Soft Modes and Related Phenomena in Materials:
A First-principles Theory

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Thanks to Ram, Gautam Menon & Janet Hunziker

Outline

First-principles Theory:
From electronic motion to behavior of Materials

Vibrations (Phonons); Soft Modes/Phonons:
Thermodynamic stability and strong response
Symmetry breaking: e.g. Ferroelectrics

Soft Modes in Engineering Problems:
1. Dynamical crack instability, Hyperelasticity
2. Stacking faults and mechanical failure in SiC

Summary: Future challenges and work

First-principles Atomistic Theory and Simulations of Molecules and Materials

First-principles Theoretical Approach:
Total Energy Function

Chemistry:	Z_I: *Atomic numbers* of atoms in a given material
Structure:	R_I: *Atomic positions* of atoms in a given material

Quantum Mechanics Electrostatic Energy

$$E_{tot}(Z_I, R_I) = E_G^{el}(Z_I, R_I) + E_{Coulomb}^{ion}(Z_I, R_I)$$

Minimum energy quantum state of electrons: *Density Functional Theory, W Kohn et al*

- Interatomic potential *T=0K*
- Hamiltonian of a collection of atoms

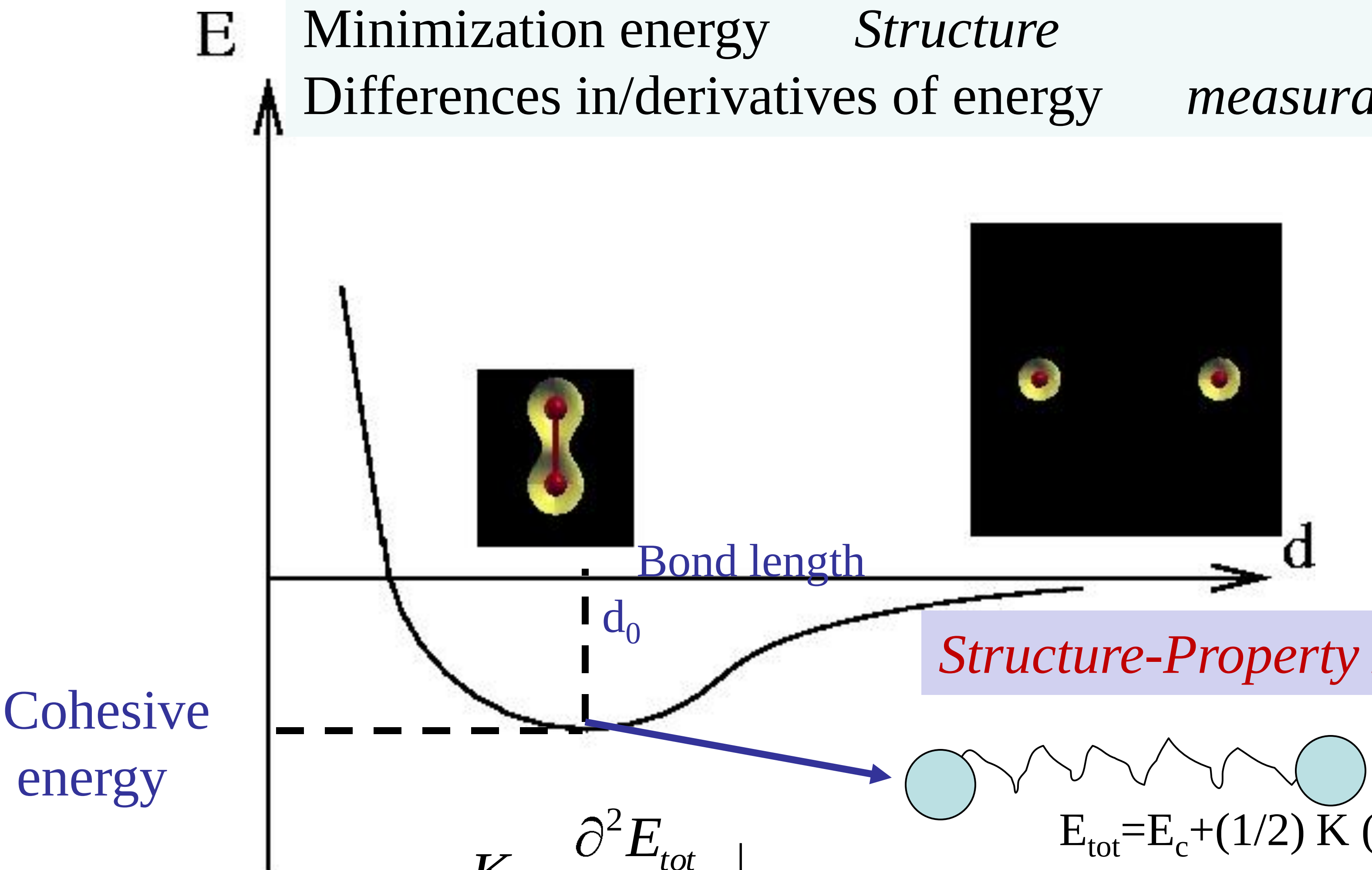
$\xrightarrow{\text{MD}}$ Monte Carlo

Free Energy
T > 0 K

From E_{tot} to Structure and Properties: e.g. O_2

Minimization energy → *Structure*

Differences in/derivatives of energy → *measurable property*



Structure-Property Relationship

$$K = \frac{\partial^2 E_{tot}}{\partial d^2}\Big|_{d=d_0}$$

$$E_{tot} = E_c + (1/2)\, K\, (d-d_0)^2$$

vibrational frequency $\omega = \sqrt{\frac{K}{M}}$

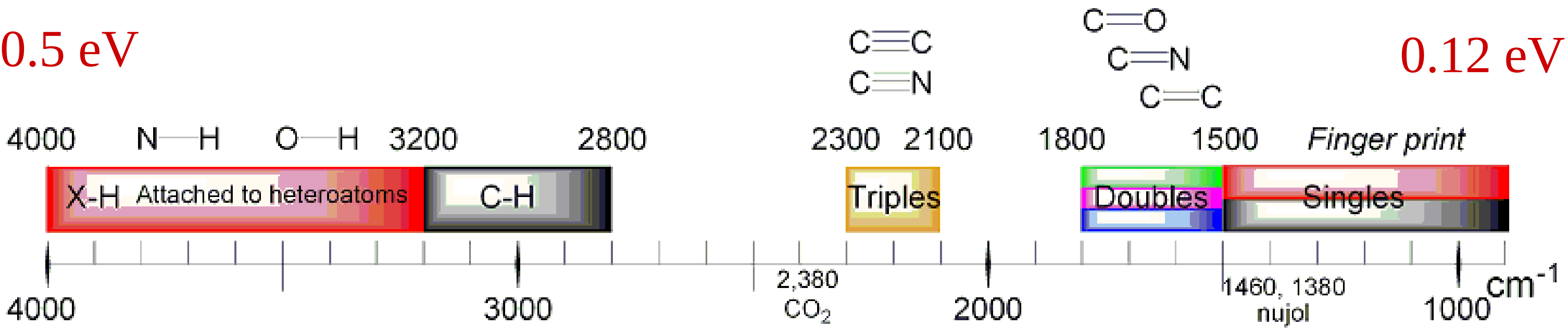
Derivatives of Free energy ↔ Physical properties at finite T

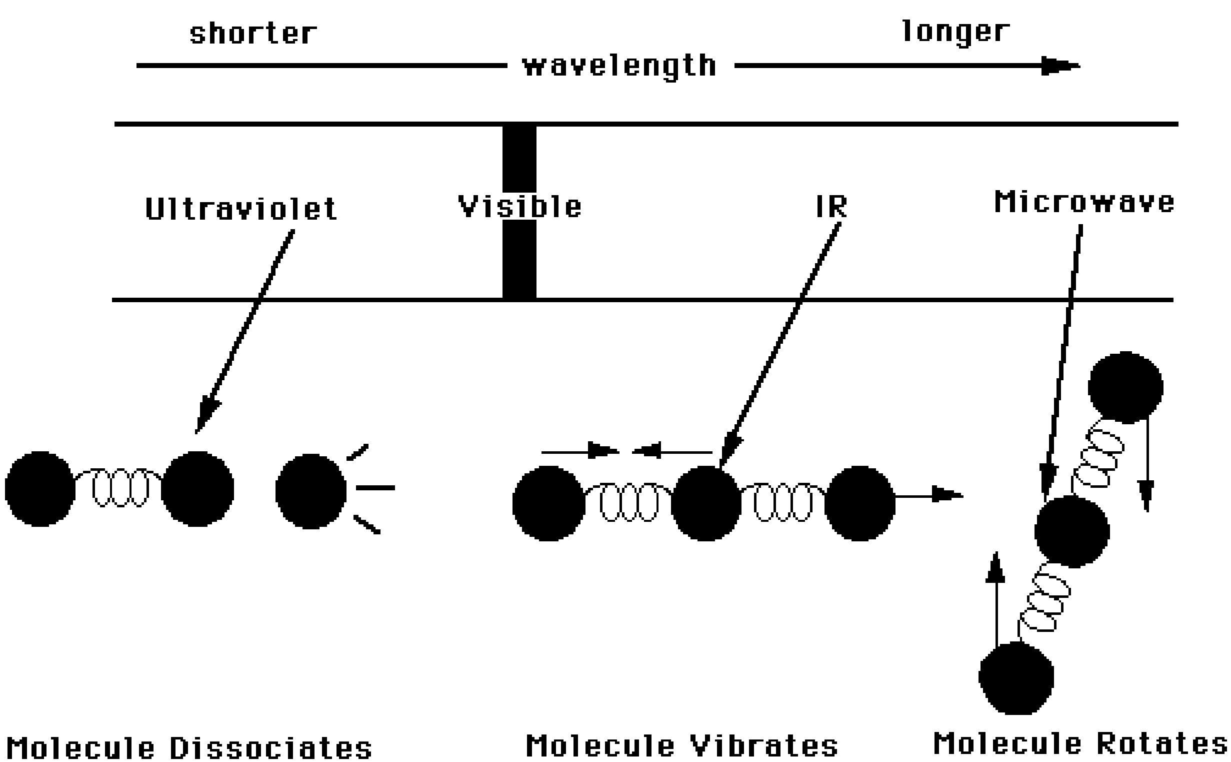
e.g. elastic modulus = $C = \frac{1}{V}\frac{\partial^2 F}{\partial \varepsilon^2}$

Soft Modes:

An Introduction

Introduction: *Vibrations*





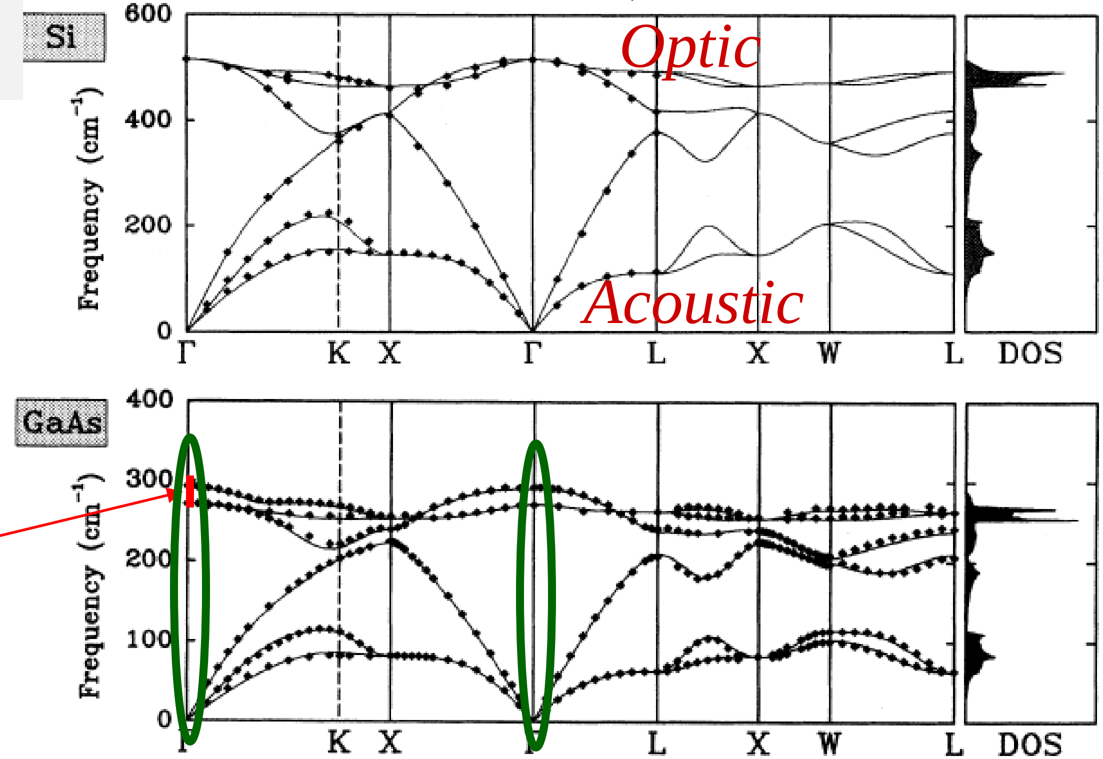
Vibrational frequency:

ω ~ measure of stiffness of a bond

Vibrations of a Crystal (phonons)

Infinitely many bonds and vibrational modes:
Bloch wave vector $k = \frac{2\pi}{\lambda}$

600 cm^{-1} ~75 meV, 900 K

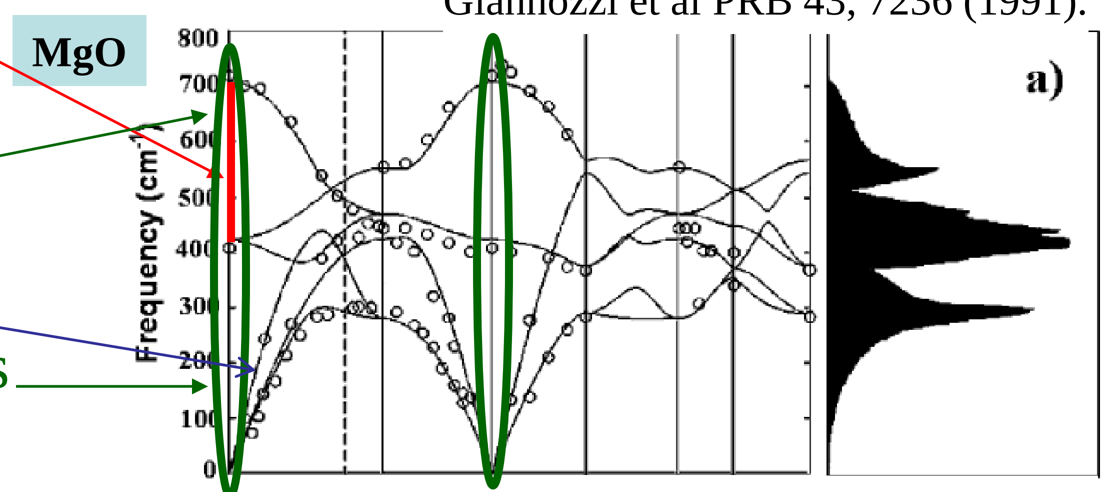


Giannozzi et al PRB 43, 7236 (1991).

LO-TO splitting:
measure of coupling
with electric field

IR and Raman

Brillouin Spectra:
long wave-length phonons



Ghose et al, Phys Rev Lett 96, 035507 (2006).

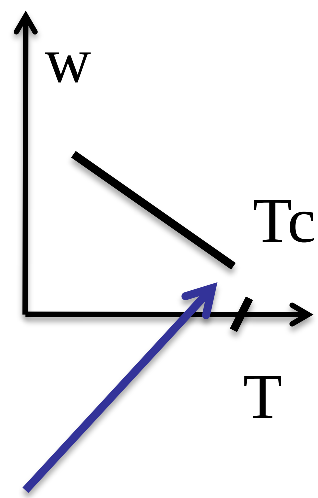
Nature 145, **147 (27 January 1940) | doi:10.1038/145147a0**.

The α-β; Transformation of Quartz

C. V. RAMAN & T. M. K. NEDUNGADI

Abstract

In the hope of obtaining an insight into these remarkable phenomena, a careful study has been made of the spectrum of monochromatic light scattered in a quartz crystal at a series of temperatures ranging from that of liquid air to nearly the transition point. Significant changes are observed which are illustrated in the accompanying illustration, reproducing part of the spectrum excited by the 4358 A. radiation of the mercury arc.



Soft mode

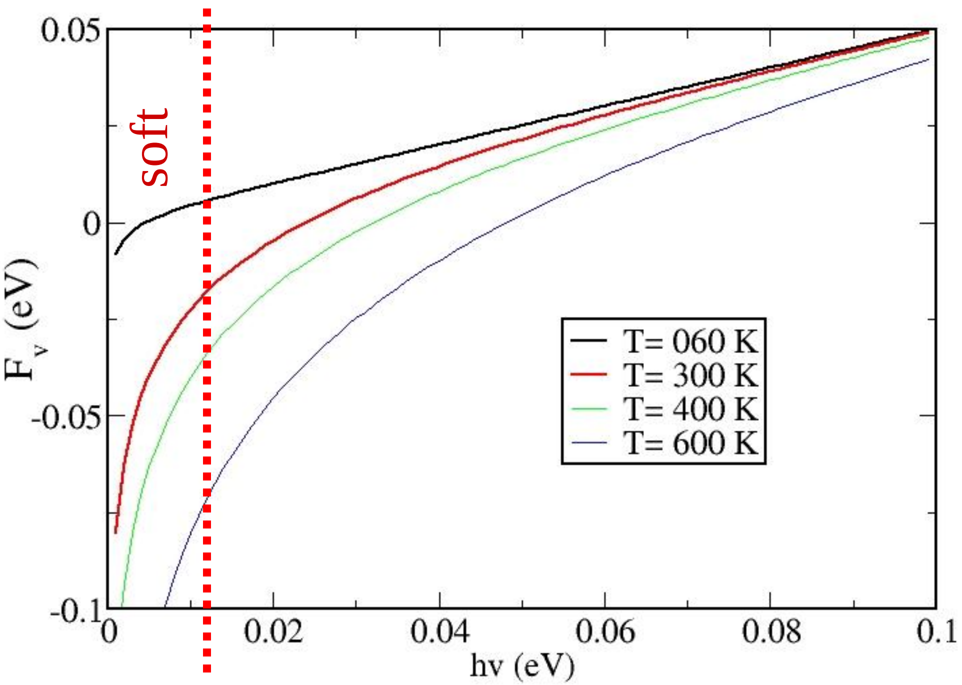
Soft Modes

CV Raman & Nedungadi, Nature (1940).
W Cochran (1959).
PW Anderson (1960).

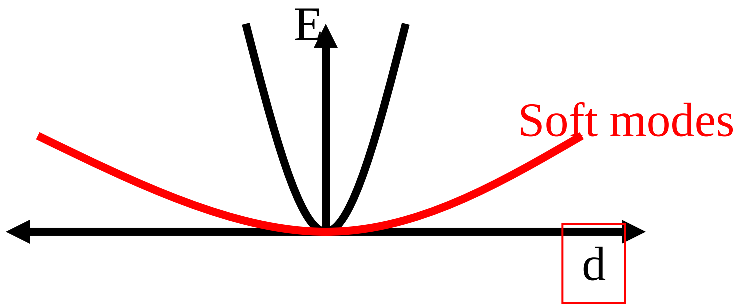
Vibrational modes of frequencies < 100 cm^{-1} (hν < 12.5 meV)

Relevance to Temperature Dependent STABILITY

Lower the frequency, greater is the entropy and lower free energy:



$$F_{vib} = +k_B T \sum_{iq} \log\left[2\sinh\left(\frac{\hbar\omega_{iq}}{2k_b T}\right)\right]$$



Soft modes give lower free energy particularly as T increases

Effects of anharmonicity are large:
T-dependent structural transitions

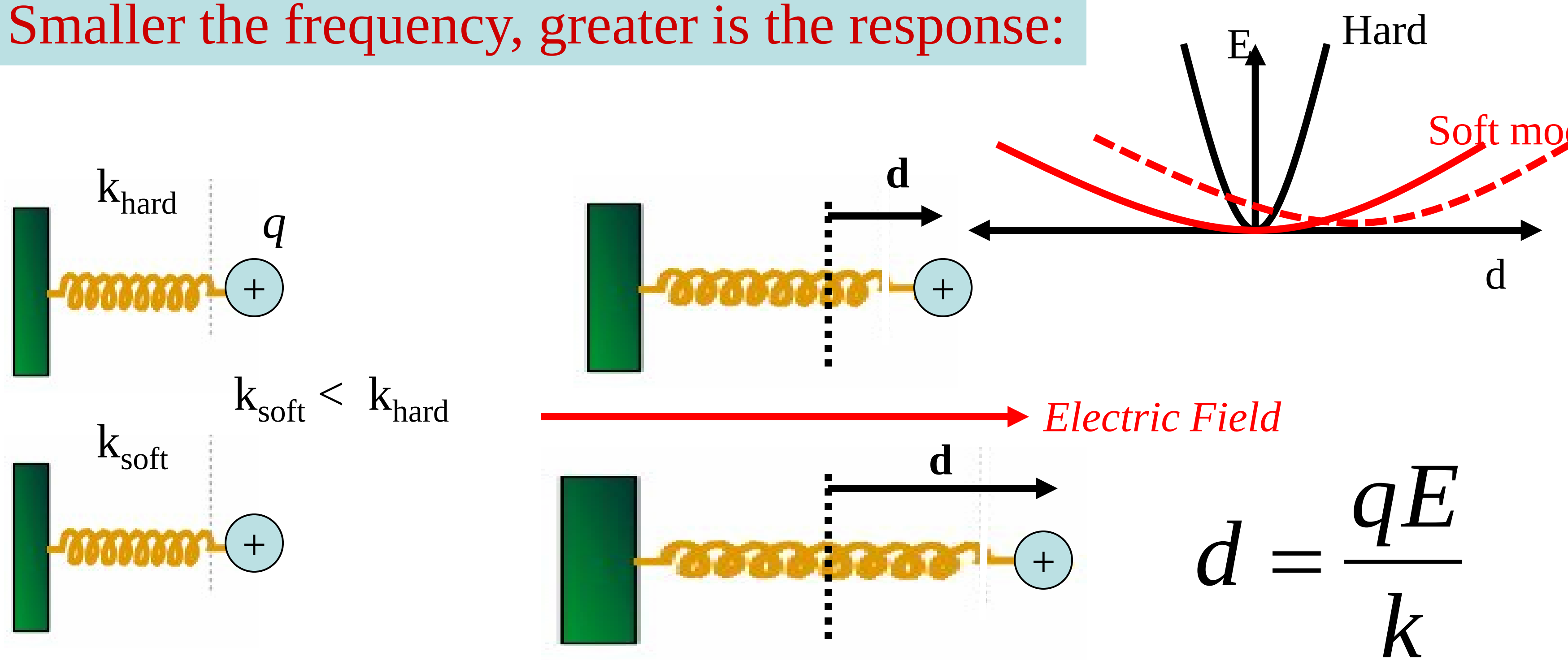
Soft Modes

Vibrational modes of frequencies < 100 cm^{-1} ($h\nu$ < 12.5 meV)

