Hands-On DFT and Beyond Workshop
September 3 2019, Barcelona

From Harmonic Vibrations to Strongly Anharmonic Heat Transport:

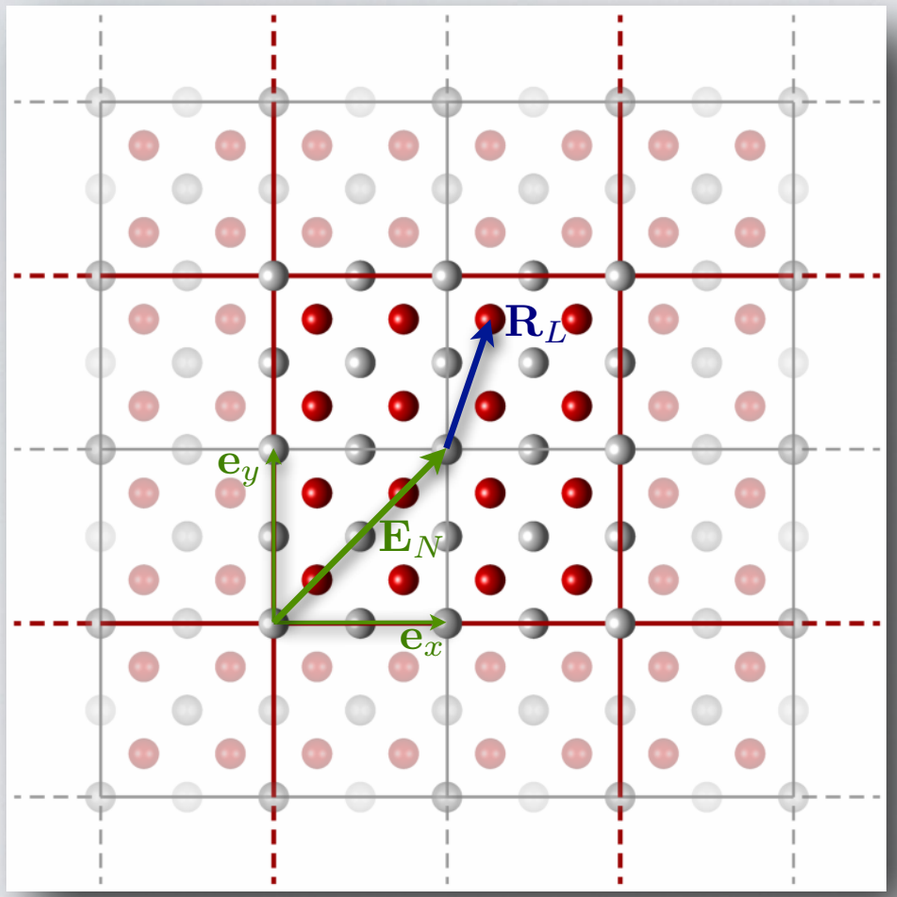
Ab initio Nuclear Dynamics in Solids

Christian Carbogno

FRITZ-HABER-INSTITUT
MAX-PLANCK-GESELLSCHAFT

CRYSTALLINE SOLIDS

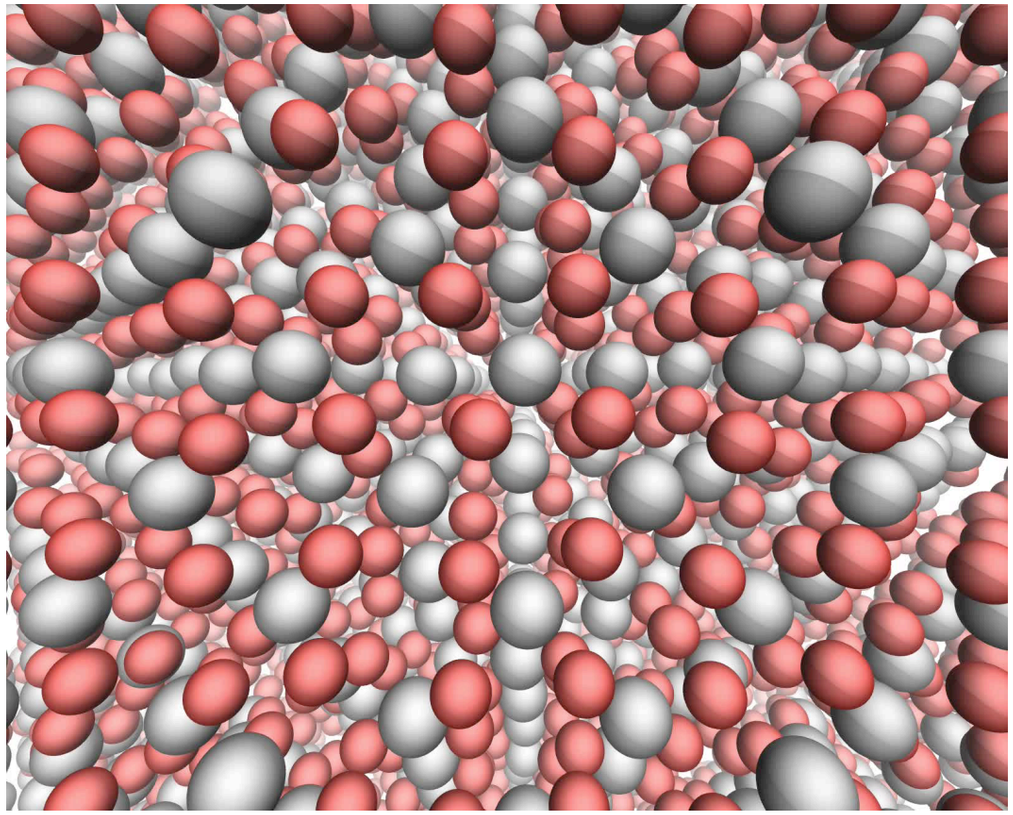
Idealized Crystal Structure



Infinite grid of
immobile atoms
with **perfect periodicity**

cf. Sergey Levchenko, Wednesday August 28

Real Materials



Everything moves!

cf. Luca Ghiringhelli, ***tomorrow****!*

Perfect periodicity disturbed!

FAILURES OF THE STATIC LATTICE MODEL

N. W Ashcroft and N. D. Mermin, "*Solid State Physics*" (1976).

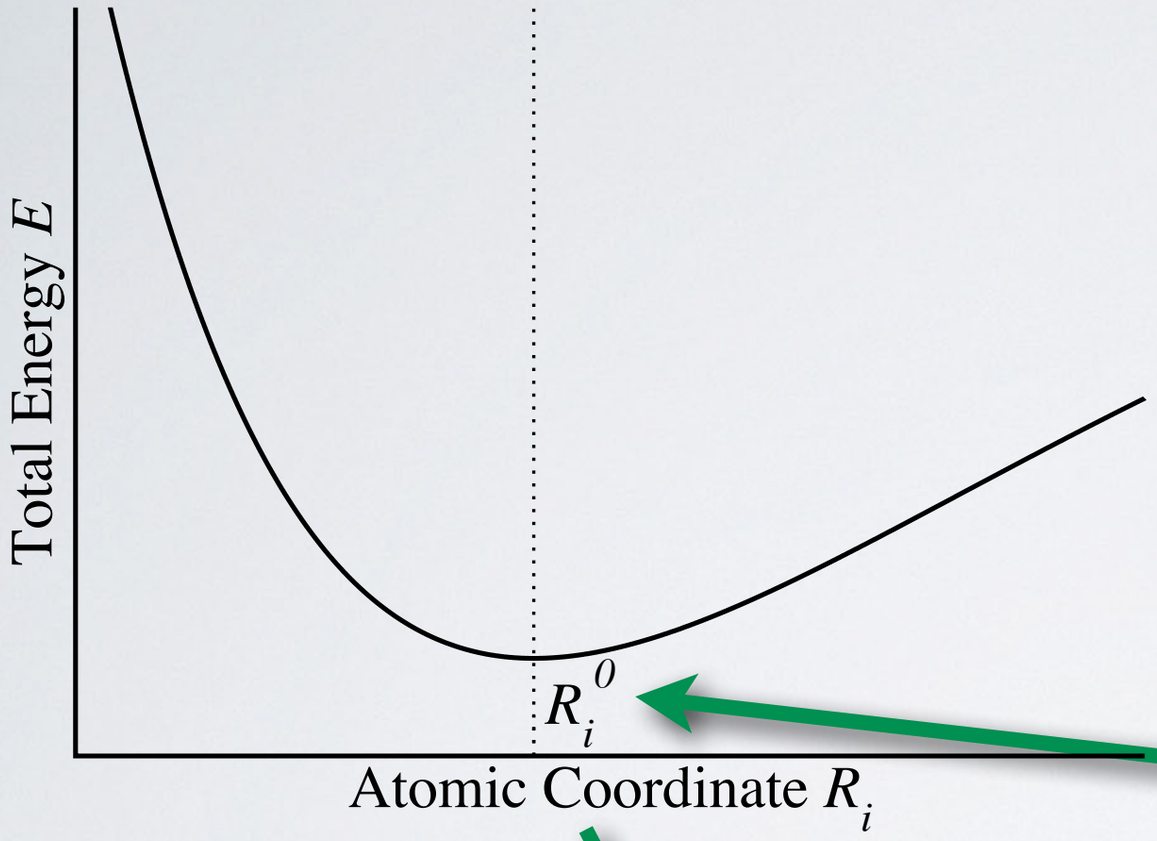
- **Inaccuracies** in the **equilibrium** properties at **0K**:
  Lattice Constants, Cohesive Energies, Elastic Constants,...

- **Failure** to describe **thermodynamic equilibrium properties**:
  Specific Heat, Thermal Lattice Expansion, Phase Transformations, ...

- **Failure** to describe **thermodynamic non-equilibrium properties:**
  - ✦ **Charge Transport:**
    Electrical AC/DC Conductivity, Superconductivity,...
  - ✦ **Heat Transport:**
    Thermal Conductivity, Transmission of Sound,...
  - ✦ **Coupling of Charge & Heat Transport:**
    Seebeck and Peltier Effect,...
  - ✦ **Interaction with Radiation:**
    X-Ray, Infrared, Neutron, ...

I. THE HARMONIC APPROXIMATION

THE HARMONIC APPROXIMATION



The total energy ***E*** is a
3N-dimensional surface:

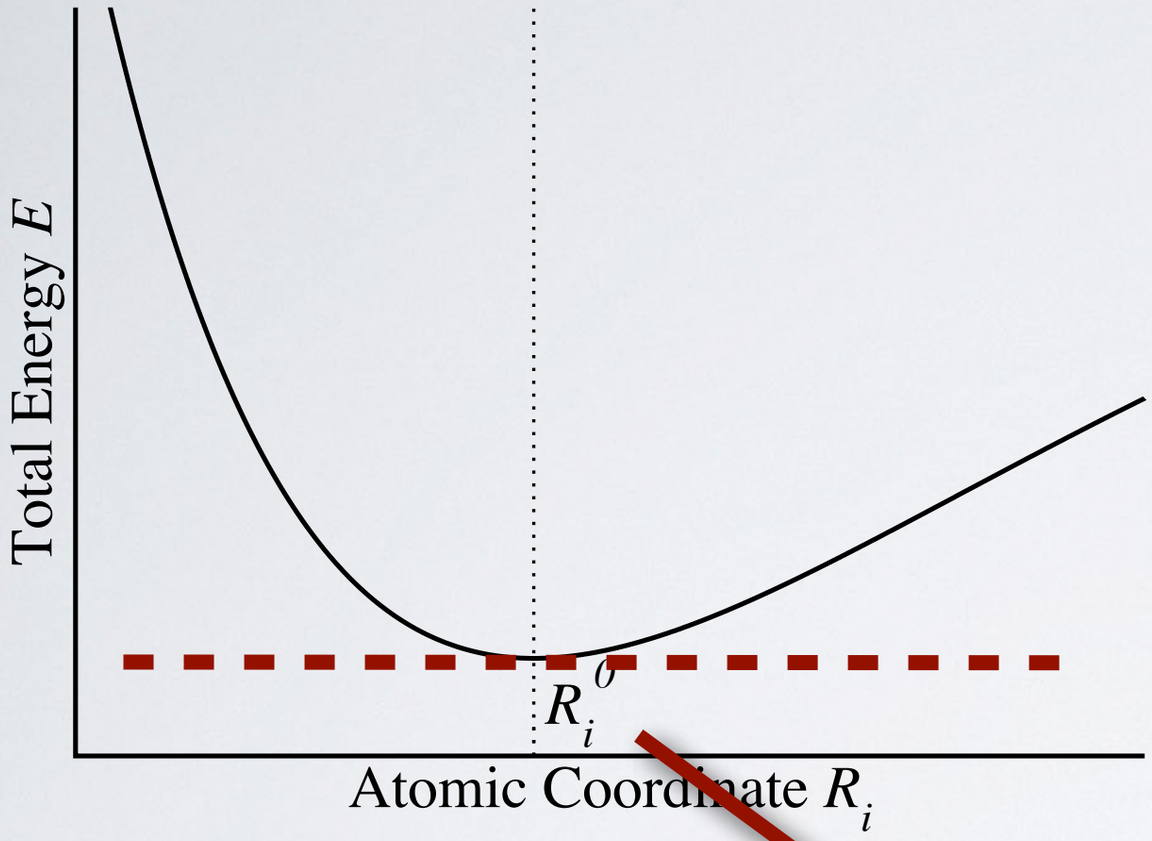
$$E = V\left(\mathbf{R}_1, \mathbf{R}_2, \cdots, \mathbf{R}_N\right)$$

Approximate by Taylor Expansion around the Static Equilibrium R_i^0

$$E\left(\{\mathbf{R}_0 + \Delta\mathbf{R}\}\right) \approx E\left(\{\mathbf{R}_0\}\right) + \cdots$$

Static Equilibrium Energy

THE HARMONIC APPROXIMATION



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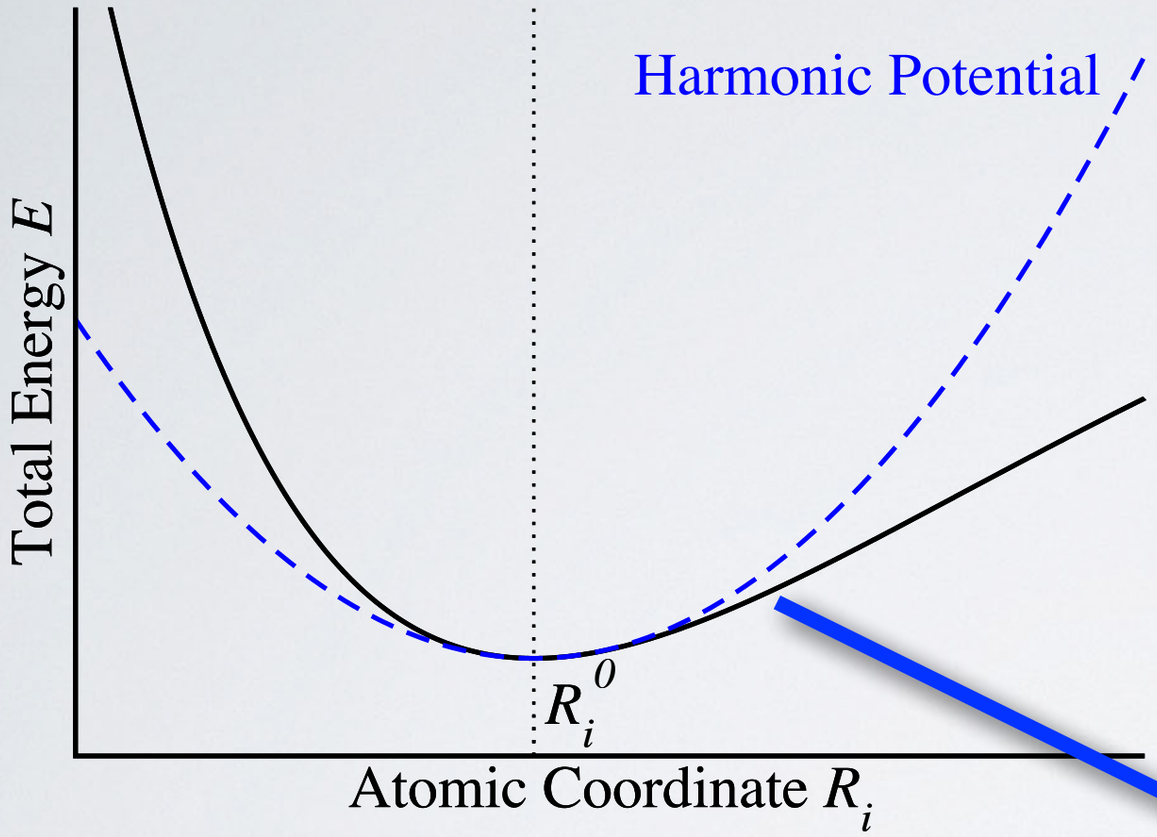
Forces vanish at $\mathbf{R_0}$

THE HARMONIC APPROXIMATION



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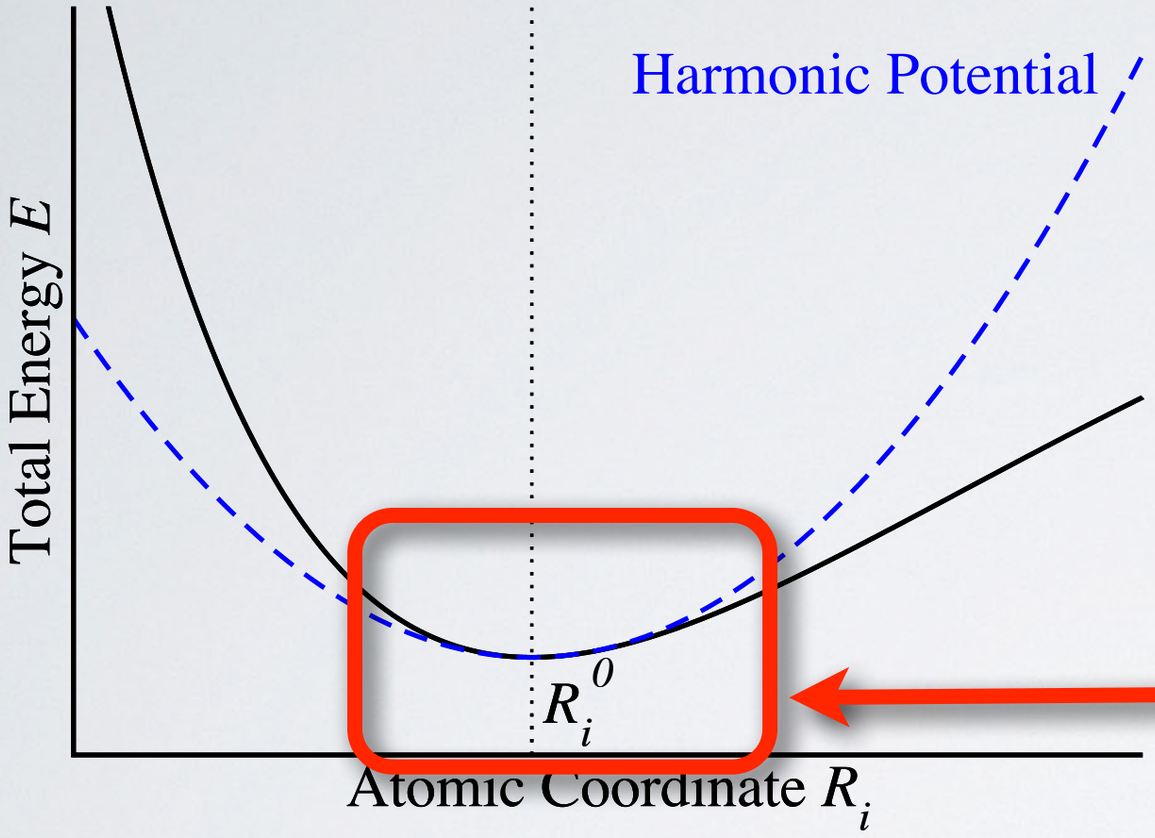
Hessian Φ_{ij}

THE HARMONIC APPROXIMATION



The total energy ***E*** is a
3N-dimensional surface:

$$E = V\left(\mathbf{R}_1, \mathbf{R}_2, \cdots, \mathbf{R}_N\right)$$

WARNING:

Harmonic Approximation is only valid for small displacements from $\boldsymbol{R^0}$!

$$E\left(\{\mathbf{R}_0 + \Delta\mathbf{R}\}\right) \approx E\left(\{\mathbf{R}_0\}\right) + \sum_i \cancel{\left.\frac{\partial E}{\partial \mathbf{R}_i}\right|_{\mathbf{R}_0} \Delta\mathbf{R}_i} + \frac{1}{2}\sum_{i,j} \left.\frac{\partial^2 E}{\partial \mathbf{R}_i \partial \mathbf{R}_j}\right|_{\mathbf{R}_0} \Delta\mathbf{R}_i \Delta\mathbf{R}_j$$

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Static Equilibrium Energy from DFT

Hessian Φ_{ij}

Determine **Hessian** aka the **Harmonic Force Constants** Φ_{ij}:

Why is this theoretically challenging?

