Breather energy spectra and reconstructive transformations of mica muscovite

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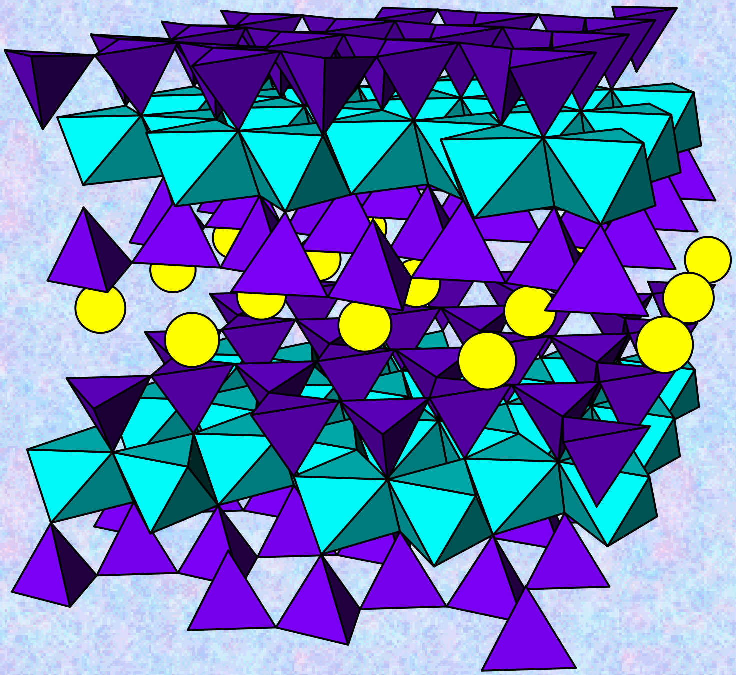
¿What is the reconstructive transformation of Mica muscovite?

muscovite

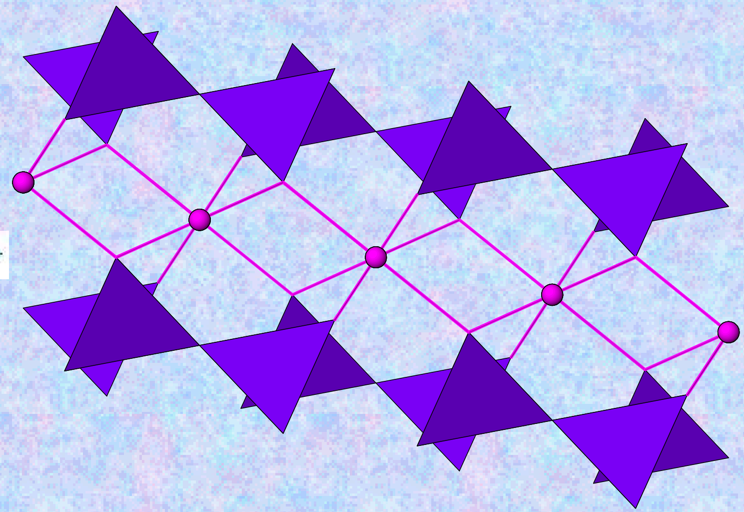
$K_2[Si_6Al_2]^{IV}[Al_4]^{VI}O_{20}(OH)_4$

Disilicate of Lutetium

$Lu_2Si_2O_7$



Lu^{3+}



300° C, 3 days

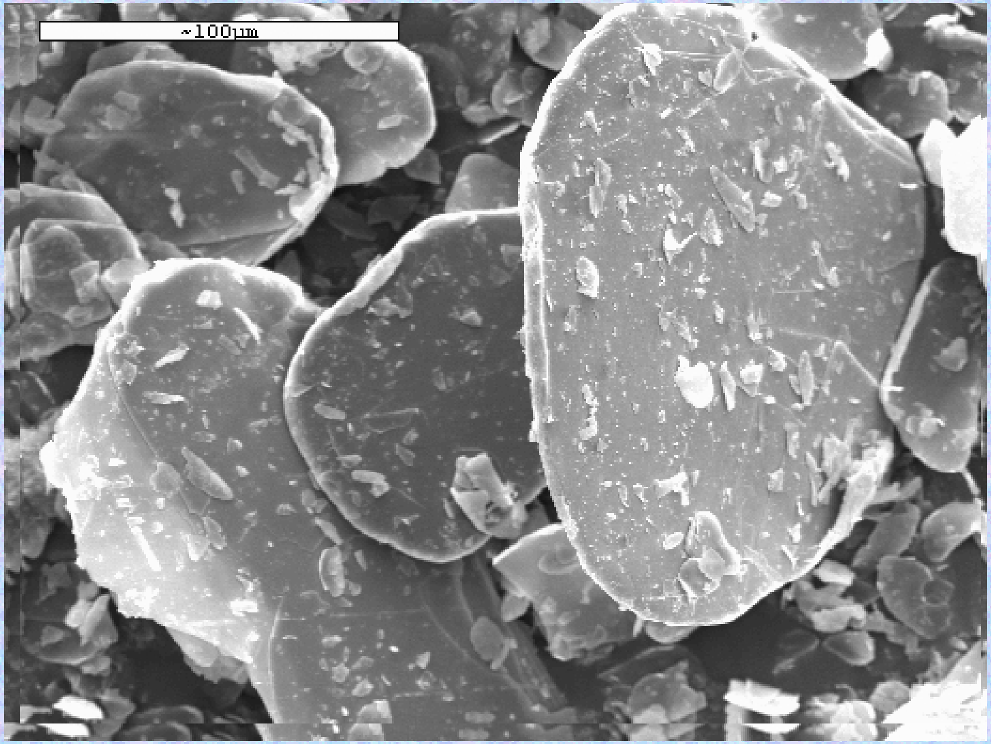
K^+

36% of muscovite transforms

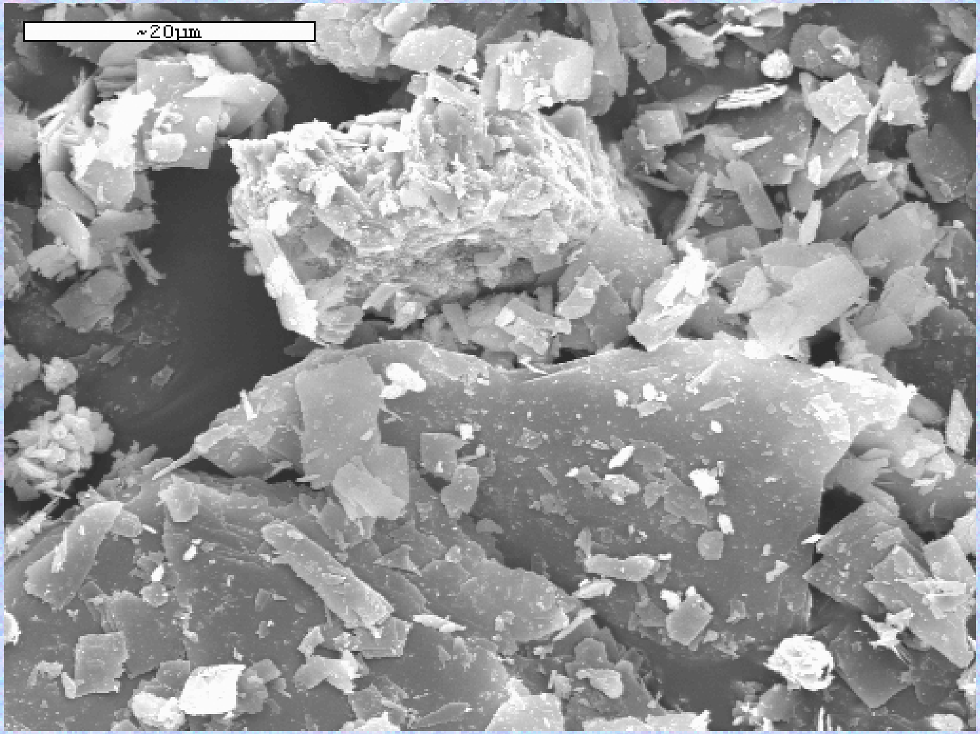
Lu^{3+}

Scanning electron microscopy with energy dispersive X-ray (EDX) analysis

Untreated muscovite



Treated muscovite

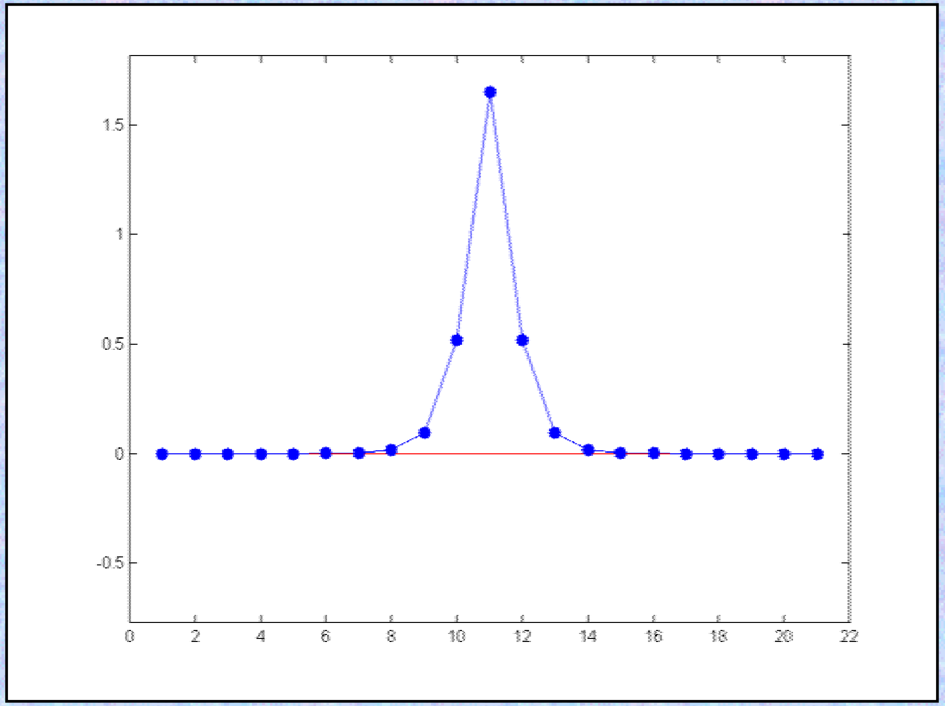


Three different types of particles: muscovite, $Lu_2Si_2O_7$ and bohemite

¿What are breathers?
¿In which systems do they appear?

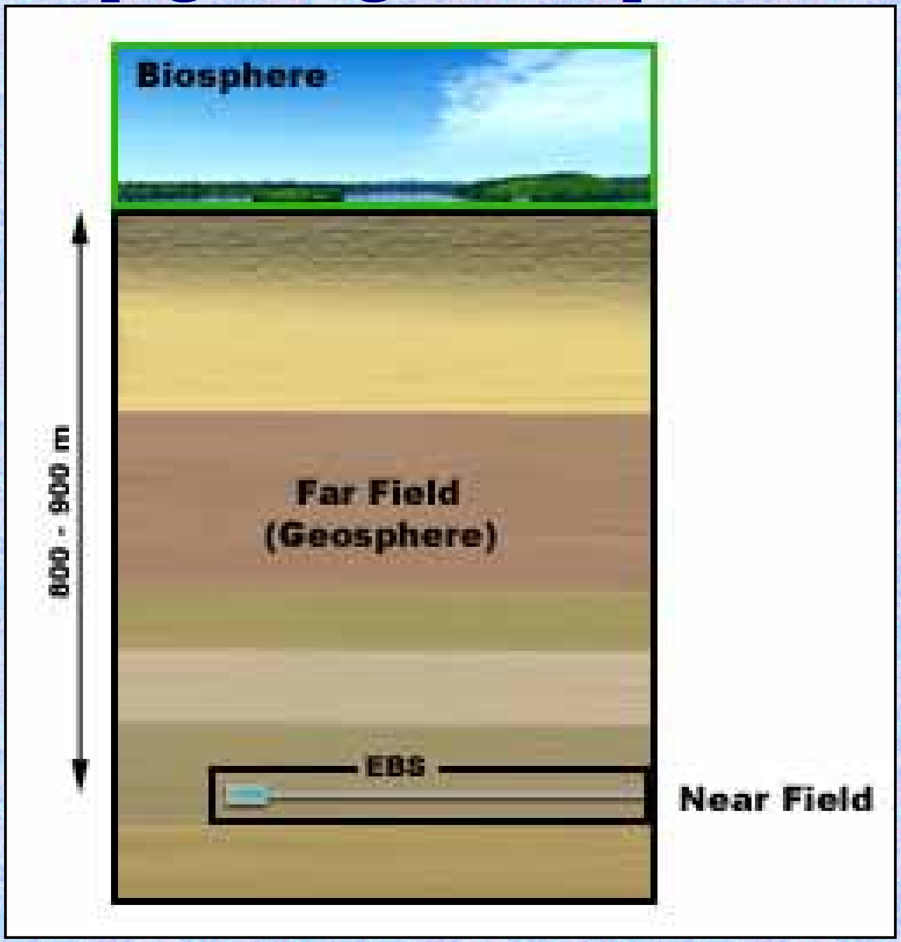
- Vibrations
- Localized
- Exact

- In systems of coupled oscillators



¿Why are we interested in reconstructive transformations?

Deep geological depositories for nuclear waste.



EBS:
Engineered barrier system

- Lutetium substitutes in the laboratory to heavy radionuclides
- The reconstructive transformation traps the radionuclides

¿What is special in the reconstructive transformation of mica and other layered silicates?

• Reconstructive transformations had been observed in silicates only about 1000 C

• **Some of the authors (MDA, MN, JMT) have recently achieved low temperature reconstructive transformations (LTRT) at temperatures 500 C lower than the lowest temperature reported before**

• **LTRT:** Low temperature reconstructive transformations.

• **UP TO NOW THERE WAS NO EXPLICATION**

¿Could breathers be the explanation?

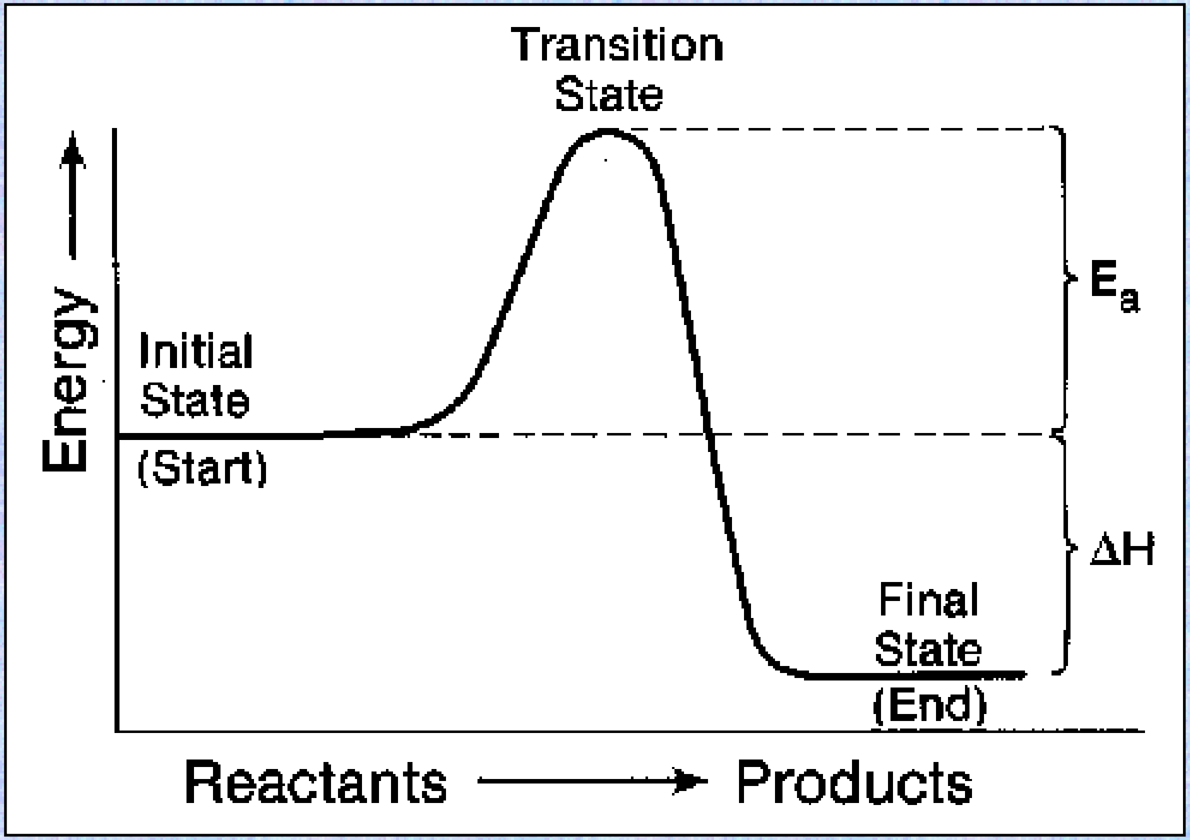
First suggested in: Mackay and Aubry [Nonlinearity, **7**, 1623 (1994)]