Analogy with electrons at or near the Fermi energy

Relevance to low-energy / temperature phenomena

Smaller the frequency, greater is the response:



$$d = \frac{qE}{k}$$

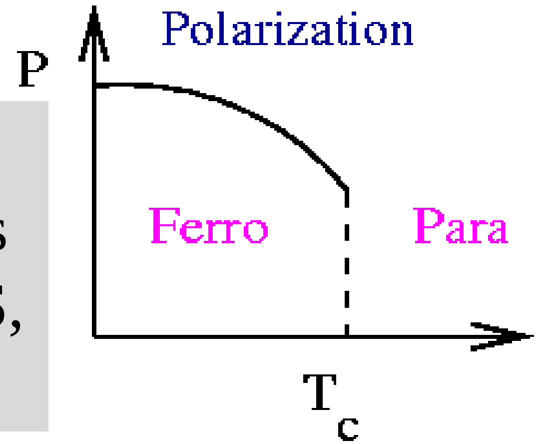
$k \sim w^2$

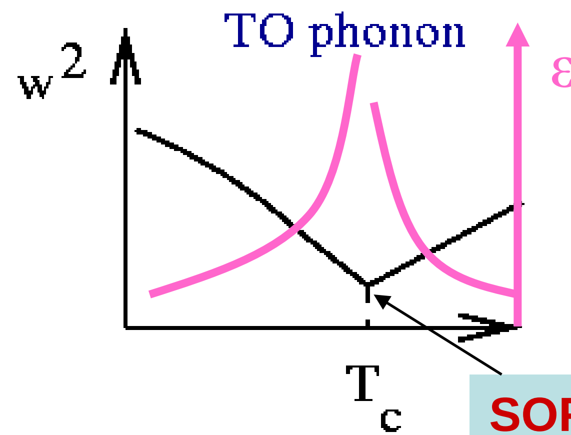
-Indicate diminishing bond-stiffness

-Soft modes dominate dielectric, pizeoelectric and other responses

Soft Modes: Ferroelectric Phase Transitions

Ferroelectrics: Smart materials used in MEMS, memory





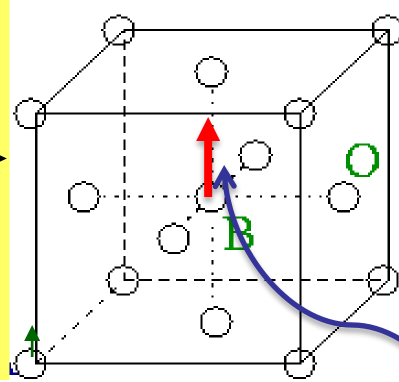
$$\varepsilon \propto \frac{1}{\omega^2}$$

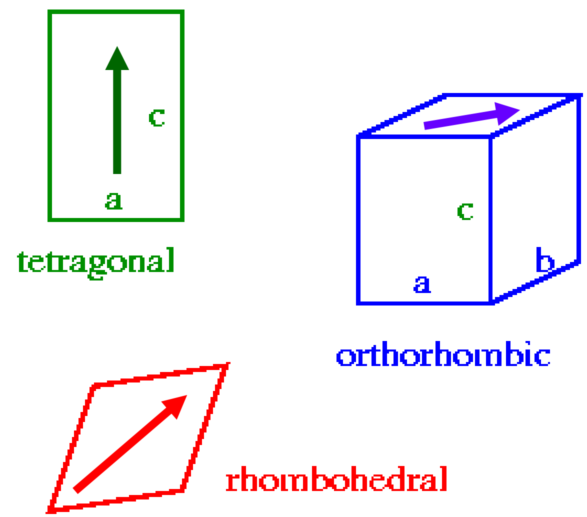
SOFT MODE

$BaTiO_3$, $PbTiO_3$, $KNbO_3$

Perovskite Ferroelectrics

SOFT MODE
Breaks the inversion $\vec{r} \rightarrow -\vec{r}$ symmetry of the cubic structure

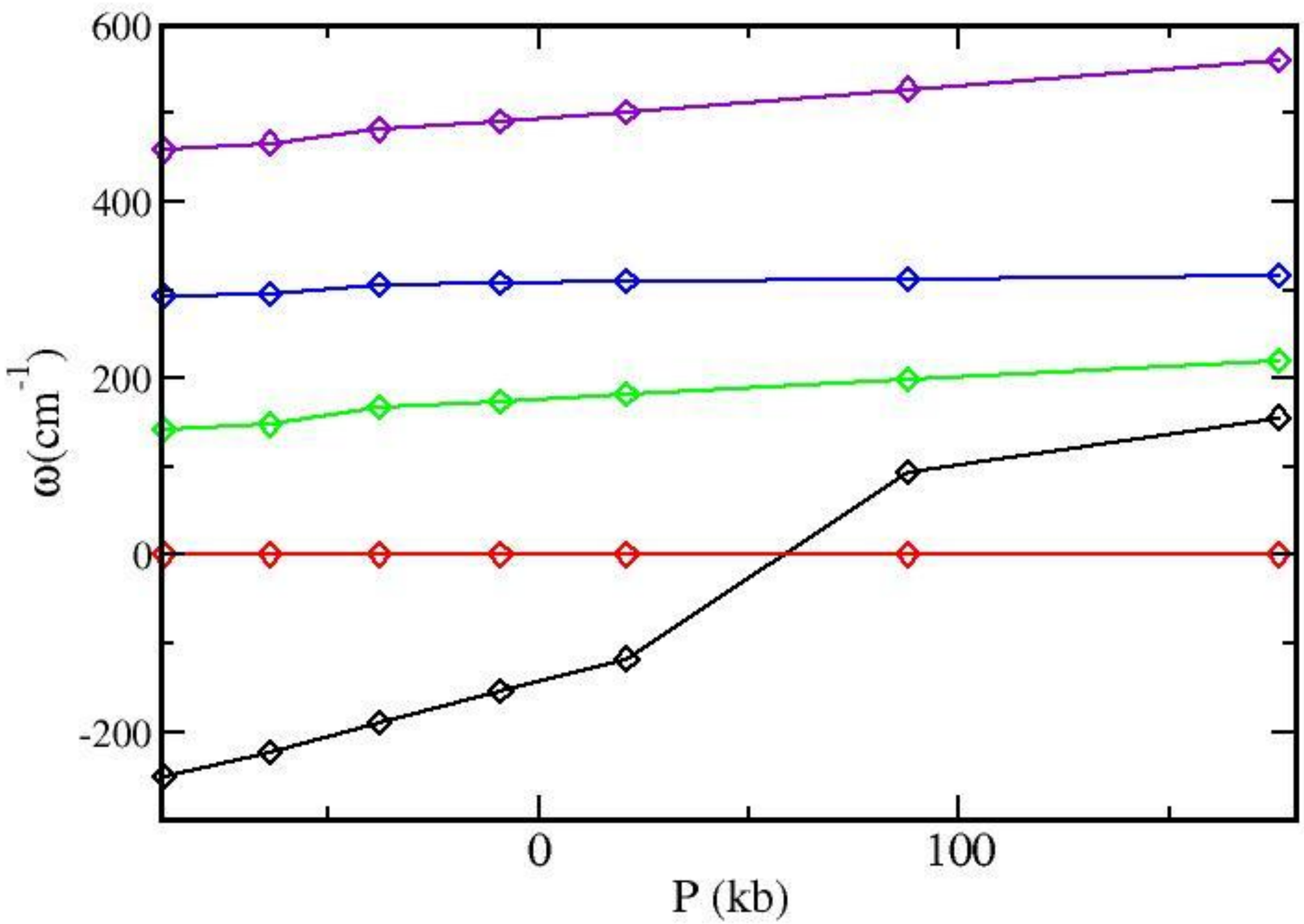




Cubic Perovskite ($T > T_c$) ($T < T_c$)

Soft mode involves atomic displacements that connect high symmetry structure to the one with broken symmetry

Pressure dependent phonons of CUBIC $BaTiO_3$

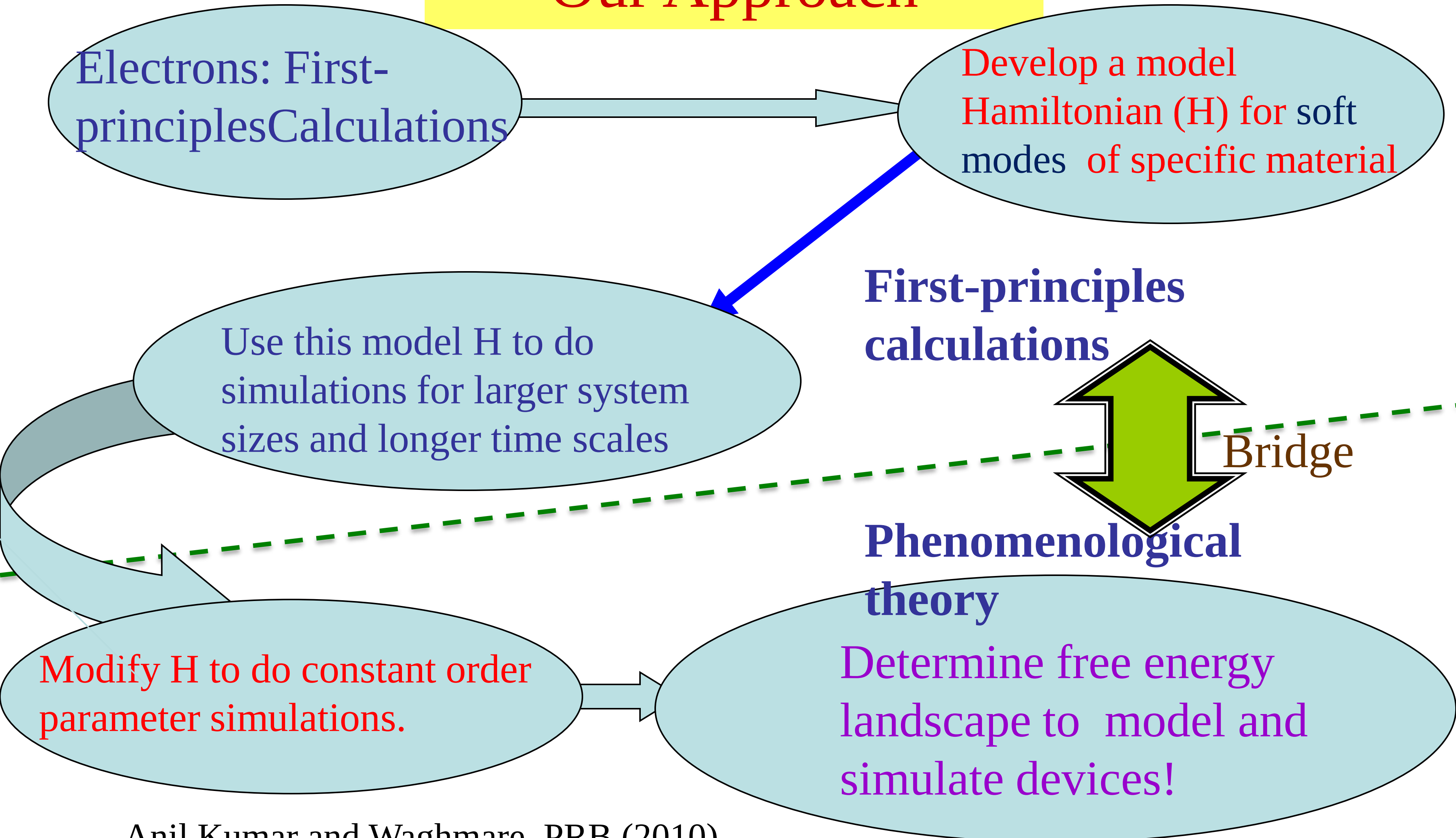


Soft modes couple most strongly with pressure *NONLINEARITY*

At high enough pressure, ferroelectricity is eliminated.