HELLMAN-FEYNMAN THEOREM

Born-Oppenheimer Approximation:

Ground State Electrons determine the **Potential Energy**

$$U(\mathbf{R}) = \langle \Psi_{\mathbf{R}}(\mathbf{r}) | \, \mathbb{H}_{\mathbf{R}} \, | \Psi_{\mathbf{R}}(\mathbf{r}) \rangle$$

Forces:

$$\mathbf{F}_i = -\frac{\partial U(\mathbf{R})}{\partial \mathbf{R}_i}$$

$$= -\langle \Psi_{\mathbf{R}}(\mathbf{r}) | \frac{\partial \mathbb{H}_{\mathbf{R}}}{\partial \mathbf{R}_i} | \Psi_{\mathbf{R}}(\mathbf{r}) \rangle - 2 \langle \Psi_{\mathbf{R}}(\mathbf{r}) | \mathbb{H}_{\mathbf{R}} | \partial \Psi_{\mathbf{R}}(\mathbf{r}) / \partial \mathbf{R}_i \rangle$$

Forces are an expectation value of the wave function and do *not* depend on *changes* in the *wave function* itself.

HIGHER ORDER DERIVATIVES

$$\mathbf{\Phi}_{ij} = -\frac{\partial \mathbf{F}_i}{\partial \mathbf{R}_j}$$

Hessian:

$$= \langle \Psi_{\mathbf{R}}(\mathbf{r}) | \frac{\partial^2 \mathbb{H}_{\mathbf{R}}}{\partial \mathbf{R}_i \partial \mathbf{R}_j} | \Psi_{\mathbf{R}}(\mathbf{r}) \rangle - 2 \langle \Psi_{\mathbf{R}}(\mathbf{r}) | \frac{\partial \mathbb{H}_{\mathbf{R}}}{\partial \mathbf{R}_i} | \partial \Psi_{\mathbf{R}}(\mathbf{r}) / \partial \mathbf{R}_j \rangle$$

Hessian **depends** explicitly on the **response** of the wave function to a **nuclear displacement**.

⇒ *Adiabatic Electron-Phonon Coupling*

2*n*+1 Theorem:

$(2n+1)^{\text{th}}$ derivative of the **energy** requires

the n^{th} derivative of the **wave function / electron density**.

X. Gonze and J.-P. Vigneron, *Phys. Rev. B* **39, 13120** (1989).

THE HARMONIC APPROXIMATION

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Static Equilibrium Energy from DFT

Hessian Φ_{ij}

Determine **Hessian** aka the **Harmonic Force Constants** Φ_{ij}:

- from **Density-Functional Perturbation Theory**
  S. Baroni, P. Giannozzi, and A. Testa, *Phys. Rev. Lett.* **58**, 1861 (1987) &
  S. Baroni, *et al., Rev. Mod. Phys.* **73**, 515 (2001).
- from **Finite Differences**
  K. Kunc, and R. M. Martin, *Phys. Rev. Lett.* **48**, 406 (1982) &
  K. Parlinski, Z. Q. Li, and Y. Kawazoe, Phys. Rev. Lett. 78, 4063 (1997).

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Static Equilibrium Energy from DFT

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Determine **Hessian** aka the **Harmonic Force Constants** Φ_{ij}:

FHI-vibes & phonopy

A. Togo, F. Oba, and I. Tanaka, *Phys. Rev. B* **78**, 134106 (2008).

- from **Finite Differences**

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THE FINITE DIFFERENCE APPROACH

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Finite differences using **normalized displacements *d*:**

$$\Phi_{ij} = \left.\frac{\partial^2 E}{\partial \mathbf{R}_i \partial \mathbf{R}_j}\right|_{\mathbf{R}^0} = -\left.\frac{\partial}{\partial \mathbf{R}_i}\mathbf{F}_j\right|_{\mathbf{R}^0} \approx -\frac{\mathbf{F}_j(\mathbf{R}_i^0 + \varepsilon\,\mathbf{d}_i)}{\varepsilon}$$

Example: Diamond Si (2 atoms in the basis):

$$\begin{pmatrix}
\Phi_{11}^{xx} & \Phi_{11}^{xy} & \Phi_{11}^{xz} & \Phi_{12}^{xx} & \Phi_{12}^{xy} & \Phi_{12}^{xz} \\
\Phi_{11}^{yx} & \Phi_{11}^{yy} & \Phi_{11}^{yz} & \Phi_{12}^{yx} & \Phi_{12}^{yy} & \Phi_{12}^{yz} \\
\Phi_{11}^{zx} & \Phi_{11}^{zy} & \Phi_{11}^{zz} & \Phi_{12}^{zx} & \Phi_{12}^{zy} & \Phi_{12}^{zz} \\
\Phi_{21}^{xx} & \Phi_{21}^{xy} & \Phi_{21}^{xz} & \Phi_{22}^{xx} & \Phi_{22}^{xy} & \Phi_{22}^{xz} \\
\Phi_{21}^{yx} & \Phi_{21}^{yy} & \Phi_{21}^{yz} & \Phi_{22}^{yx} & \Phi_{22}^{yy} & \Phi_{22}^{yz} \\
\Phi_{21}^{zx} & \Phi_{21}^{zy} & \Phi_{21}^{zz} & \Phi_{22}^{zx} & \Phi_{22}^{zy} & \Phi_{22}^{zz}
\end{pmatrix}$$

Hessian has **36** entries:
⇒ 6 displacements ***d*** required

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\end{pmatrix}$$

Space Group Analysis

$$\begin{pmatrix}
\Phi_{11}^{xx} & \Phi_{11}^{xy} & \Phi_{11}^{xz} & -\Phi_{11}^{xx} & \Phi_{12}^{xy} & 0 \\
0 & \Phi_{11}^{xx} & \Phi_{11}^{yz} & \Phi_{11}^{yz} & -\Phi_{11}^{xx} & 0 \\
0 & \Phi_{12}^{xy} & \Phi_{11}^{xx} & -\Phi_{11}^{xz} & -\Phi_{11}^{xy} & -\Phi_{11}^{xx} \\
-\Phi_{11}^{xx} & -\Phi_{11}^{xy} & -\Phi_{11}^{xz} & \Phi_{11}^{xx} & -\Phi_{12}^{xy} & 0 \\
0 & -\Phi_{11}^{xx} & -\Phi_{11}^{yz} & -\Phi_{11}^{yz} & \Phi_{11}^{xx} & 0 \\
0 & -\Phi_{12}^{xy} & -\Phi_{11}^{xx} & \Phi_{11}^{xz} & \Phi_{11}^{xy} & \Phi_{11}^{xx}
\end{pmatrix}$$

Hessian has **5 unique, non-zero** entries:
⇒ Only **1** displacement ***d*** required

THE HARMONIC APPROXIMATION

...in Molecules:

N ... Number of atoms

⇓

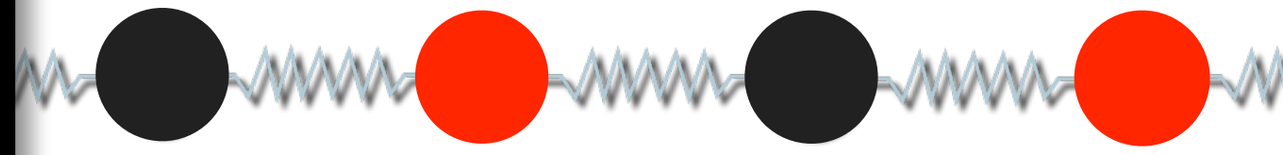
Degrees of Freedom: ***3N***

Dimension of Hessian: $9N^2$

Wednesday August 28:

⇒ *Practical Session I , Maria Dragoumi*

...in Crystalline Solids:



N ... Number of atoms

⇓

Degrees of Freedom: ***3N***

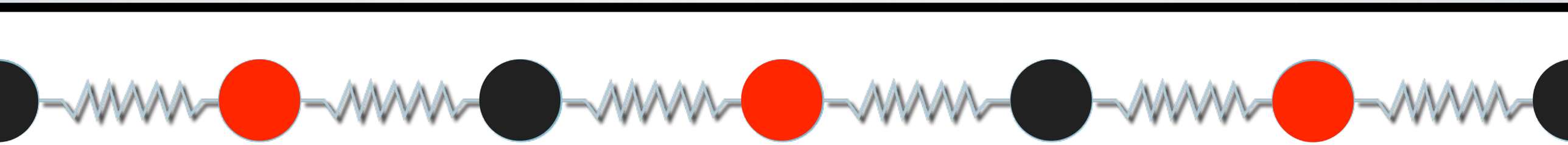
Dimension of Hessian: $9N^2$

BUT:

$N \rightarrow \infty$

PERIODIC BOUNDARY CONDITIONS

cf. Sergey Levchenko, "Periodic Structures", Wednesday August 28



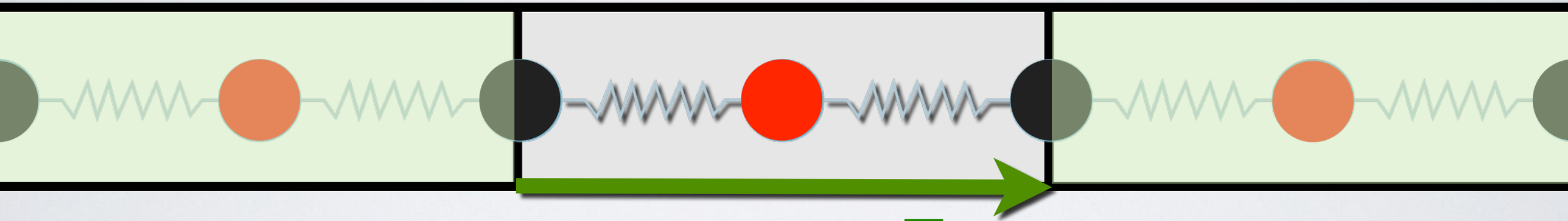
PERIODIC BOUNDARY CONDITIONS

cf. Sergey Levchenko, "Periodic Structures", Wednesday August 28

Unit Cell with N_p atoms

Periodic Images

Periodic Images



Lattice vector: $\mathbf{E}_0$

Real Space:

Hessian Φ_{ij} with $i,j \rightarrow \infty$

Fourier Transform

$$D_{i'j'}(\mathbf{q}) = \sum_j \frac{e^{i\left(\mathbf{q}\cdot\left(\mathbf{R}^0_j - \mathbf{R}^0_{j'}\right)\right)}}{\sqrt{M_{i'} M_{j'}}} \Phi_{i'j}$$

Reciprocal Space:

Dynamical Matrix $D_{i'j'}(q)$ with $i',j' \leq N_p$

VIBRATIONS IN A CRYSTAL 101

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Reciprocal Space:
Dynamical Matrix $D_{i'j'}(q)$
with $i',j' \leq N_p$

Fourier Transform can be truncated since
$\Phi_{ij} = 0$ for large $|R_j^0 - R_{j'}^0|$

Hessian Φ_{ij}
with **finite** number
of non-zero entries

Dynamical Matrix $D_{i'j'}(q)$
known for the **whole**
reciprocal space

VIBRATIONS IN A CRYSTAL 101

e.g. N. W Ashcroft and N. D. Mermin, "*Solid State Physics*" (1976)
also see Sergey Levchenko, Wednesday August 28

Dynamical matrix:

$$D_{i'j'}(\mathbf{q}) = \sum_j \frac{e^{i\left(\mathbf{q}\cdot(\mathbf{R}^0_j - \mathbf{R}^0_{j'})\right)}}{\sqrt{M_{i'}M_{j'}}}\,\Phi_{i'j}$$

Equation of Motion becomes an **Eigenvalue** Problem:

$$\mathbf{D}(\mathbf{q})\;[\nu(\mathbf{q})] = \omega^2(\mathbf{q})\;[\nu(\mathbf{q})]$$

Analytical Solution in Real Space:

Superposition of Harmonic Oscillations

$$\mathbf{R}_j(t) \;=\; \mathbf{R}^0_j + \mathfrak{Re}\left(\sum_s \frac{A_s}{\sqrt{M_i}} e^{i\left(\mathbf{q}\cdot(\mathbf{R}^0_j - \mathbf{R}^0_{j'}) - \omega_s(\mathbf{q})t\right)} \cdot [\nu_s(\mathbf{q})]_{j'}\right)$$

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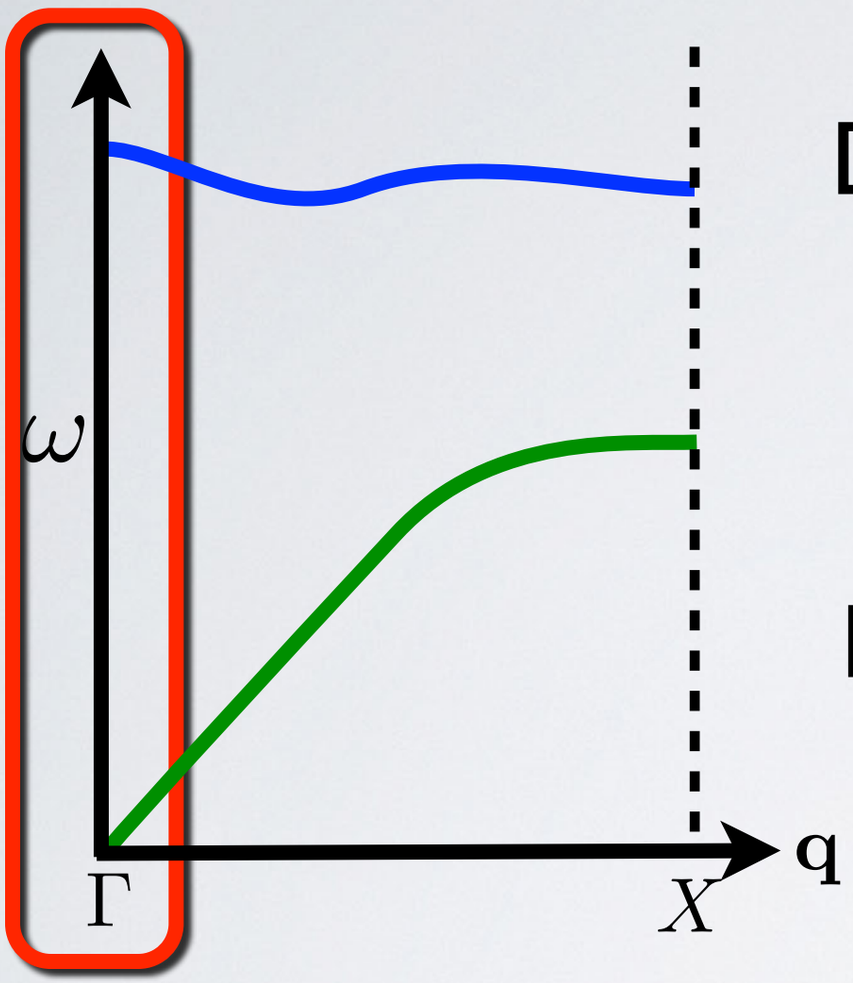

Dynamical matrix:

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= I

Eigenvalue problem:

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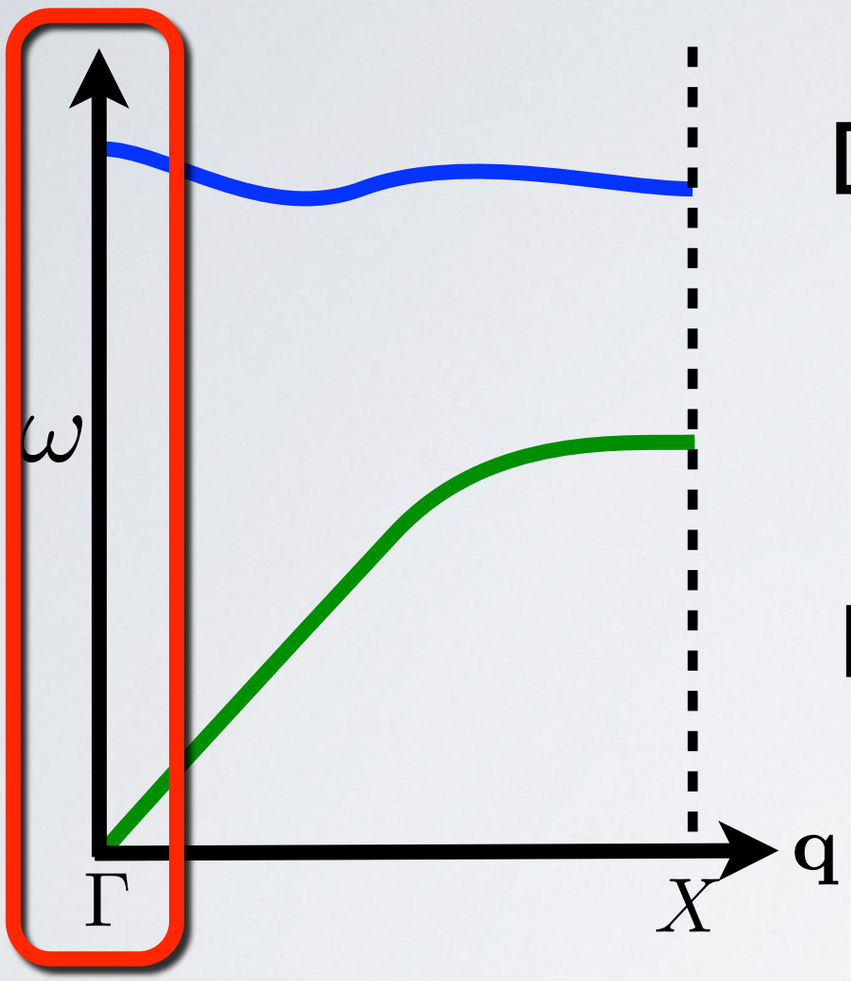

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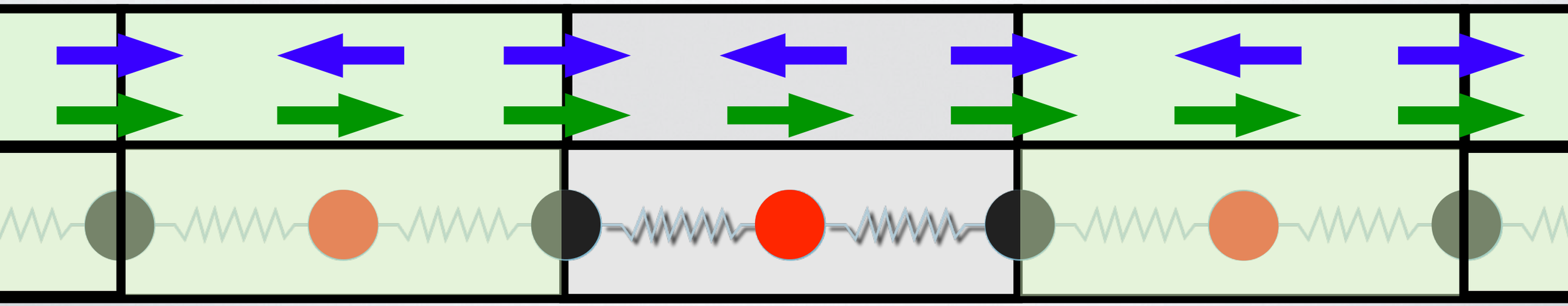