¿What influence may have breathers? Reaction speed and statistics

Arrhenius law: $\kappa = A \exp(-E_{\mathbf{a}}/RT)$

Transition state theory

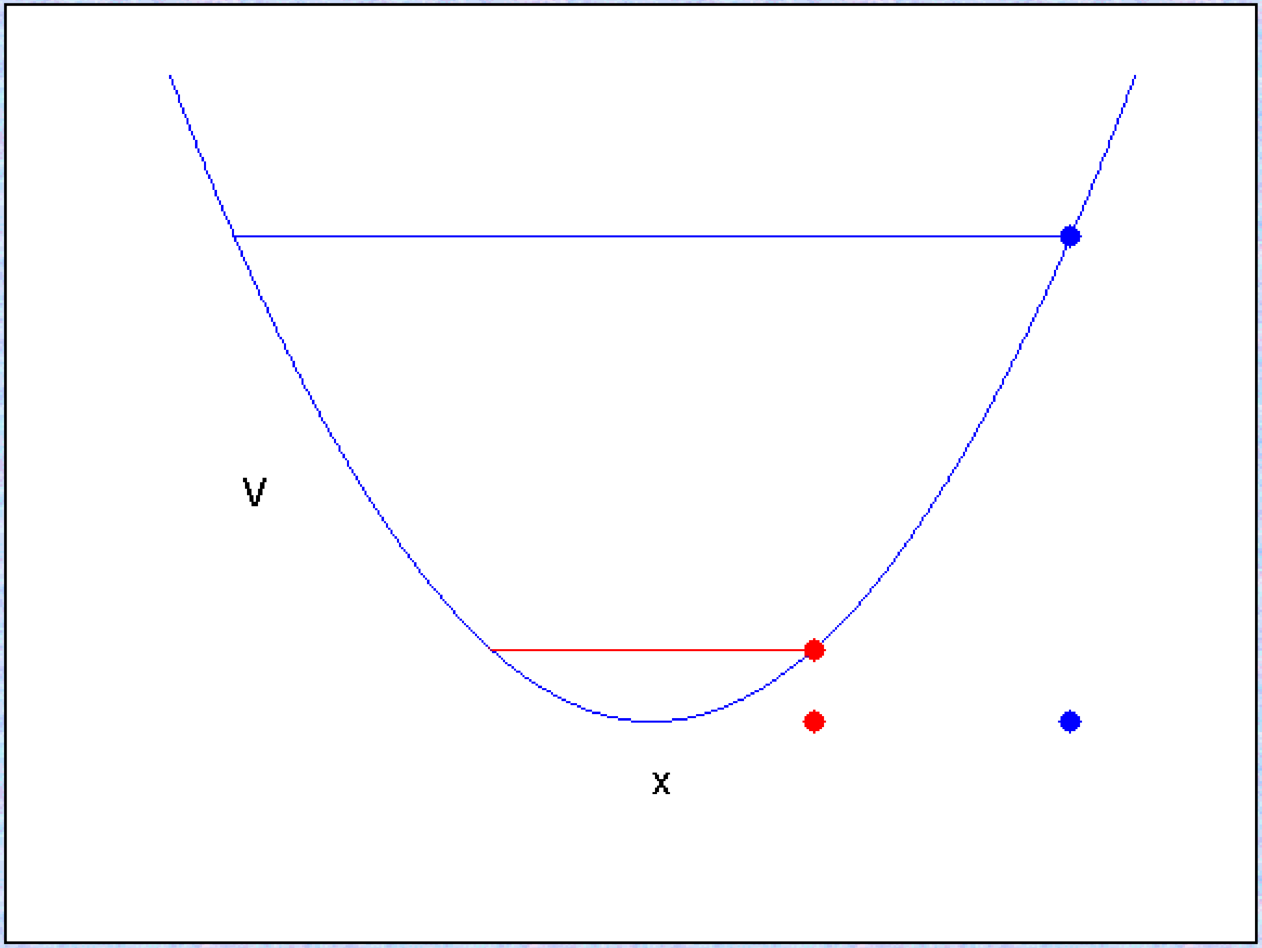
$E_{\mathbf{a}}$~100-200 KJ/mol



Outline of the talk

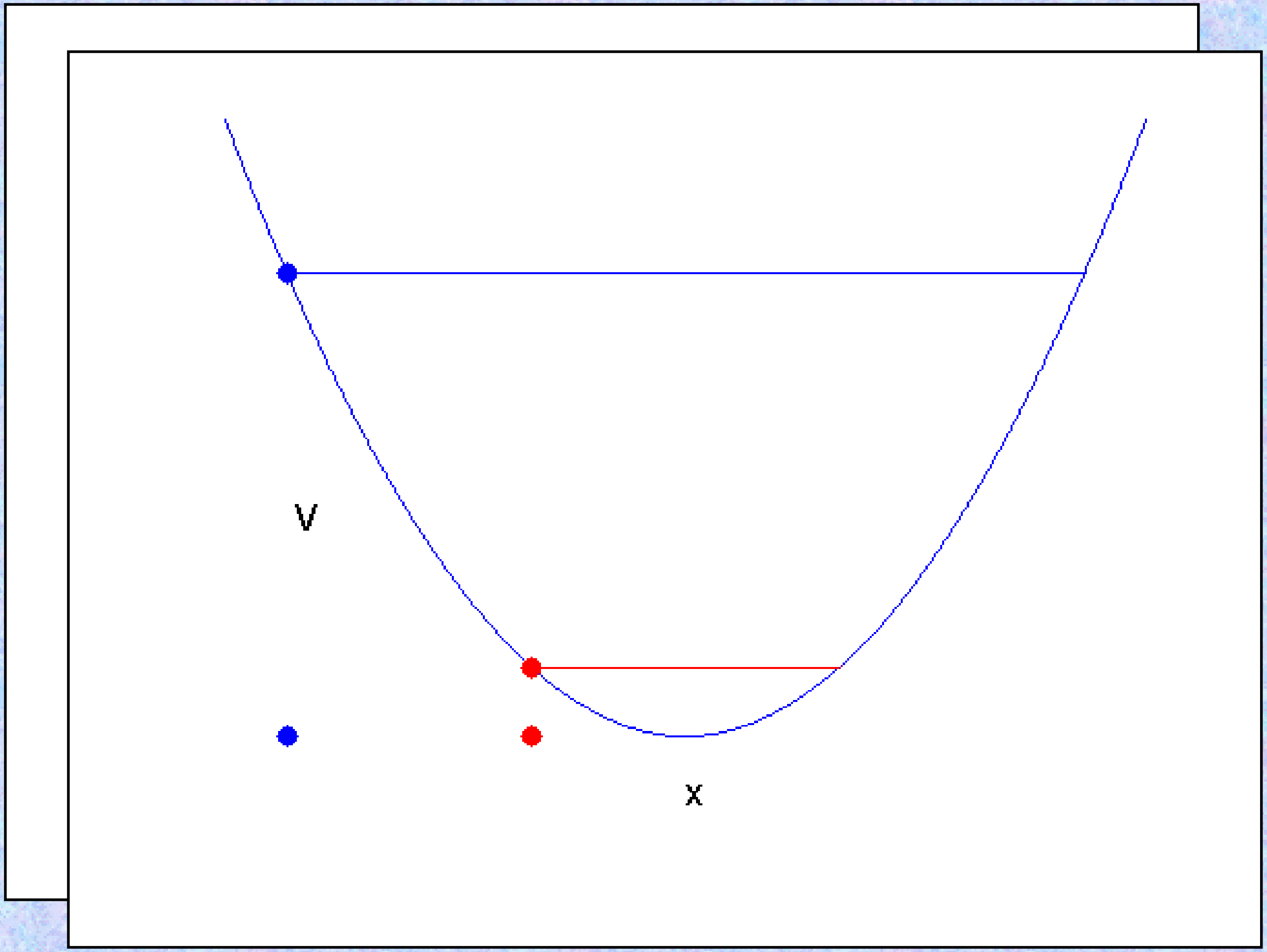
- Non linear oscillator with hard, soft and mixed potential
- Phonons and breathers
- Breathers in a model of mica muscovite
- Phonon and breather statistics
- Numerical results and modification of breather statistics
- Estimation of the influence on the reaction speed
- Other evidences on breathers in muscovite
- Conclusions

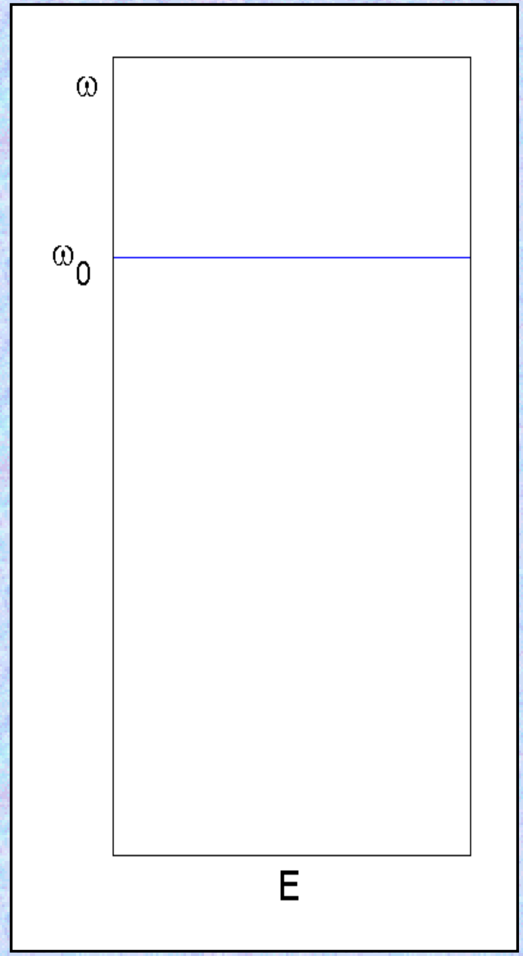
Isolated linear oscillator (1): F=-k x, V= ½ k x^2



$$x=A\cos(\omega_0 t+\varphi_0)$$

Isolated linear oscillator (2): F=-k x, V= ½ k x^2

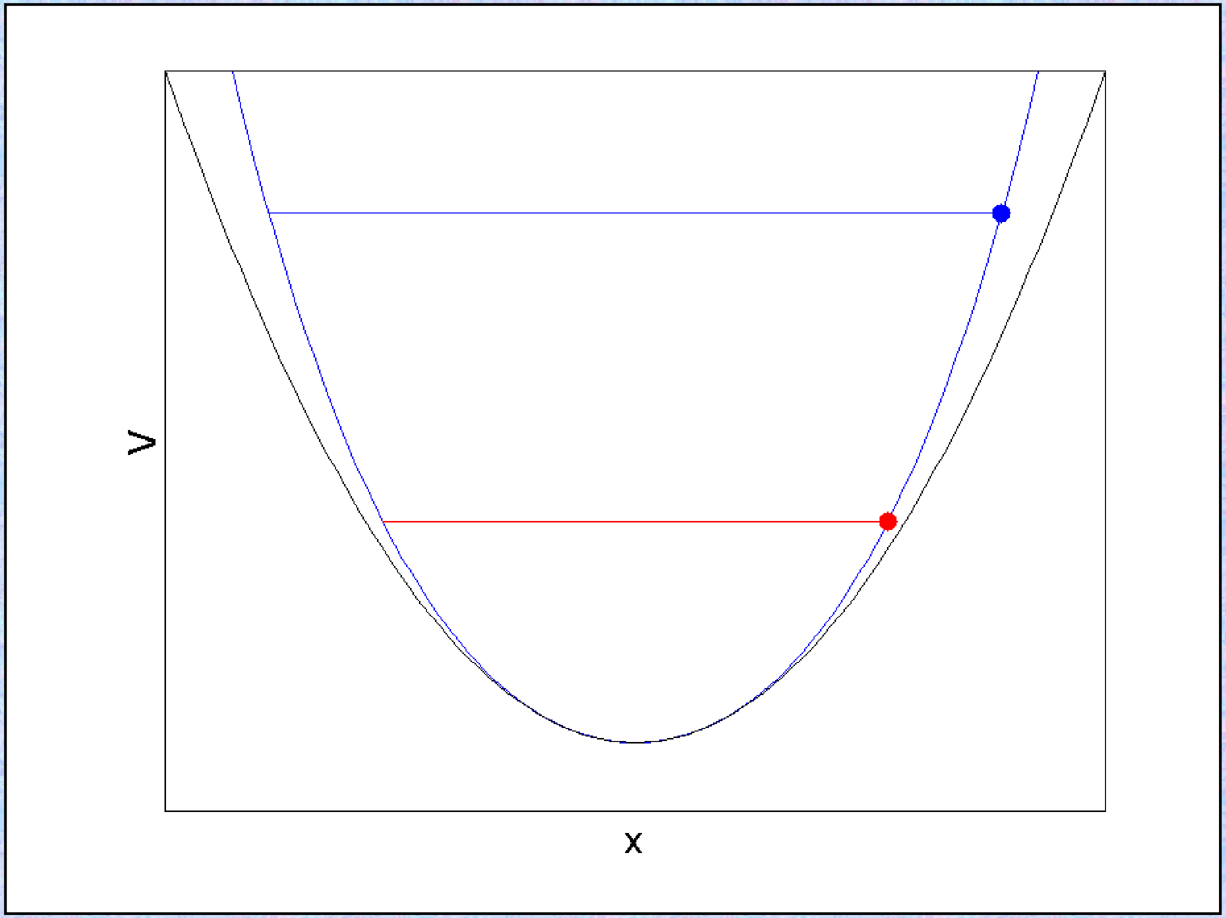




T ● = T ●

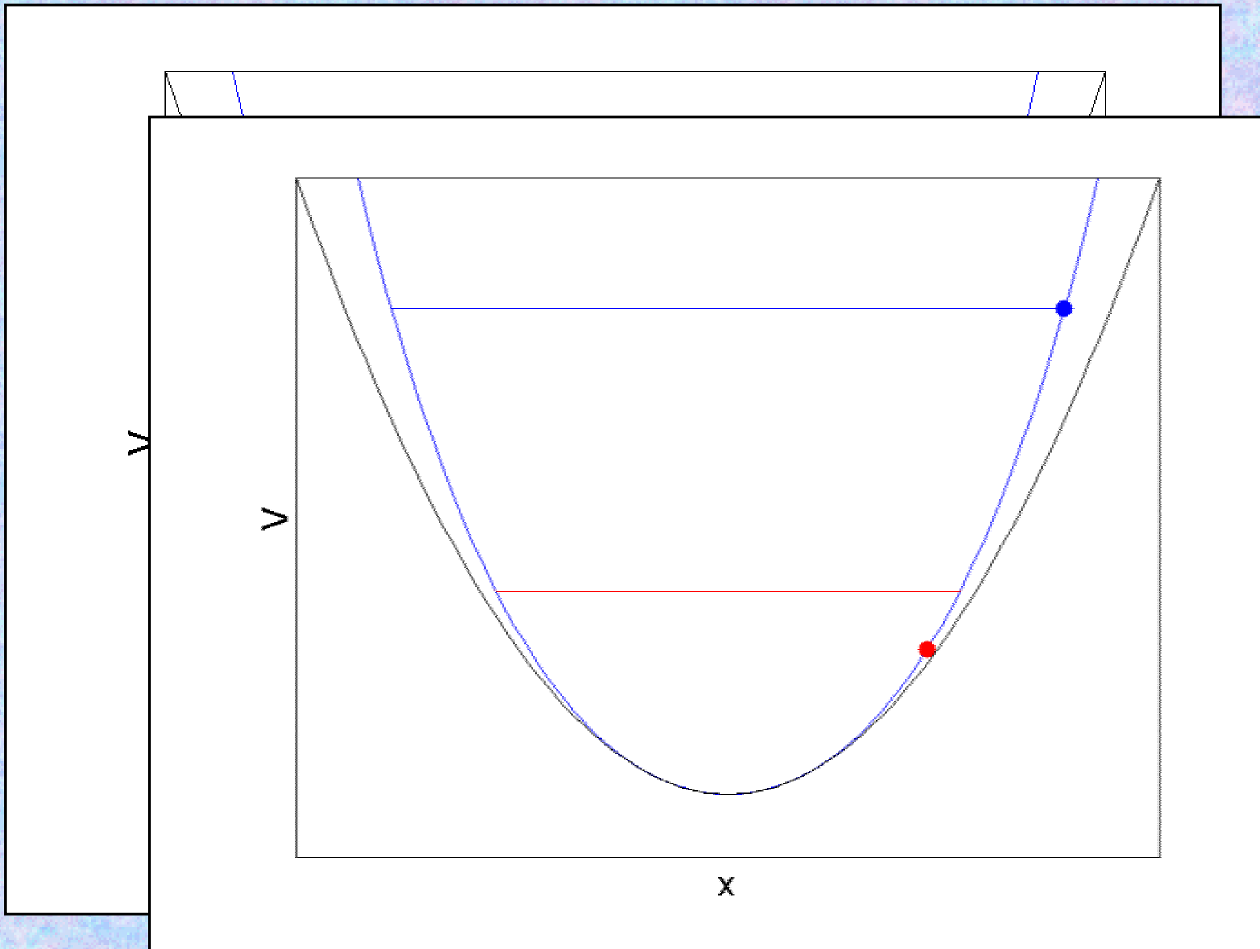
$\omega_0 \neq \omega_0(E)$

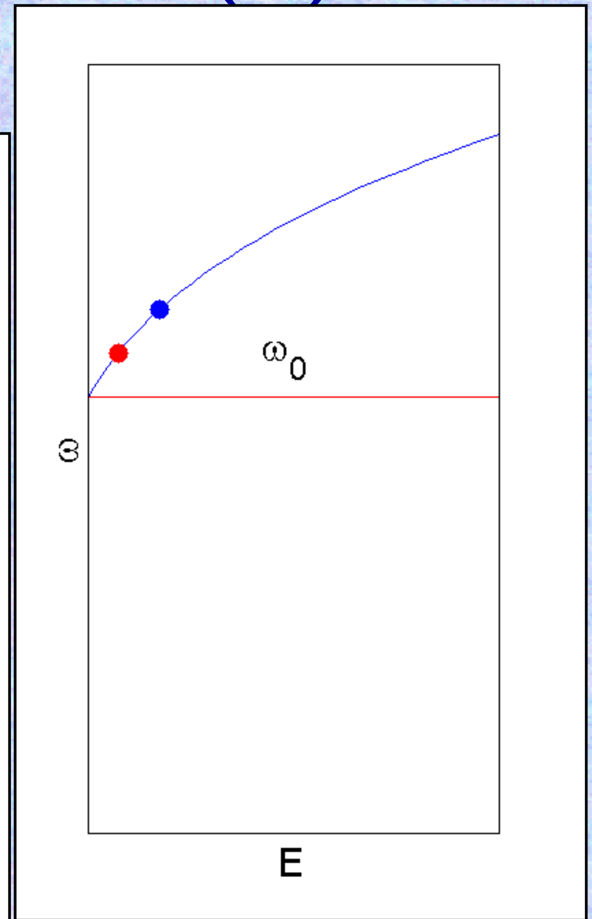
Oscillator with hard potential (1)

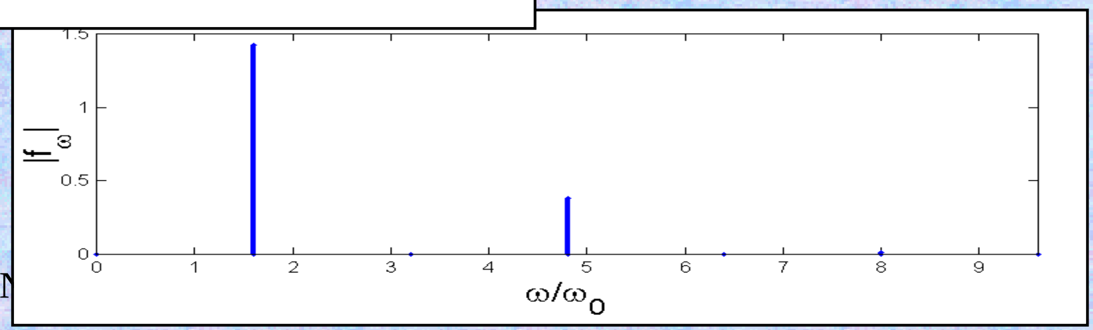


$V=\frac{1}{2}(\omega_0)^2x^2+\frac{1}{4}x^4$

Oscillator with hard potential (2)

