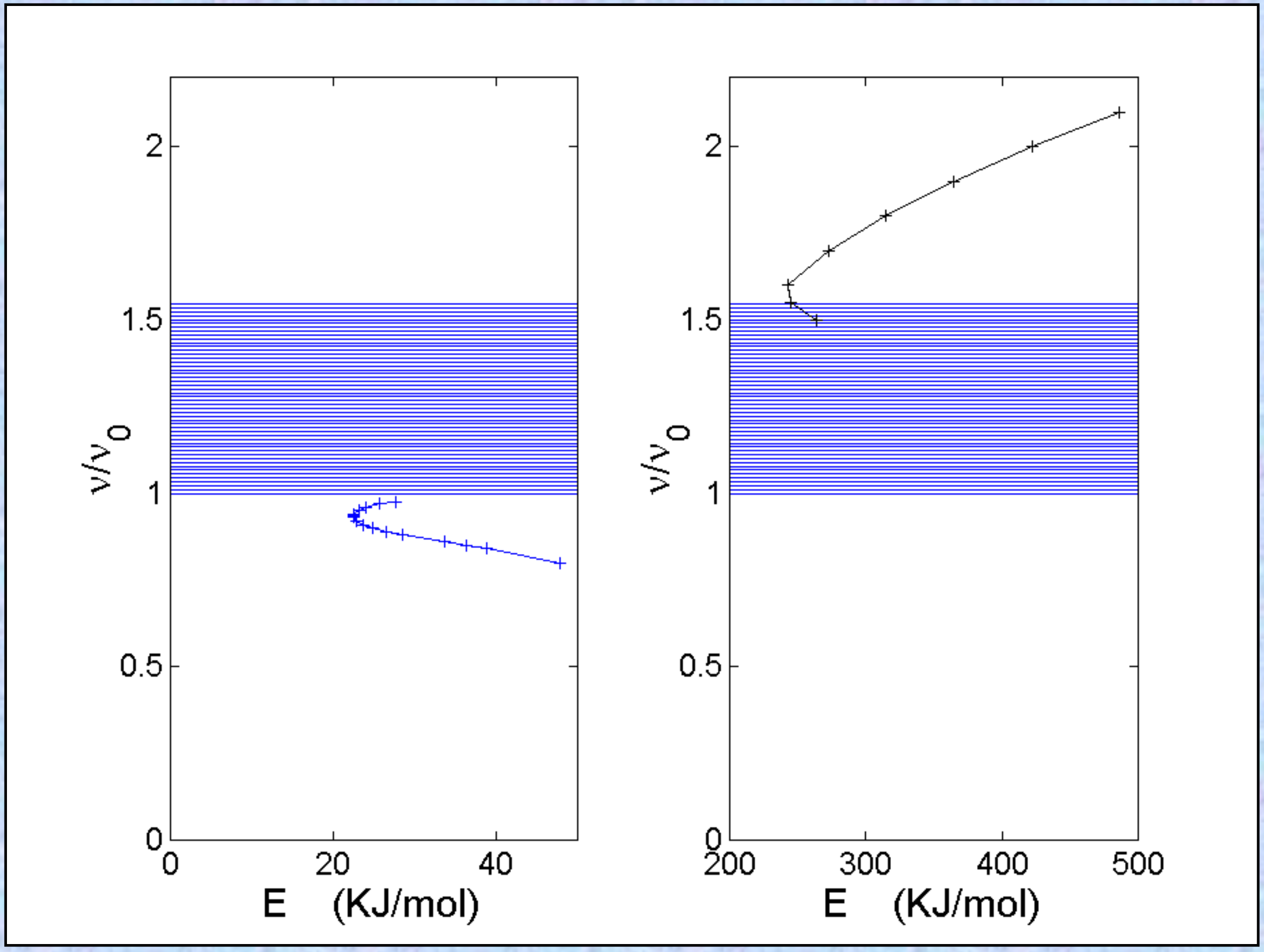
Energy density profiles for two soft breathers



$\nu_b = 0.97\nu_0$, E =25.6 kJ/mol $\nu_b = 0.85\ \nu_0$, E =36.3 kJ/mol

$\nu_0 = 167.5\ cm^{-1} \sim 5 \cdot 10^{12}$ Hz

Breather frequency versus energy



ν_0= 167.5cm^{-1}
~ 5·10^{12} Hz

Mimimum energies
Δ_s = 22.4 kJ/mol

Δ_h = 240 kJ/mol

Activation energy
estimated in
100-200 kJ/mol

BREATHERS HAVE LARGER ENERGIES THAN THE ACTIVATION ENERGY

2D breather statistics: Piazza et al, 2003

1.- They have a minimum energy: Δ

2.- Rate of breather creation: $B(E) \;\alpha\; \exp(-\beta E)$, $\beta=1/k_B T$

3.- Rate of breather destruction: $D(E) \;\alpha\; 1/(E-\Delta)^{z}$

Large breathers live longer.