Also why Ferroelectrics are strong di- and piezo-electrics

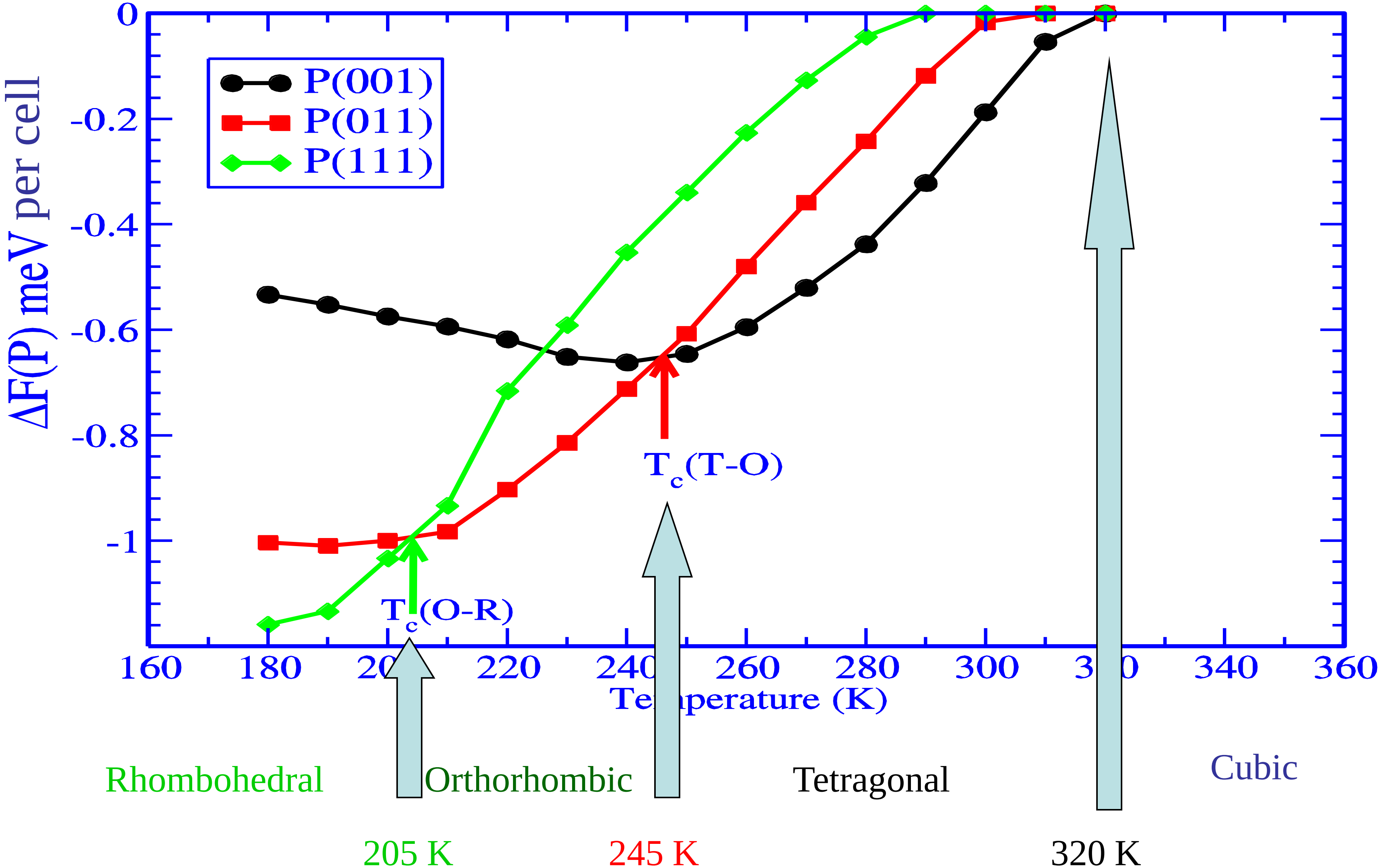
Our Approach



Anil Kumar and Waghmare, PRB (2010)

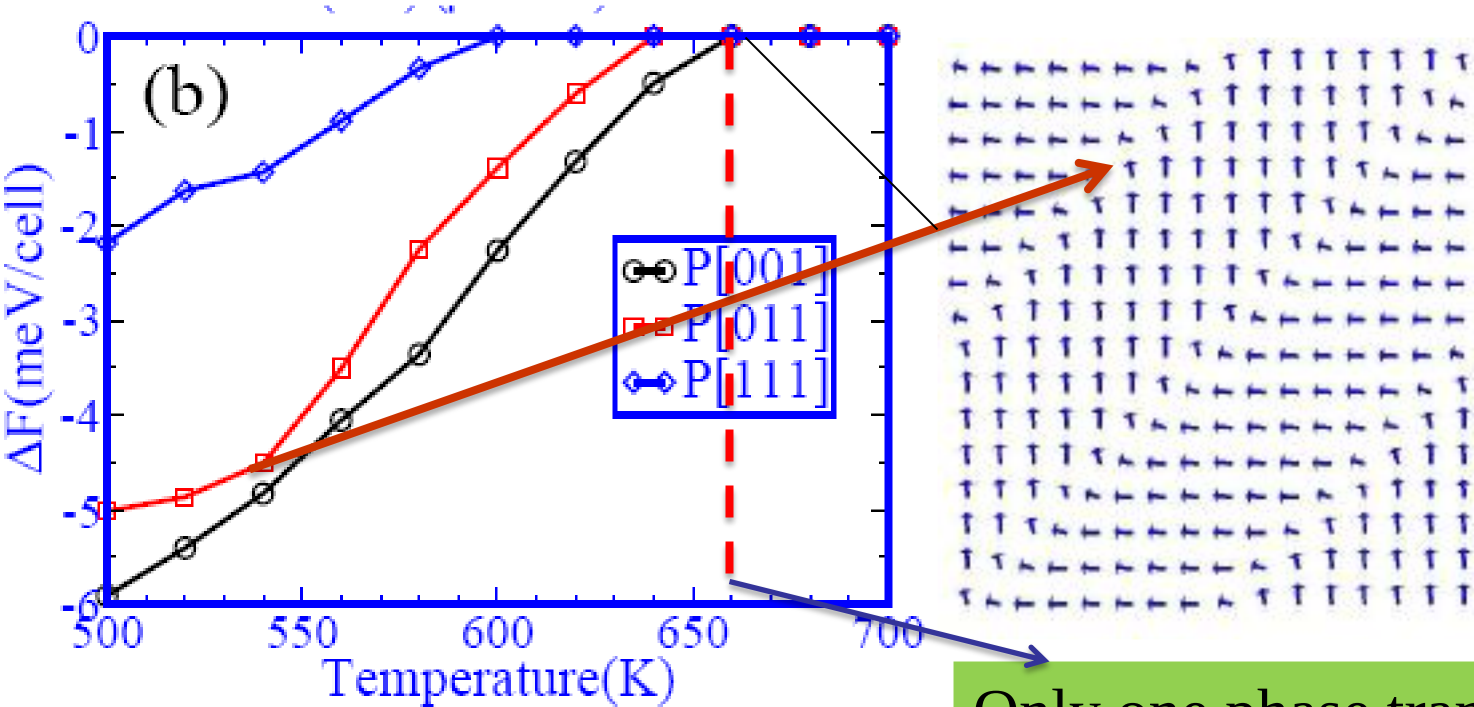
This powerful approach brings out the fundamental origin of remarkable contrast between $BaTiO_3$ and $PbTiO_3$.

Free Energy for different phases of $BaTiO_3$



A sequence of three phase transitions!

Free Energies: $PbTiO_3$



Only one phase transition P_z

90° domains:
Arise from the strong piezoelectric coupling

Nano-scale structure relevant to technological applications: memory

$PbTiO_3$ is rather different from $BaTiO_3$ and more extensively used in applications!

Anil Kumar and Waghmare, PRB (2012)
T Nishimatsu, Anil Kumar, Waghmare et al (2012)

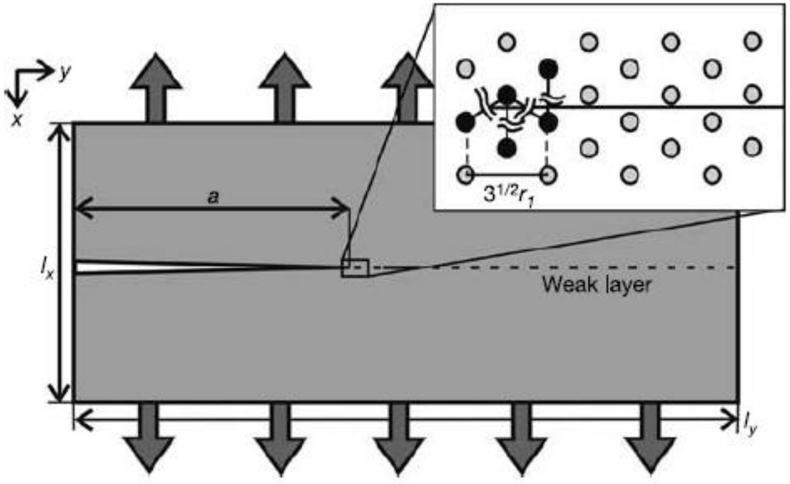
Soft Modes Relevant to Engineering Problems!

Mechanical Failure of Materials

Fracture or mechanical failure is singularly important to technological applications

Crack propagation is the main mode of material failure.

A multi-scale process: from bond breaking to blunting through dislocation emission, void formation



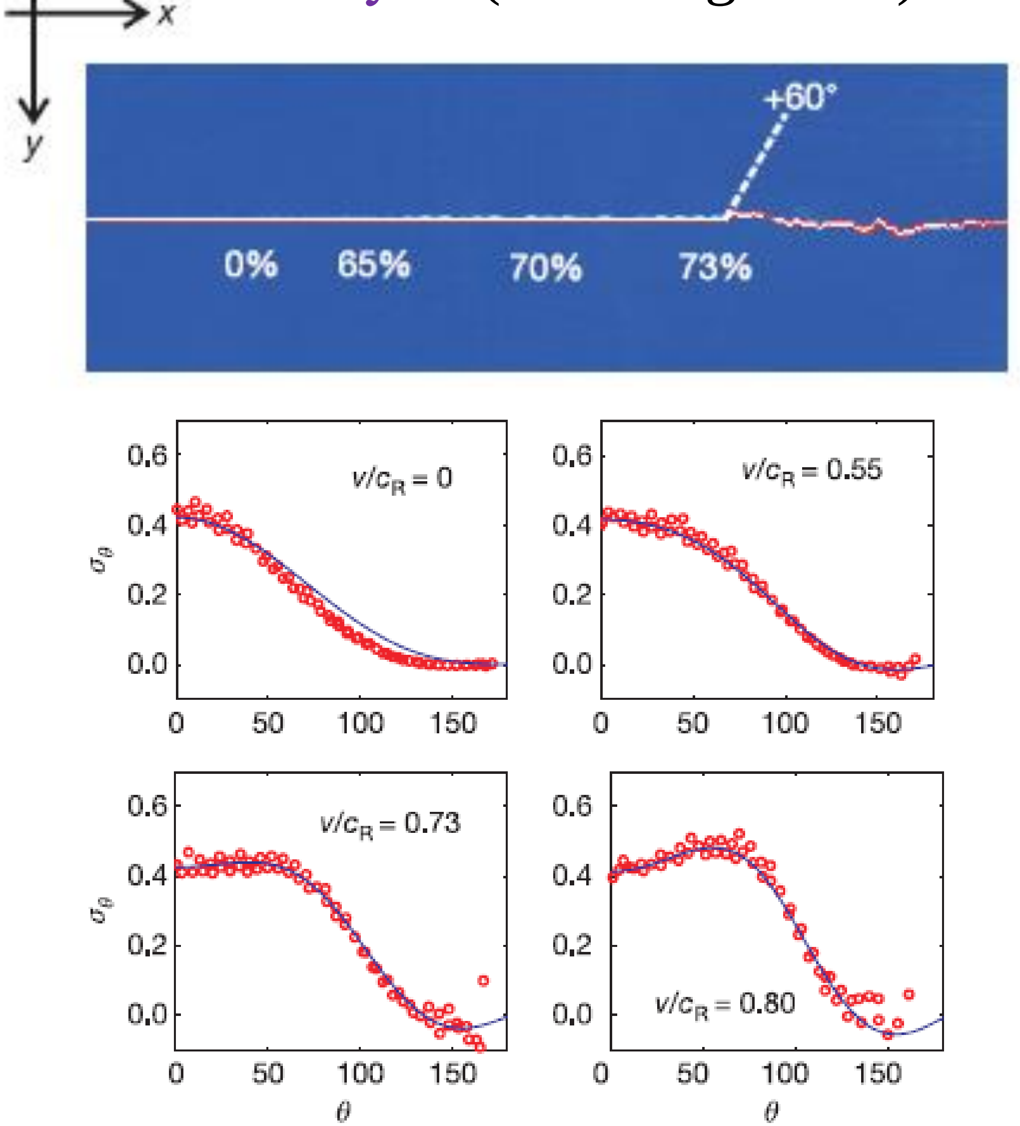
Buehler et al, Nature 426, 141 (2003)