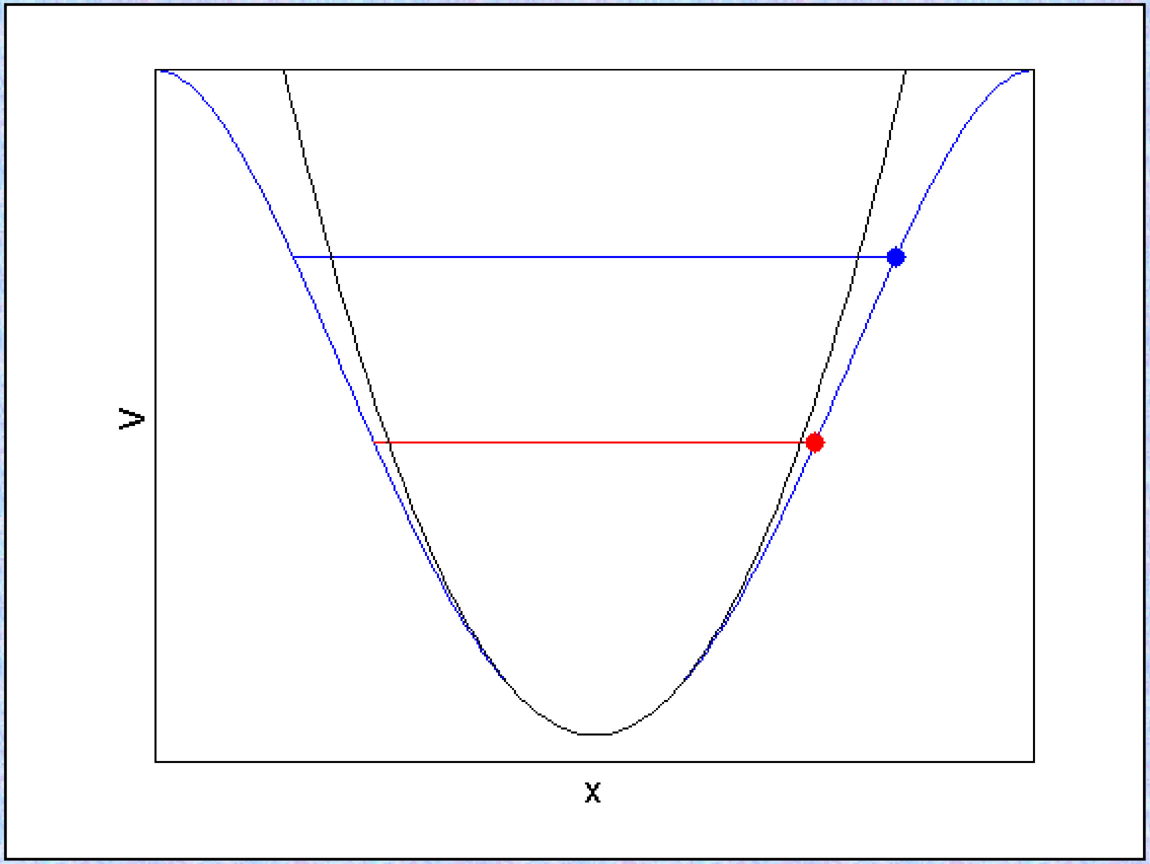






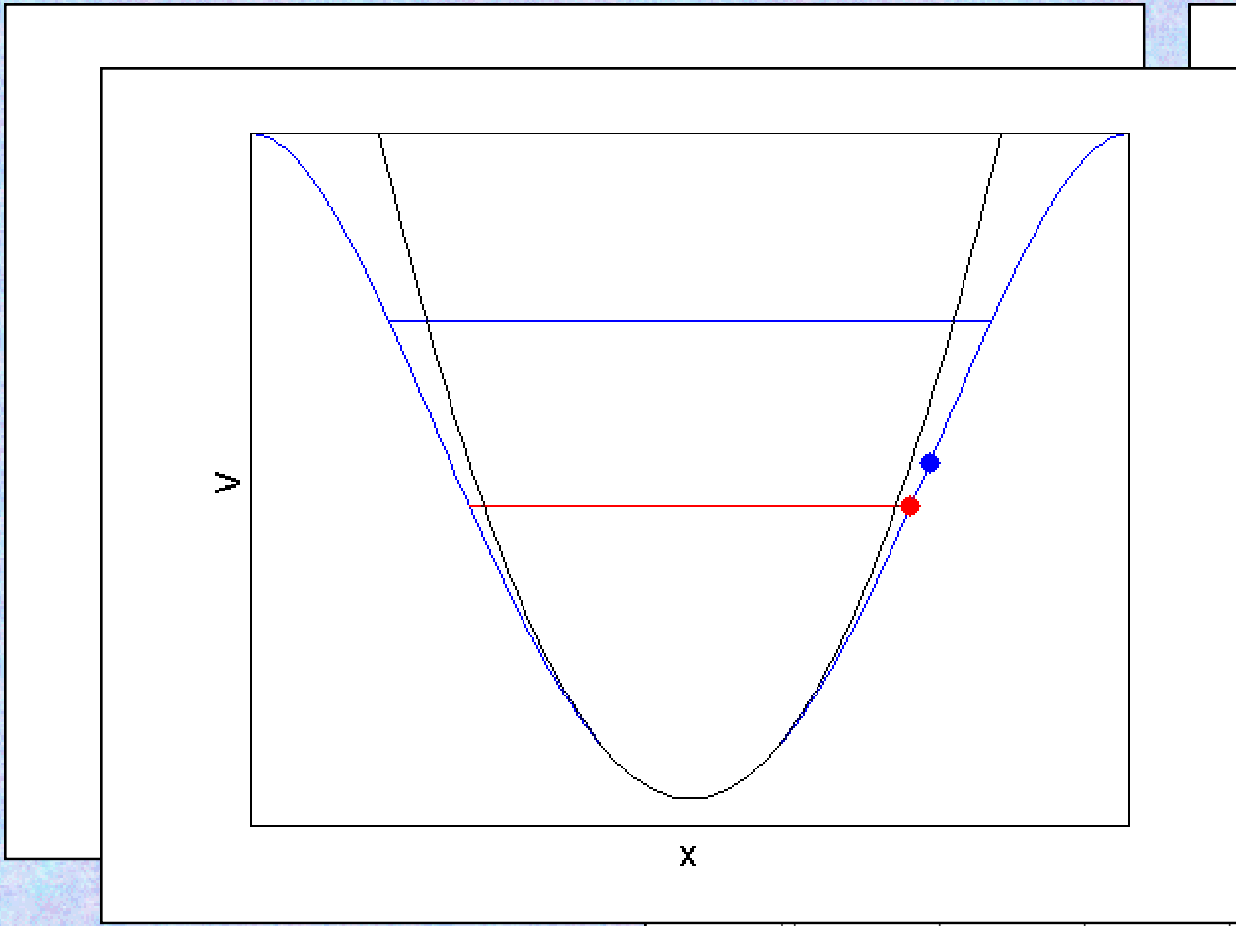
T ● < T ●

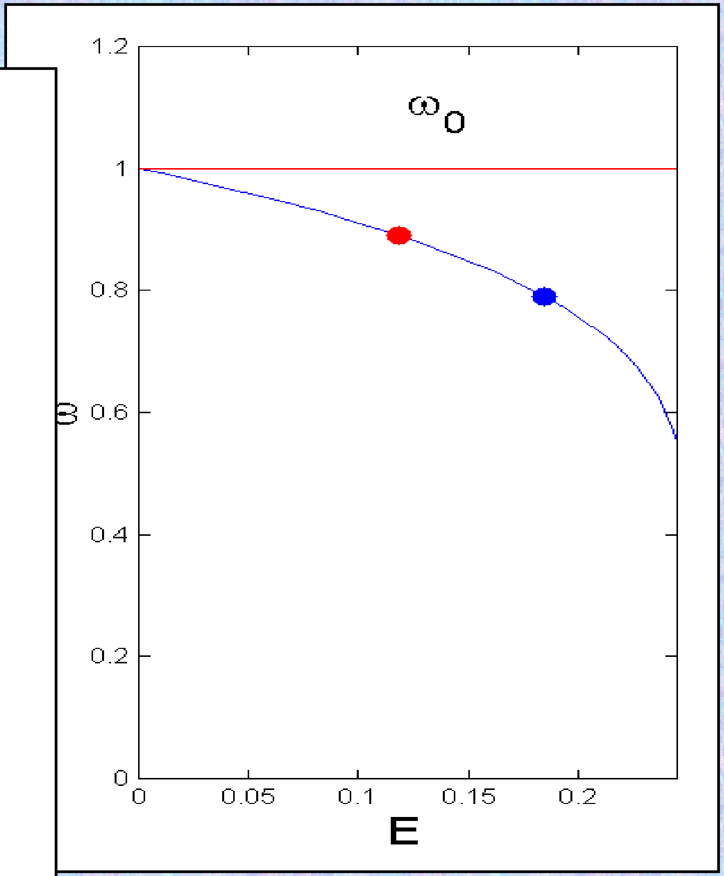
Oscillator with soft potential (1)



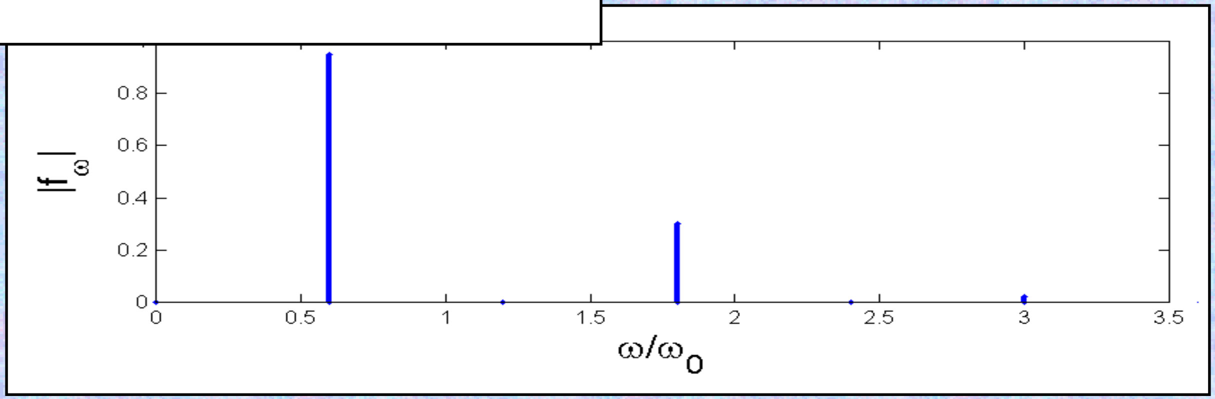
$V = \frac{1}{2} (\omega_0)^2 x^2 - \frac{1}{4} x^4$

Oscillator with soft potential (2)





T● > T●



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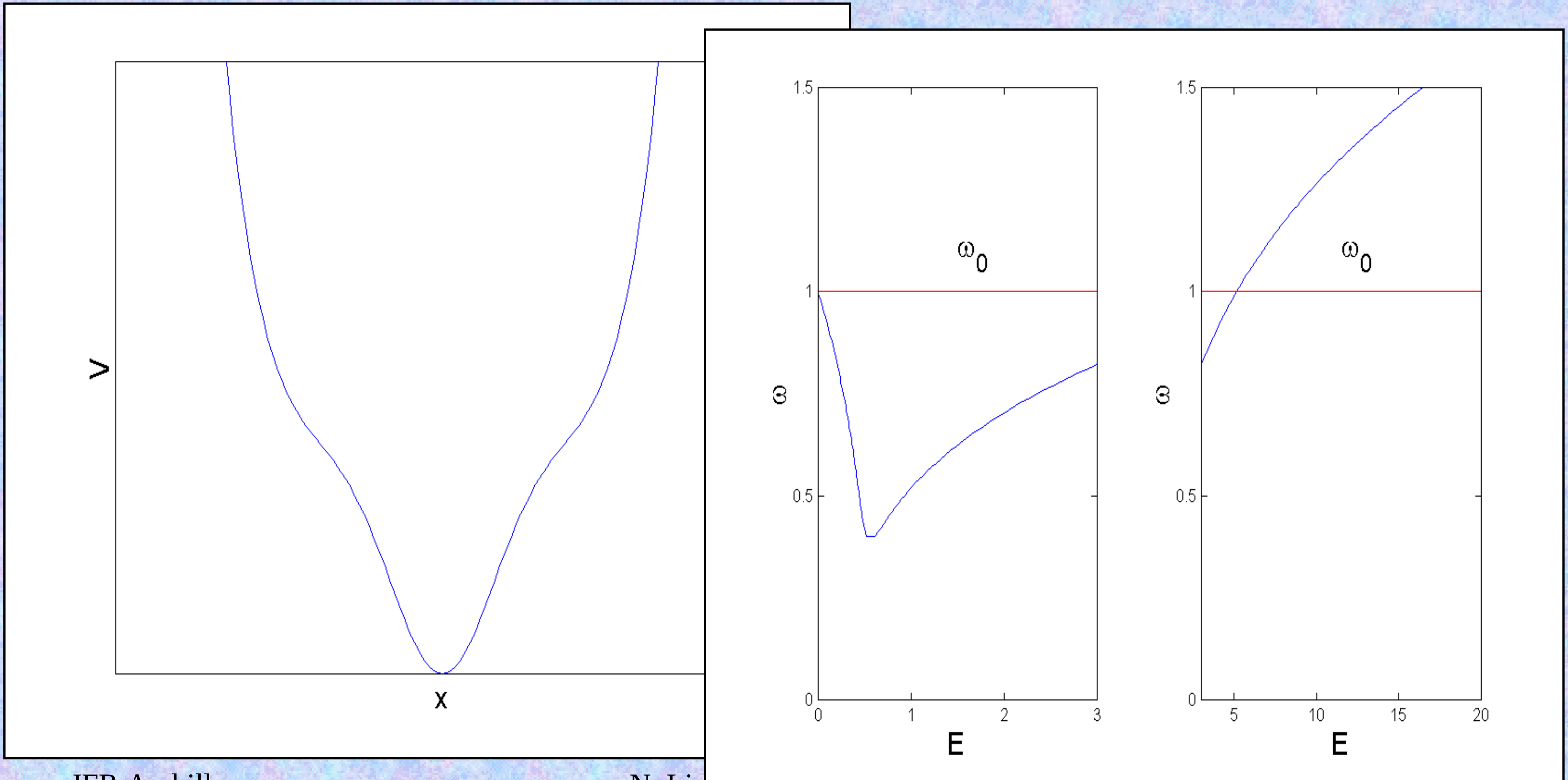
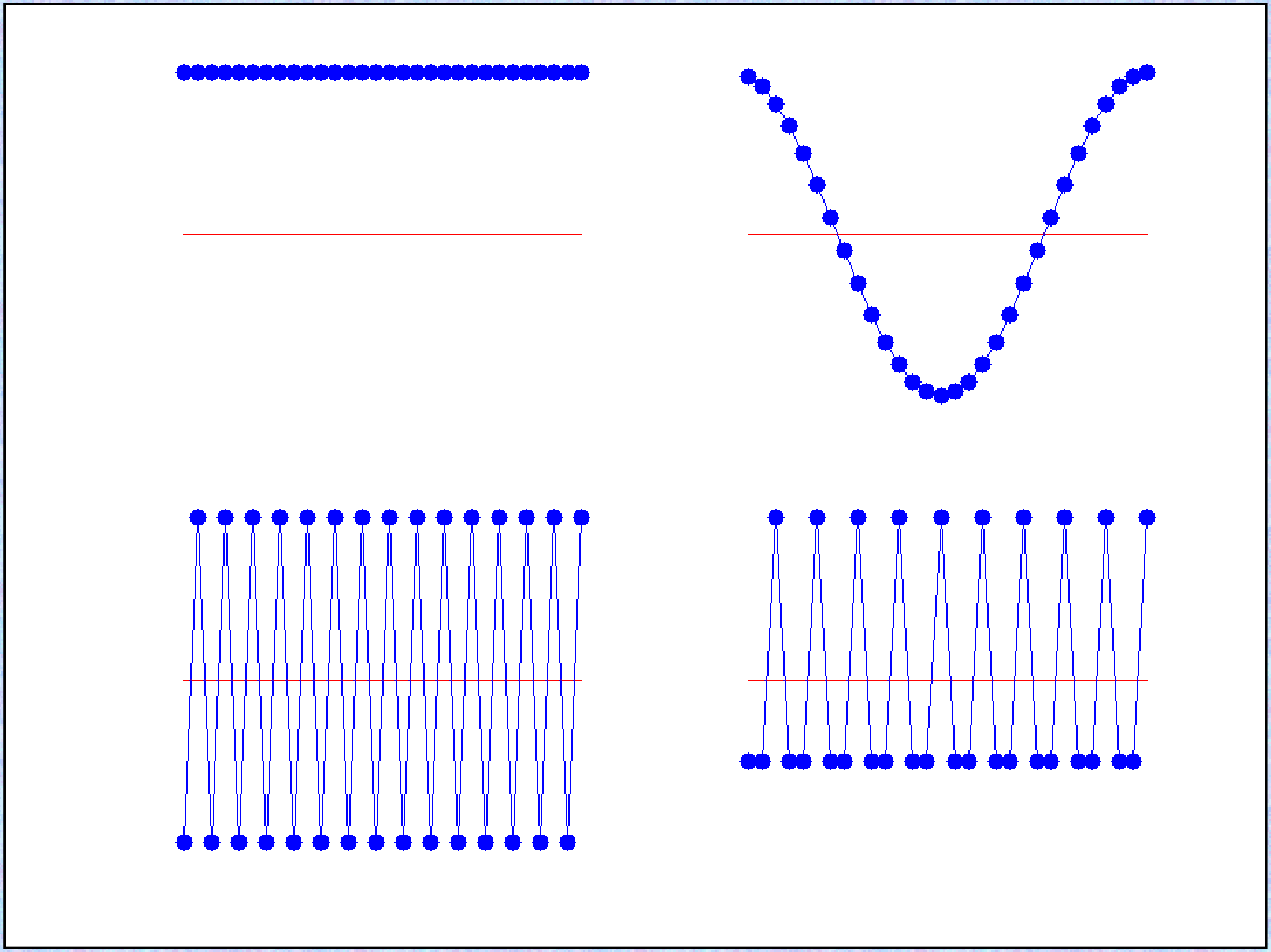
Nonlinear oscillator with mixed potential

Potential $V(x)=D(1-e^{-bx^2})+\gamma x^6$



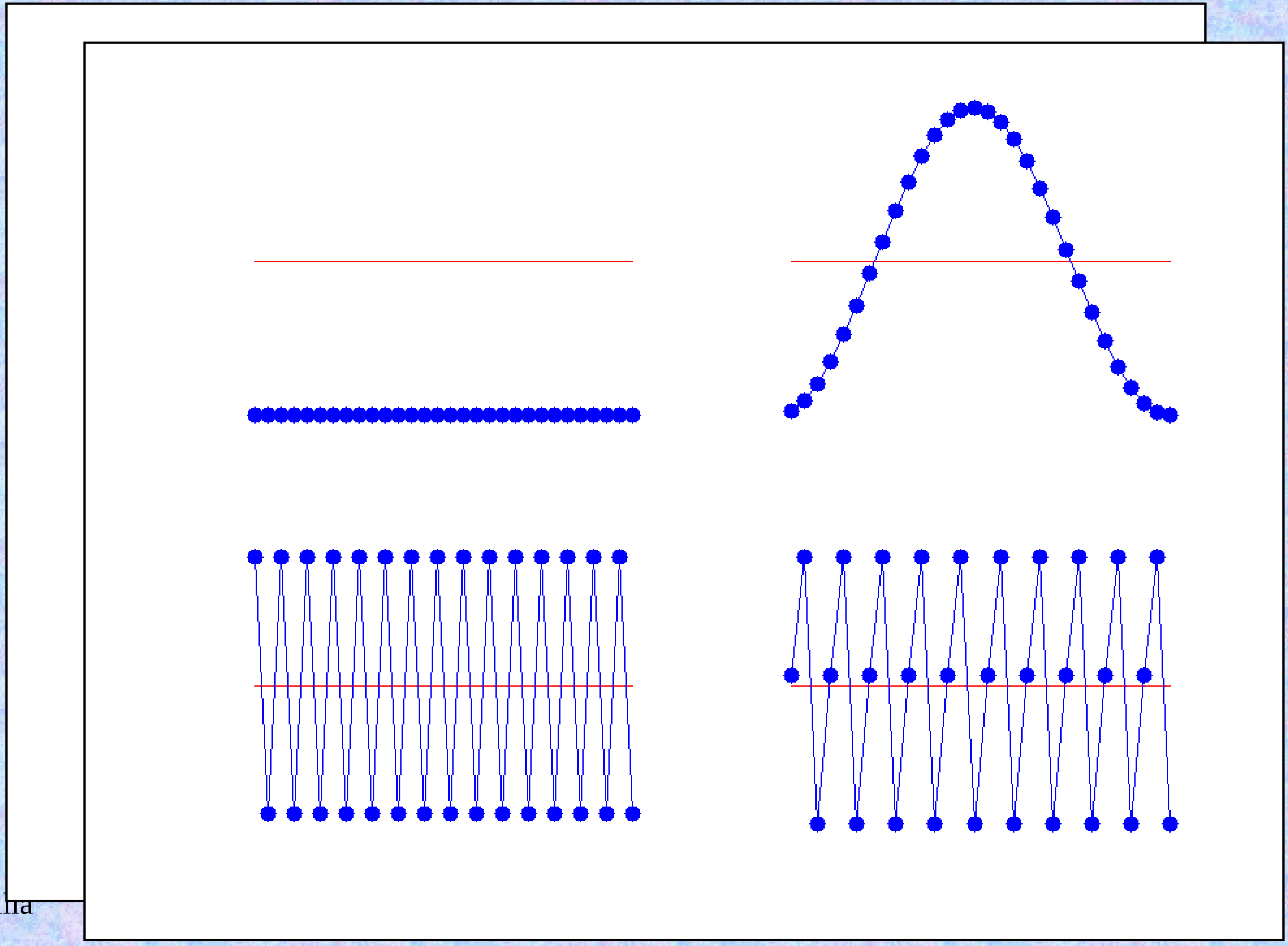
Lattice of coupled linear oscillators (1)