4.- Thermal equilibrium: if $P_b(E)\,dE$ is the probability that a breather energy is between E and E+dE:

$$D(E)\,P_b(E)\,dE = A\,B(E)\,dE, \qquad A \neq A(E)$$

5.- Normalization: $\int_0^\infty P_b(E)\,dE = 1$

Breathers statistics. Results.

1.-$P_b(E)= \beta^{z+1} (E- \Delta)^z \exp[- \beta(E- \Delta)]/\Gamma(z+1)$

2.- $<E>=\Delta+(z+1)\, k_B T$

3.- Most probable energy: $E_p= \Delta+ z\, k_B T$

3.-Fraction of breathers with energy above *E*:

$$C_b(E)=\Gamma(z+1)^{-1}\, \Gamma(z+1, \beta[E-\Delta])$$

4.- Mean number of breathers per site with energy above E:

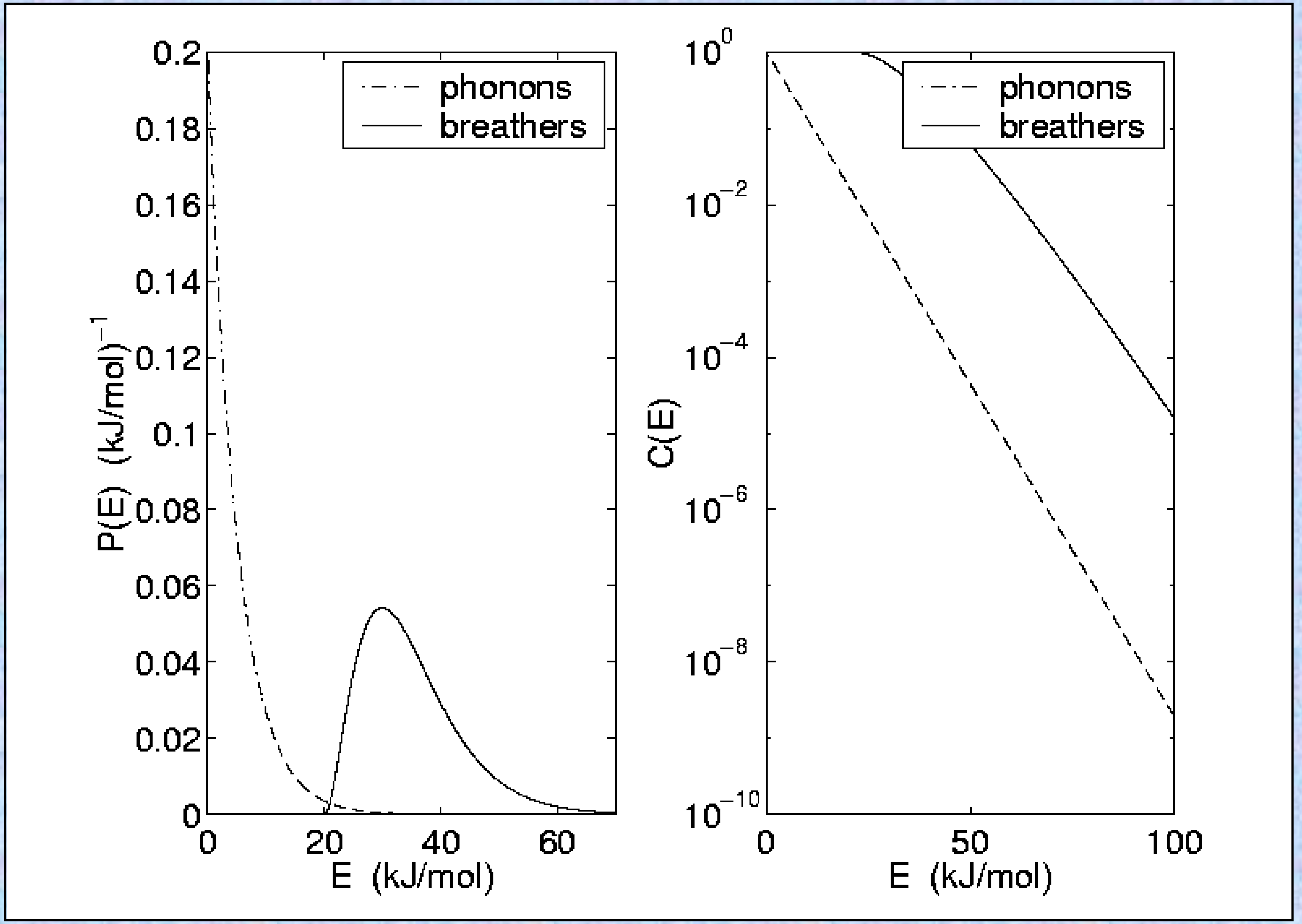
$$n_b(E)=<n_b>C_b(E)$$

$<n_b>$=mean number of breathers per site $\sim 10^{-3}$

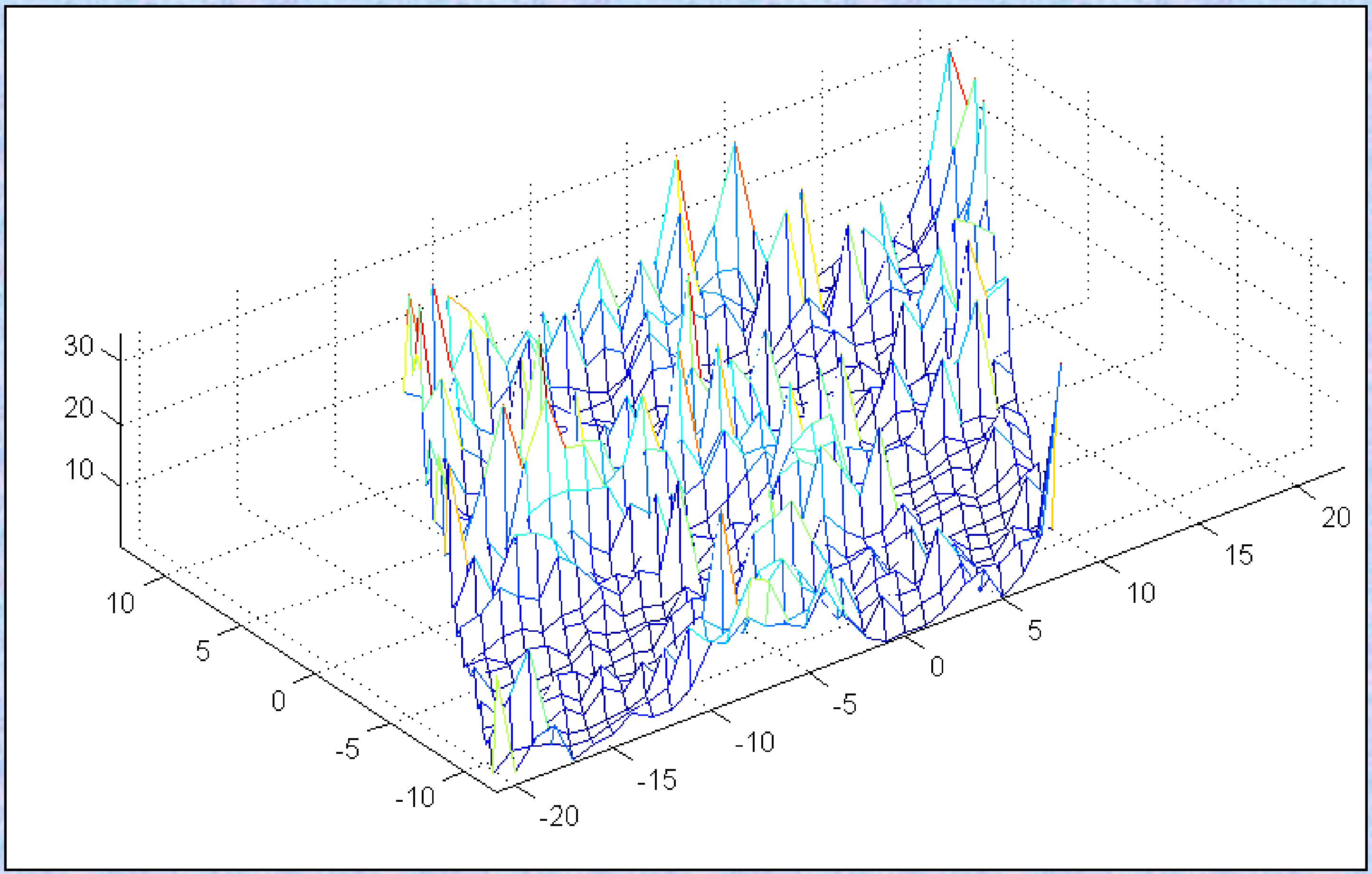
-Function gamma and first incomplete gamma function:

$$\Gamma(z+1)= \int_0^\infty y^z \exp(-y)dy, \quad \Gamma(z+1,x)= \int_x^\infty y^z \exp(-y)dy$$