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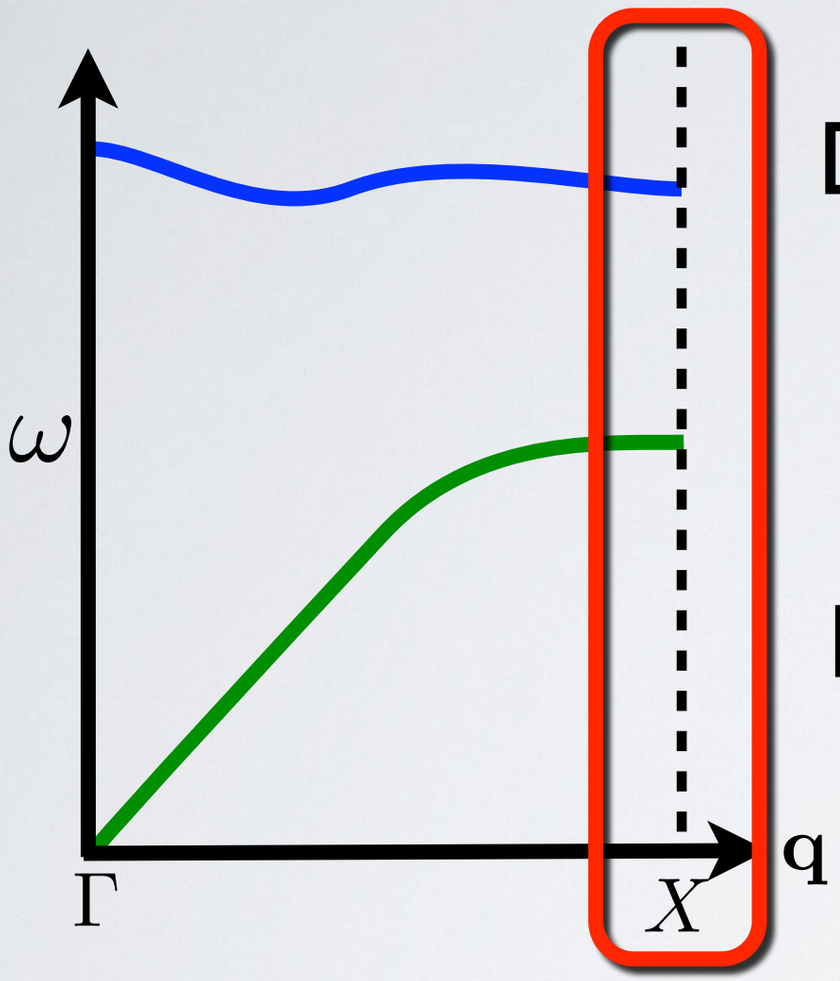

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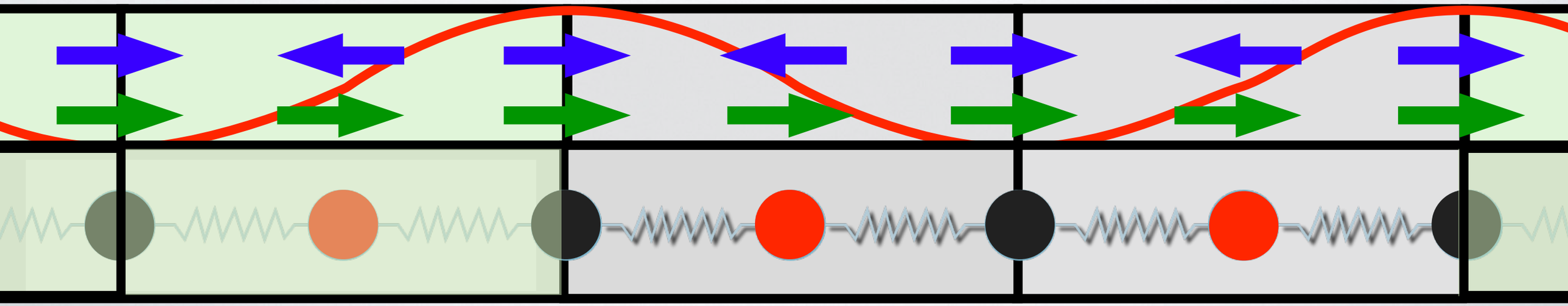

VIBRATIONS IN A CRYSTAL 101

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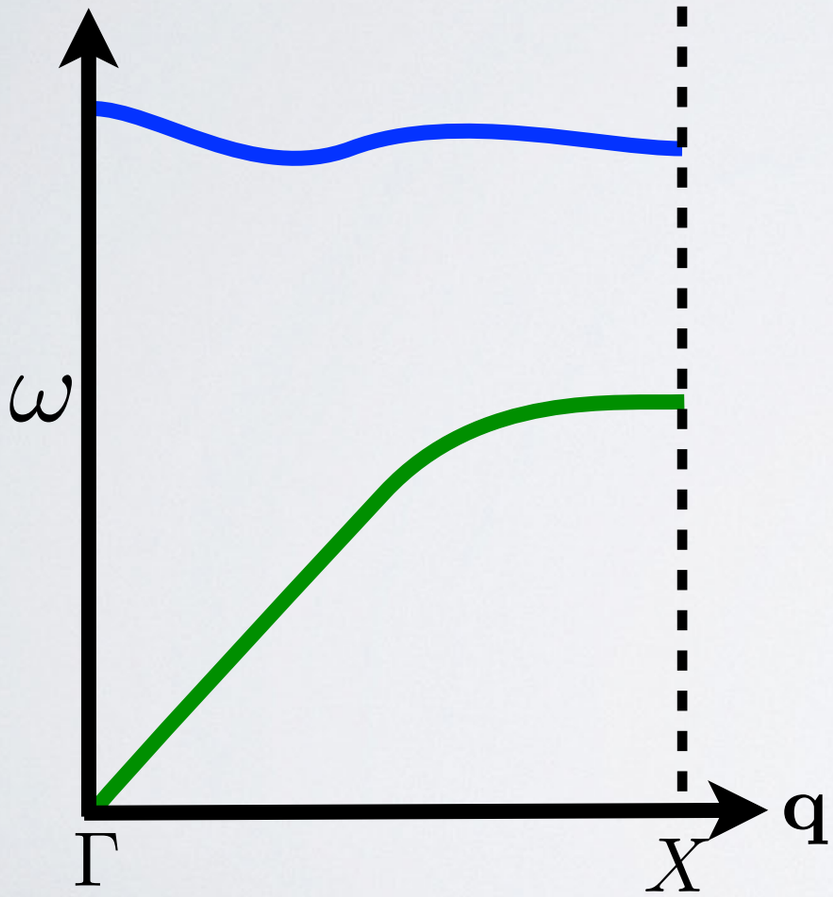
For N_p atoms in the unit cell there are:



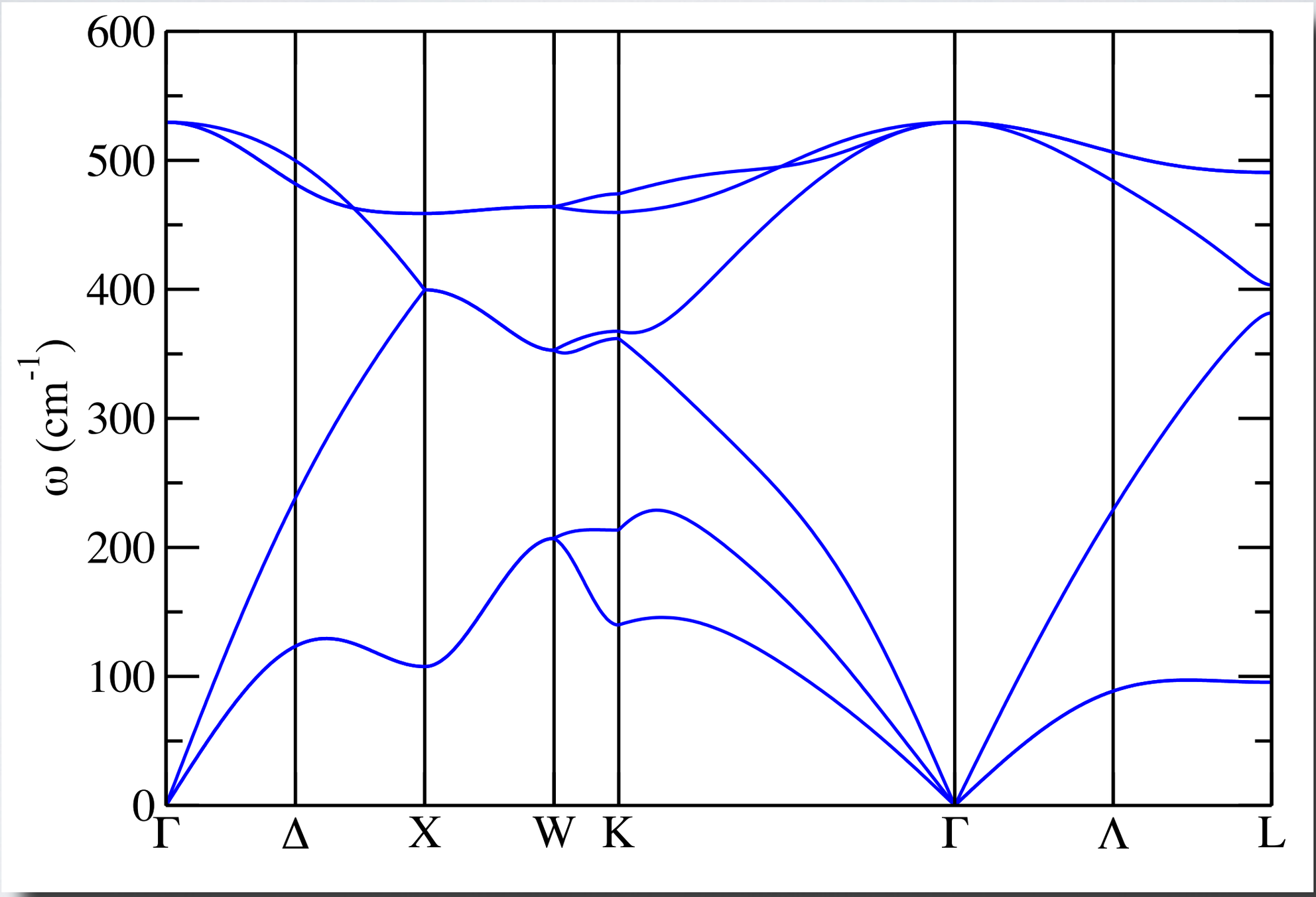
3 Acoustic modes:

- Atoms in unit cell in-phase
- Acoustic modes vanish at $\mathbf{\Gamma}$
- Strong (typically linear) dispersion close to $\mathbf{\Gamma}$

$(3N_p - 3)$ Optical modes:

- Atoms in unit cell out-of-phase
- $\omega > 0$ at $\mathbf{\Gamma}$ (and everywhere else)
- Weak dispersion

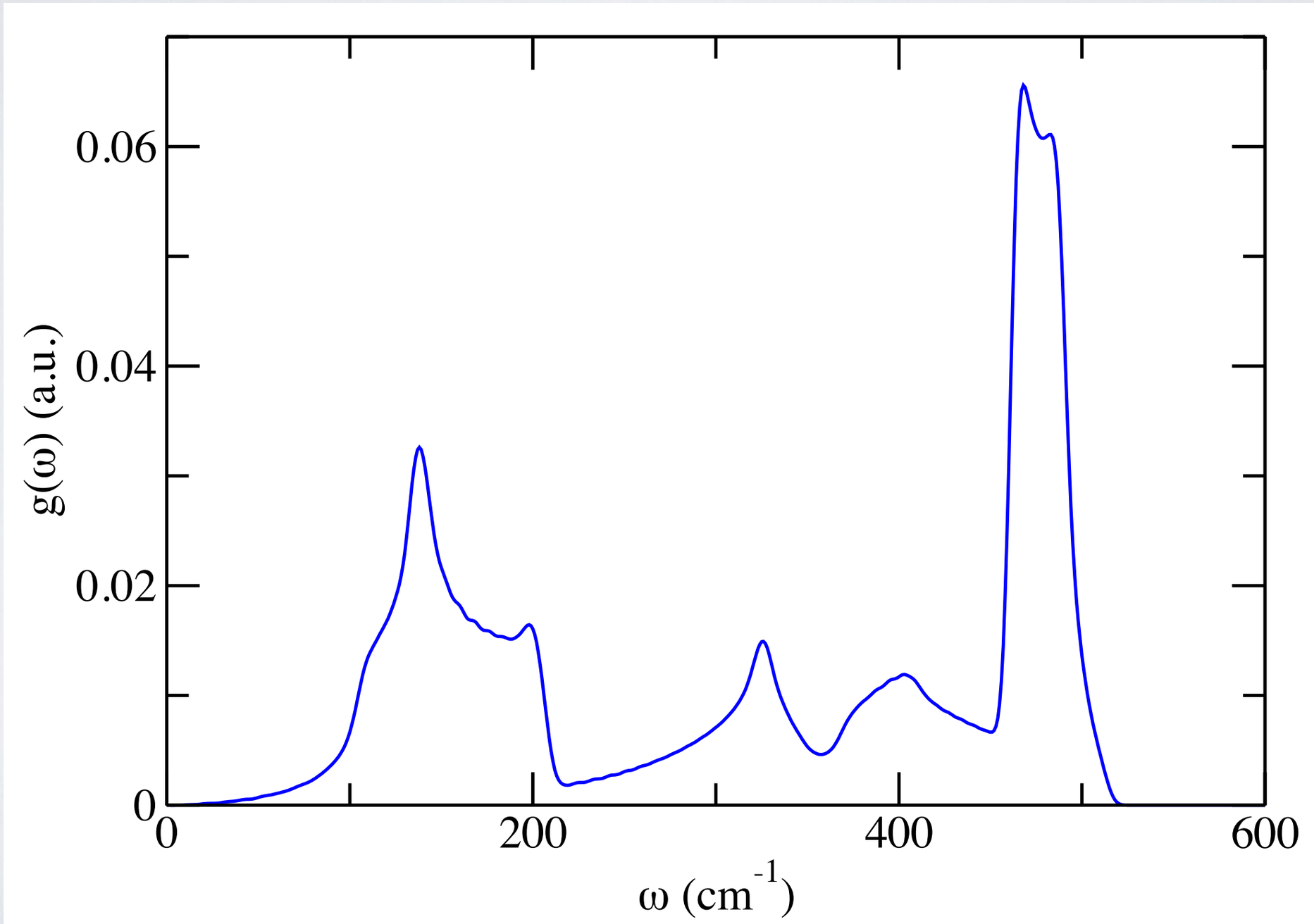
VIBRATIONAL BAND STRUCTURE



Silicon, diamond structure

VIBRATIONAL DENSITY OF STATES

$$g(\omega) = \sum_s \int \frac{d\mathbf{q}}{(2\pi)^3} \delta(\omega - \omega(\mathbf{q})) = \sum_s \int_{\omega(\mathbf{q})=\omega} \frac{dS}{(2\pi)^3} \frac{1}{|\nabla\omega(\mathbf{q})|}$$



ATTENTION:
QUANTUM-NUCLEAR EFFECTS

Classical Limit: Equipartition Theorem

Each mode carries $\langle E_s(\mathbf{q}, T)\rangle = k_B T$

Quantum-mechanical Solution: Bose-Einstein

Each mode carries

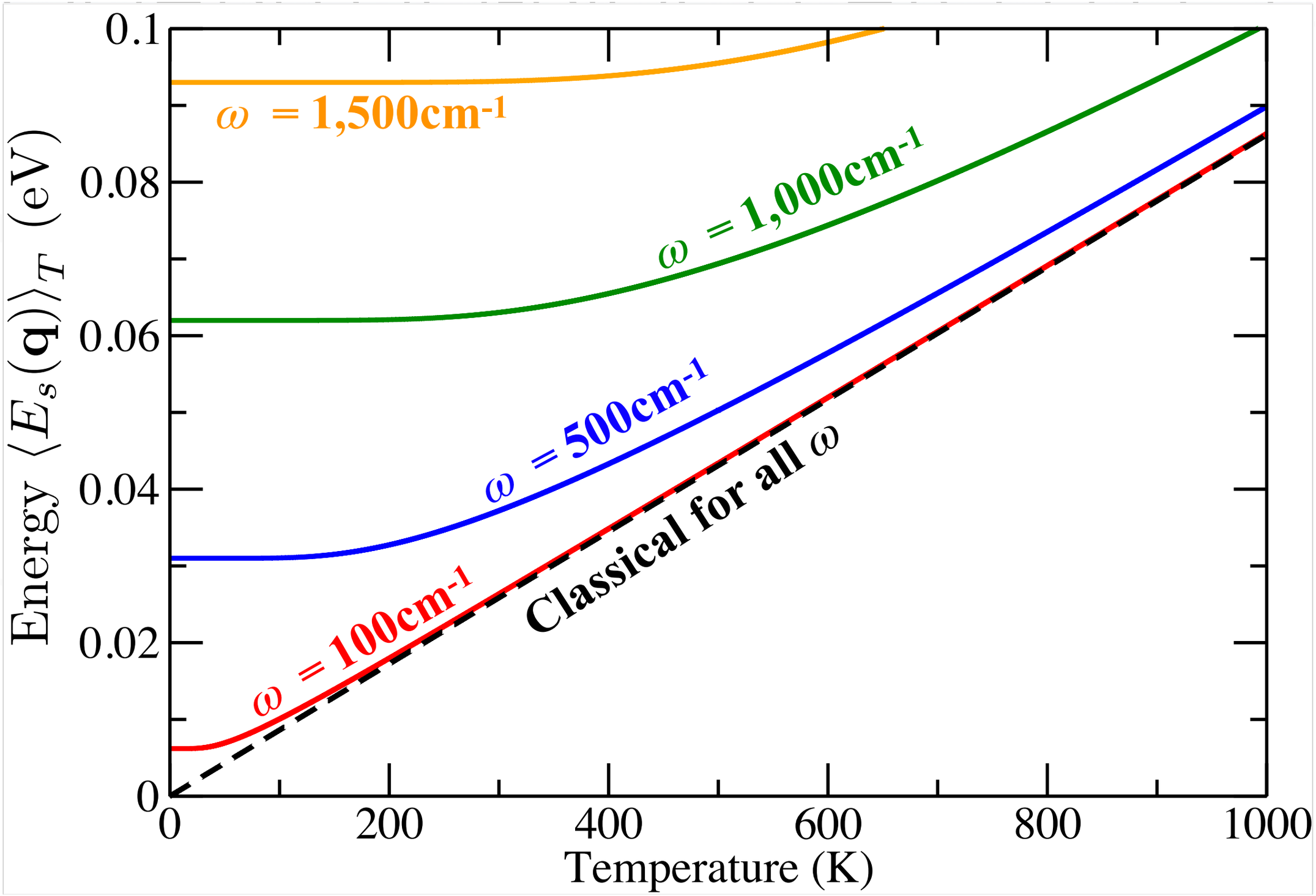
$$\langle E_s(\mathbf{q}, T)\rangle = \hbar\omega_s(\mathbf{q}) \left(n_{\mathrm{BE}}(\omega_s(\mathbf{q}), T)) + \frac{1}{2} \right)$$

ATTENTION:

QUANTUM NUCLEAR EFFECTS

Cla

Qu



THE HARMONIC FREE ENERGY

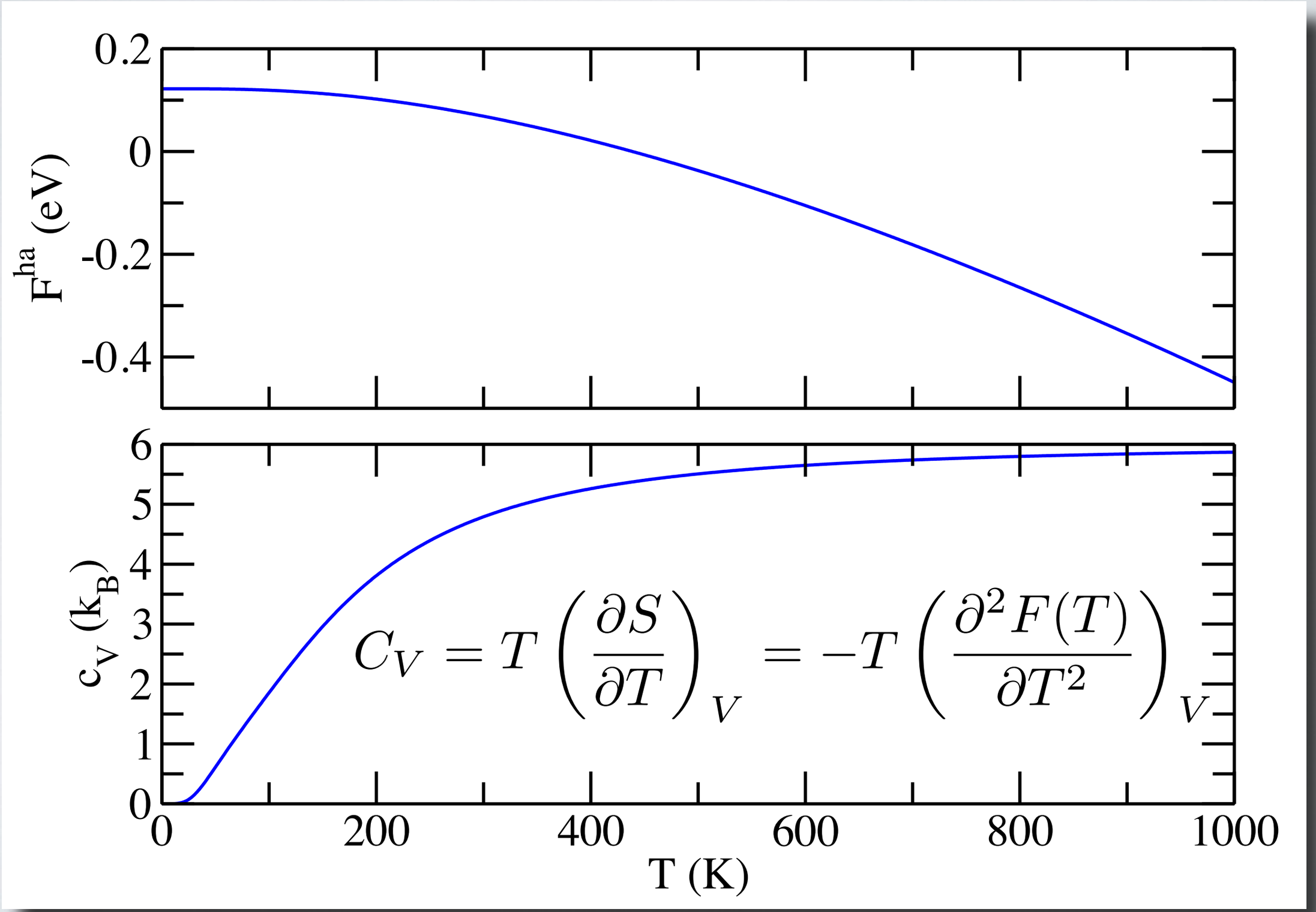
$$
\begin{aligned}
F^{ha}(T) &= E(\{\mathbf{R}_0\}) \\
&+ \int d\omega \; g(\omega) \frac{\hbar\omega}{2} \\
&+ \int d\omega \; g(\omega) \; k_B T \ln\left(1 - e^{\left(-\frac{\hbar\omega}{k_B T}\right)}\right)
\end{aligned}
$$