Phonons: $x_n = A \cos(\omega_q t - q n)$



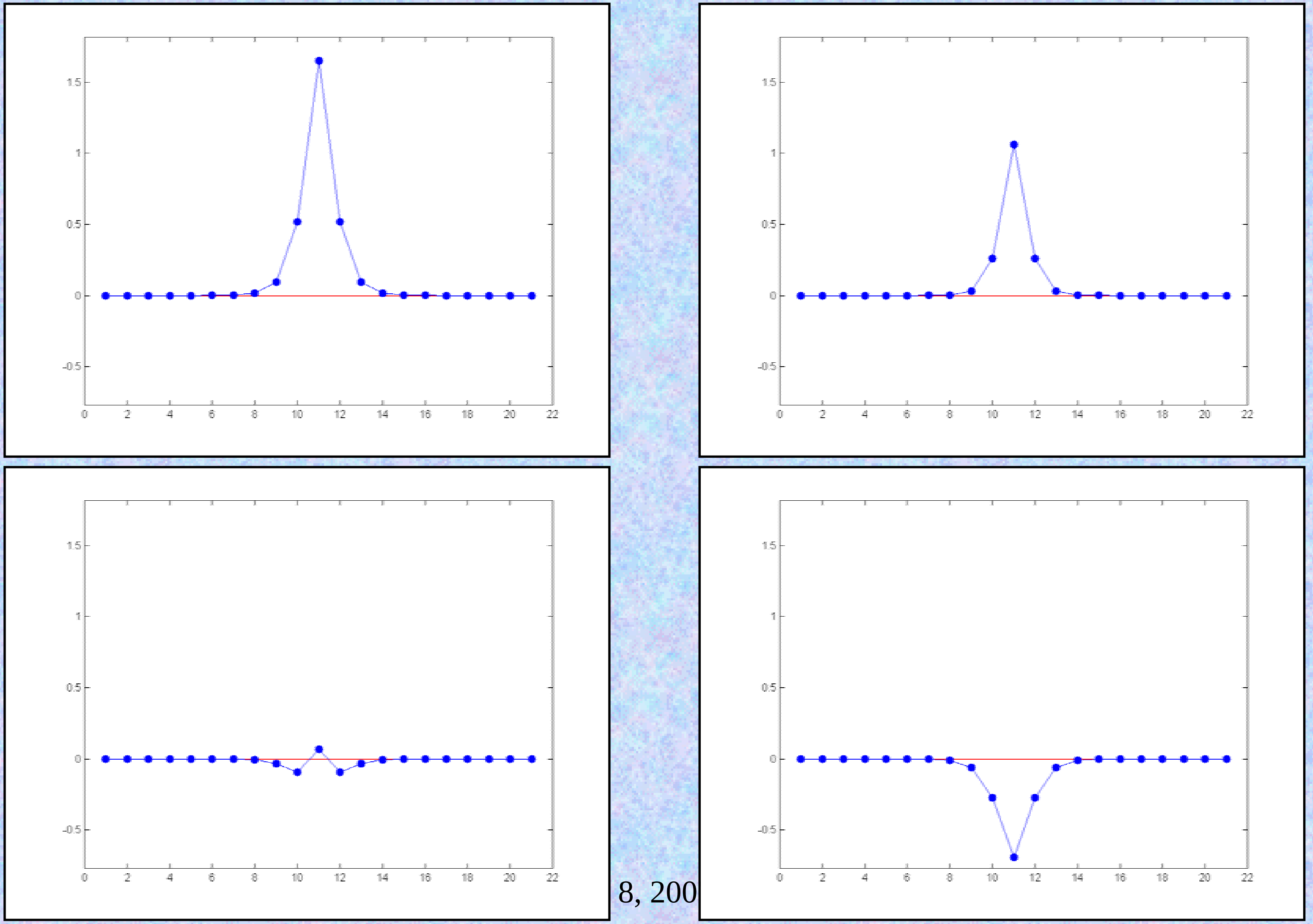
Lattice of coupled linear oscillators (2)

Phonons: $x_n = A \cos(\omega_q t - q\, n)$

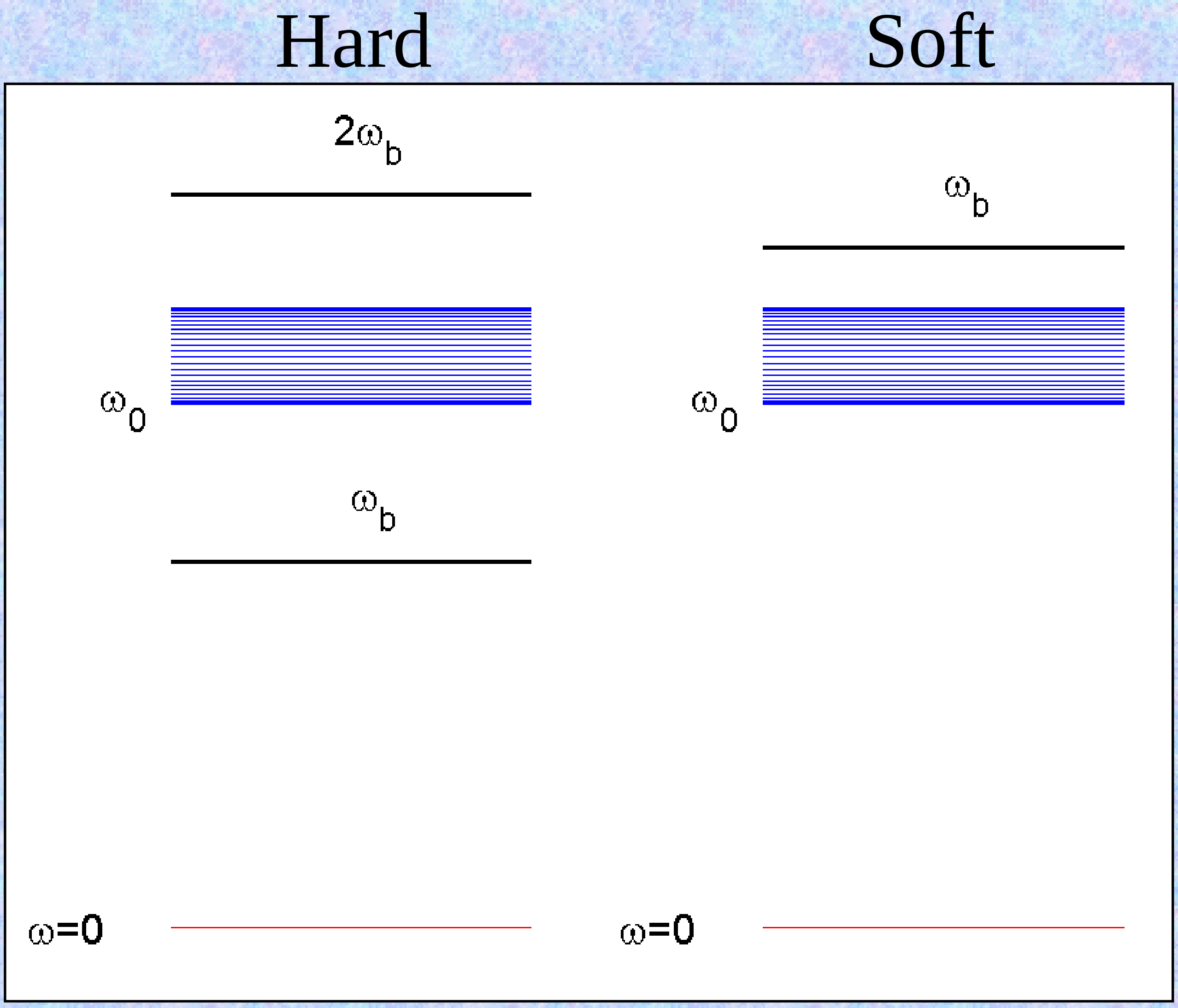


Lattice of coupled nonlinear oscillators. Breathers.

- Exact, periodic and localized solution



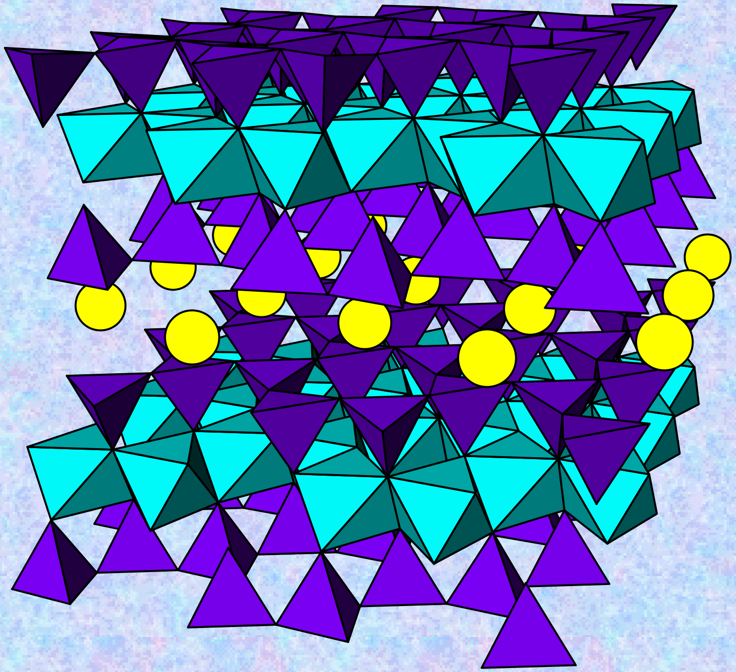
Breather frequency and phonon band

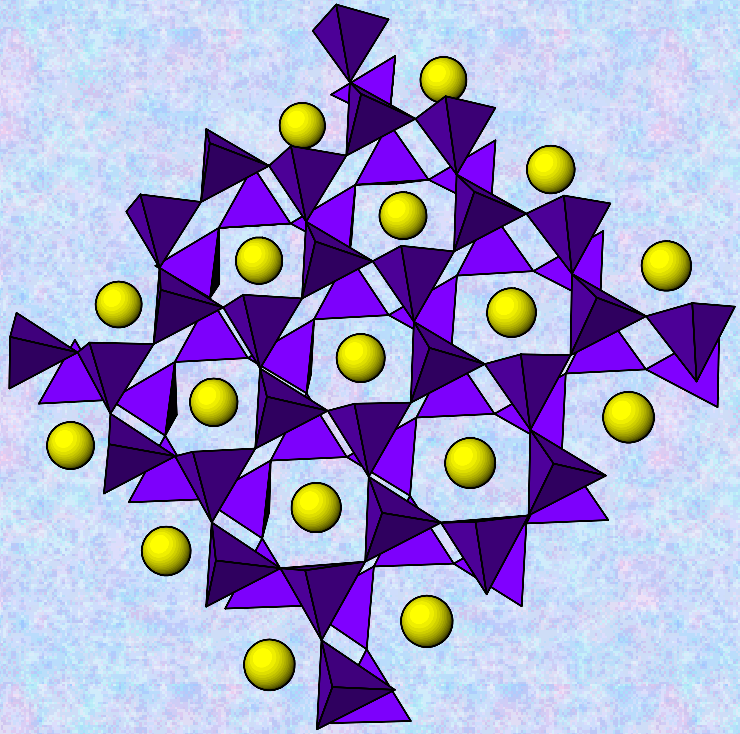


$n\omega_b \notin [\omega_0, \omega_{f,max}]$

$\omega_b'(E) \neq 0$

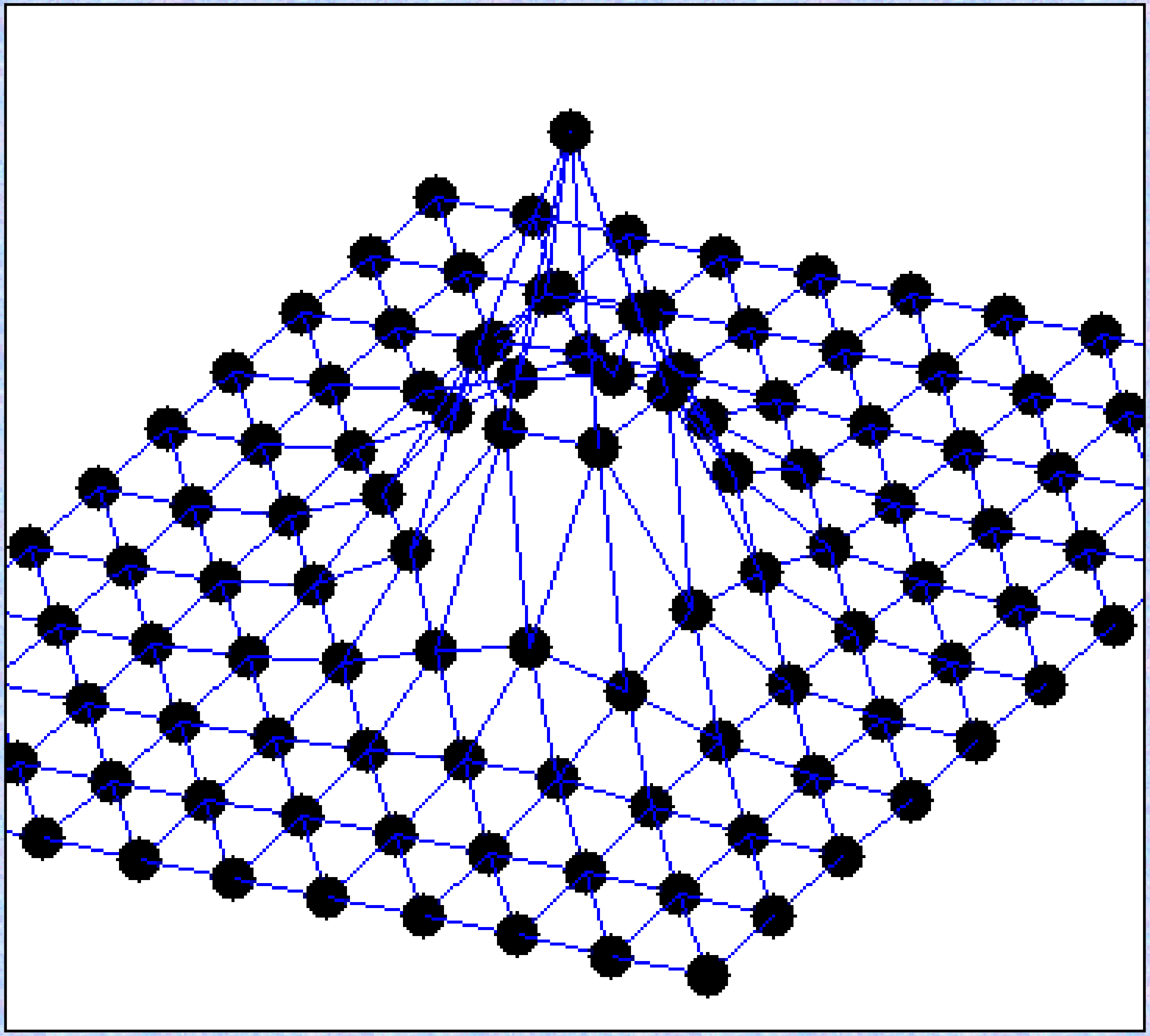
Example: mica muscovite





K$^+$

A 2D breather in the cation layer



Hypothesis: influence of discrete breathers on the reaction speed

Objectives:

- Calculate 2D breathers in the cation layer of mica muscovite
- ¿Have they large enough energy to bring about the increase in reaction speed?
- ¿Is their number large enough?