Griffith's energy balance:
$G = 2\,\gamma_S$

How fast can a crack propagate?

Crack Propagation and Instability

Yoffe's analysis (Phil Mag. 1951) on a linear elastic continuum



Buehler et al, Nature 426, 141 (2003)

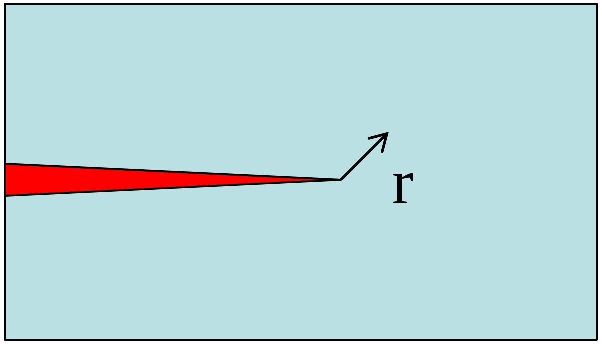
Crack propagation along a straight line for low speeds

For **v > 0.73 c_R** (Rayleigh speed) stress near a crack becomes bimodal, and the crack deviates from the straight path.

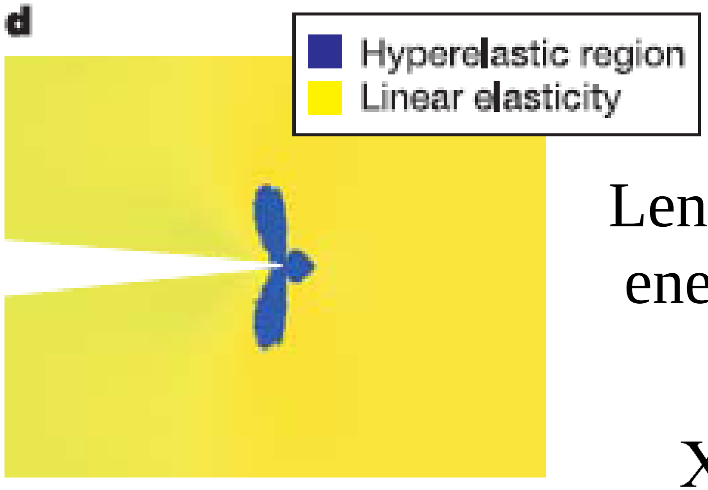
→ *Roughening, branching*

Experiments, however, show much smaller critical crack speeds (< 0.4 c_R)

Inglis (1913): Stress near the crack tip diverges as $\dfrac{1}{\sqrt{r}}$



Large stresses and deformations near the crack tip: ***Linear elasticity invalid?***

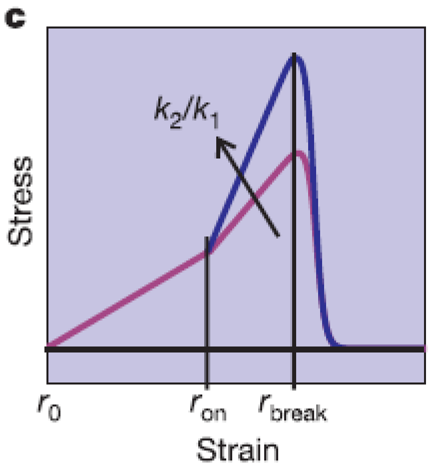


MD simulations on a model potential with linear and nonlinear elastic terms

Gao et al, Nature 439, 3-7 (06)

Length-scale for energy release

$$X = \beta \frac{\gamma_s E}{\sigma^2}$$



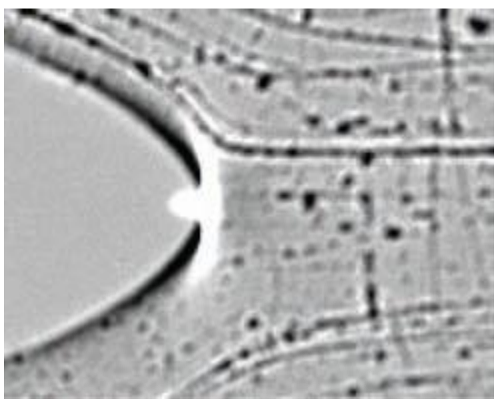
Hyperelasticity local to the crack governs the crack instability

What happens in real materials?

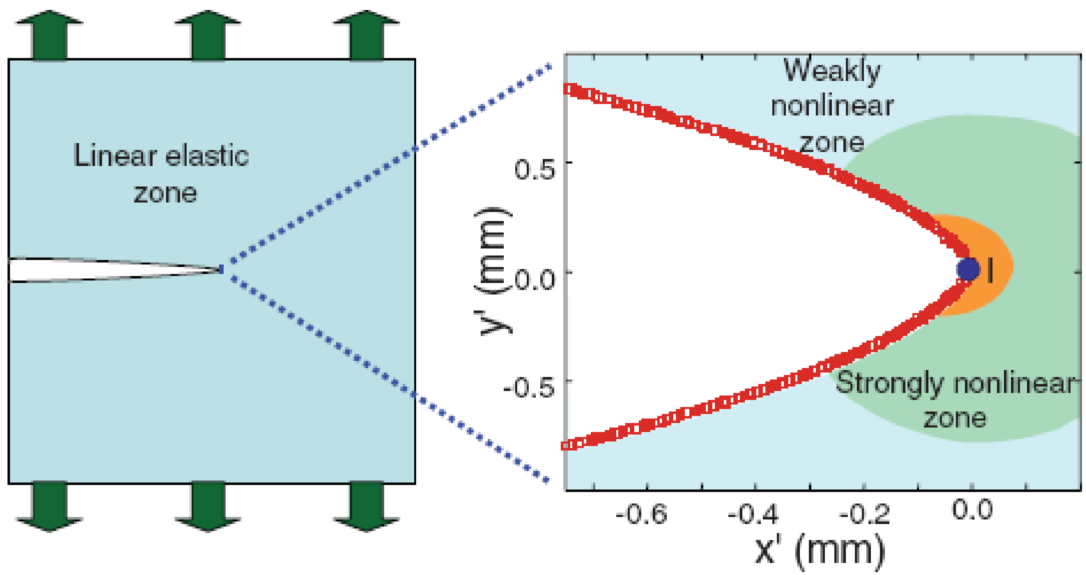
Experimental evidence for hyperelasticity near a moving crack

Fineberg et al, Science 327, 1359 (2010)

Polyacrylamide gels (large strains are possible, cracks move much slower (2 m/s) than in glass (1200 m/s)): a neo-hookean brittle material



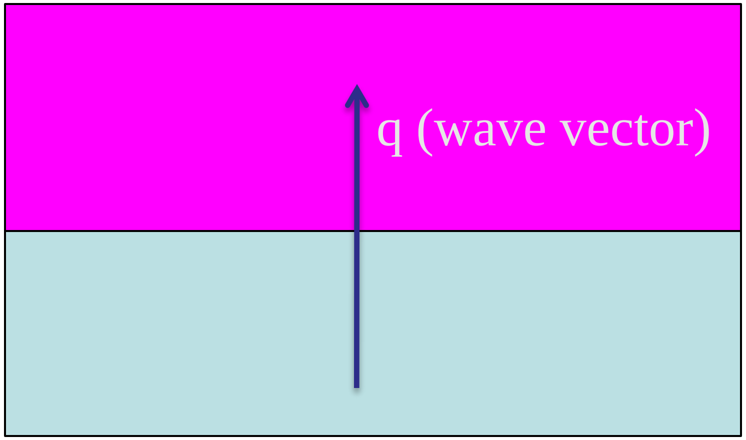
Tracers in the gel imaged



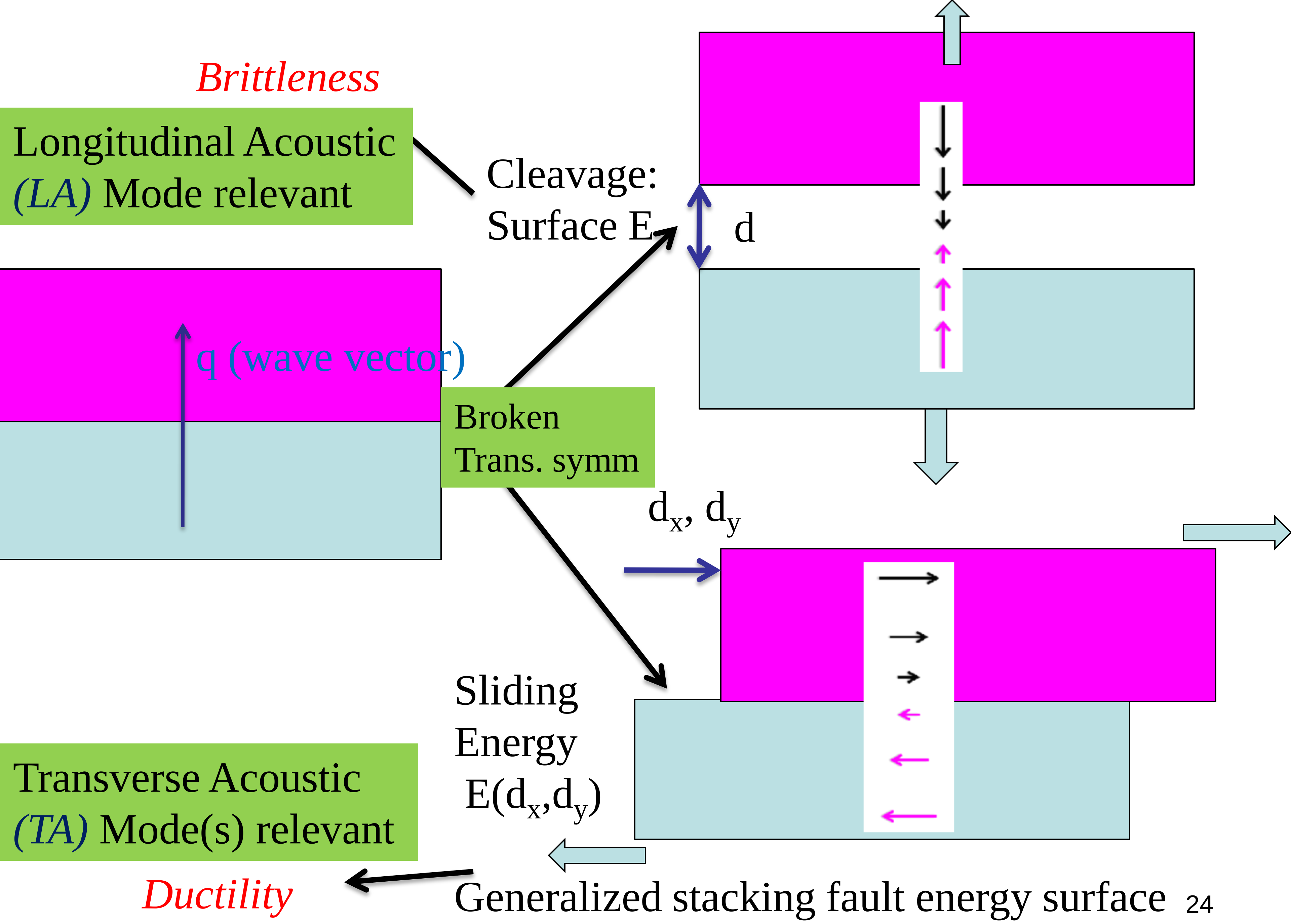
Hierarchy of hyper-elastic regions near the crack tip:
can this help in sorting out the puzzle of critical crack speed?