Static Equilibrium Energy

Zero-point vibration

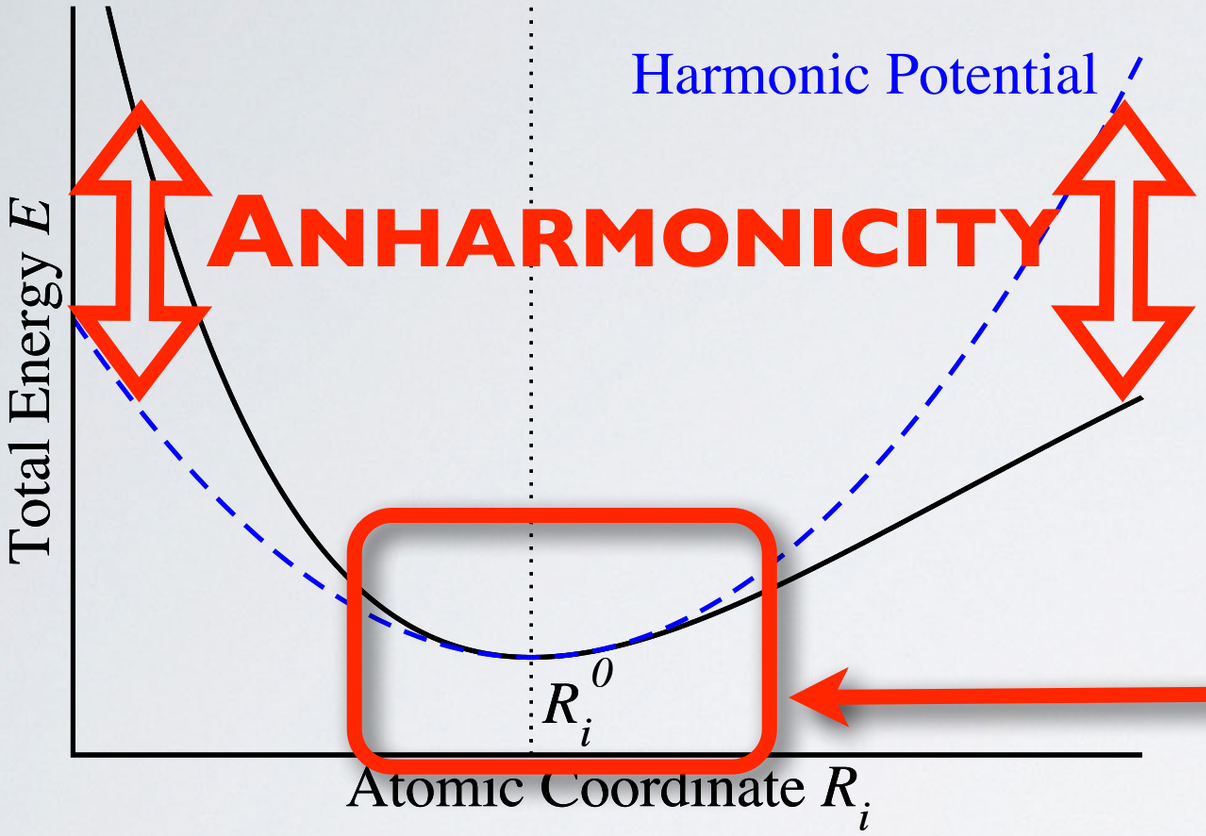
Thermally induced vibrations

FREE ENERGY AND HEAT CAPACITY



II. ANHARMONICITY

THE HARMONIC APPROXIMATION

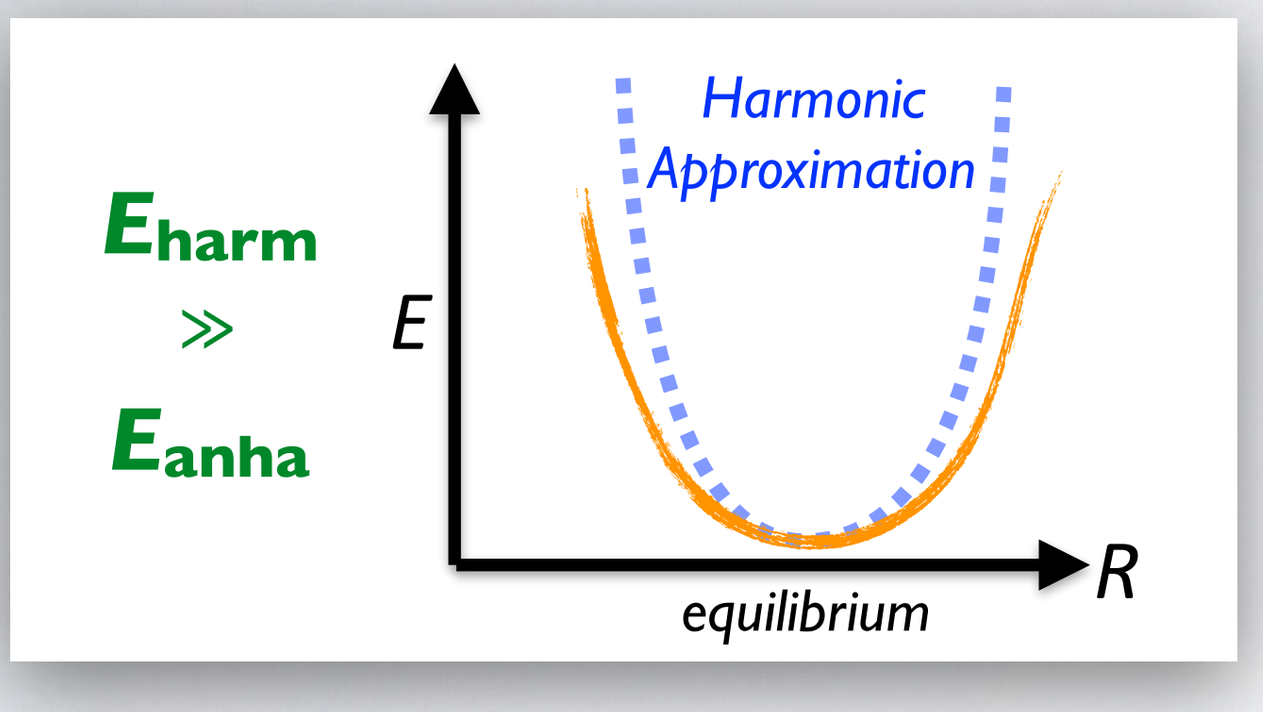


WARNING:

Harmonic Approximation is only valid for small displacements from R^0!

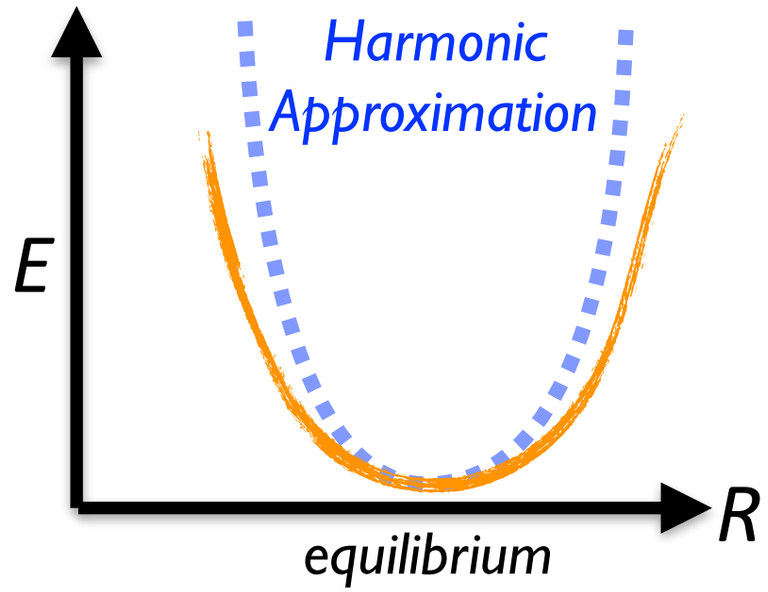
At elevated temperatures the harmonic approximation becomes increasingly **inaccurate** – and often **terribly misleading**!

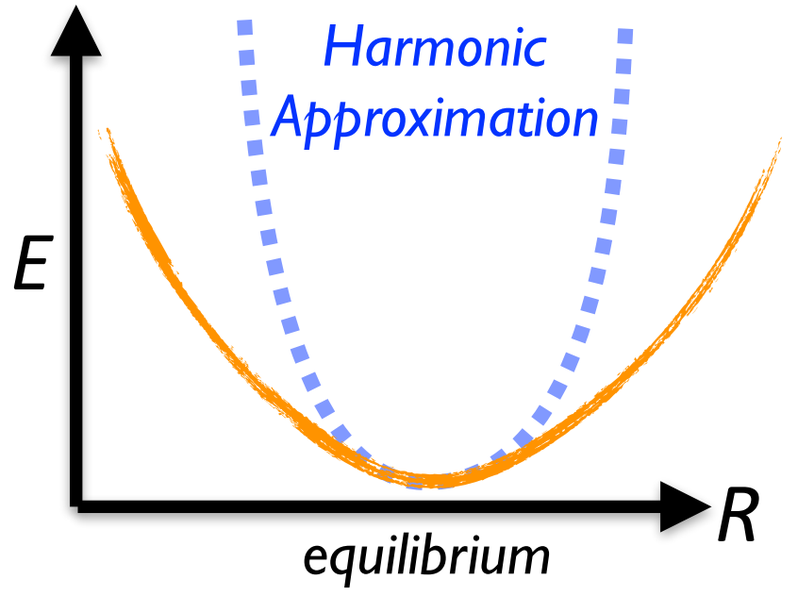
What is Anharmonicity?



What is Anharmonicity?

$E_{harm} \gg E_{anha}$

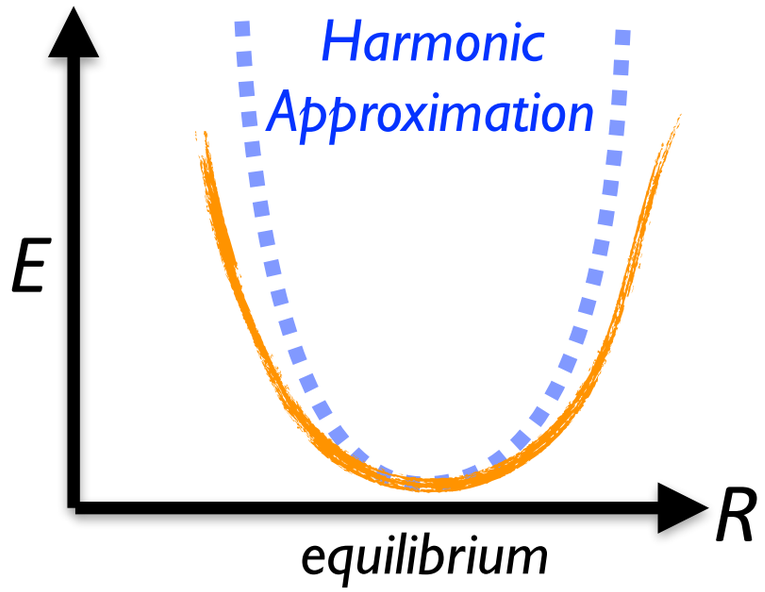


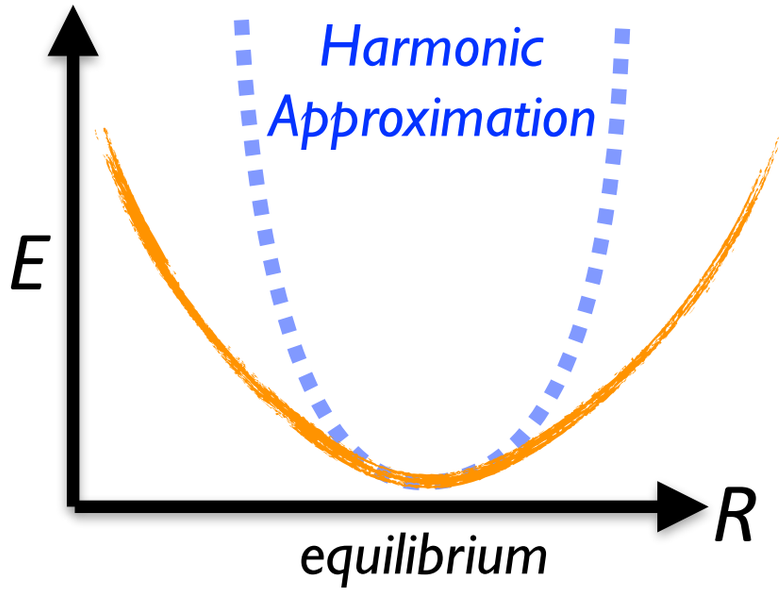


$E_{harm} \approx E_{anha}$

What is Anharmonicity?

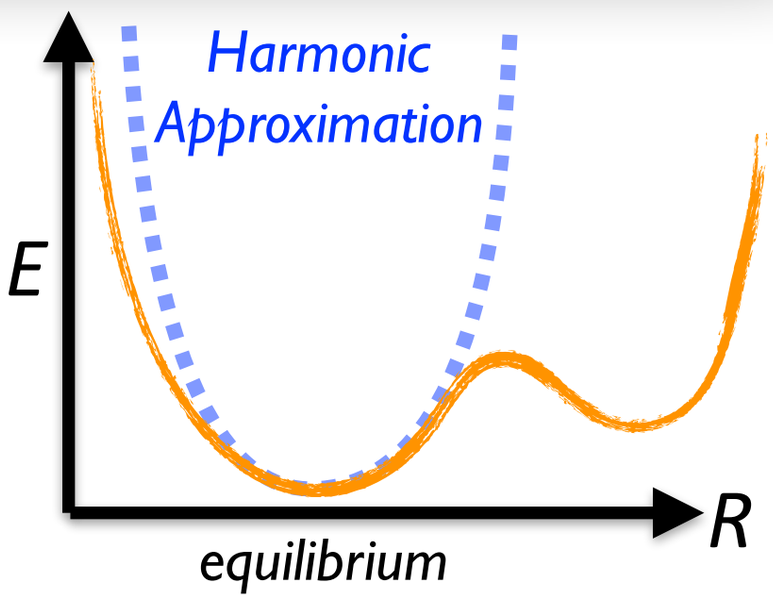
$E_{harm} \gg E_{anha}$





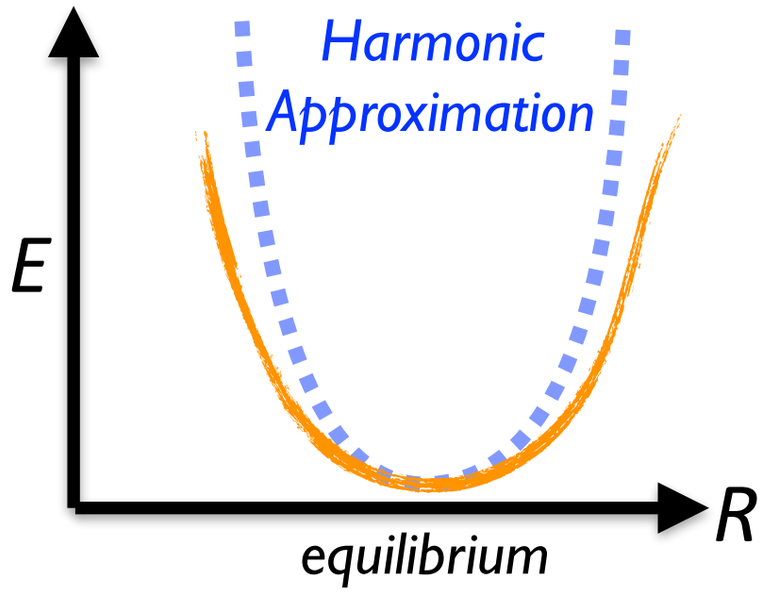
$E_{harm} \approx E_{anha}$

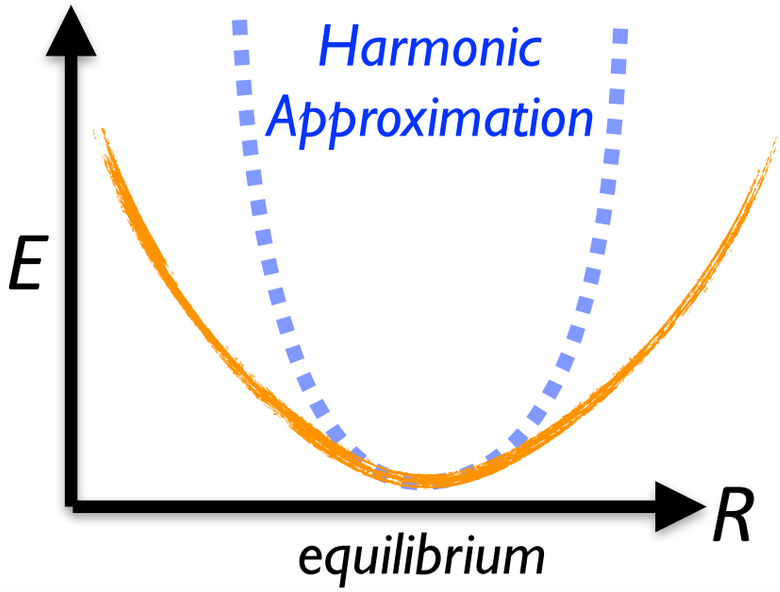
$E_{harm} \ll E_{anha}$



What is Anharmonicity?