Mathematical model

Hamiltonian:

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

Harmonic coupling

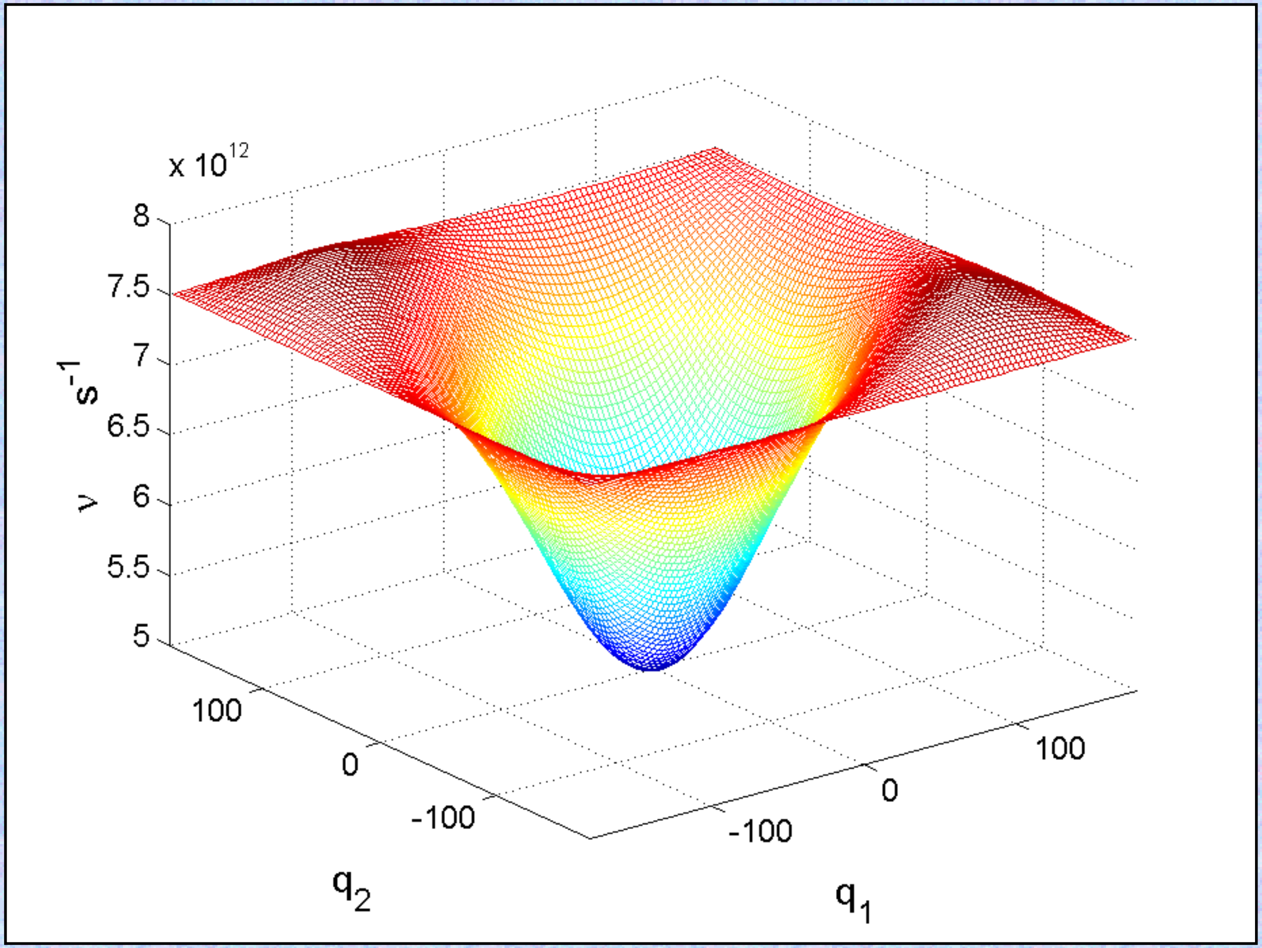
- k=10±1 N/m (D. R. Lide Ed., *Handbook of Chemistry and Physics*, CRC press 2003-2004)

On-site potential *V*

- Assignment of far infrared (30-230 cm−1) bands through dichroic experiments, [Diaz et al, *Clays Clay Miner*., **48**, 433 (2000)] with linear frequency ν_0=143 cm^{-1} = 5.03 THz
- Nonlinearity of the potential unknown

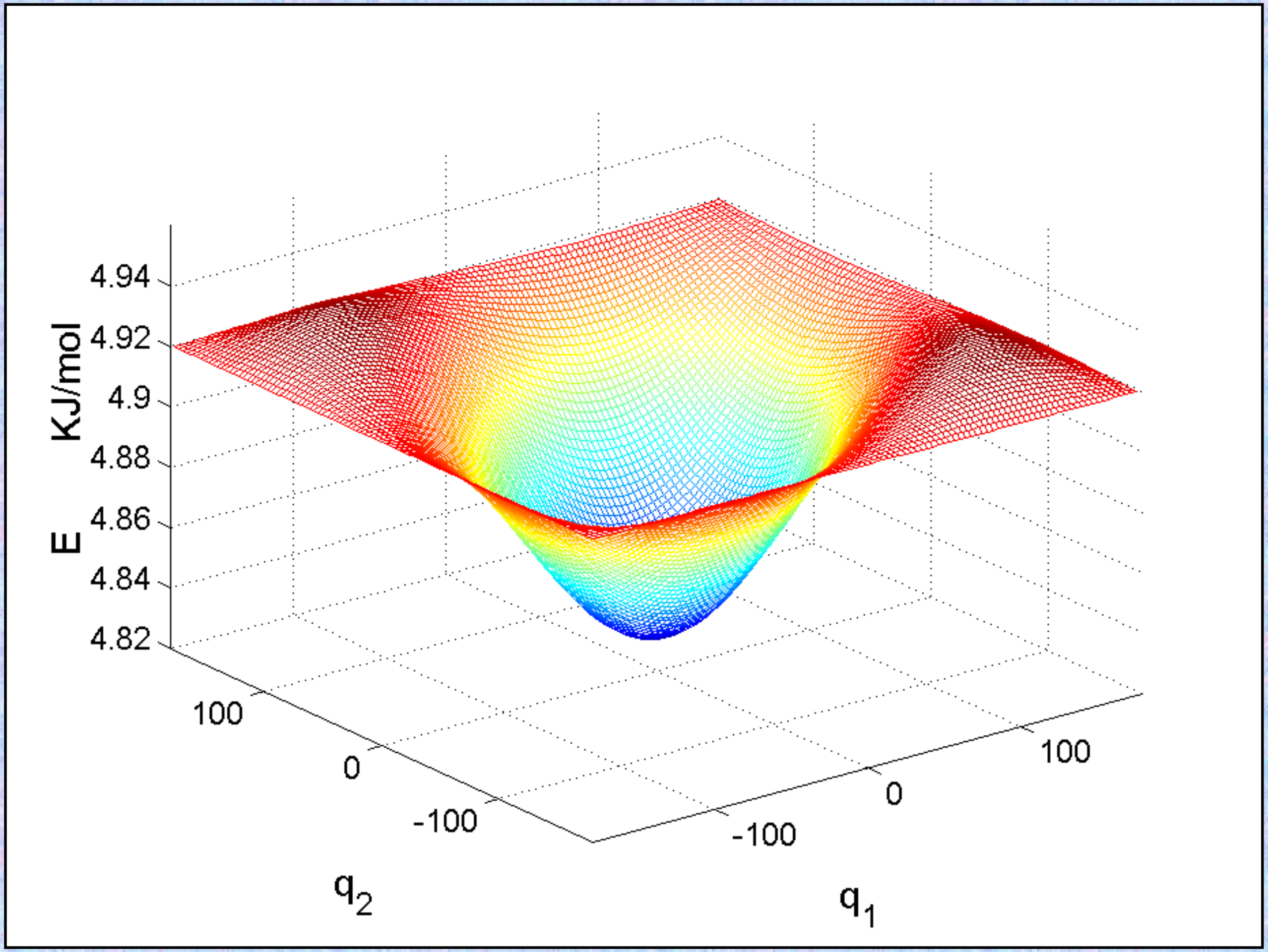
Phonon band

$\nu_f \in [5\ ,\ 7.8]$ THz



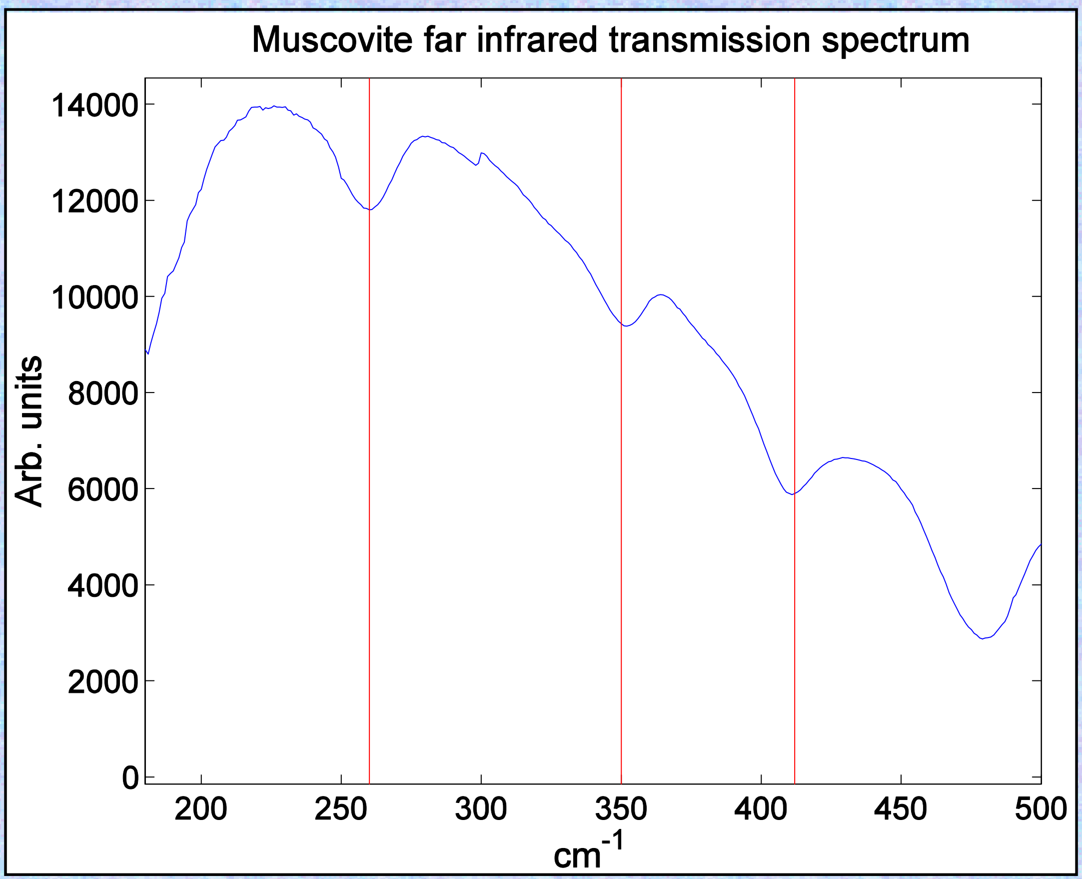
$$\nu^2 = (\nu_0)^2[1+4\ \varepsilon(\mathrm{sen}^2(q_1/2)+\mathrm{sen}^2(q_1/2)+\mathrm{sen}^2(q_2/2-q_1/2))]$$

Mean energy of each phonon mode



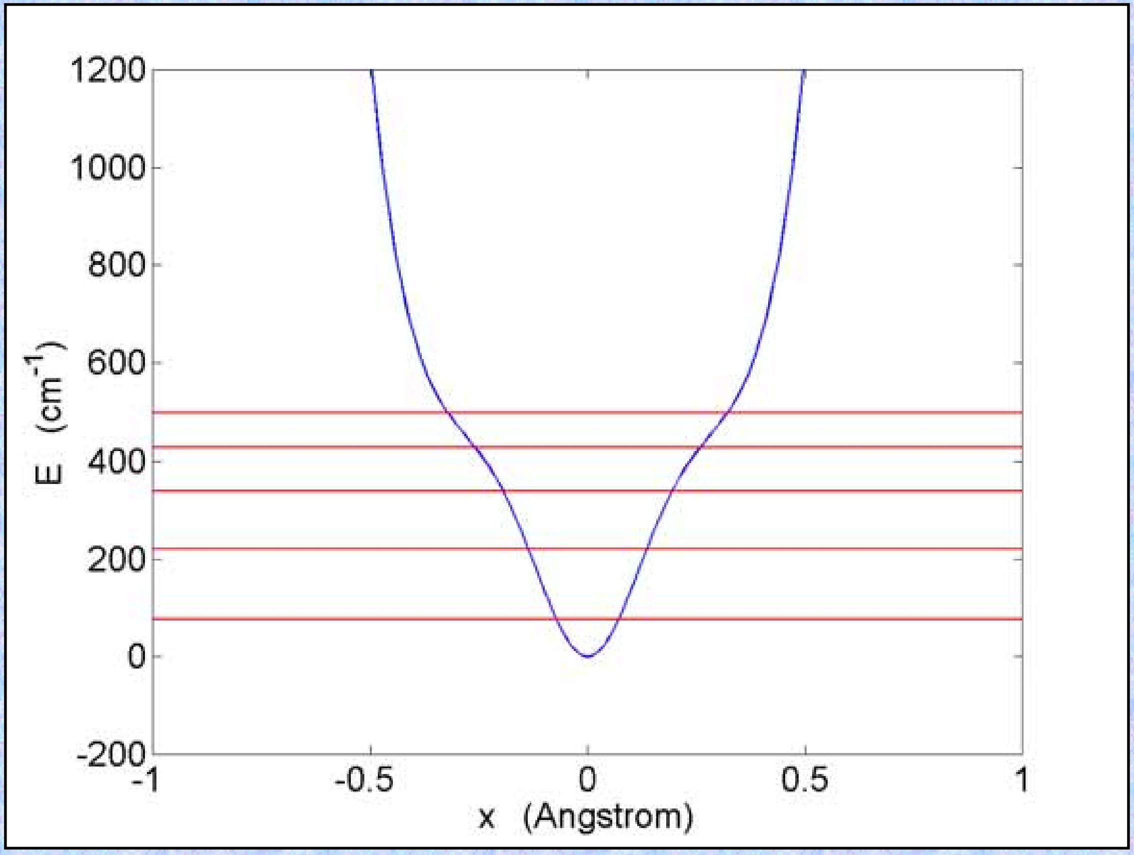
$\langle E_{ph} \rangle = (n+0.5)\, h\nu$, $n = 1/(e^{\beta h\nu} - 1)$, T=573 K