Symmetry and Soft Modes in the Context of Cracks or Faults: *planar defects*

Translational symmetry of the lattice:
momentum (ђq) conservation



Soft modes should have wave vector perpendicular to the plane. What about atomic displacements?

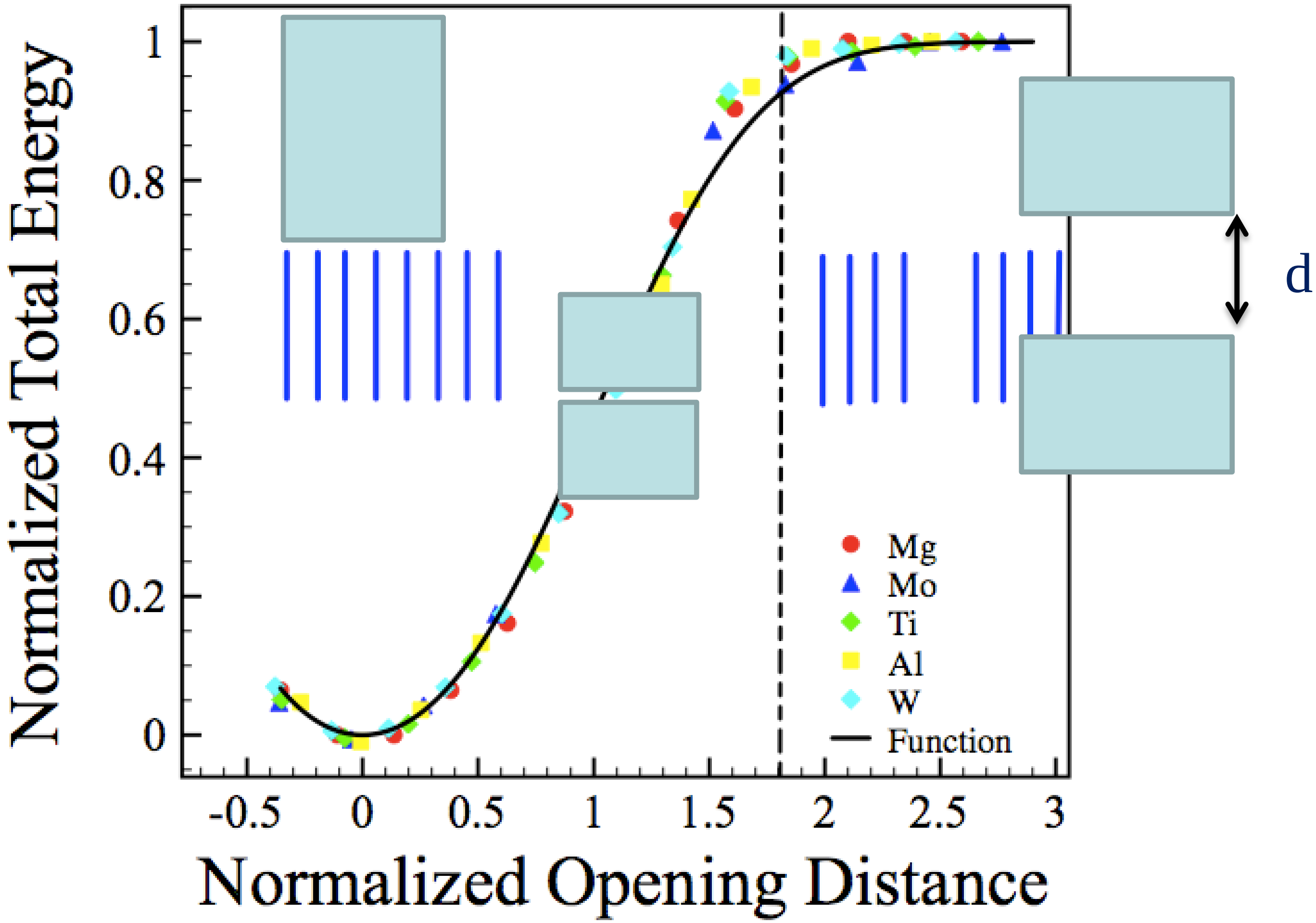

Brittleness
Longitudinal Acoustic *(LA)* Mode relevant
Cleavage: Surface E
d
q (wave vector)
Broken Trans. symm
d_x, d_y
Sliding Energy $E(d_x,d_y)$
Transverse Acoustic *(TA)* Mode(s) relevant
Ductility
Generalized stacking fault energy surface

Crack opening in metal crystals:

LA soft modes

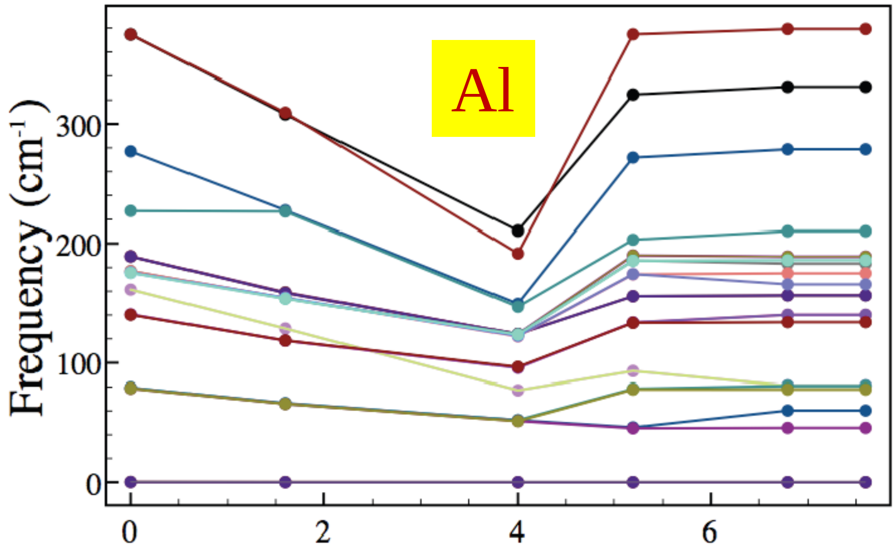
Sandeep Kumar, Nelson Dzade, U Ramamurty and U V Waghmare (2012).

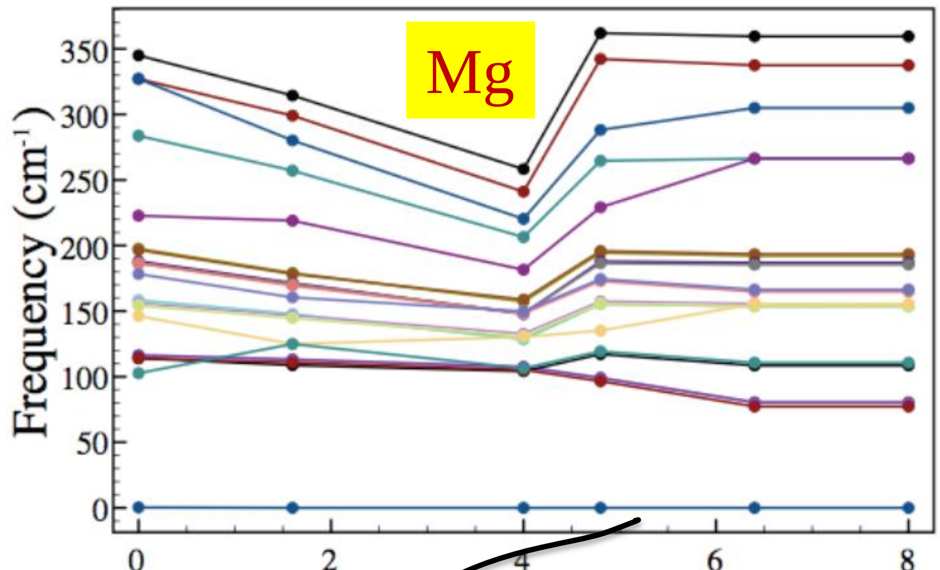
Universal Binding Energy: Cleavage

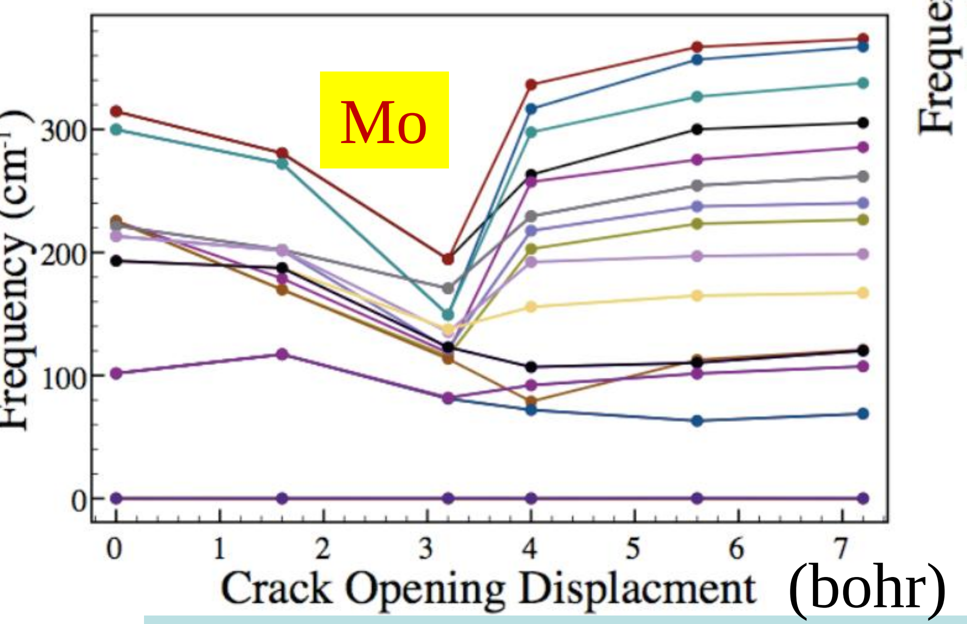


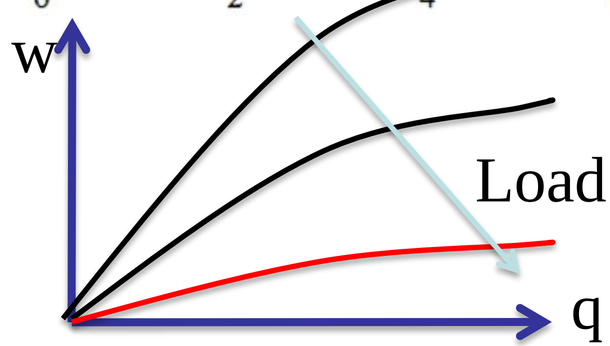
$$\varphi(\delta) = 2\gamma_s - 2\gamma_s \left(1 + \delta\sqrt{\frac{Y}{2\gamma_s \mathcal{L}}}\right) e^{-\delta\sqrt{\frac{Y}{2\gamma_s \mathcal{L}}} - \left(\lambda\delta\sqrt{\frac{Y}{2\gamma_s \mathcal{L}}}\right)^3}$$