Probability density and cumulative probability. Breathers accumulate at higher energies

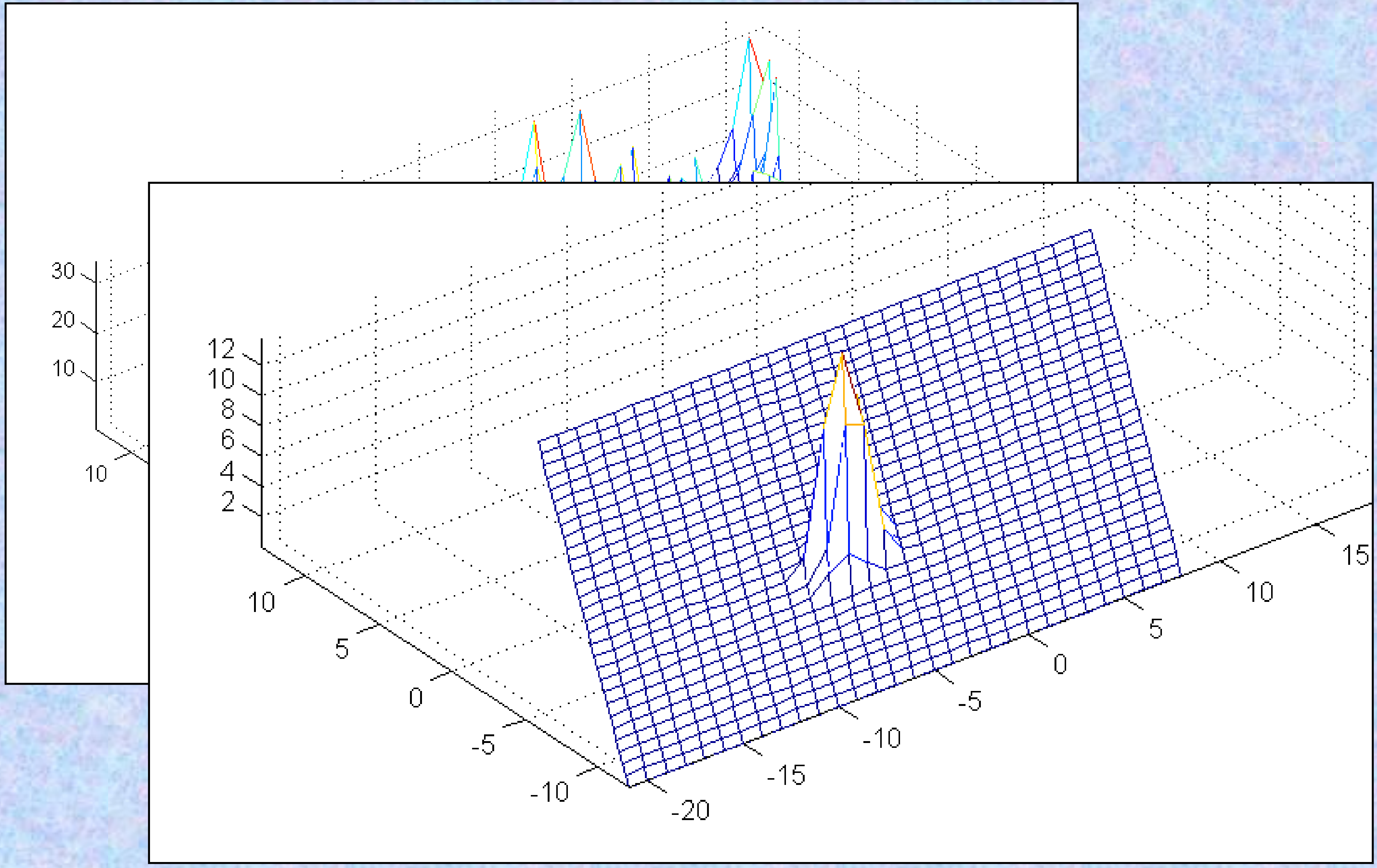


Numerical simulations in mica. Before cooling.