Far infrared spectrum performed at LADIR-CNRS



Bands are assigned tentatively to K^+ higher order transitions

Fitting of the nonlinear on-site potential

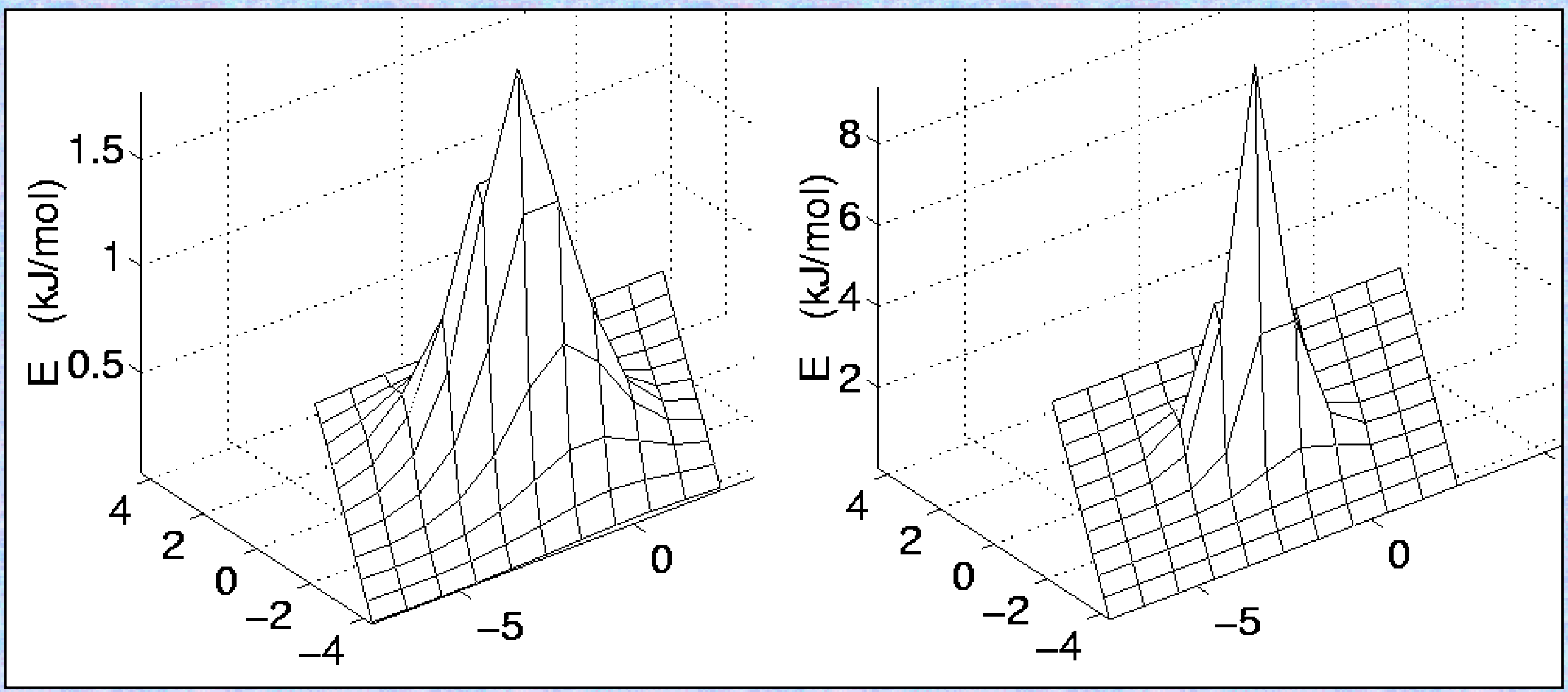


$V(x) =$
$D\,(\,[1-\exp(-\,b^2\,x^2)\,]+\gamma\,x^6)$

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

Choice consistent with the space available for K^+ $2{\cdot}1.45$ Å

Energy density profiles for two soft breathers

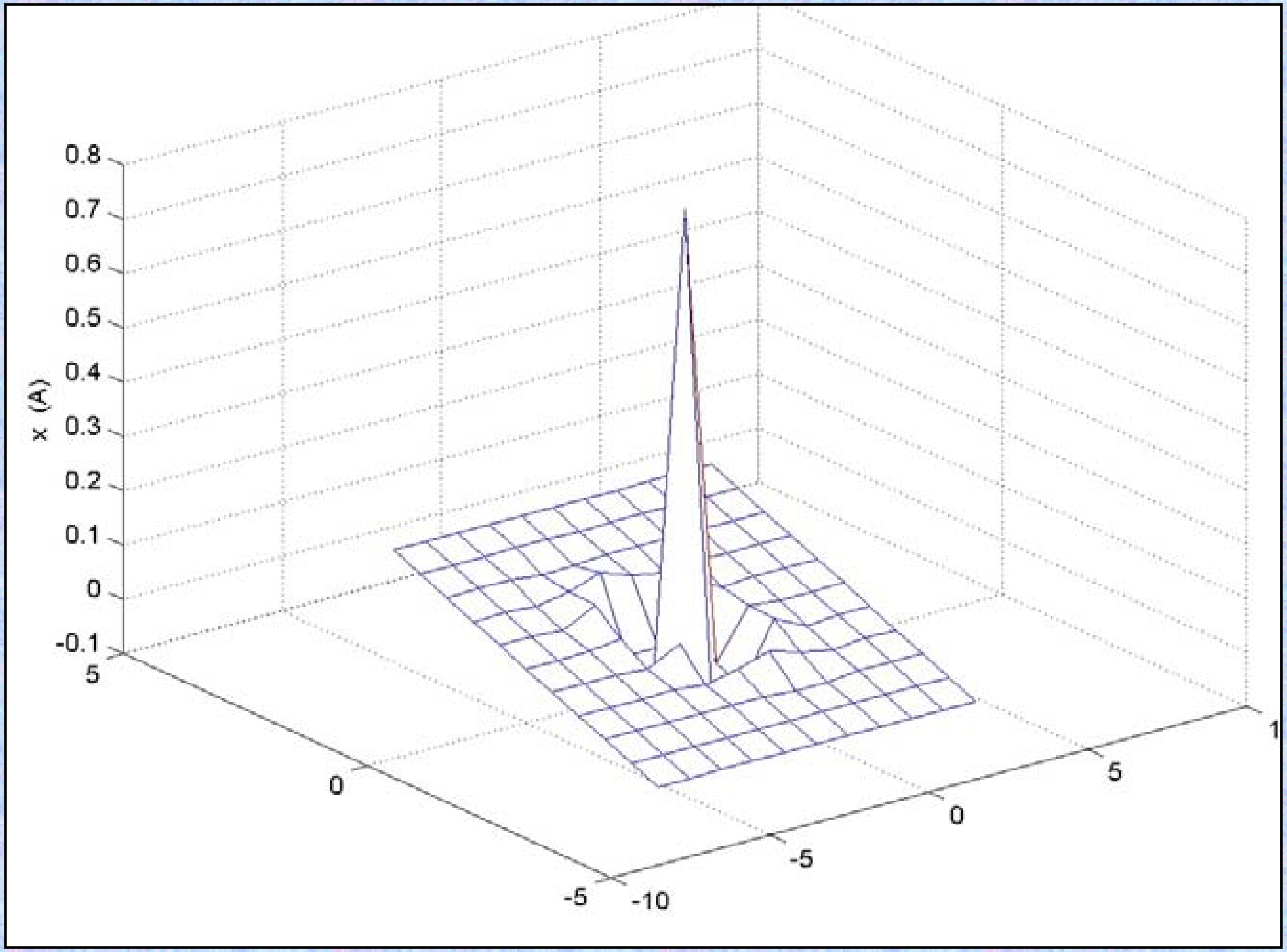


ν_b=0.97ν_0, E =25.6 kJ/mol

ν_b =0.85 ν_0, E =36.3 kJ/mol

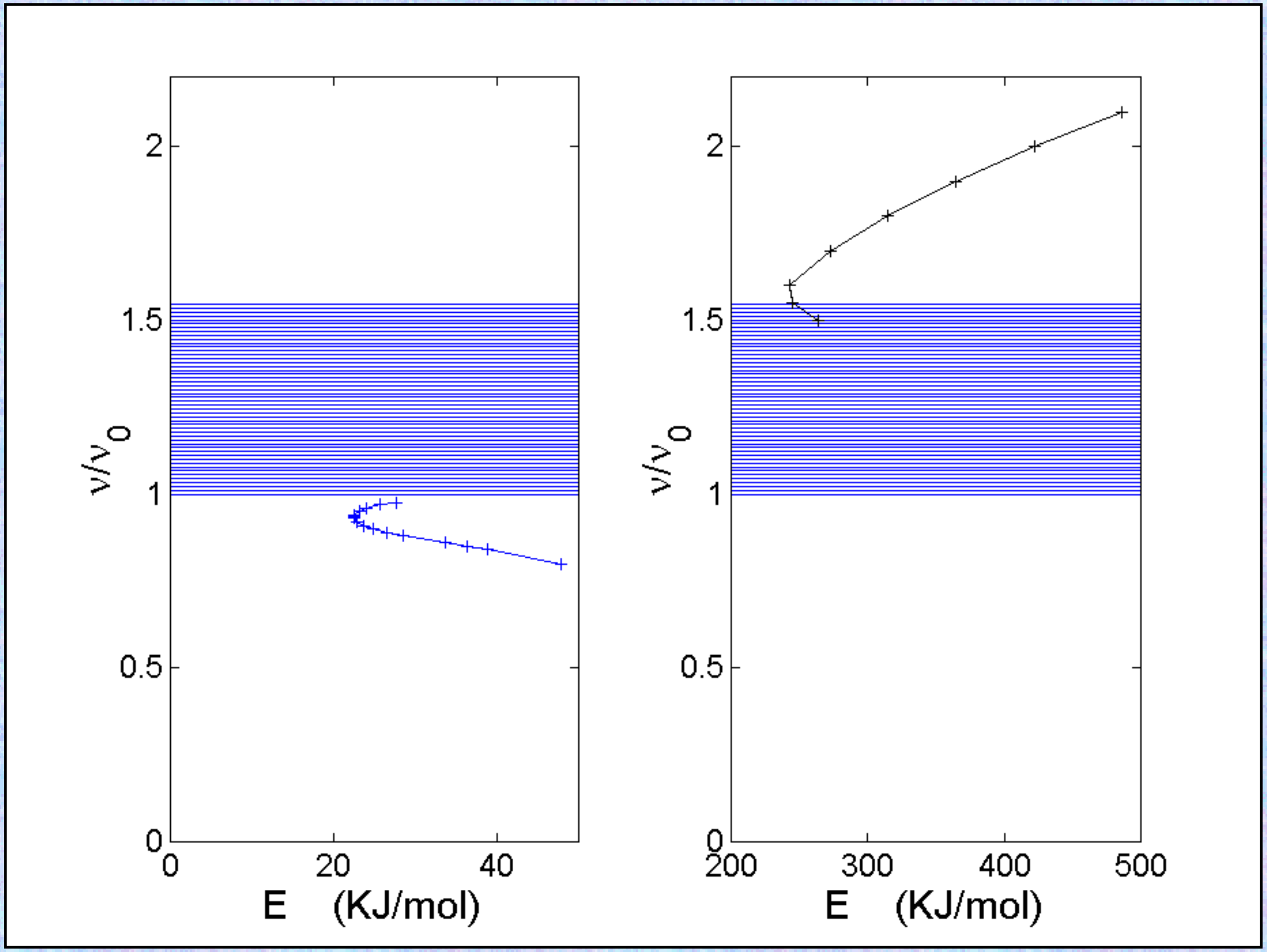
ν_0= 167.5 cm^{-1} ~ 5·10^{12} Hz

Profile of a hard breather



$\nu=1.7\nu_0= 8.54$ THz, E=272 KJ/mol

Breather frequency versus energy



$\nu_0 = 167.5 \text{cm}^{-1}$

$\sim 5 \cdot 10^{12}$ Hz

Minimum energies

Δ_s = 22.4 kJ/mol

Δ_h = 240 kJ/mol

BREATHERS HAVE LARGER ENERGIES THAN THE ACTIVATION ENERGY

¿How many phonons? ¿How many breathers? ¿With which energies?

Phonons: fraction of phonons per site with energy larger than E_a : $C_{ph}(E_a) = \exp(-E_a/RT)$

Breathers:

- Numerically: $\langle n_B \rangle \sim 10^{-3}$ per K^+
- Theory: Piazza et al, Chaos **13,** 589 (2003)]

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.- $\langle E\rangle = \Delta + (z+1)\, k_B T$

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:

$$n_b(E) = \langle n_b\rangle C_b(E)$$

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

-Function gamma and first incomplete gamma function:

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

Breathers statistics. Results.

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

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

3.- Most proba

3.-Fraction of

$C_b($

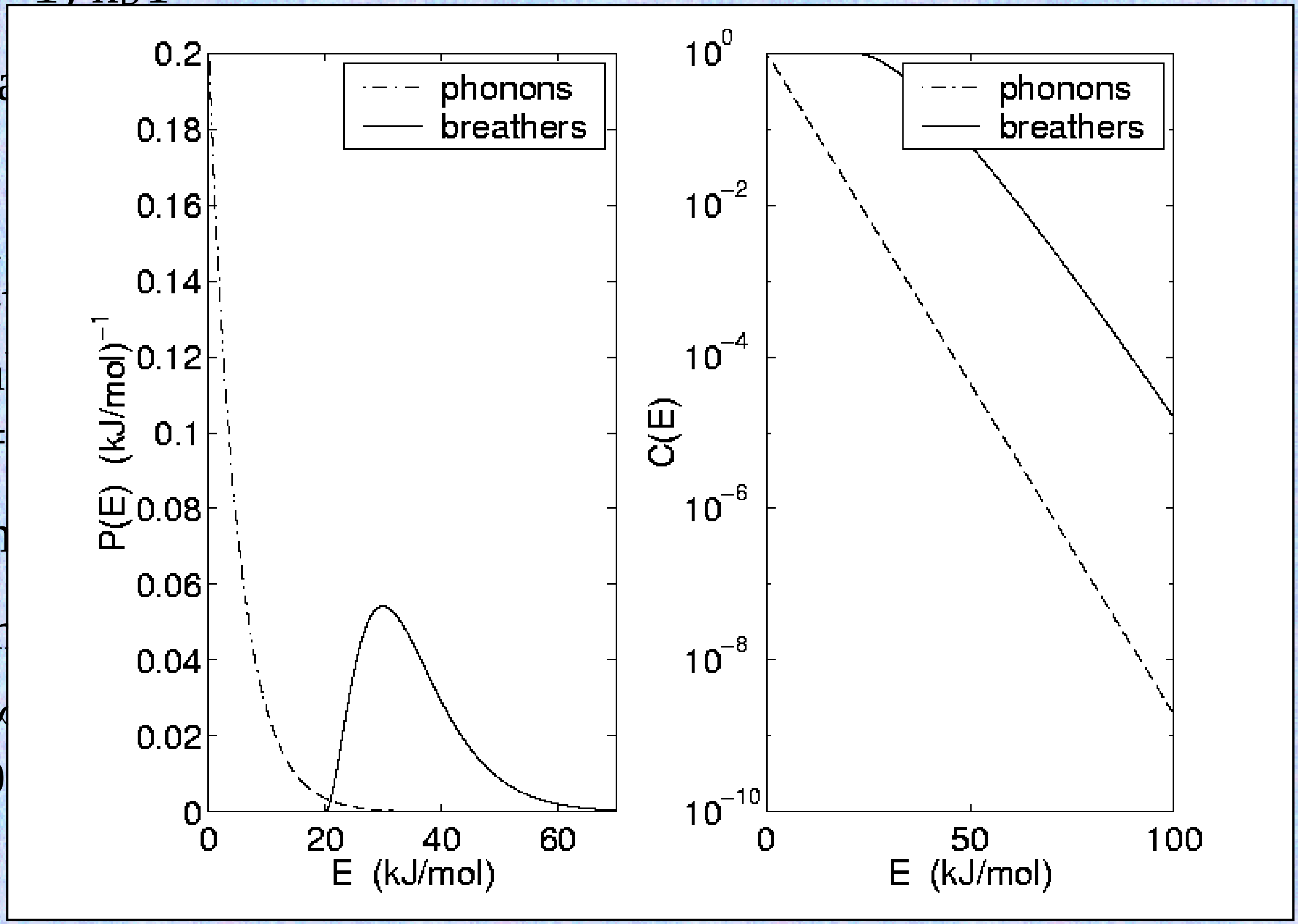
4.- Mean num

$n_b(E)=$

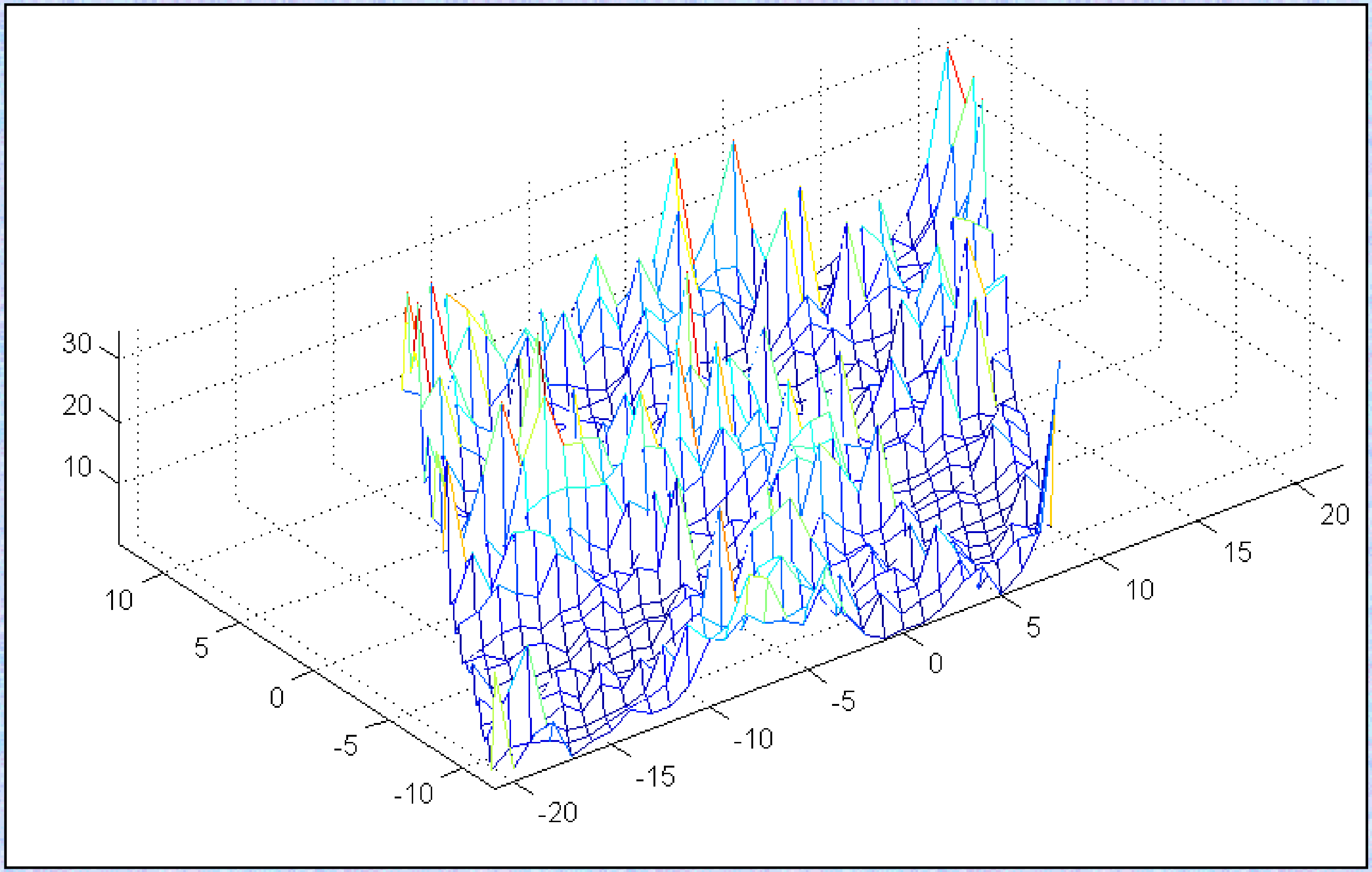
$\langle n_b \rangle = n$

-Function gam

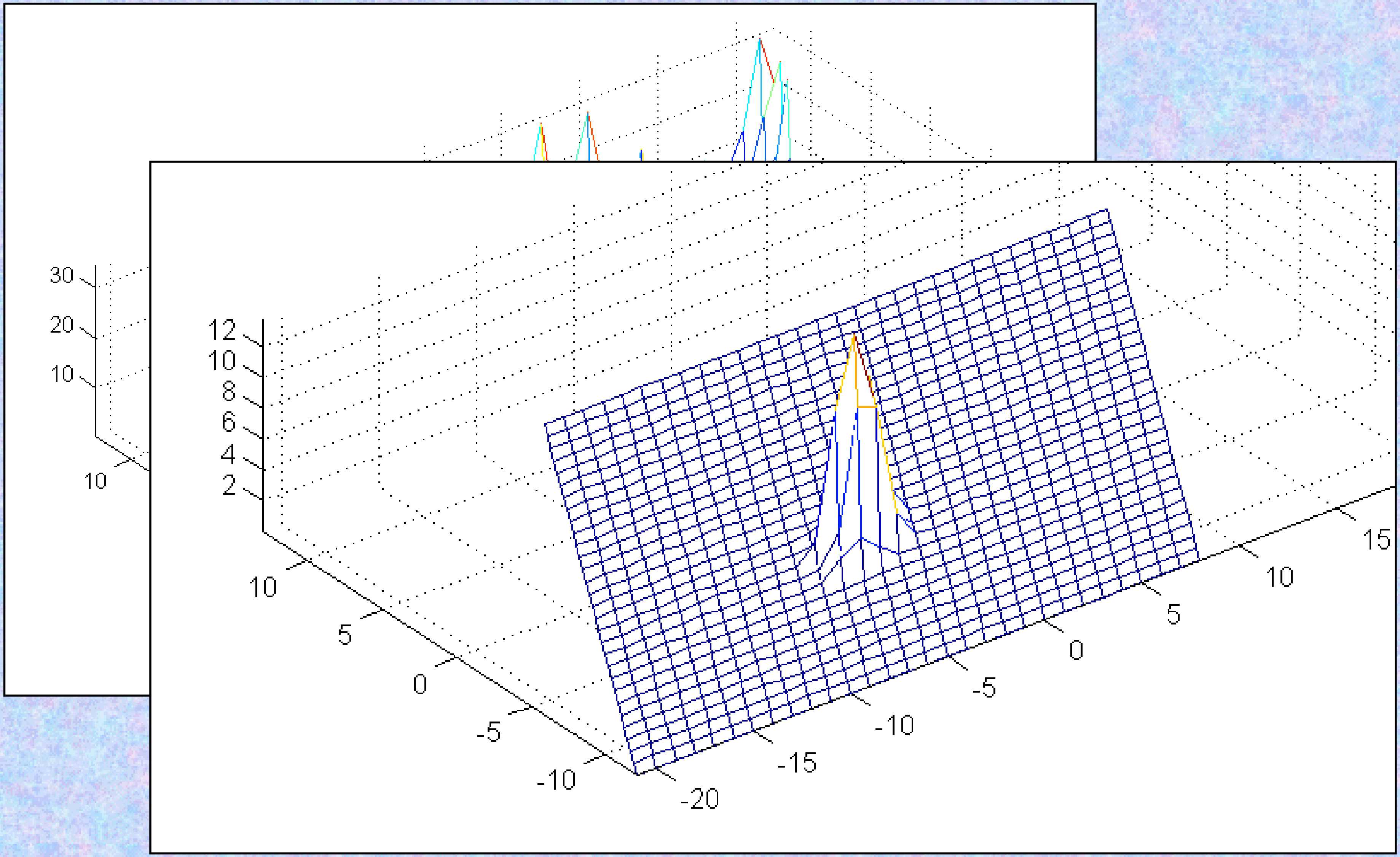
$\Gamma(z+1)= \int_0^\infty$



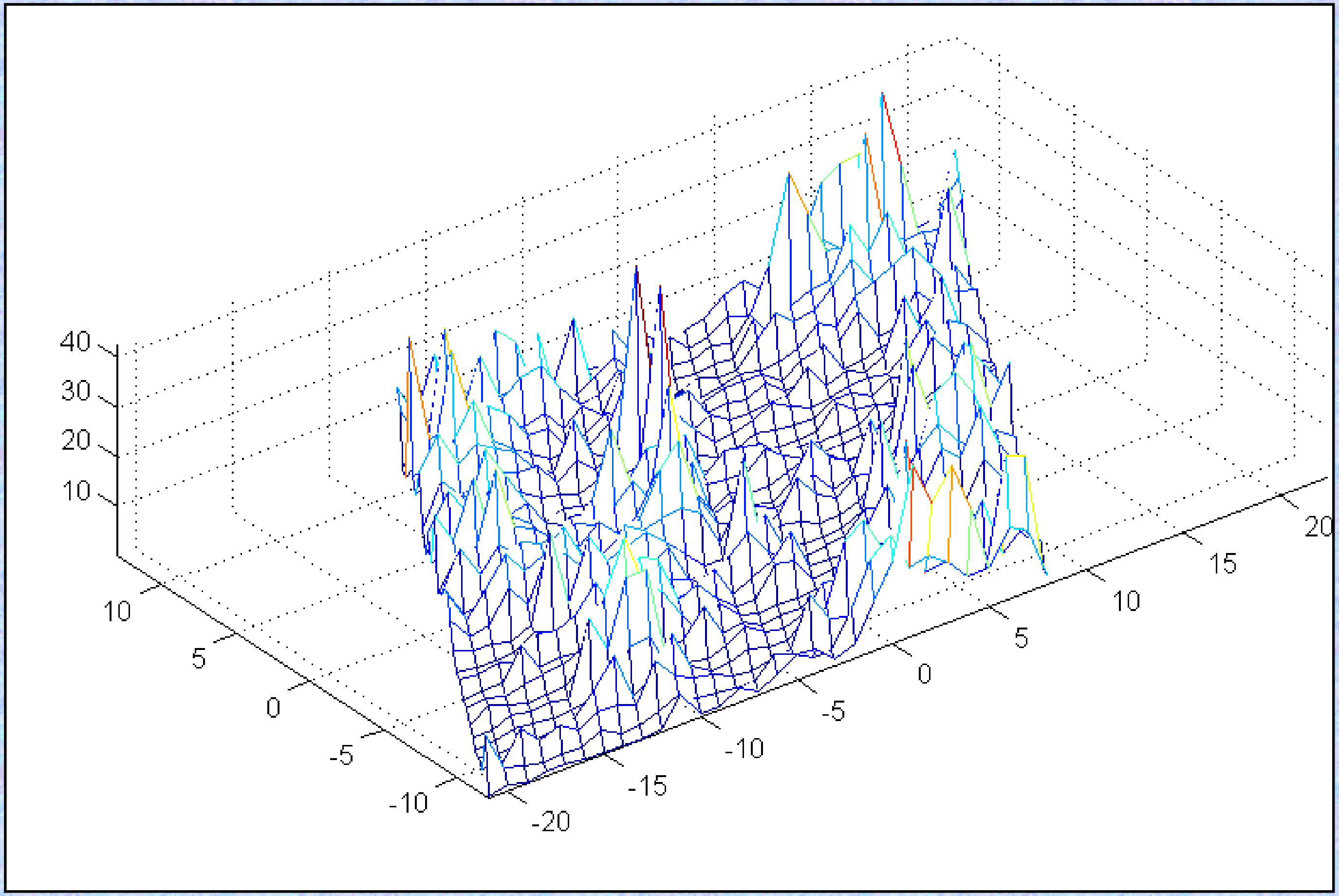
Numerical simulations in mica (1a)