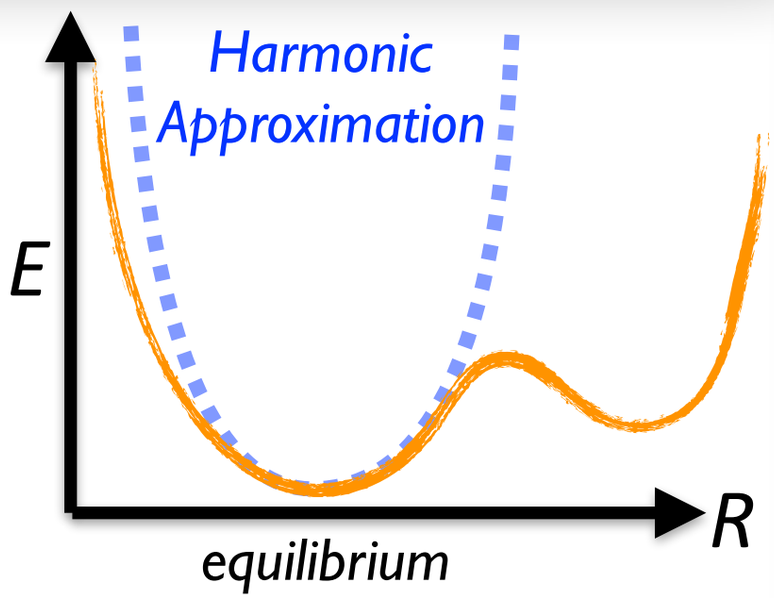
$E_{harm} \gg E_{anha}$

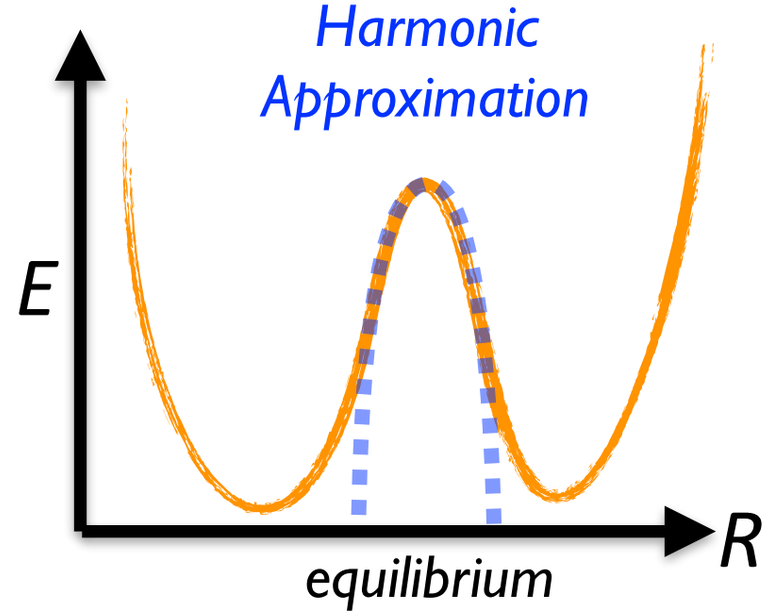




$E_{harm} \approx E_{anha}$

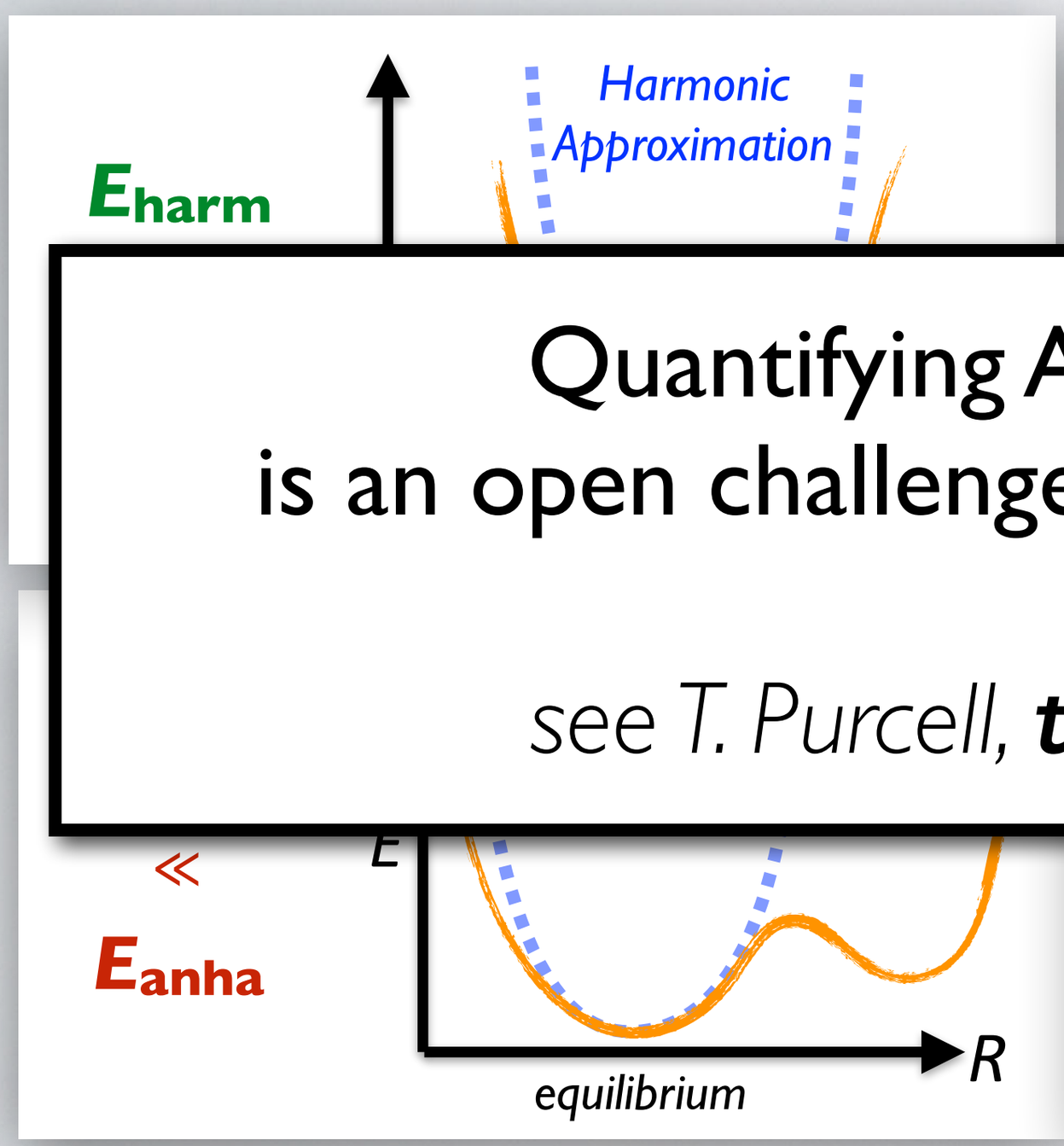
$E_{harm} \ll E_{anha}$

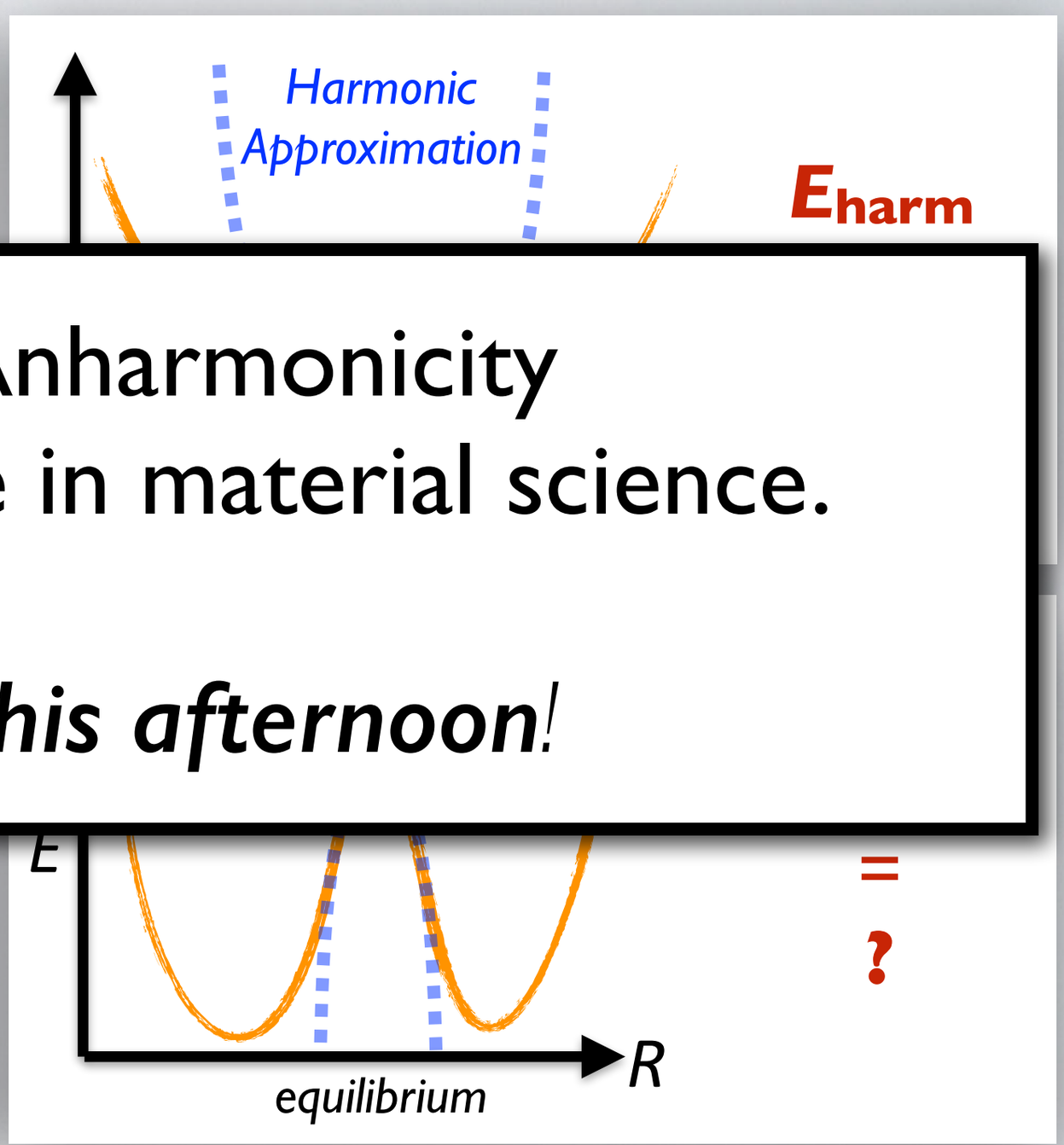




$E_{harm} = ?$

What is Anharmonicity?

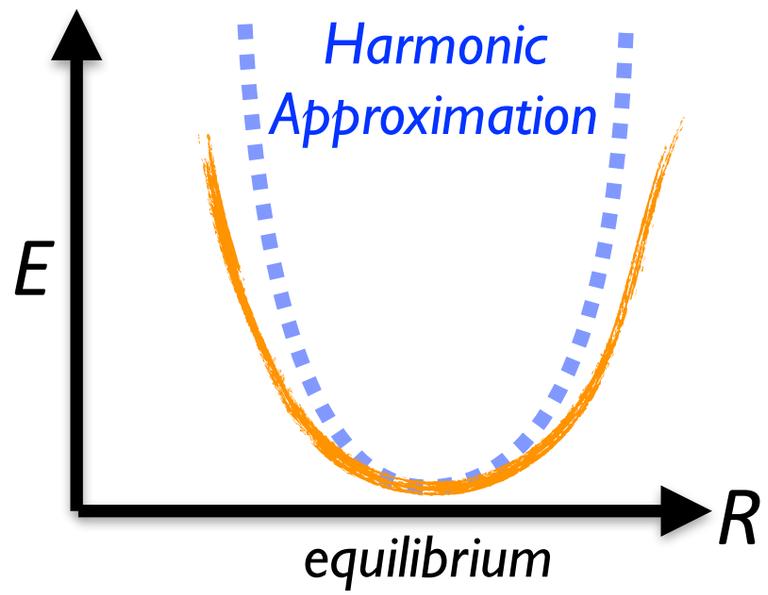




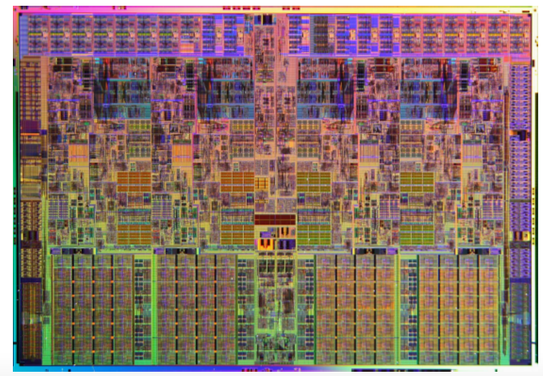
Quantifying Anharmonicity
is an open challenge in material science.

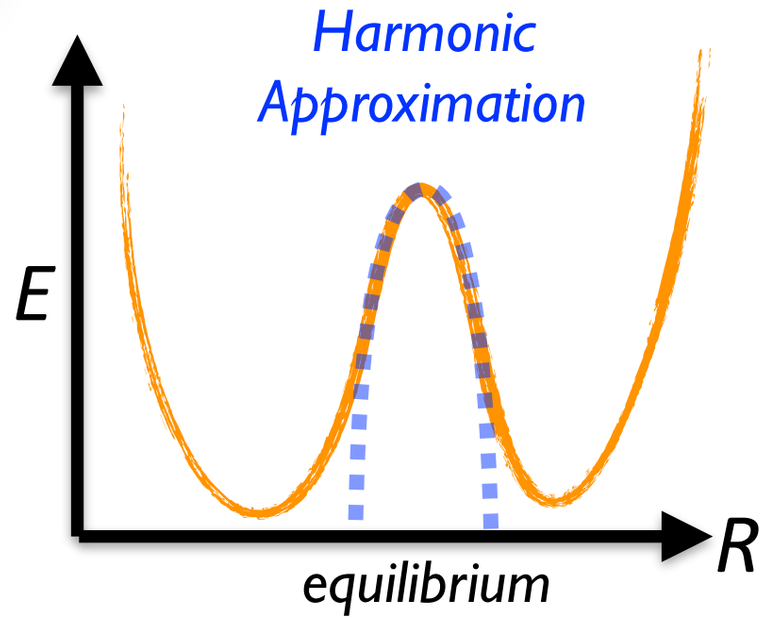
see *T. Purcell*, ***this afternoon***!

$E_{harm} \gg E_{anha}$



Si: Thermal conductivity **huge** (~250 W/mK)

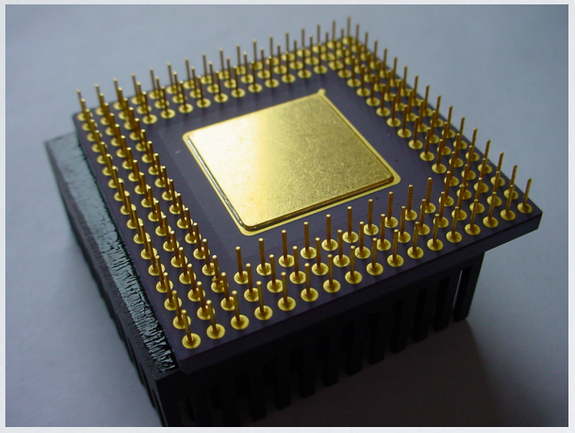




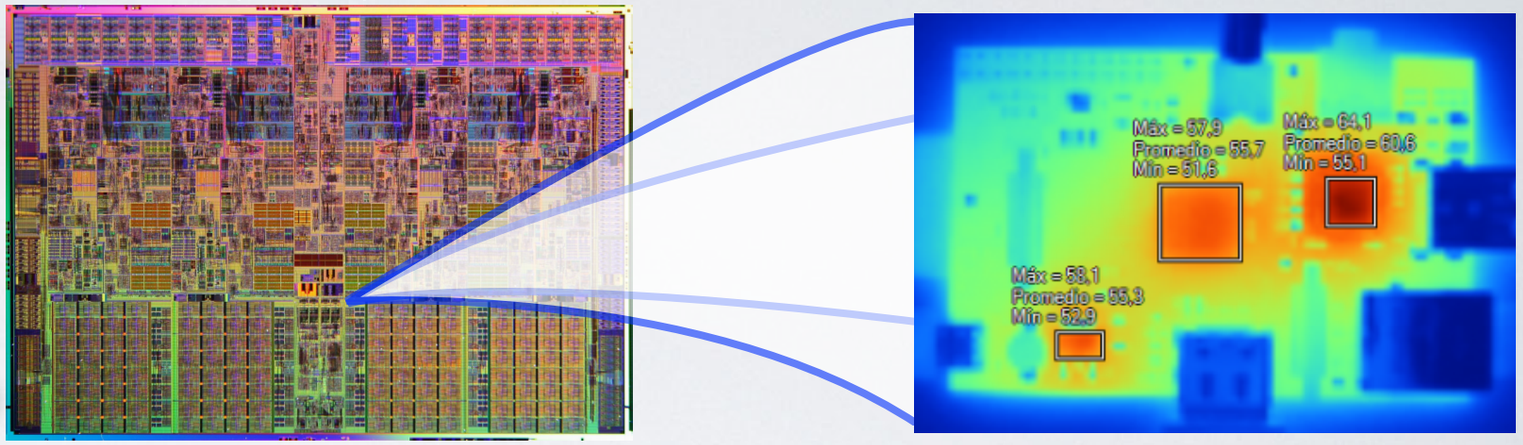
$E_{harm} = ?$

Semiconductor Technology

486 (1995): 10^6 Trans.



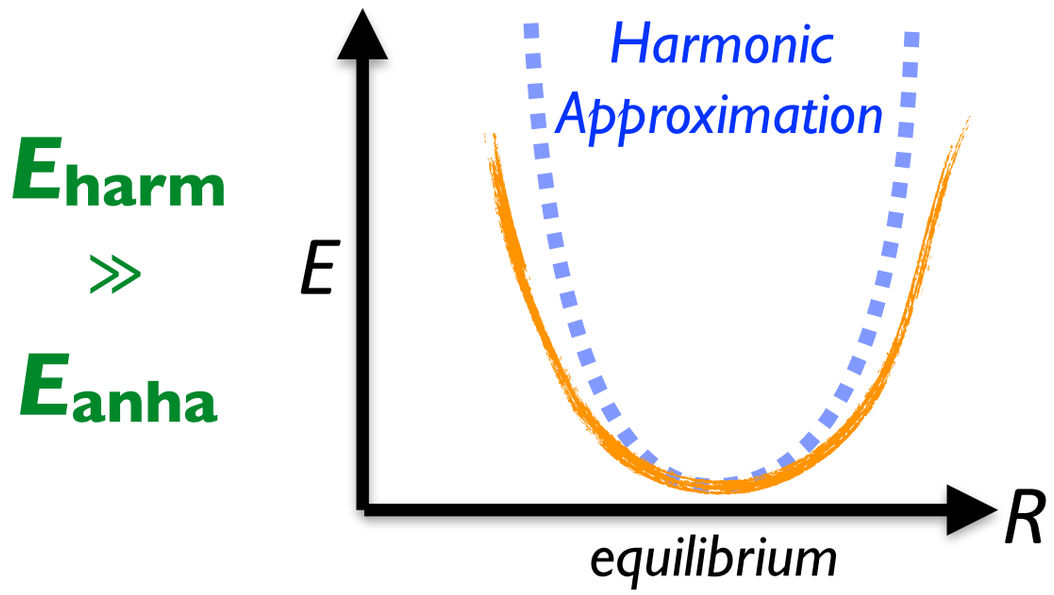
Haswell (2015): $>10^9$ Trans.



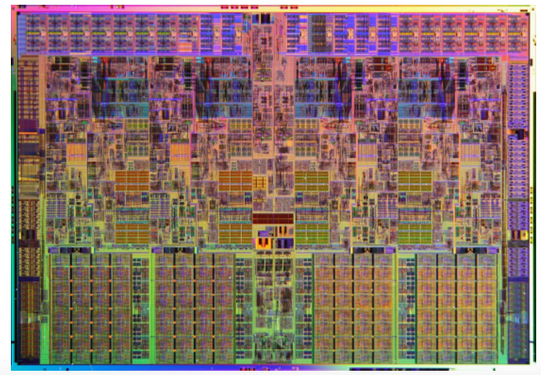
Miniaturization has lead to **enormous** transistor densities

Miniaturization has lead to **local** hot spots at the **nanoscale**.

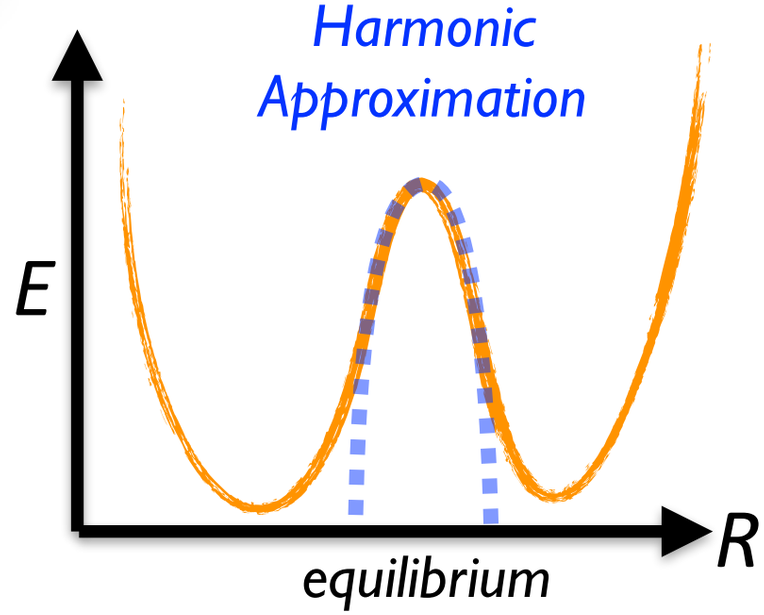
Understanding heat transport on the **nanoscale** and **increasings** its efficiency essential for next-generation CPUs.