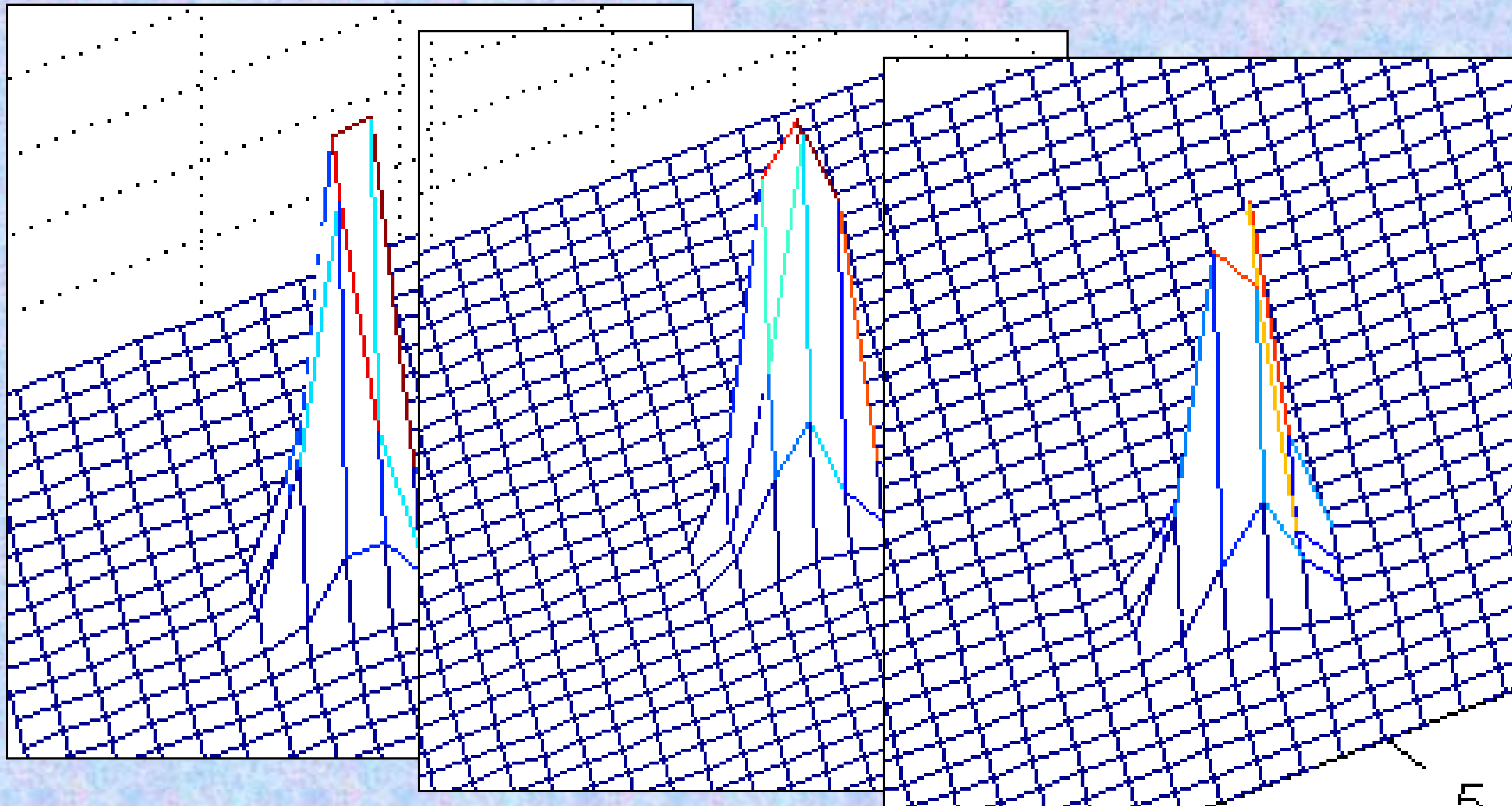


Random velocities and positions. Thermal equilibrium. Cooling at the borders.