Significant softening of LA mode just before the crack opens up



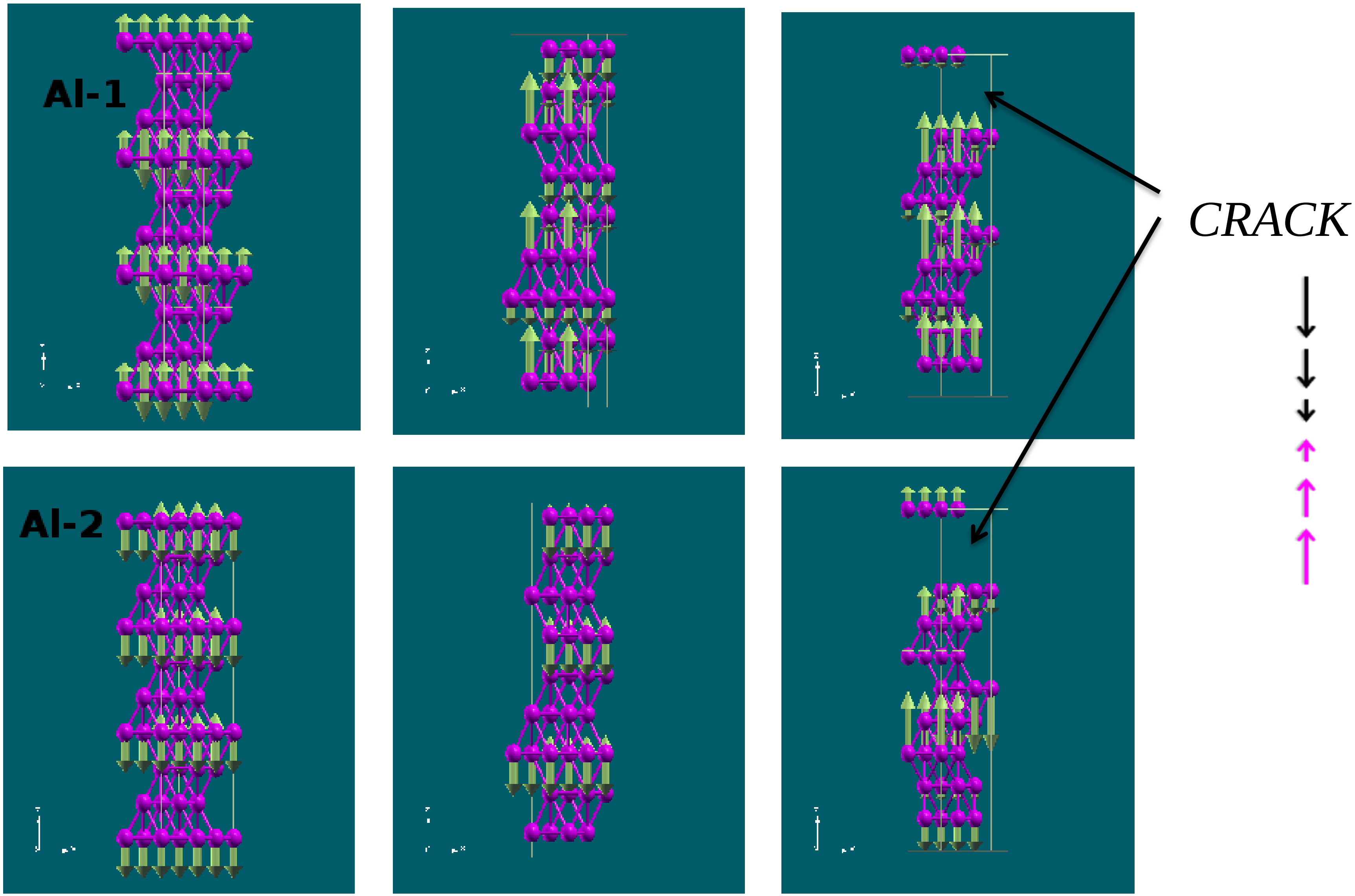






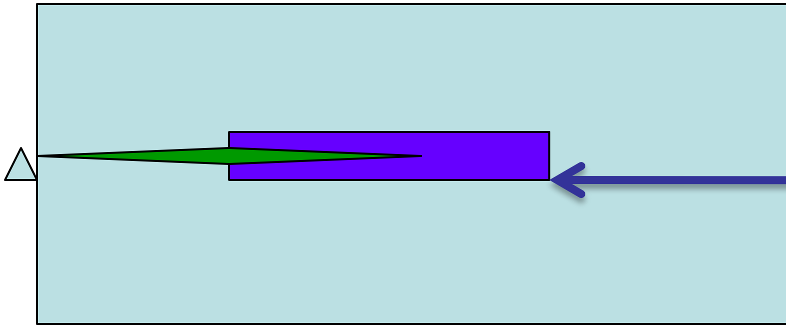
Lowering of uniaxial elastic constant: *Hyperelasticity*

First-principles Evidence for Soft modes: Longitudinal Acoustic



Prediction: slowing down of sound perpendicular to crack!

First-principles based Elastodynamic Model Analysis

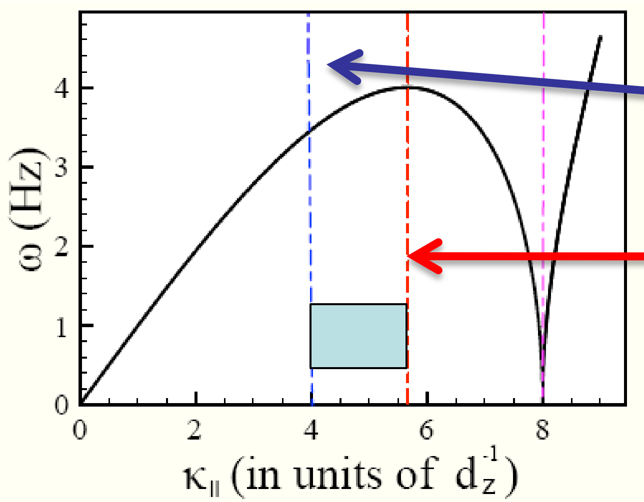


Hyperelastic zone d_z

Lower **elastic modulus**

$$\frac{E^H}{E^0} = 0.21\text{-}0.25$$

For a wave localized around the crack:



Size of Hyperelastic zone: d_z~50 nm

Localization of a wave within d_z

Stable solution

Wave velocity is lower

Yoffe analysis

Critical crack speed
for dynamical instability

$$\mathcal{V}_C = \begin{cases} 0.39\ \mathcal{V}_R & \text{for } \nu = 0 \\ 0.35\ \mathcal{V}_R & \text{for } \nu = 0.5 \end{cases}$$

(Expt:
0.33-0.40 v_R)

Summary (Crack Propagation)

•Argued **softening of LA phonons** as the crack opens up.

•Verified and estimated it from first-principles:
Hyperelasticity *emerges naturally as a consequence of broken translational symmetry.*

•Elastodynamic analysis to estimate **critical crack speeds** and explain why they are much lower than the Yoffe value.

SiC

Mechanical Stability of
semi-conducting SiC

Tiju Thomas, D Pandey, U Waghmare, Phys Rev B (R) 77, 121203 (2007).

SiC: a promising technological material both as a bulk and at nano-scale

(see a review by Melinon et al, Nature Materials 6, 479 (2007)).

Bulk SiC: mechanical hardness, optical properties (large band gap), bio-compatibility, high-temperature stability, chemical inertness, shock resistant, high refractive index

1950: Shockley predicted SiC would replace Si

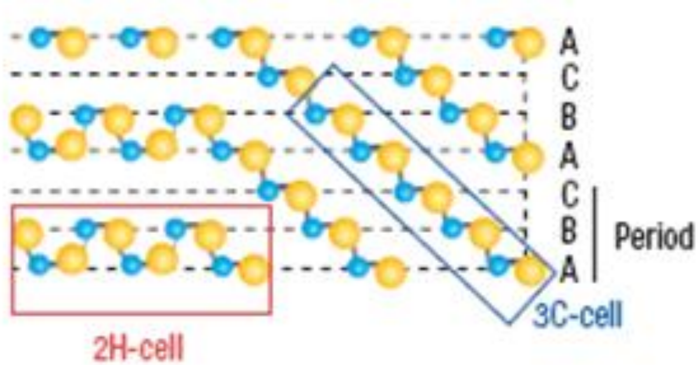
Many applications from power electronics to catalysis

Nano-form of SiC: Atomic engineering of nano-structures to tune properties

Clusters,

Nano-wires, nano-tubes,

Heterostructures

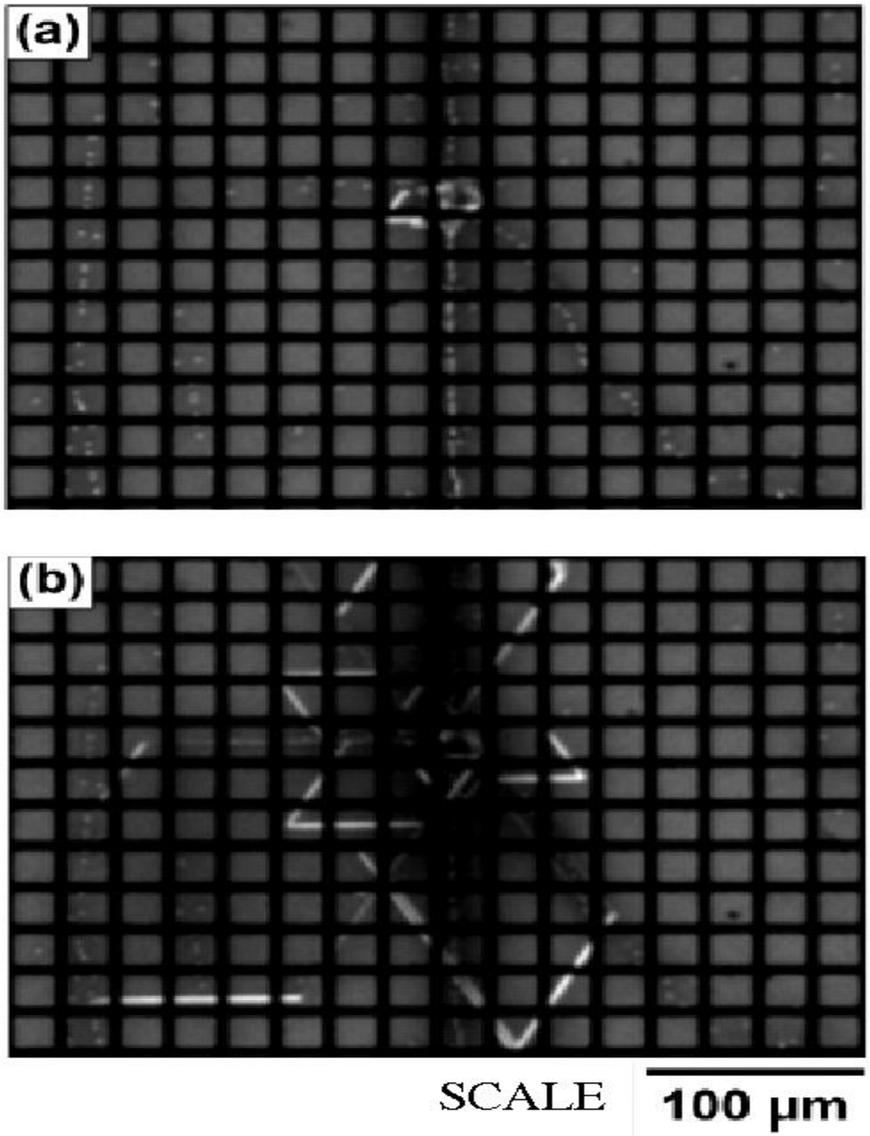


Ultra-high quality SiC crystals: Nakamura et al, Nature 430, 1010 (2004)