Si: Thermal conductivity **huge** (~250 W/mK)



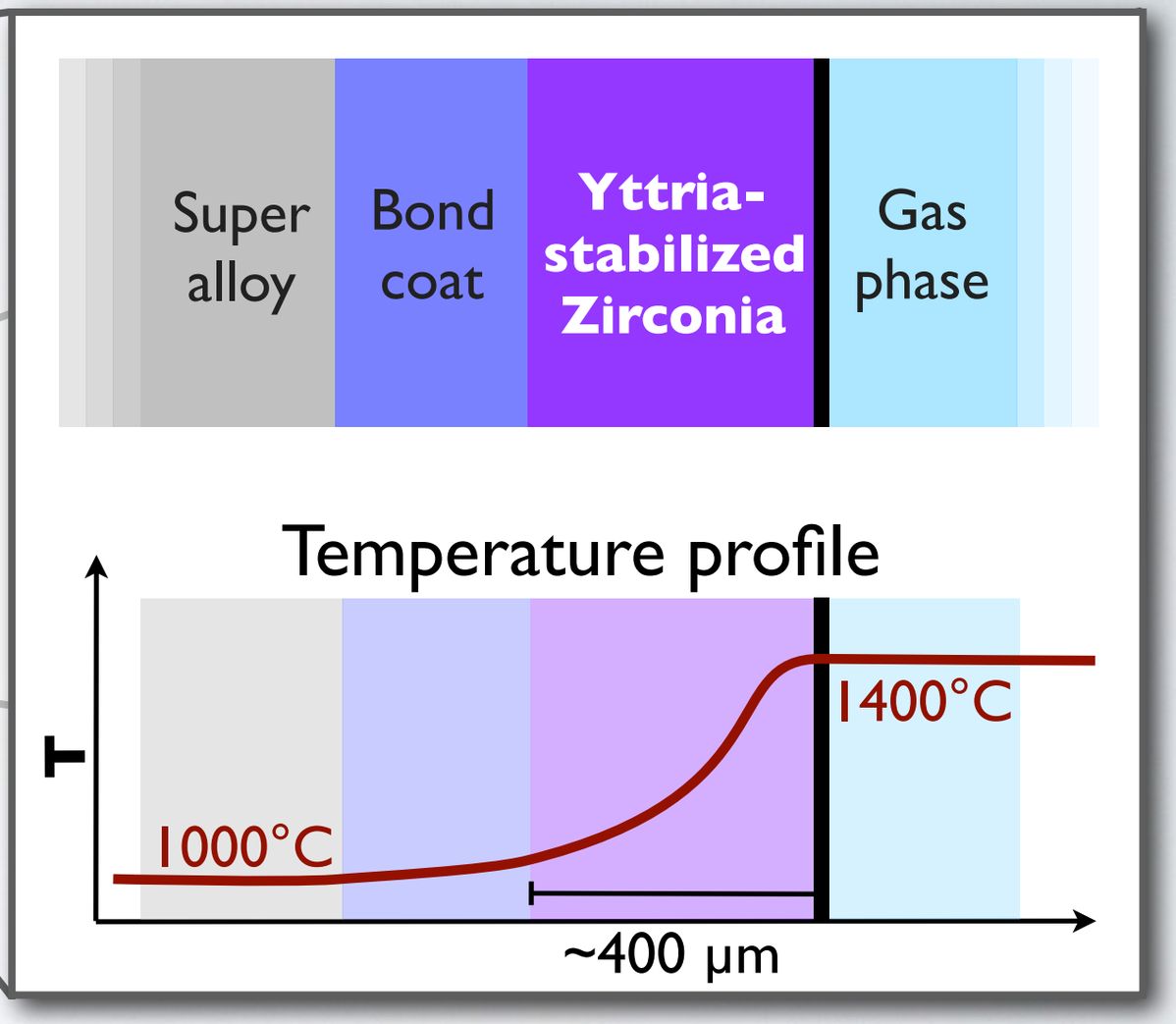
ZrO_2: Thermal conductivity **minute** (~3 W/mK)



E_{harm} = ?

Thermal-Barrier Coatings

CFM 56-7 airplane engine



Suppressing heat transport in **thermal barrier coatings** has driven the fuel-efficiency increase over the last 30 years.

D. R. Clarke & C. G. Levi, *Ann. Rev. Mat. Res.*, **33**, 383 (2003).

TECHNOLOGICAL EDGE CASES

ZrO_2: Thermal conductivity **minute** (~3 W/mK)

Suppress heat transport even further!

TECHNOLOGICAL EDGE CASES

ZrO_2: Thermal conductivity **minute** (~3 W/mK)

Suppress heat transport even further!

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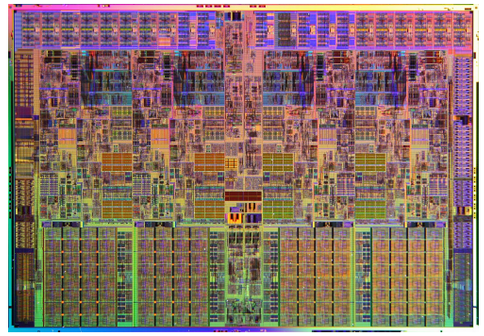


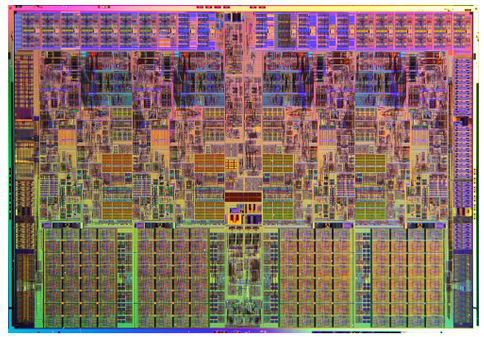
Boost heat transport even further!

TECHNOLOGICAL EDGE CASES

ZrO_2: Thermal conductivity **minute** (~3 W/mK)

Suppress heat transport even further!

Si: Thermal conductivity **huge** (~250 W/mK)



Boost heat transport even further!

First Principles Theory

A **quantitative theory** of **anharmonicity** is **required** to achieve a **qualitative understanding** of the **underlying mechanisms**!

THERMODYNAMIC EQUILIBRIUM IN A NUTSHELL

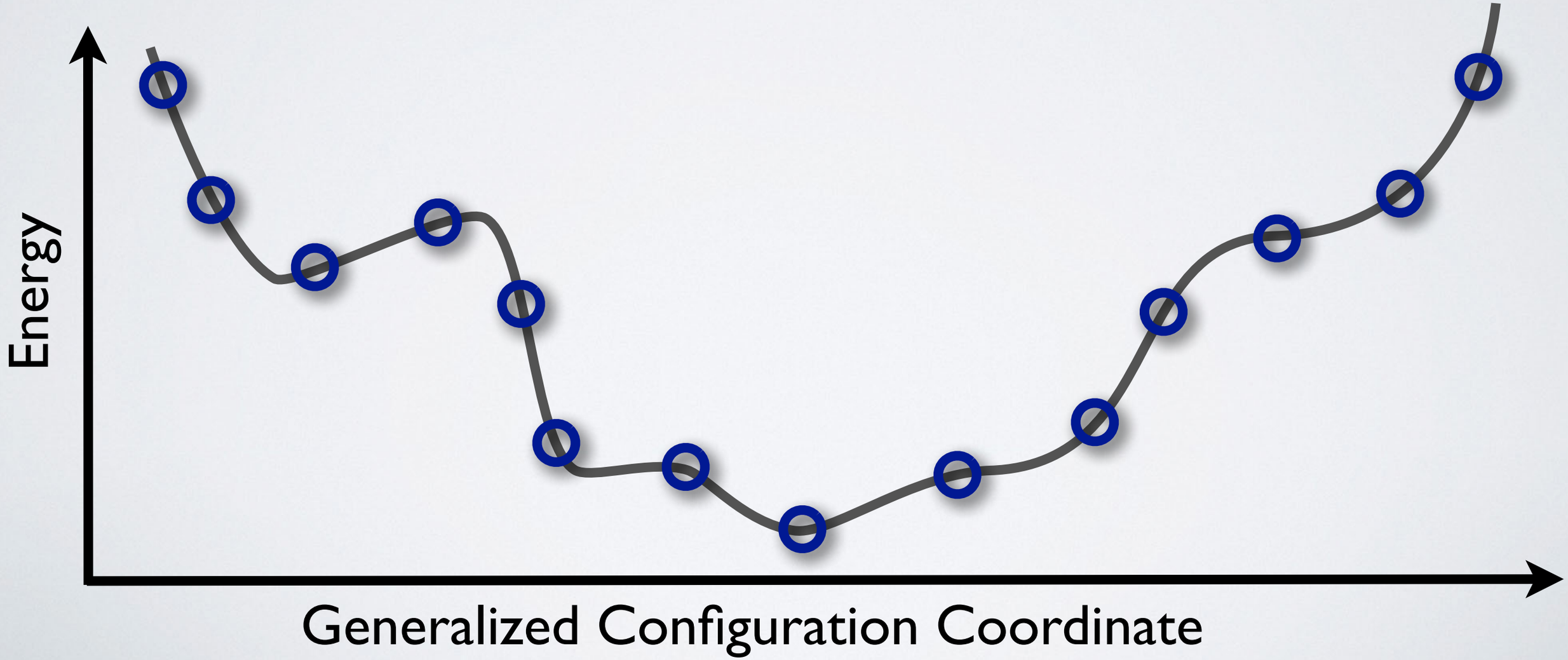
A classical system with **N atoms**, a **Volume V** and a **Temperature T** is described by its **canonical partition function Z(T,V,N)** viz. its **Helmholtz Free Energy F(T,V,N)**.

$$
\begin{aligned}
F(T,V,N) &= -k_B \ln\left(Z(T,V,N)\right) \\
&= -k_B \ln\left(\frac{1}{N!\hbar^{3N}} \int \exp\left(-\frac{\mathcal{H}(\{\mathbf{x}_i\},\{\mathbf{p}_i\})}{k_B T}\right) \{d^3\mathbf{x}_i\}\{d^3\mathbf{p}_i\}\right)
\end{aligned}
$$

Calculating the energy of **all possible configurations {x_i}** is **numerically unfeasible** even for very small systems.

THERMODYNAMIC AVERAGE

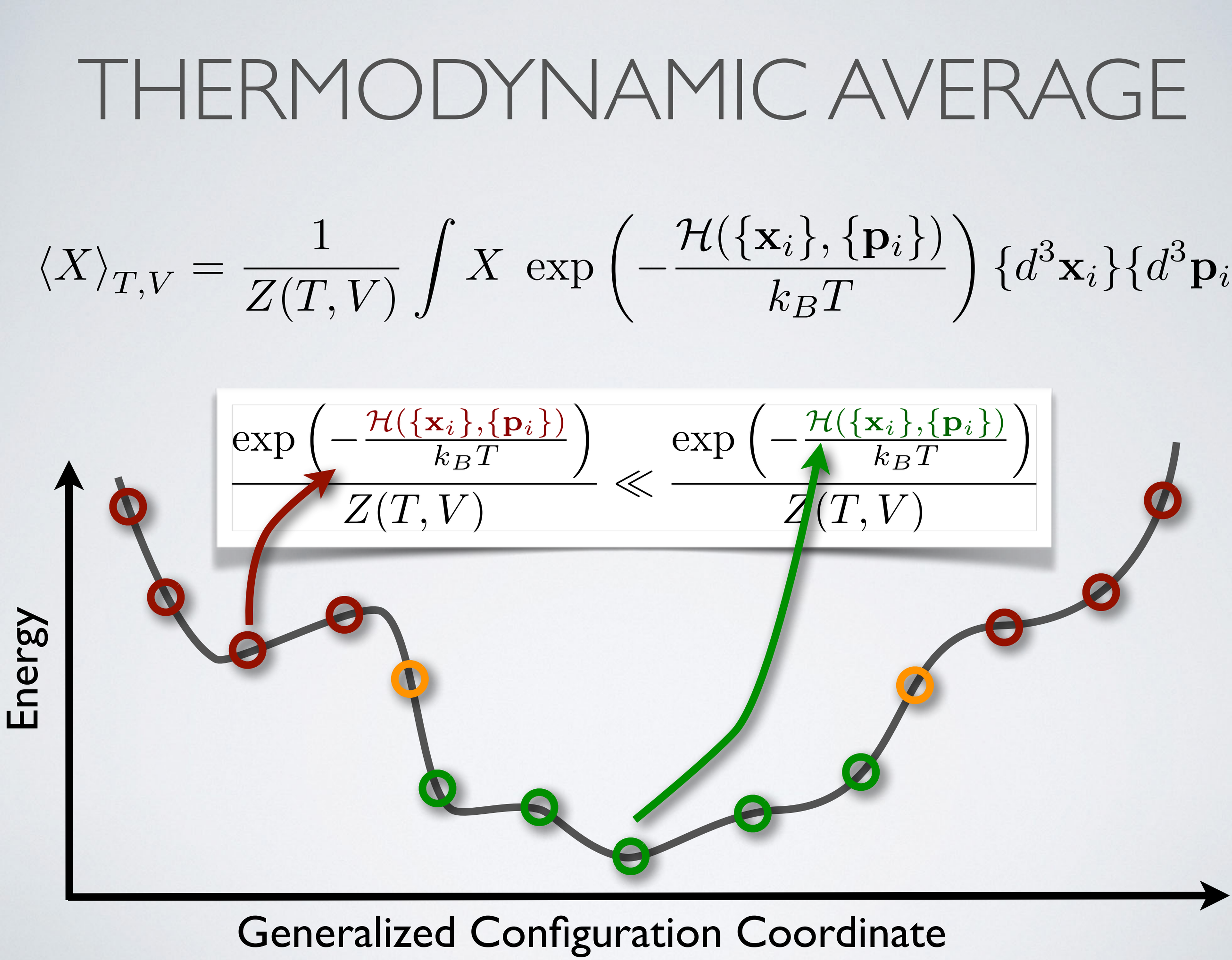
$$\langle X \rangle_{T,V} = \frac{1}{Z(T,V)} \int X \ \exp\left(-\frac{\mathcal{H}(\{\mathbf{x}_i\},\{\mathbf{p}_i\})}{k_B T}\right) \{d^3\mathbf{x}_i\}\{d^3\mathbf{p}_i\}$$



THERMODYNAMIC AVERAGE

$$\langle X \rangle_{T,V} = \frac{1}{Z(T,V)} \int X \ \exp\left(-\frac{\mathcal{H}(\{\mathbf{x}_i\},\{\mathbf{p}_i\})}{k_B T}\right) \{d^3\mathbf{x}_i\}\{d^3\mathbf{p}_i\}$$

$$\frac{\exp\left(-\frac{\mathcal{H}(\{\mathbf{x}_i\},\{\mathbf{p}_i\})}{k_B T}\right)}{Z(T,V)} \ll \frac{\exp\left(-\frac{\mathcal{H}(\{\mathbf{x}_i\},\{\mathbf{p}_i\})}{k_B T}\right)}{Z(T,V)}$$

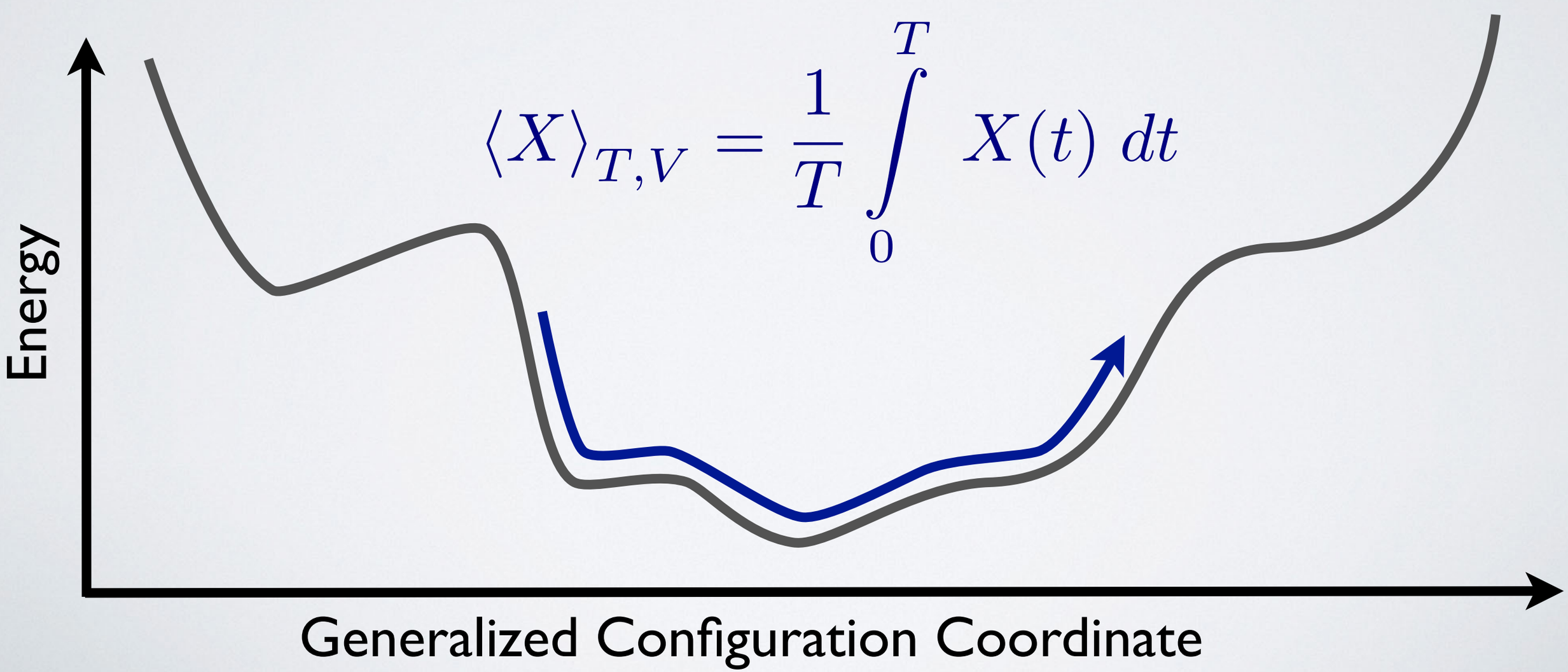


ERGODIC HYPOTHESIS

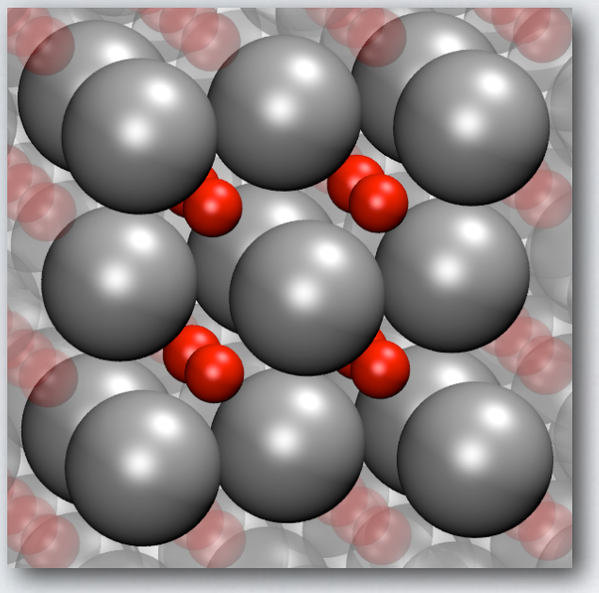
All accessible micro-states are **equiprobable**
over a long period of time:

The Time Average is equal to the Ensemble Average!

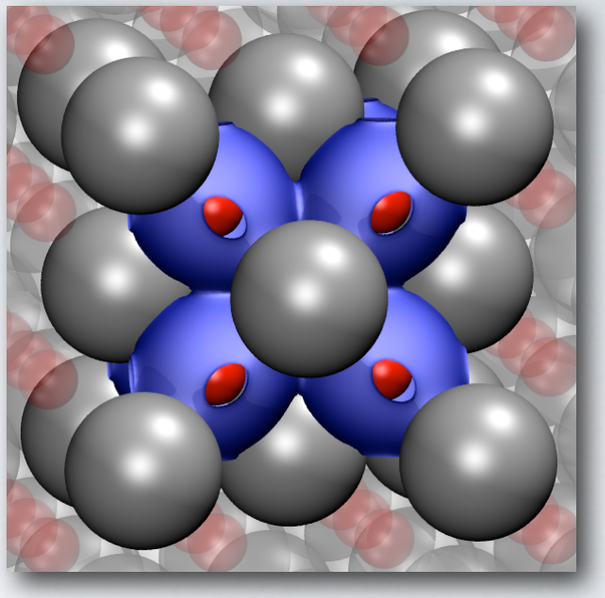
$$\langle X \rangle_{T,V} = \frac{1}{T} \int_0^T X(t)\, dt$$



AB INITIO MOLECULAR DYNAMICS



Electronic Structure Theory Code



Input:
Geometry, Species

Output:
total **energy** & **forces**

Update geometry

Iterative Approach: Explore the Dynamics of the Atoms!