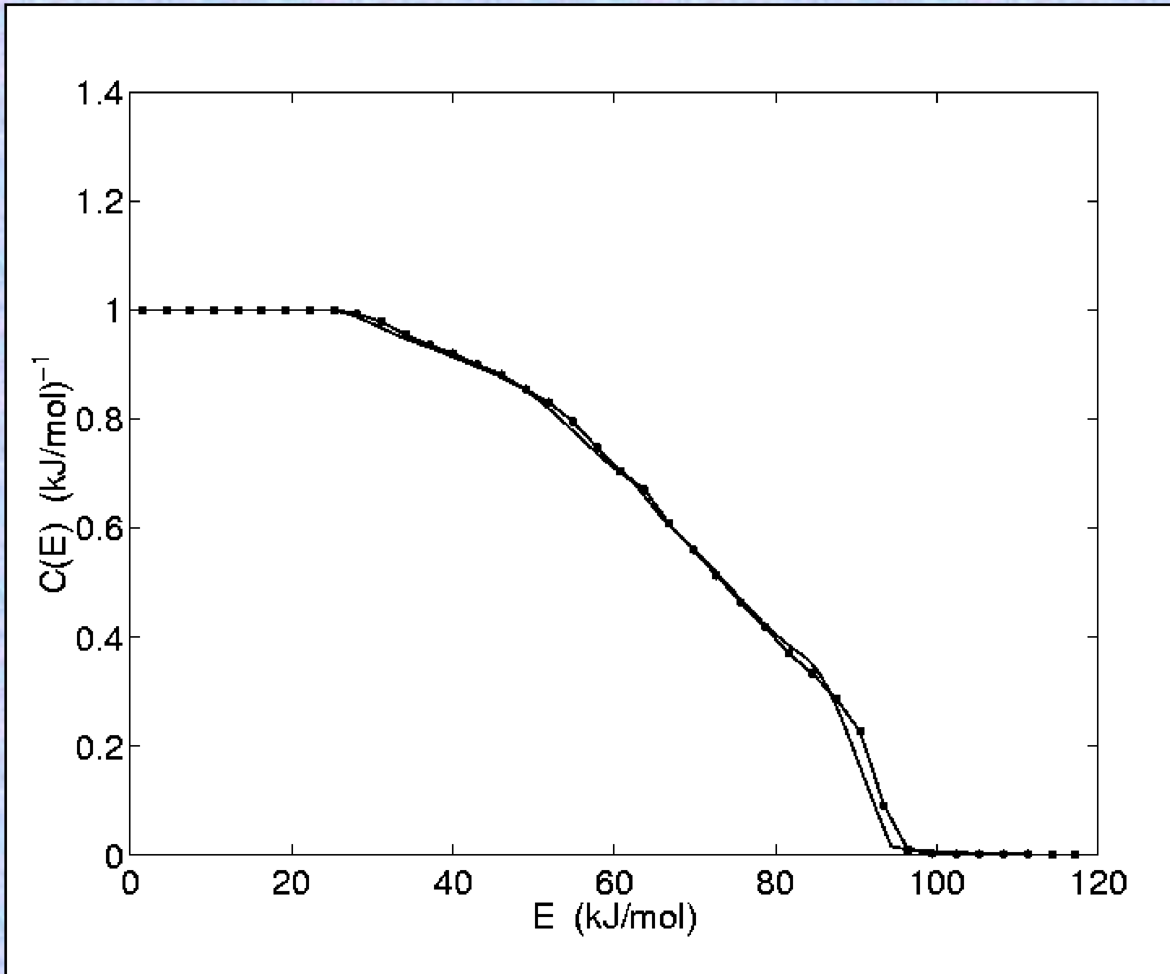
Numerical simulations in mica. After cooling.