News Report on BBC (25/8/04): Doors Open for Si Replacement

Material Failure Problem: Stacking fault expansion in SiC

Ha, Skowronski, Sumakeris, Paisley and Das, Phy. Rev. Lett. 92, 175504 (2004)



OEM showing development of rhombic stacking faults in the basal plane of 4H-SiC when used in p-i-n diode

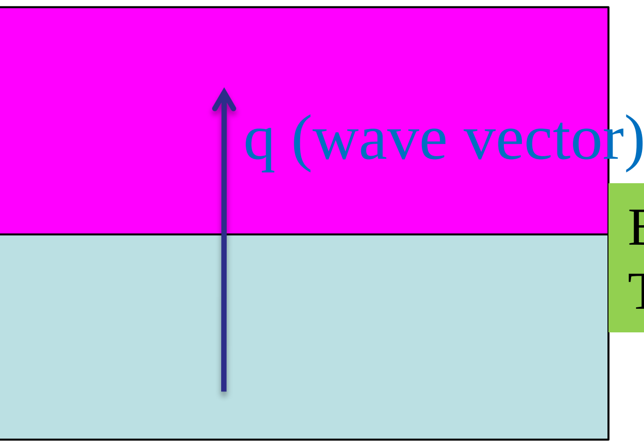
(a) Virgin diode

(b) Diode after 5 minutes of biasing at 50 A/cm^2

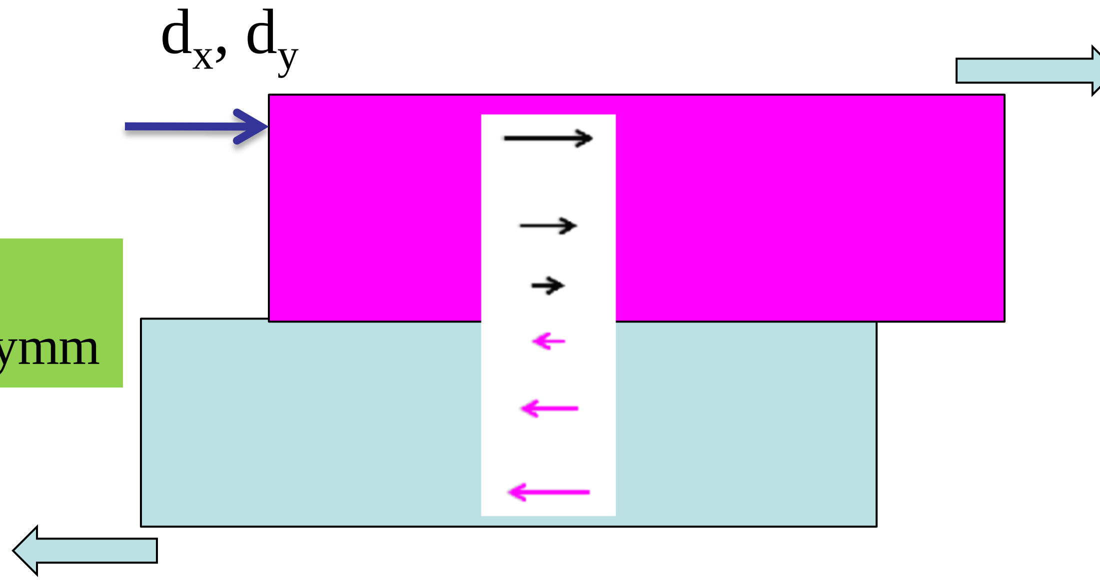
Degraded performance: ΔV changes by up to 1 V!

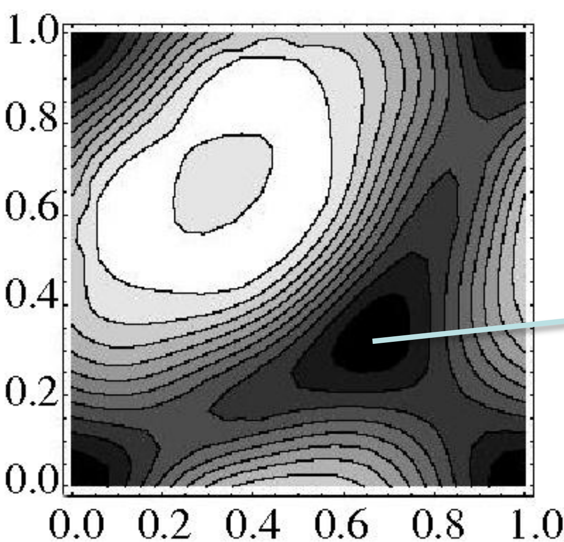
Fundamental Problem
Stacking Fault: Part of the crystal slips with respect to the other half, creating *misregistry* between adjacent crystal planes

Symmetry and Soft Modes Relevant to Stacking Faults



Broken
Trans. symm



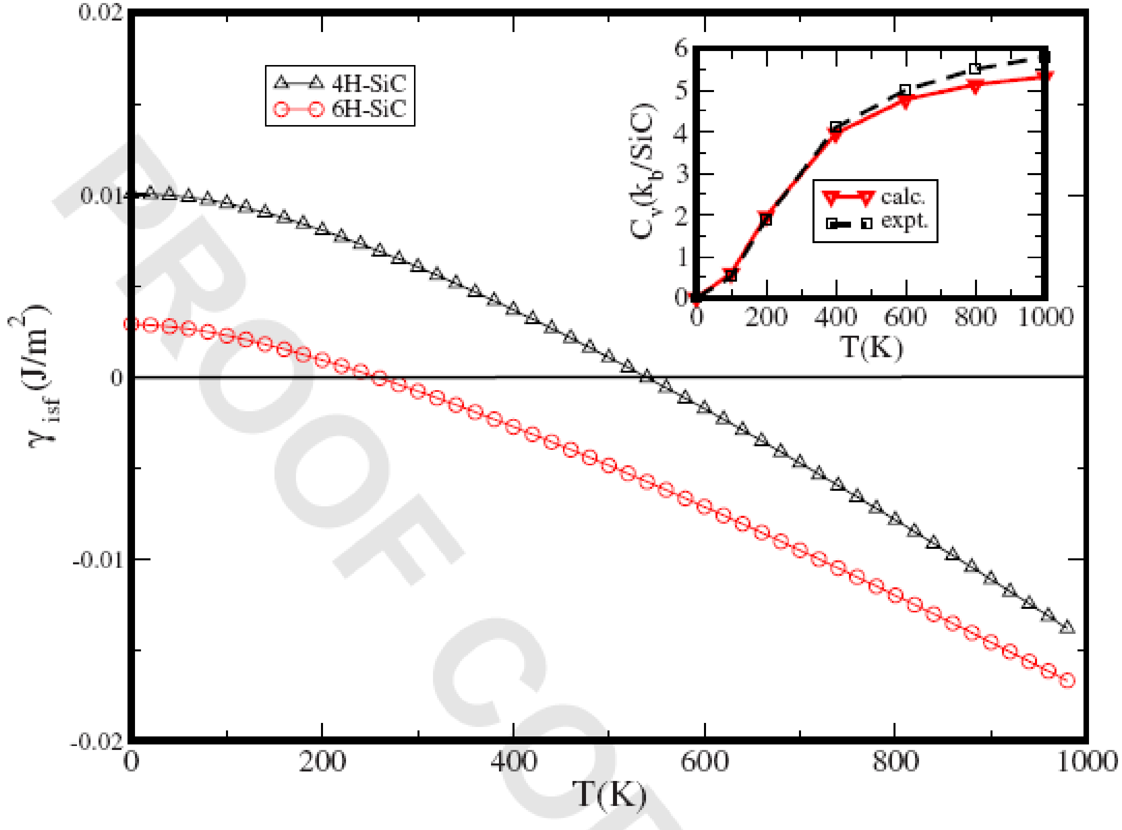


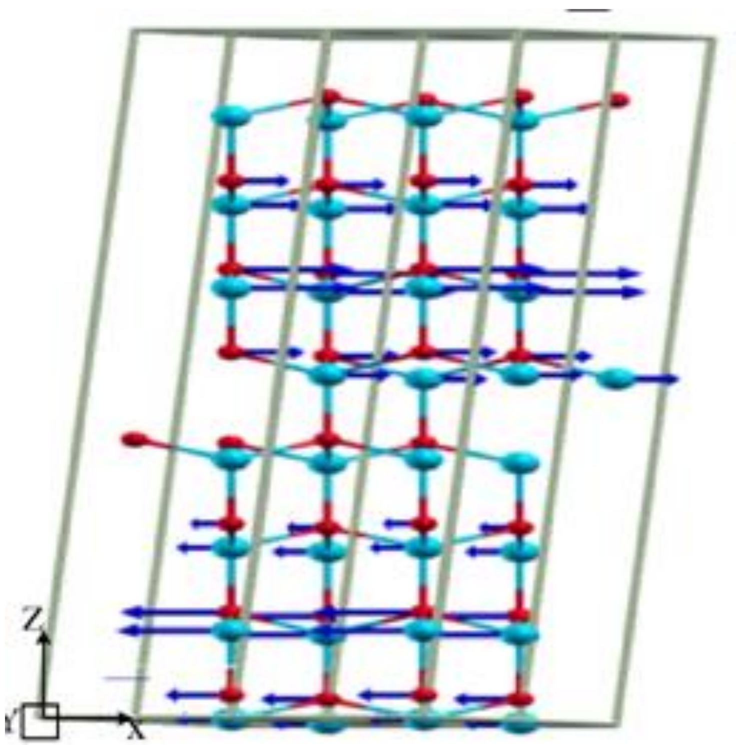
Sliding Energy $E(d_x,d_y)$
Generalized stacking fault energy surface

Stacking Fault

We expect Soft modes:
Transverse Acoustic Mode(s)

Stacking fault energy of 4H-SiC





Soft mode

(1) Vibrational contribution to free energy is dominant

(2) $\gamma_s(T) < 0$ for T > 260 K

► stabilizes the faulted structure at elevated temperatures:
observed stacking fault expansion.

Origin of this: Soft modes!

Prediction to be verified experimentally: *Shear waves will be slown down.*

Summary

First-principles Simulations *(an Interdisciplinary tool):*
from molecules to design of alloys
Understand mechanisms, complement experiments

Symmetries and Soft Modes in Materials (e.g. TO phonon in FE):
Thermodynamic Stability and *Sensitivity* to External Fields

Engineering Problems: Cracks and Stacking Faults
soft LA (dilational) and TA (shear) phonon modes:
Hyperelasticity emerges naturally from broken translational symmetry

Future: Larger systems Correlated materials

1. Expand the range of applicability of first-principles techniques
2. Combination of first-principles modeling and knowledge-based algorithms: *design novel materials*