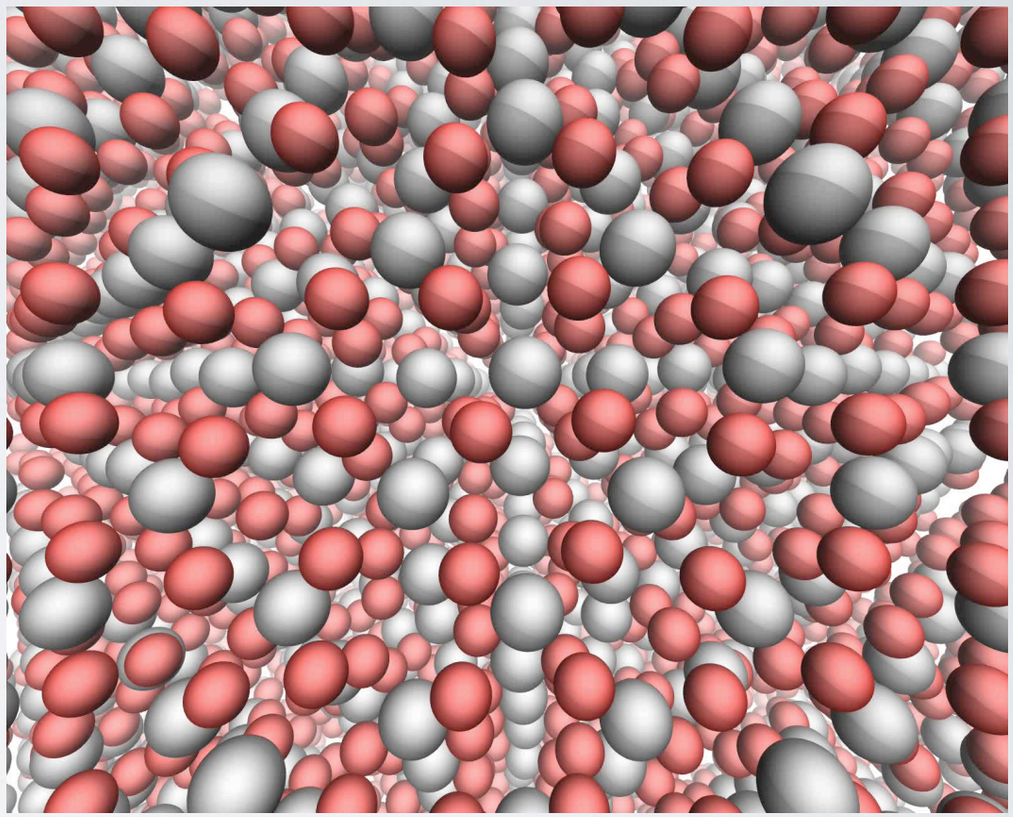
AB INITIO MOLECULAR DYNAMICS

Numerical Integration
of the **equations of motion**

L. Verlet, *Phys. Rev.* **159**, 98 (1967).

$$M_I \ddot{\mathbf{R}}_I(t) = \mathbf{F}_I(\mathbf{R}_1(t), \cdots, \mathbf{R}_N(t))$$

Initial conditions have to be specified!



The **Verlet Algorithm** conserves the number of particles **N**, the volume **V**, and the energy **E**.

⇒ **Micro-canonical Ensemble**

PHASE DIAGRAM OF ZrO_2

Monoclinic

Tetragonal

Cubic

0 K

500 K

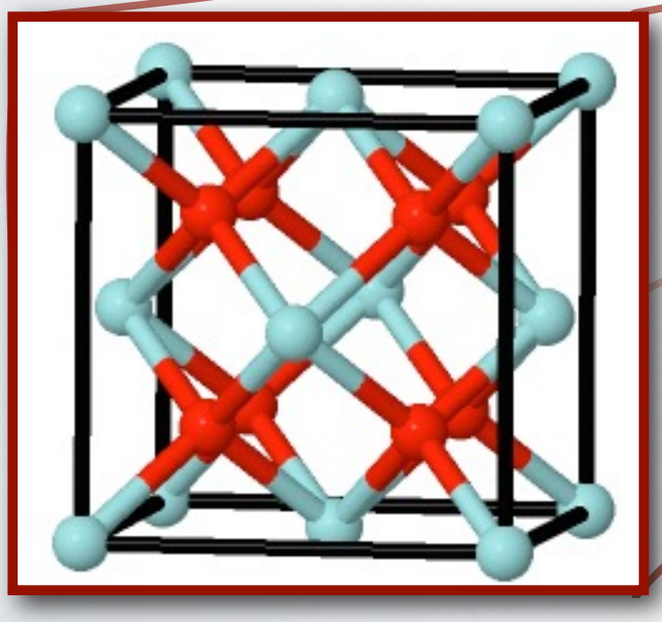
1000 K

1500 K

2000 K

2500 K

3000 K



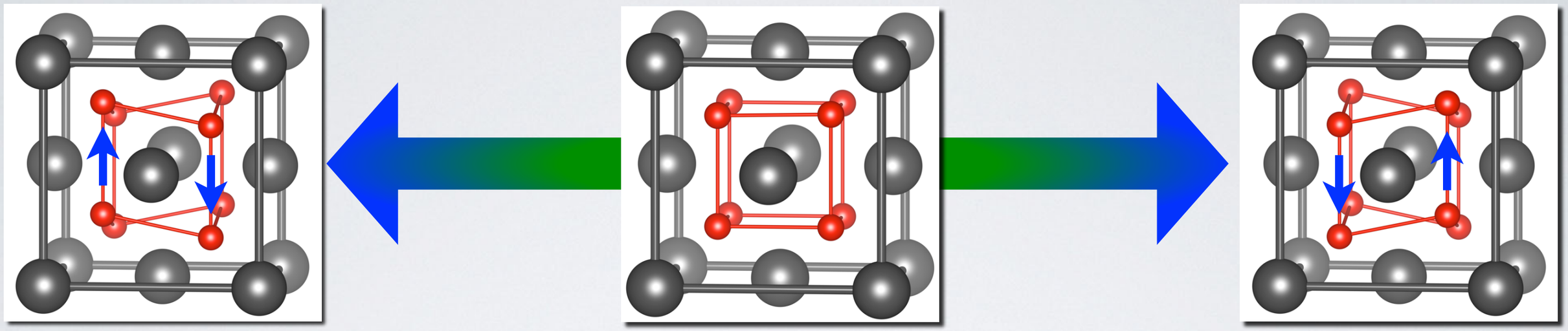
T > 2400°C

„Cubic“

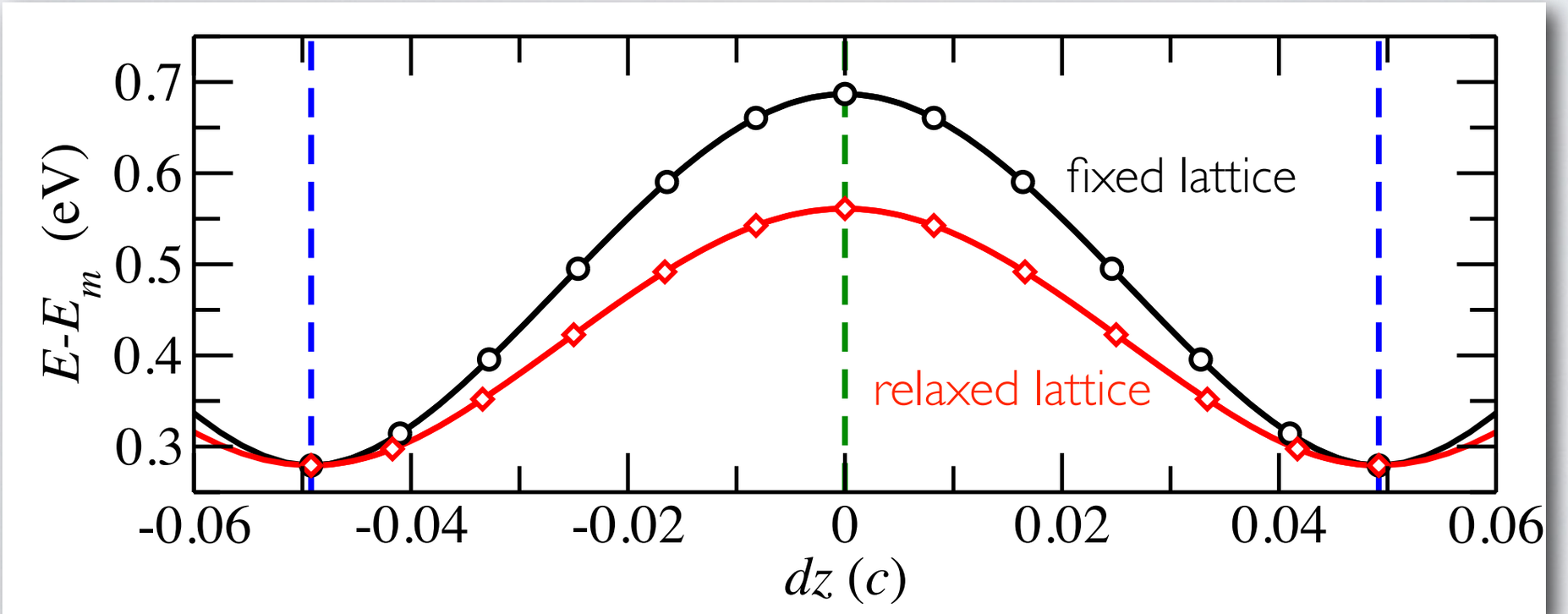
Fluorite Structure

The Tetragonal-Cubic Phase Transition

Tetragonal | Cubic | Tetragonal

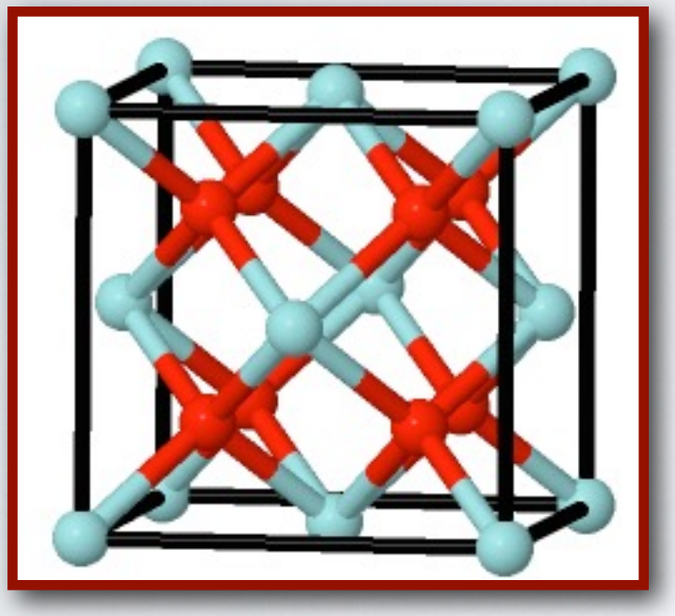


dz < 0 ***dz = 0*** ***dz > 0***

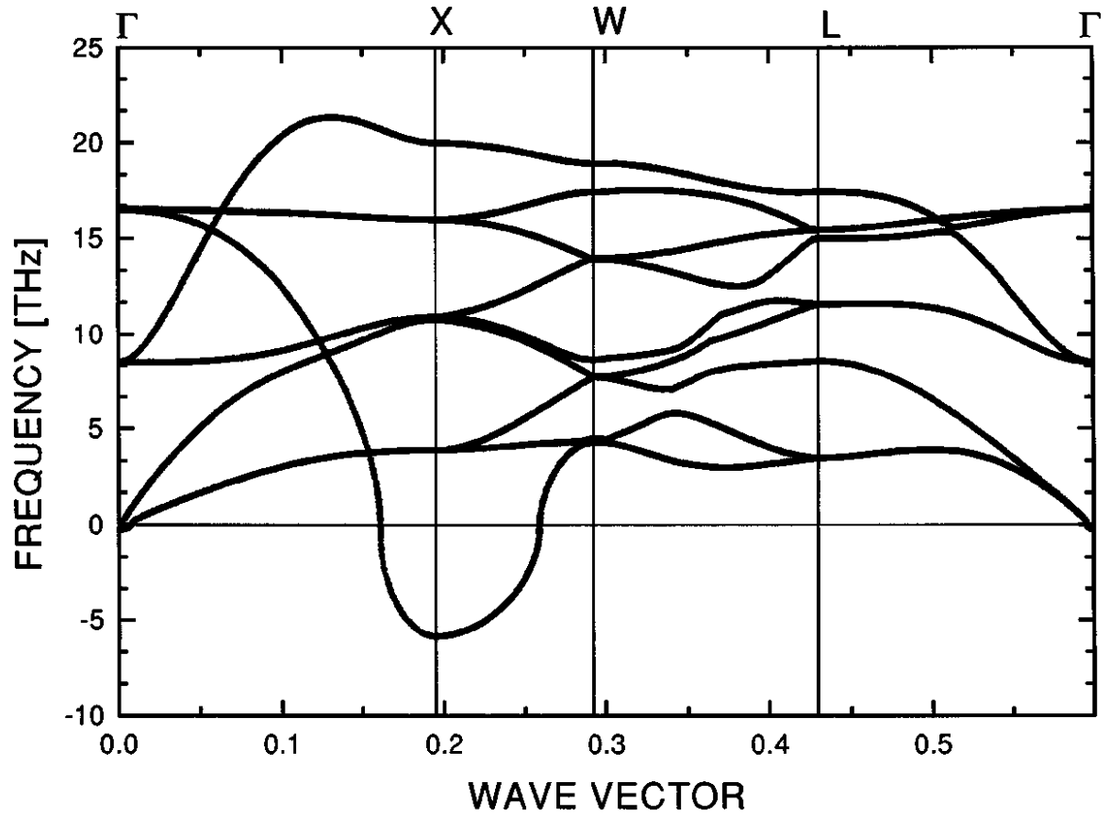


S. Fabris, A.T. Paxton, and M.W. Finnis, *Phys. Rev. B* **63**, 094101 (2001).
M. Sternik and K. Parlinski, *J. Chem. Phys.* **123**, 204708 (2005).

THE SOFT MODE OF CUBIC ZrO_2



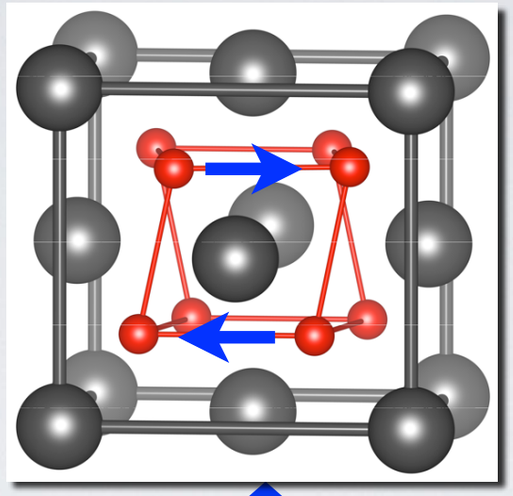
„Cubic“
Fluorite Structure



K. Parlinski, Z. Q. Li, and Y. Kawazoe,
Phys. Rev. Lett. **78**, 4063 (1997).

Cubic Zirconia exhibits a ***soft mode (imaginary mode):***

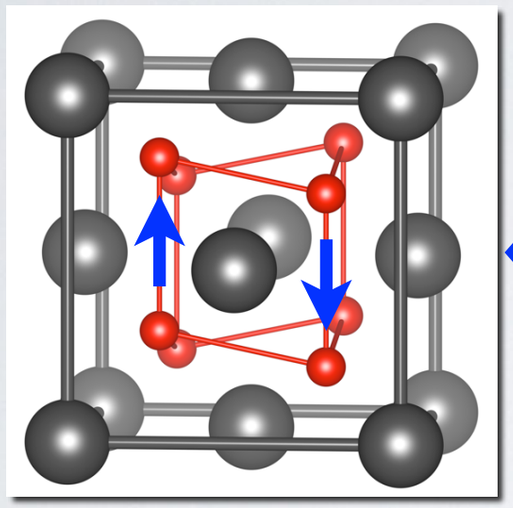
$$\mathbf{D}(\mathbf{X})\ [\nu(\mathbf{X})] = \omega^2(\mathbf{X})\ [\nu(\mathbf{X})] \quad \Rightarrow \quad \omega_1^2(\mathbf{X}) < 0$$