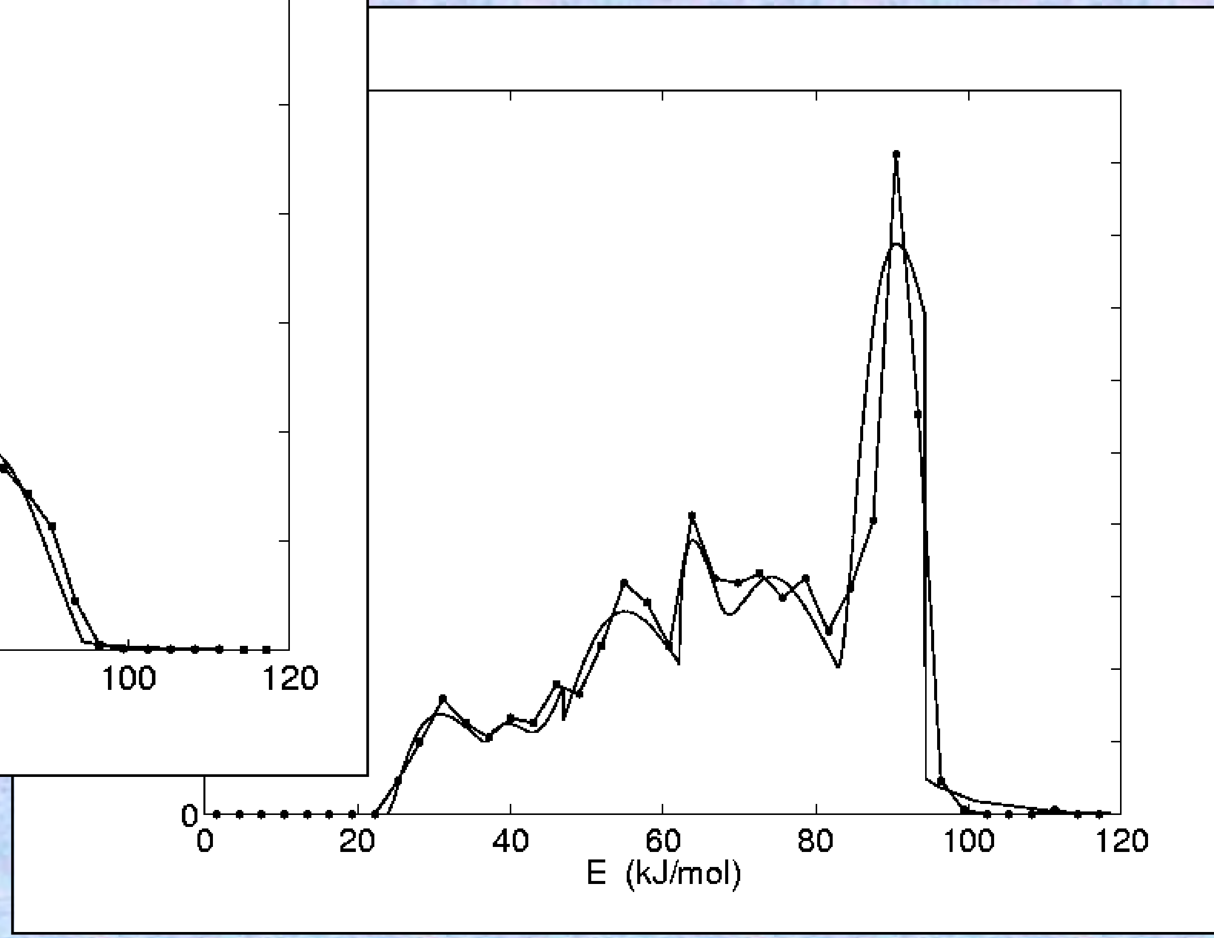


Multiple types of breathers and multibreathers. Breathers with maximum energy. Modification of the theory



Cumulative probability and probability density for breathers in mica





•-- Numerical

— Theoretical

Estimations

For E_a~100-200 kJ/mol, T=573 K:

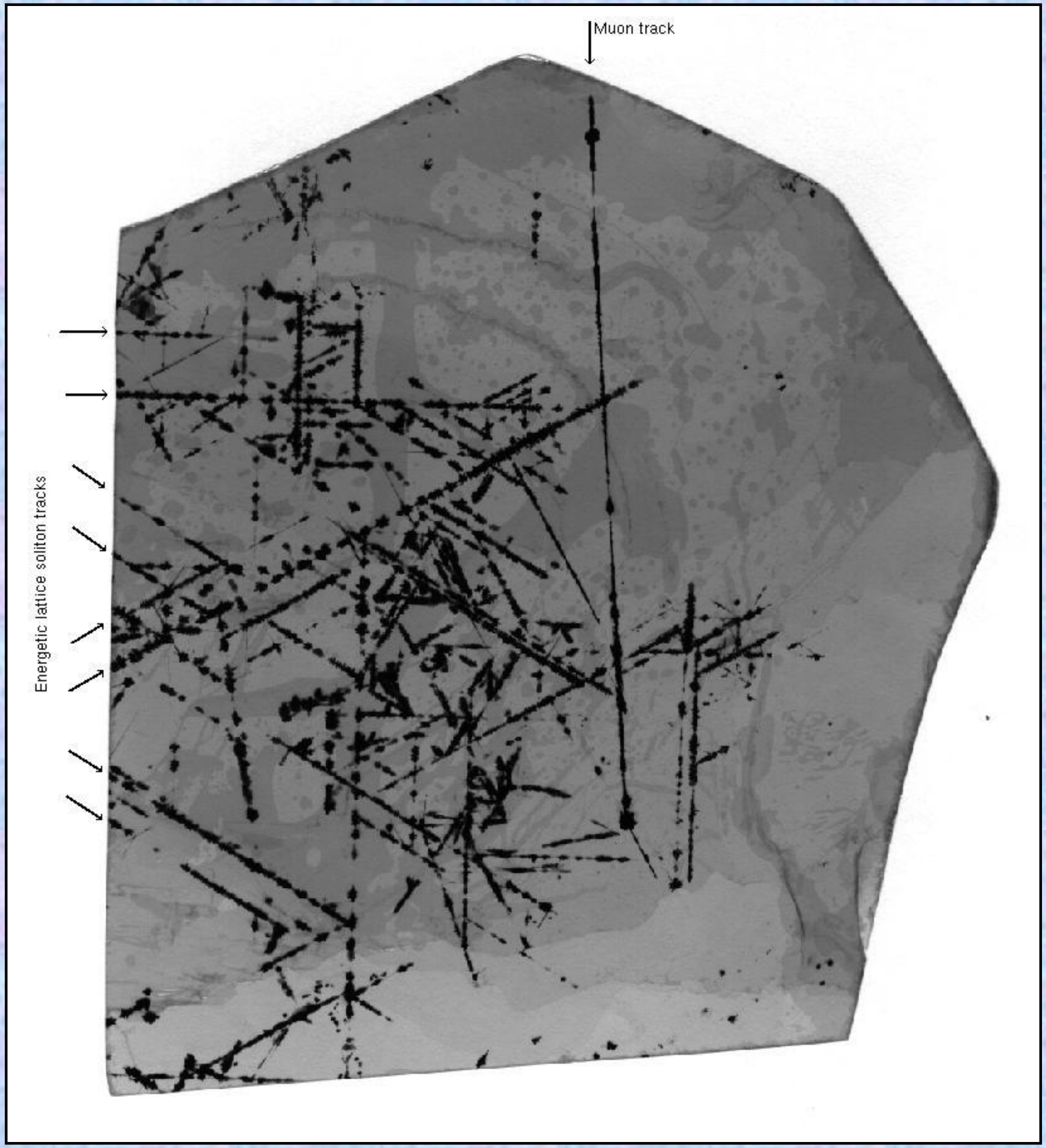
$$\frac{\text{Number of breathers}}{\text{Number of phonons}} = 10^4\text{-}10^5 \qquad \text{(with } E \geq E_a\text{)}$$