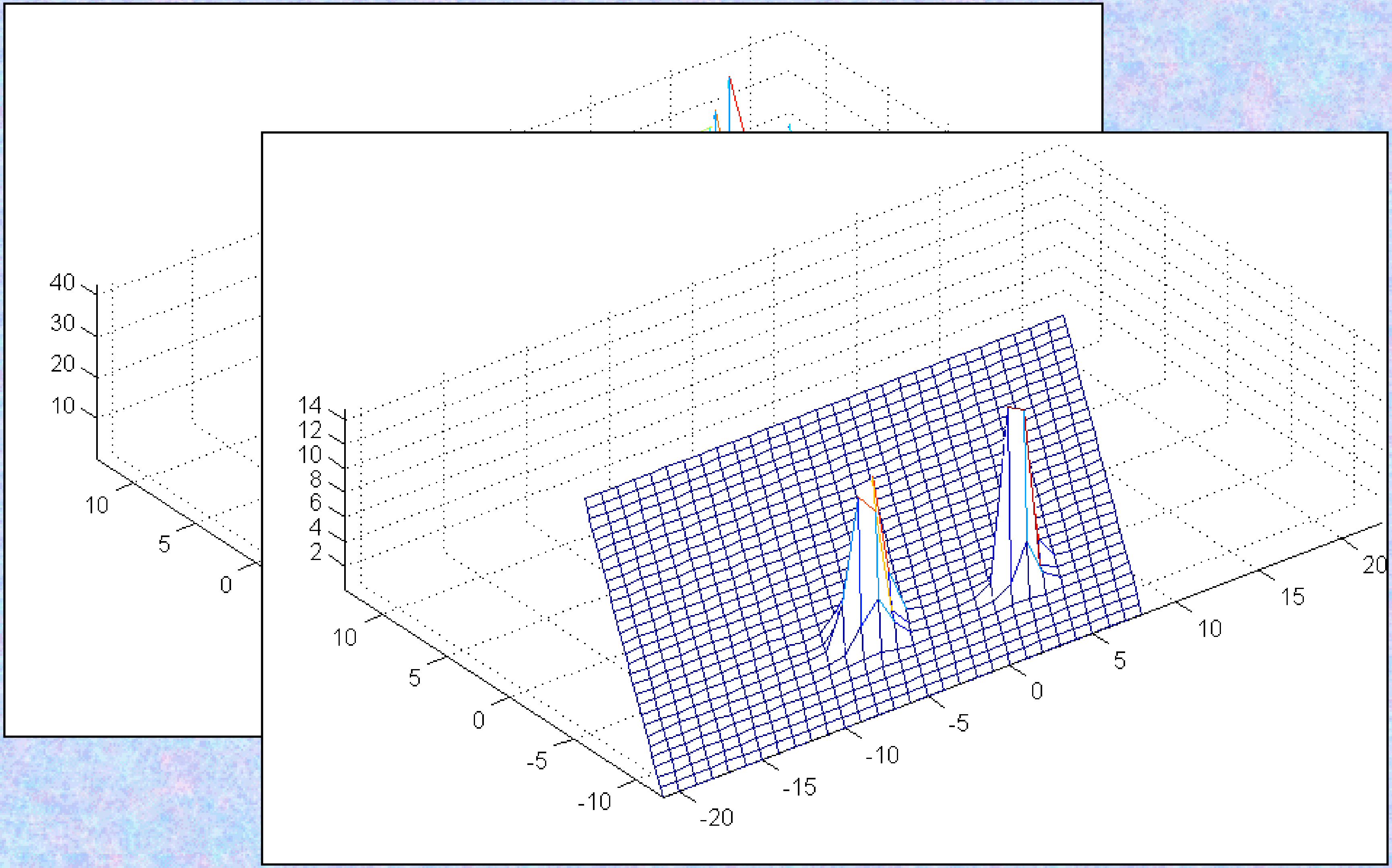
Numerical simulations in mica (1b)



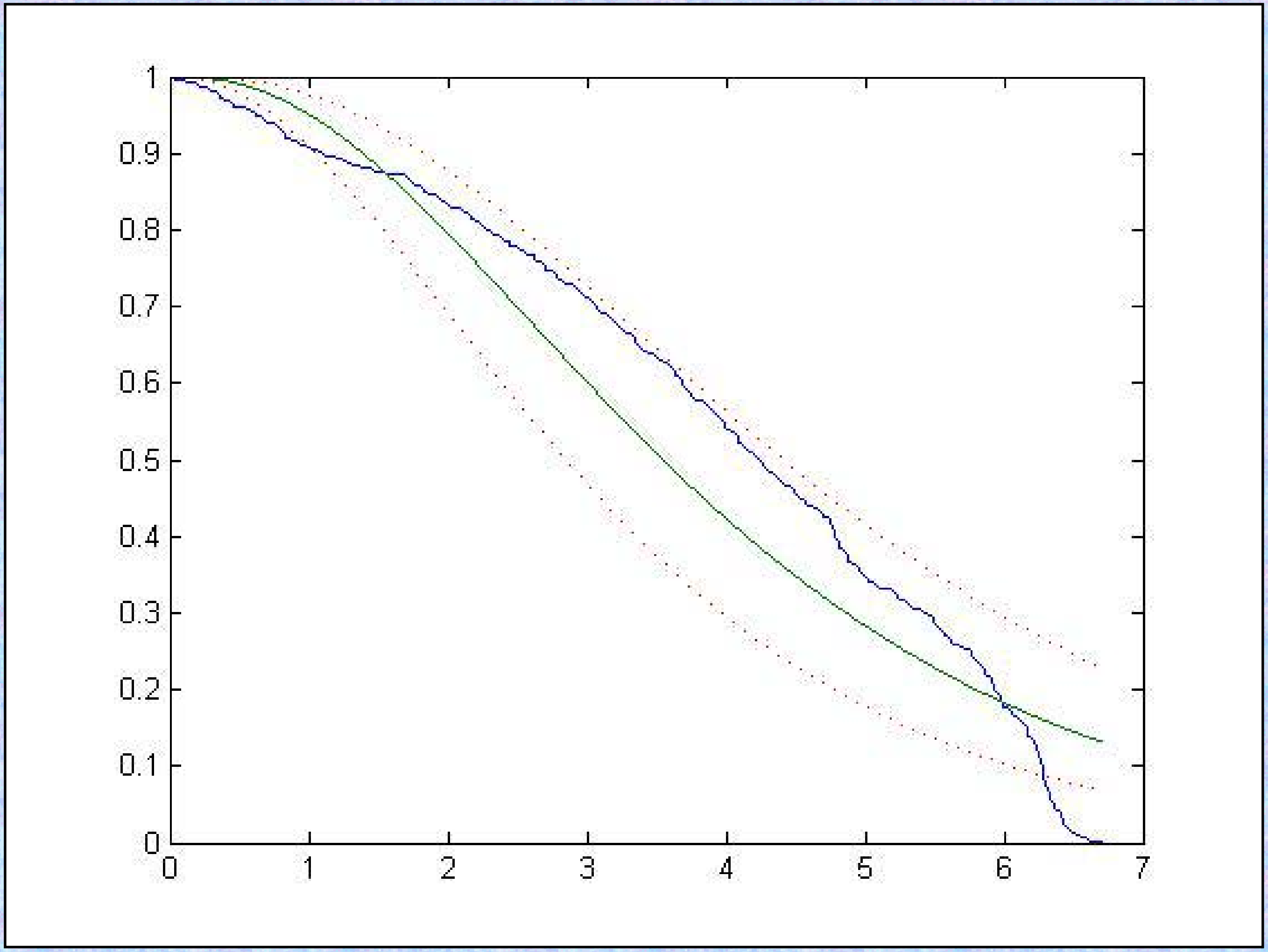
Numerical simulations in mica (2a)



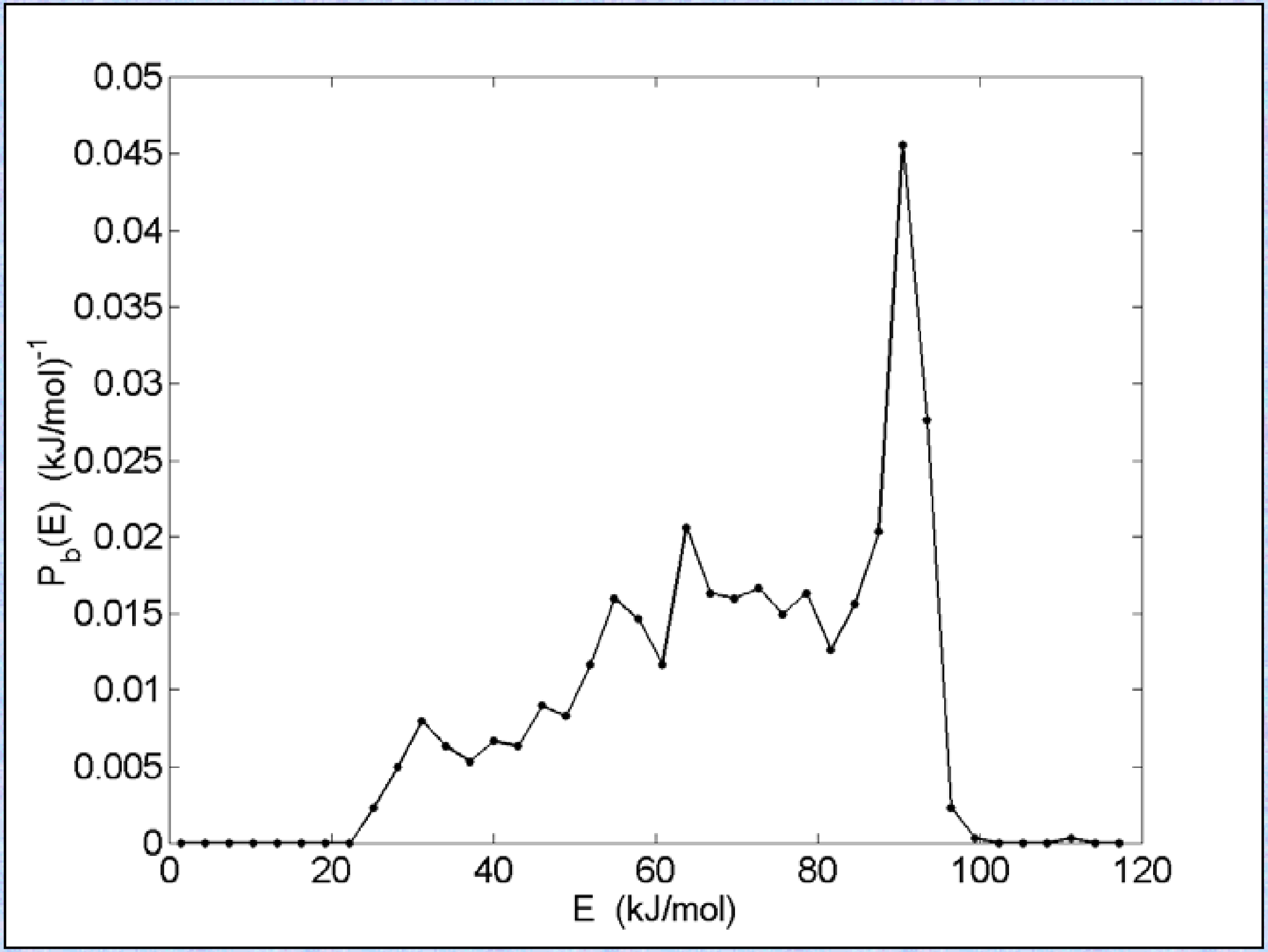
Numerical simulations in mica (2b)



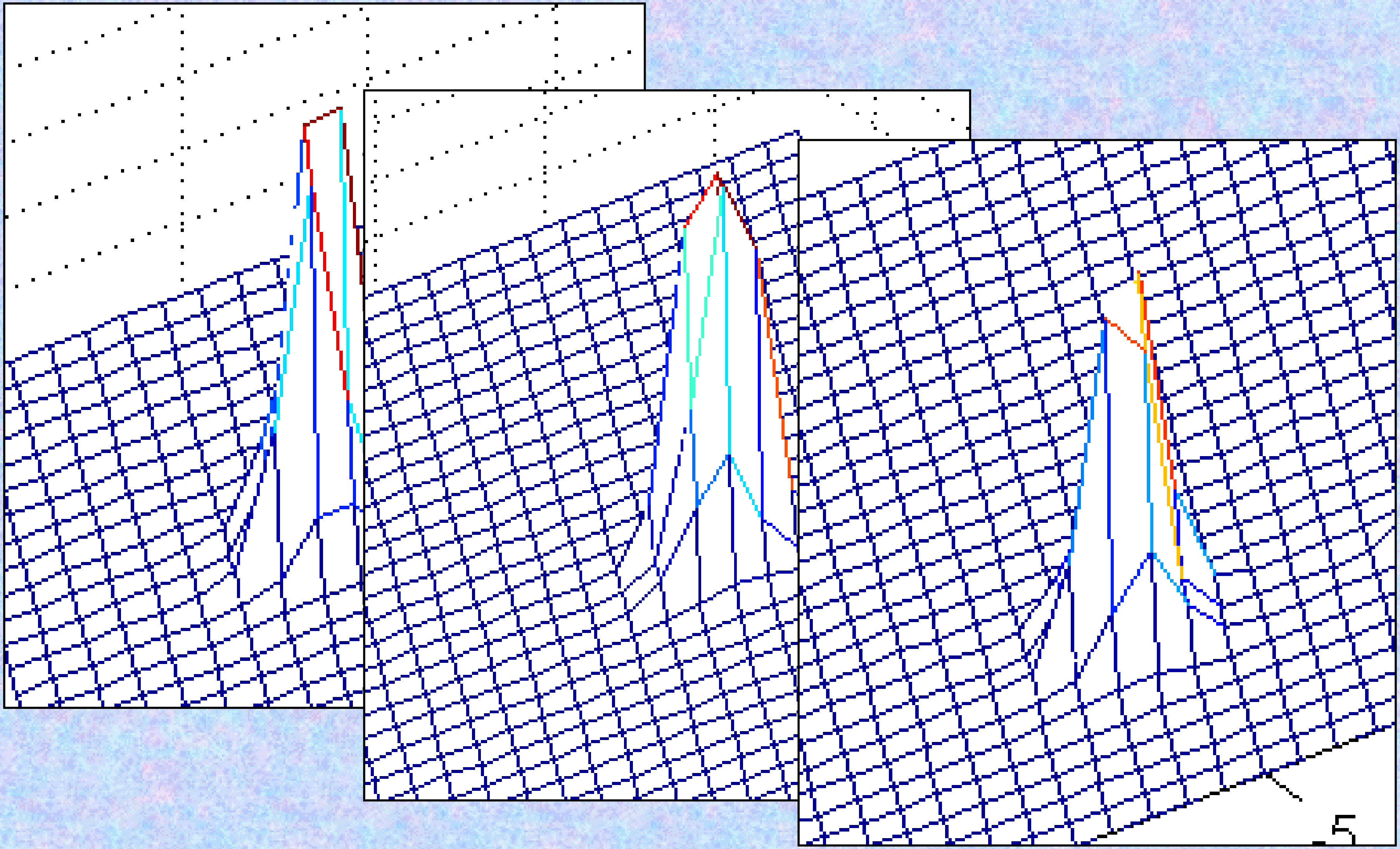
Attempt to fit $C_b(E)$: failure.



Total failure: $P_b(E)$



Reason: multiple breather types



Modification of the theory. Breathers with maximum energy

1.- Multiple breather types

2.- Differences:

- Minimum energy Δ
- Parameter z
- Maximum energy E_M !! :
  - Normalization: $\int_0^{E_M} P_b(E)\, dE=1$
- Different probability for each type of breather:

$$P(\Delta, z, E_M, ?)$$

Breathers with maximum energy. Results.

1.- Probability density:

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

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

$$C_b(E)=1- \gamma(z+1, \beta[E-\Delta])/ \gamma(z+1, \beta[E_M-\Delta])$$

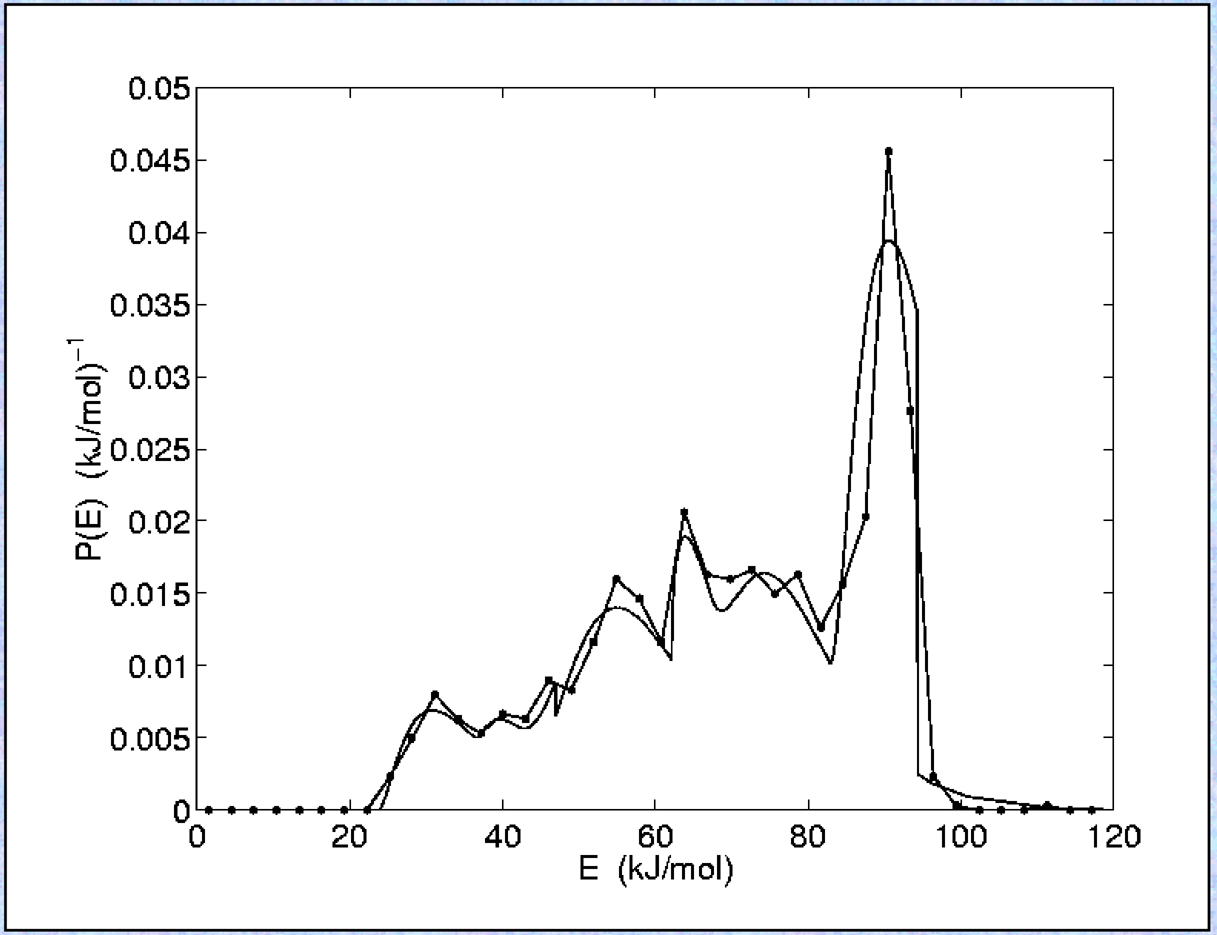
- Second incomplete gamma function:

$$\gamma(z+1,x)= \int_0^x y^z \exp(-y)dy$$

Breather energy spectrum

Δ (kJ/mol)	23.9	36.6	41.4	62.2	67.3	82.9
z	1.50	1.17	3.00	0.52	2.07	1.80
E_M (kJ/mol))	-	46.9	-	-	-	94.4
probability	0.103	0.026	0.281	0.097	0.202	0.290

Density probability for breathers in mica

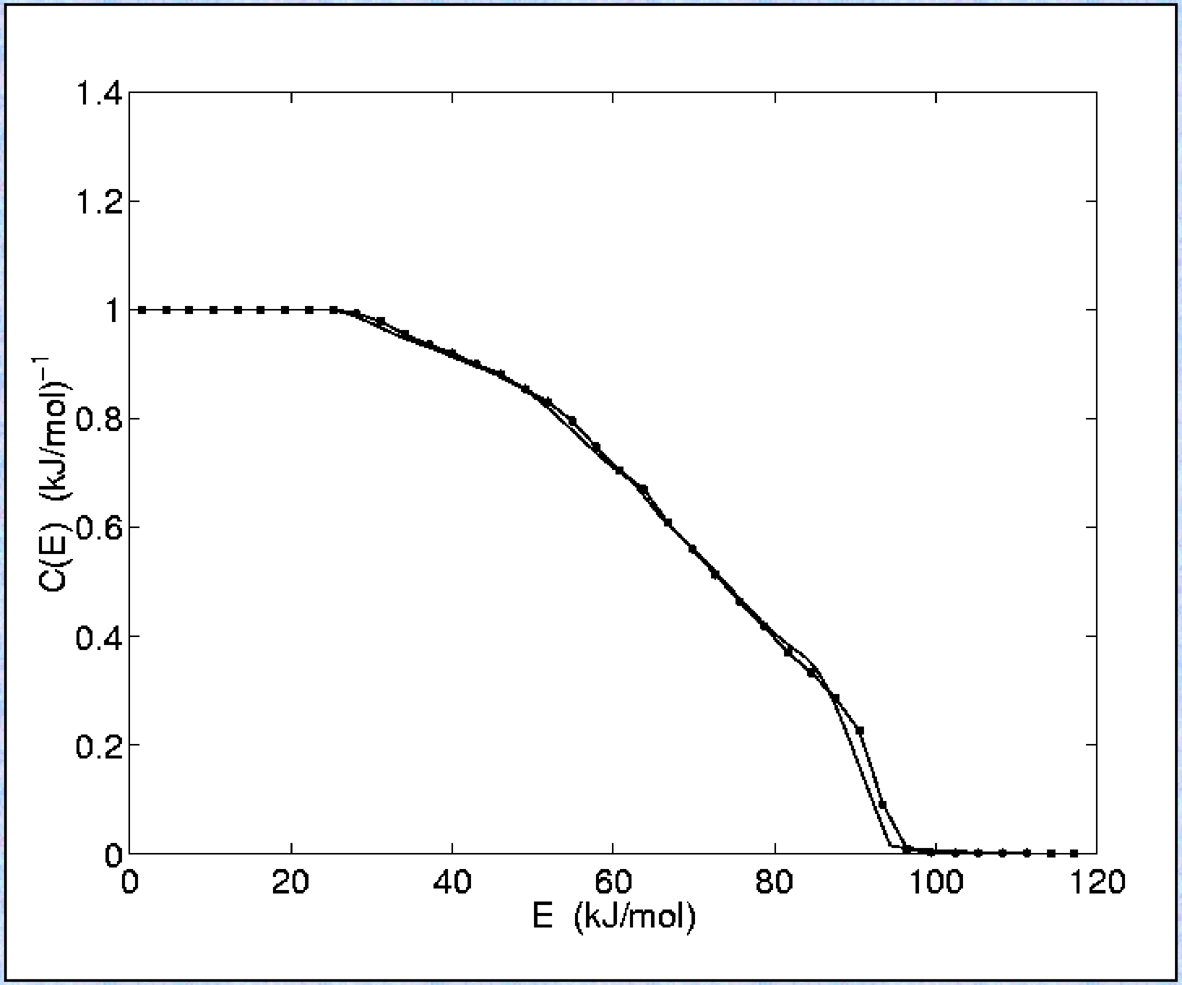


--•-- Numerical

— Theoretical

Accumulate probability:

Fraction of breathers with energy equal or larger than E



--•-- 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 years,

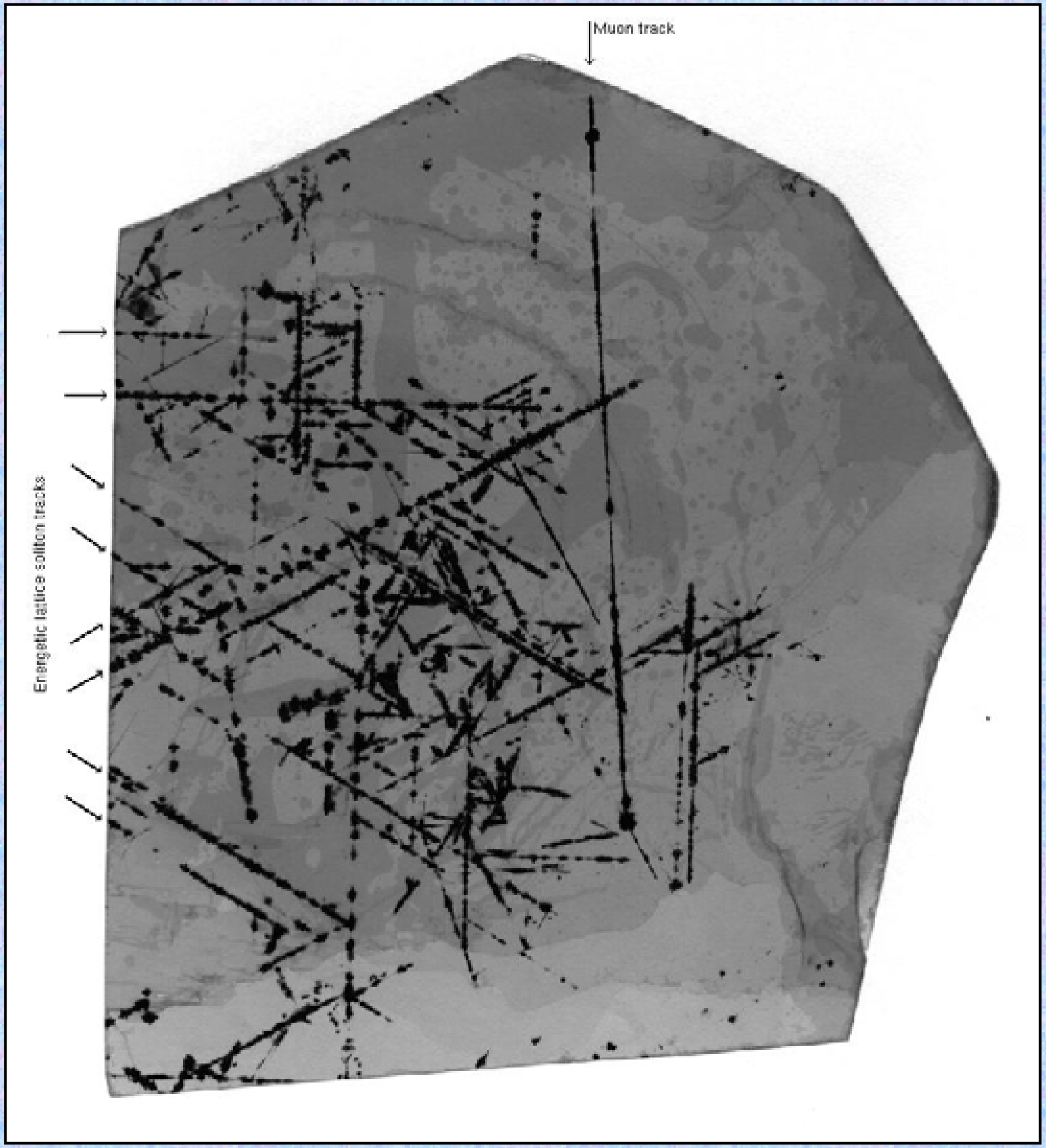
Moreover, breather can localize more the energy delivered, which will increase further the reaction speed

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

Other possible evidences for breather existence in mica muscovite

- Black tracks in natural mica
- Numerical studies of moving breathers
- Sputtering

Quodons in mica muscovite



Black tracks: Fe_3O_4

Cause:

• 0.1% Particles:

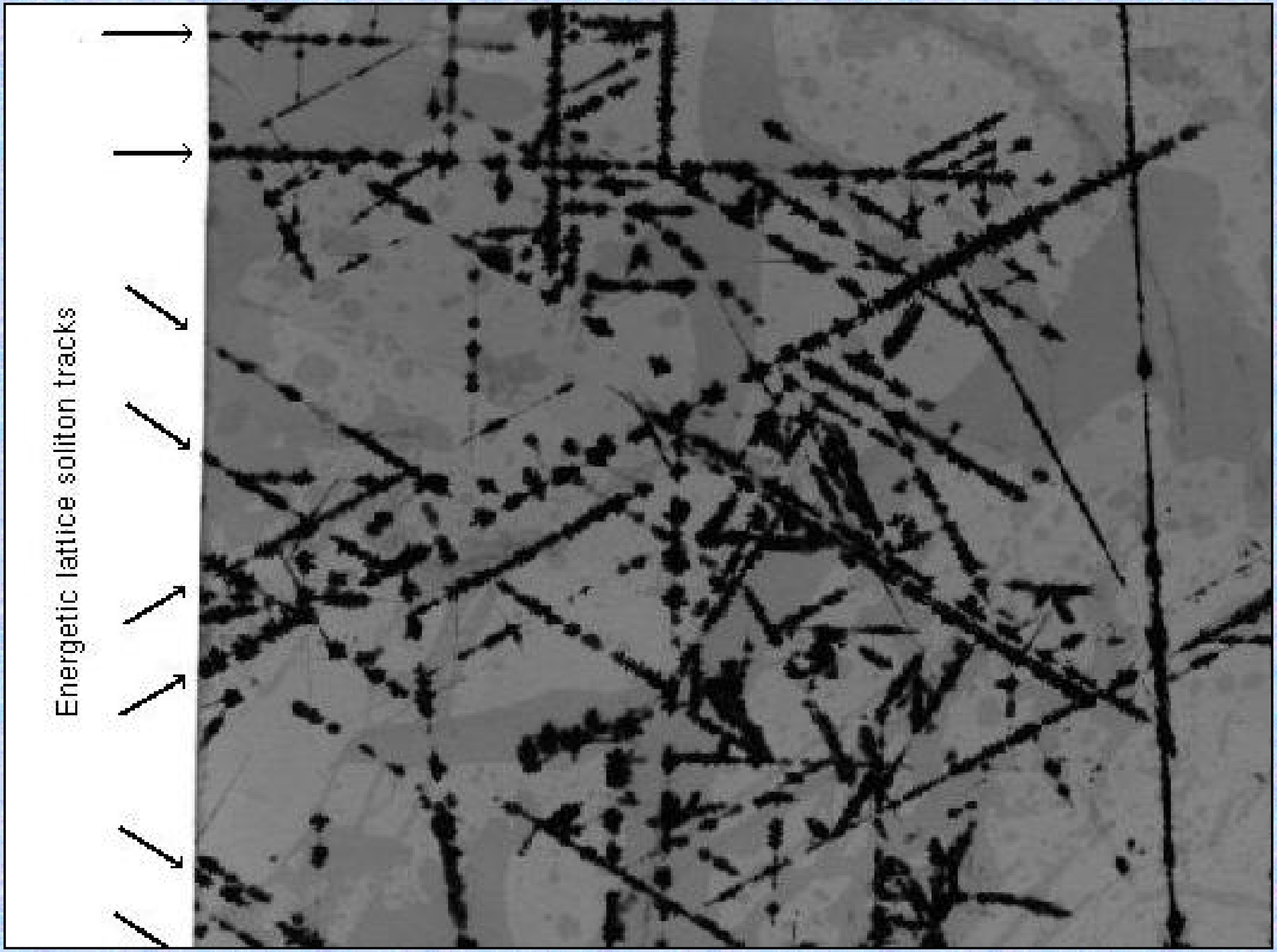
•muons: produced by interaction with neutrinos

• Positrons: produced by muons' electromagnetic interaction and K decay

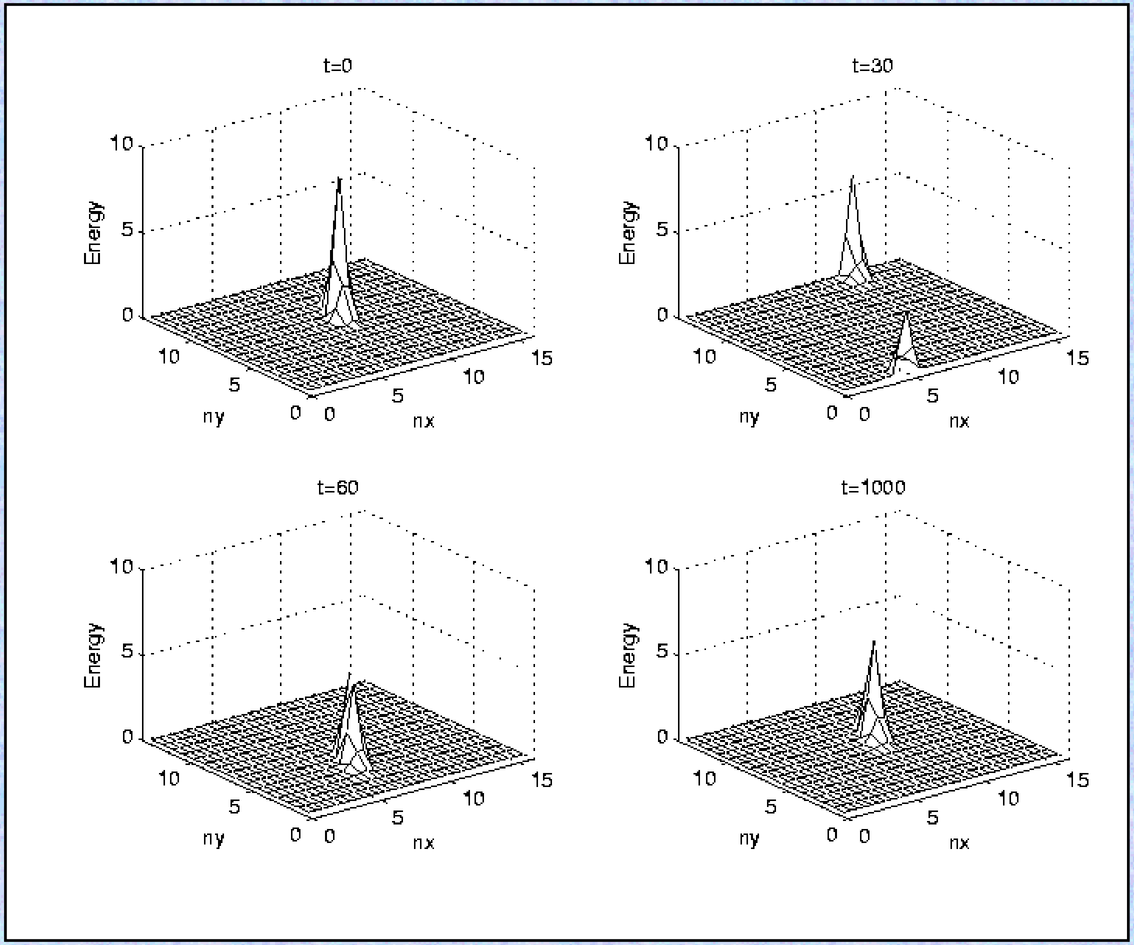
• 99.9% **Unknown**

¿Lattice localized vibrations: quodons?

Black tracks are along lattice directions within the K^+ layer



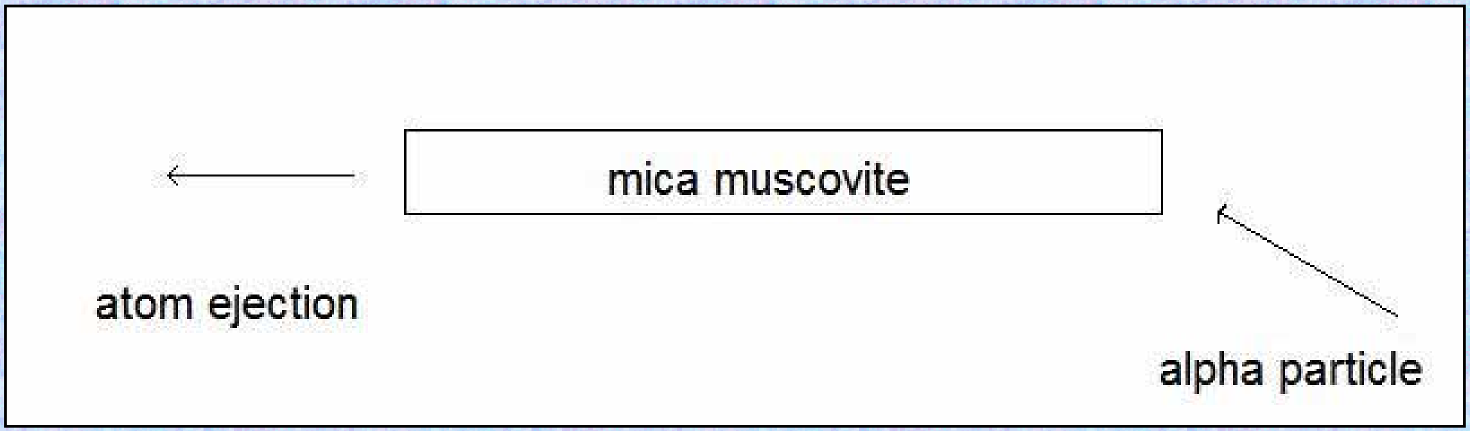
Numerical simulations in a 2D hexagonal lattice



No apparent dispersion in 1000~10000 lattice units

Localized moving breathers in a 2D hexagonal lattice.
JL Marín, JC Eilbeck, FM Russell, Phys. Lett A 248 (1998) 225

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) 10004

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 breathers in the cation layer

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Discrete breathers for understanding reconstructive mineral processes at low temperatures, JFR Archilla, J Cuevas, MD Alba, M Naranjo and JM Trillo, J. Phys. Chem. B 110, 24112, 2006