Reaction time without breathers: 80 a 800 años,

Moreover, breather can loaclize more the energy delivered, which will increse further the reaction speed

THERE ARE MUCH LESS BREATHERS THAN LINEAR MODES, BUT MUCH MORE WITH ENERGYABOVE THE ACTIVATION ENERGY

Other evidences: quodons in mica muscovite



Black tracks: Fe_3O_4

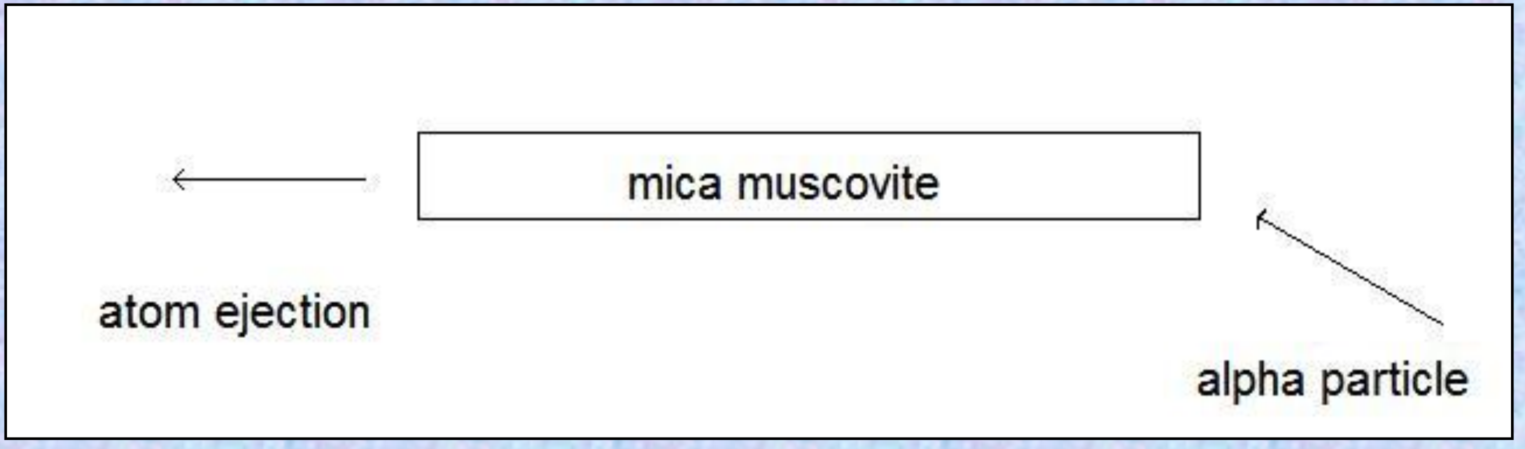
Cause:

- 0.1% Particles:
  - muons: produced by interaction with neutrines
  - positrons: produced by muons' electromagnetic interaction and K decay

- 99.9% **Unknown**

¿Lattice localized vibrations: quodons?

Other evidences: Sputtering



Trajectories along lattice directions within the K^+ layer

Evidence for moving breathers in a layered crystal insulator at 300K

FM Russell y JC Eilbeck, Europhysics Letters, **78** (2007) 1004

CONCLUSIONS

1. Breathers within the cation layer have larger energies than the activation energy

2. There are much more breathers than linear modes with enough energy, which can explain the observed increase in the reaction speed

3. There are other evidences on the existence of breather in the cation layer

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Bibliography

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