dy > 0

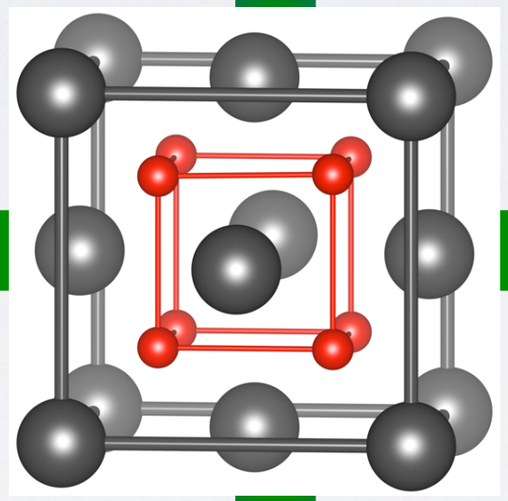
dz,dx = 0

Tetragonal

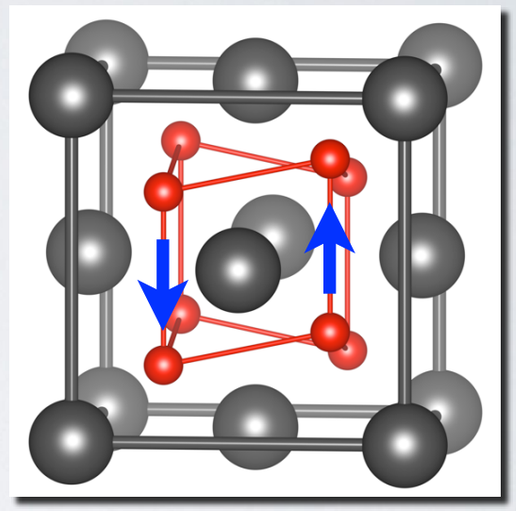


dz < 0

dx,dy = 0

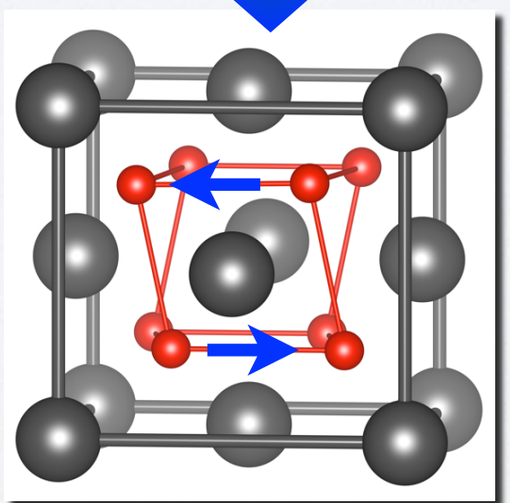


Tetragonal



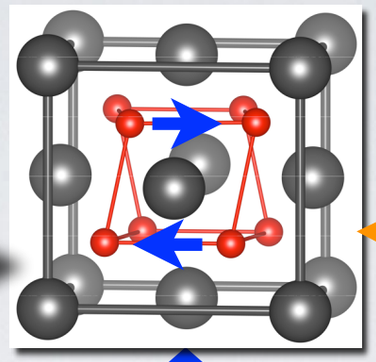
dz > 0

dx,dy = 0



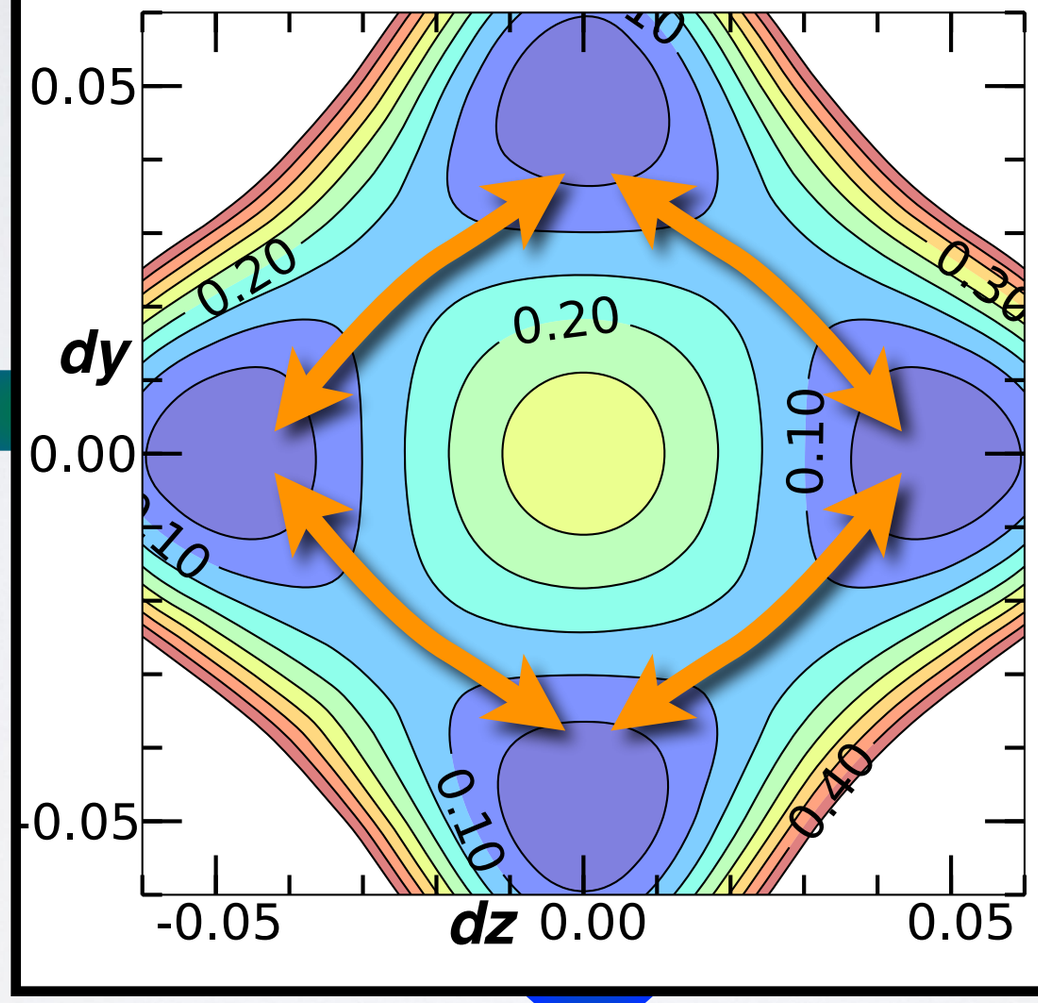
dy < 0

dz,dx = 0

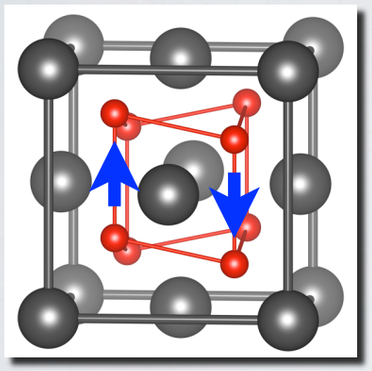


dy > 0
dz,dx = 0

Switches

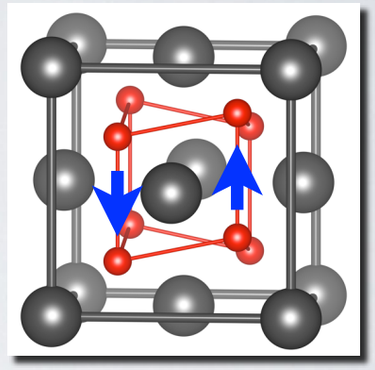


Tetragonal

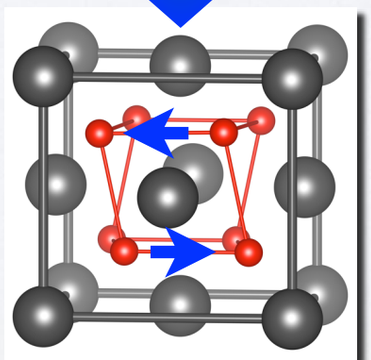


dz < 0
dx,dy = 0

Tetragonal

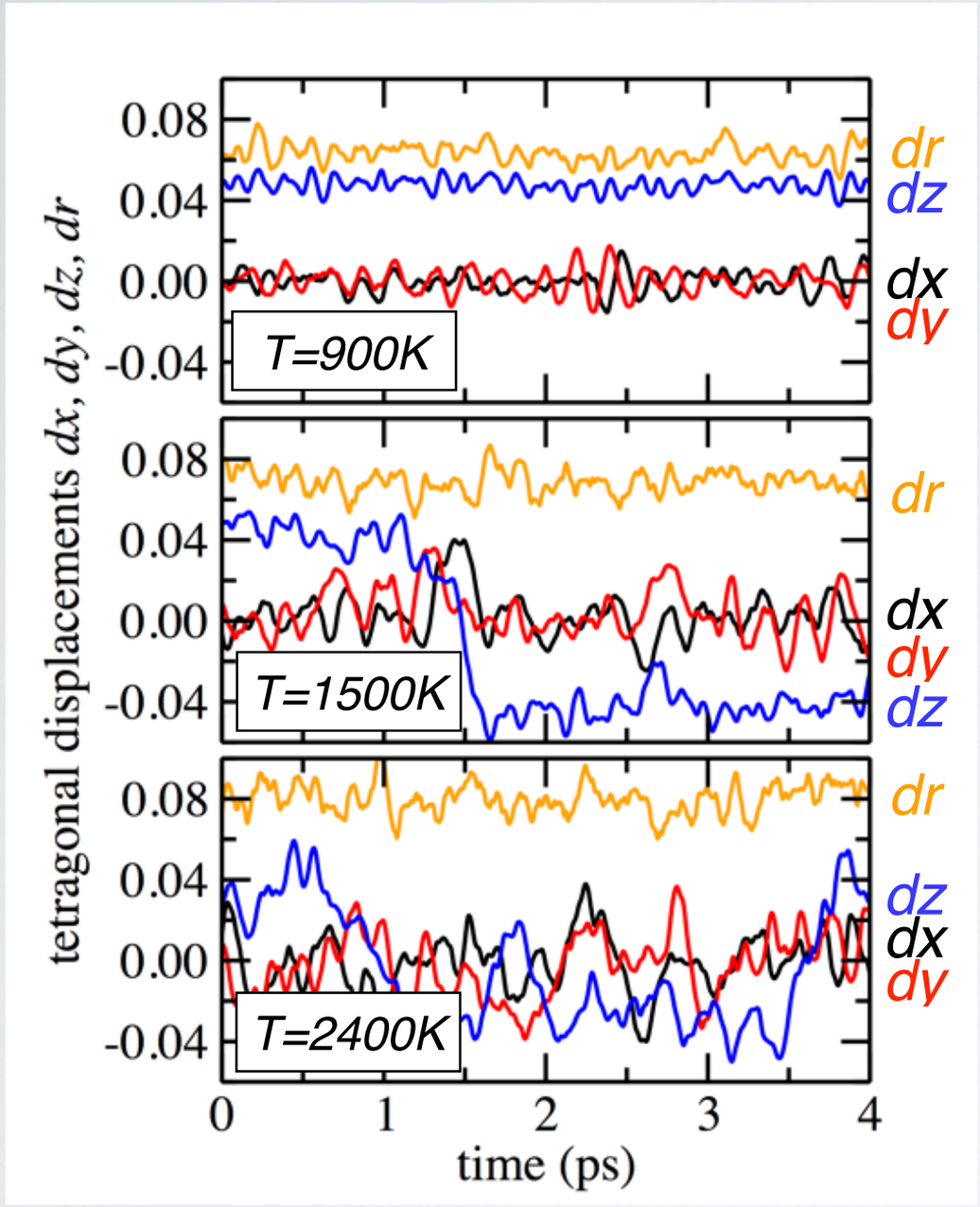


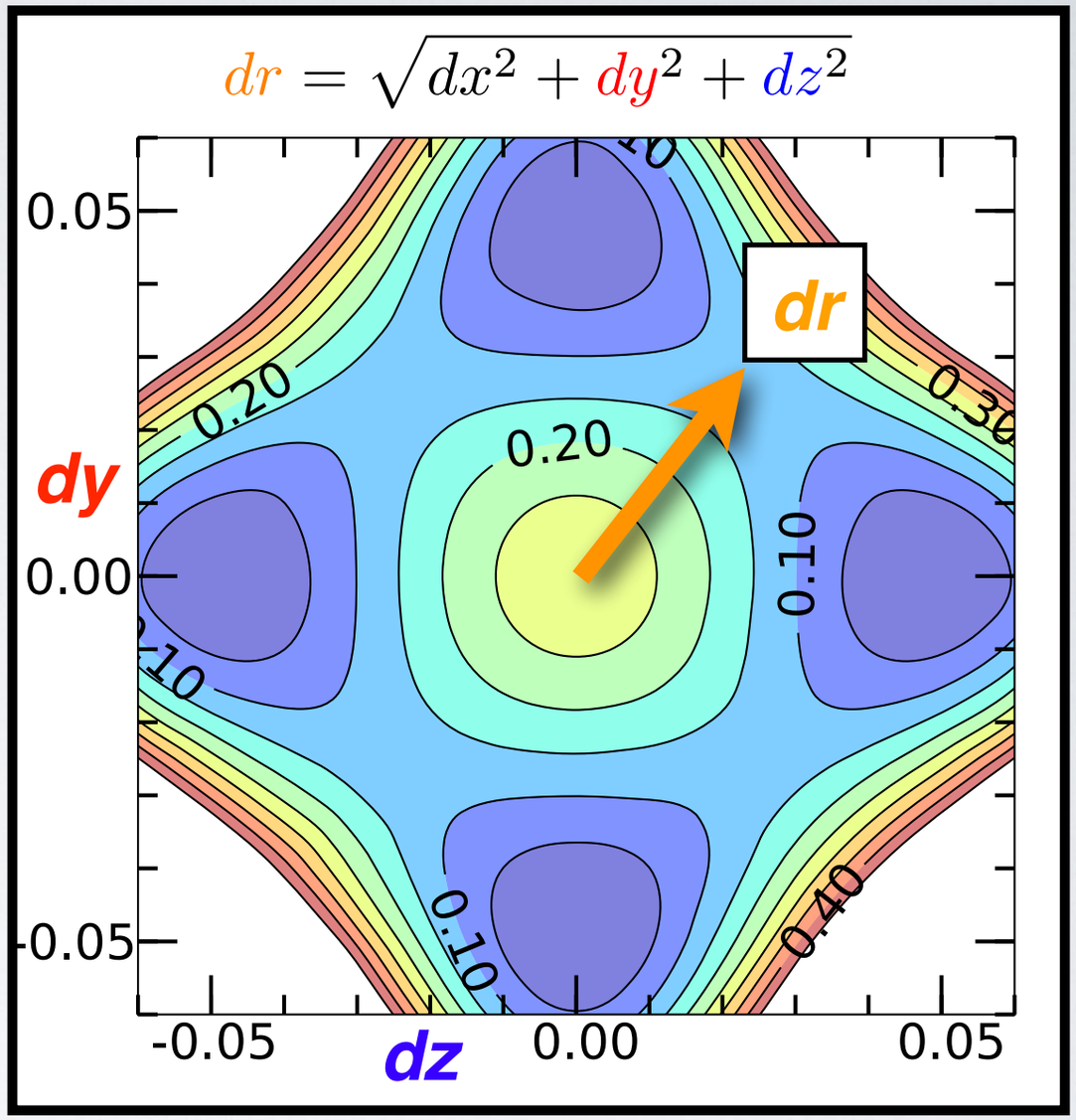
dz > 0
dx,dy = 0



dy < 0
dz,dx = 0

Ab initio MD Evidence



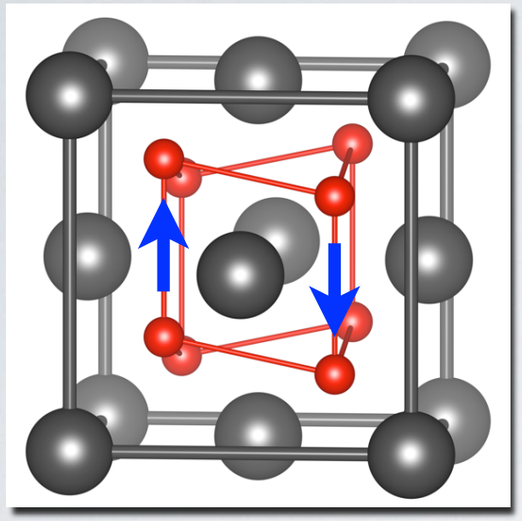


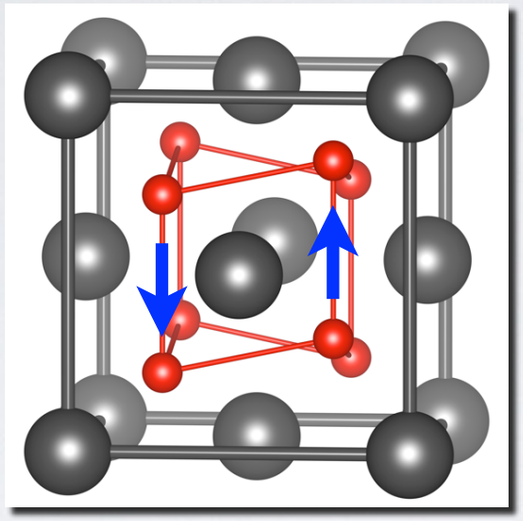
Distance from cubic geometry $dr = \sqrt{dx^2 + dy^2 + dz^2}$ always conserved!

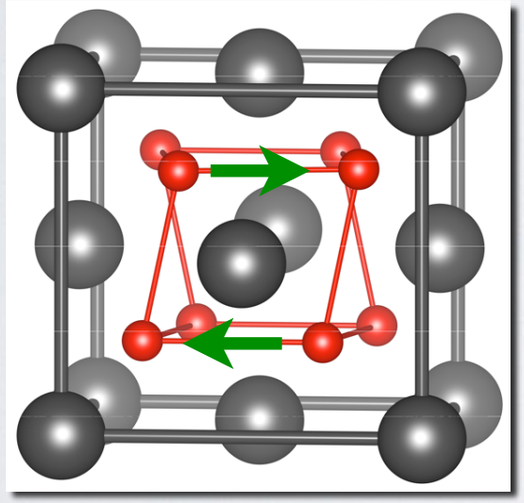
Cubic Structure is **never** realised at a **microscopic** level!

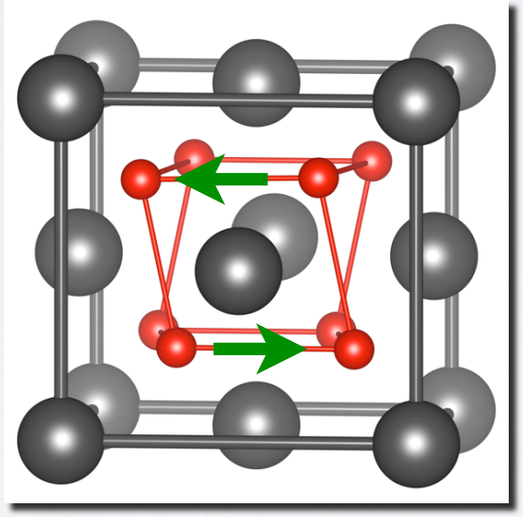
The Dynamics of Zirconia

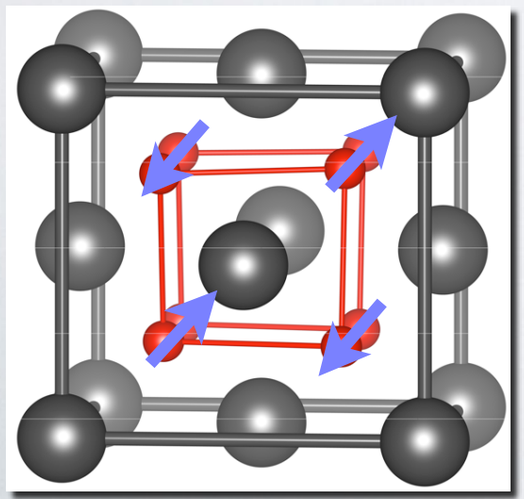
C. Carbogno, C. G. Levi, C. G. Van de Walle, and M. Scheffler *Physical Review B* 90, 144109 (2014).

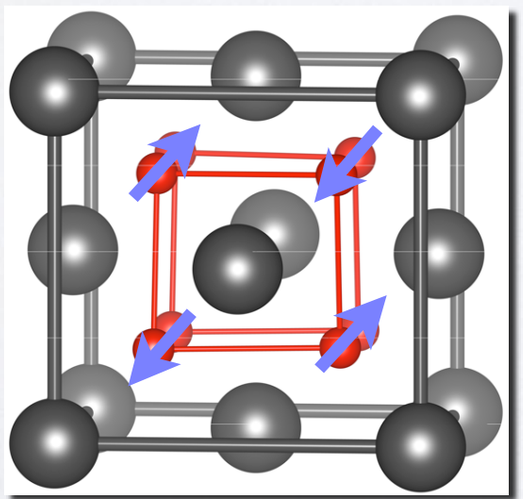












ZrO_2 exhibits **not one**, **but six degenerate** equilibrium configurations.

⇓

Switches between these configurations occur quite **frequently**.

⇓

Severe violation of the harmonic approximation.

SUMMARY I

We have introduced the harmonic approximation under periodic boundary conditions.

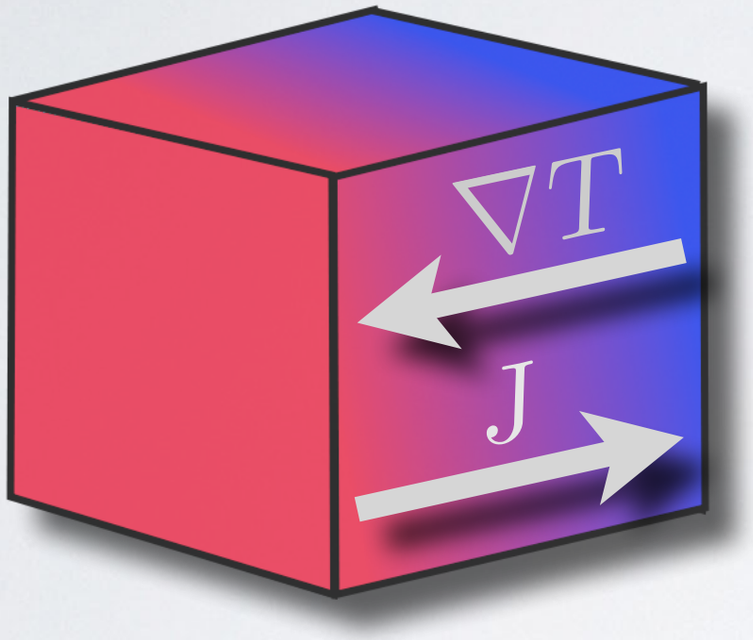
The harmonic approximation can be very useful to approximatively asses dynamic and thermodynamic effects at low temperatures.

The harmonic approximation becomes increasingly inaccurate at elevated temperatures and must be handled with care under such thermodynamic conditions.

III. HEAT TRANSPORT

HEAT TRANSPORT

Macroscopic Effect:



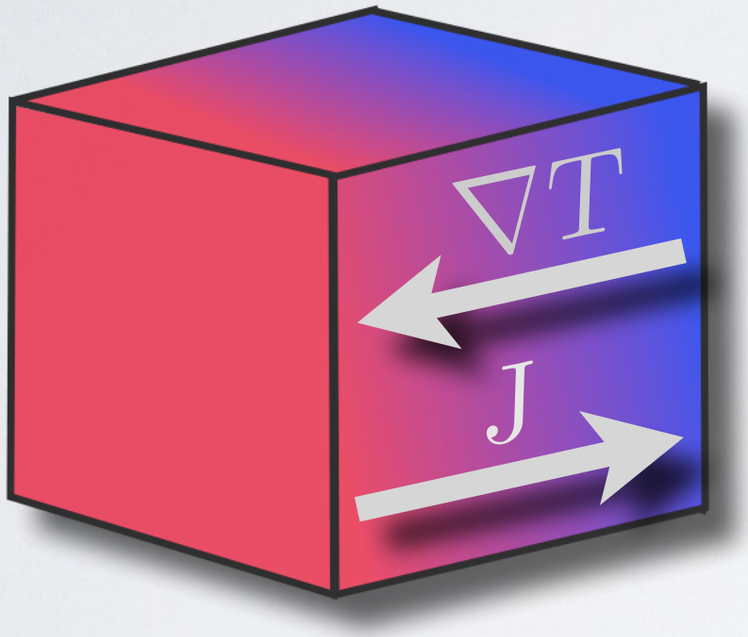
Fourier‘s Law:

$$\mathbf{J} = -\kappa \, \nabla T = -\alpha \, \rho \, c_V \, \nabla T$$

HEAT TRANSPORT

Macroscopic Effect:

$$\kappa = \kappa_{\text{photon}} + \kappa_{\text{elec.}} + \kappa_{\text{nucl.}}$$



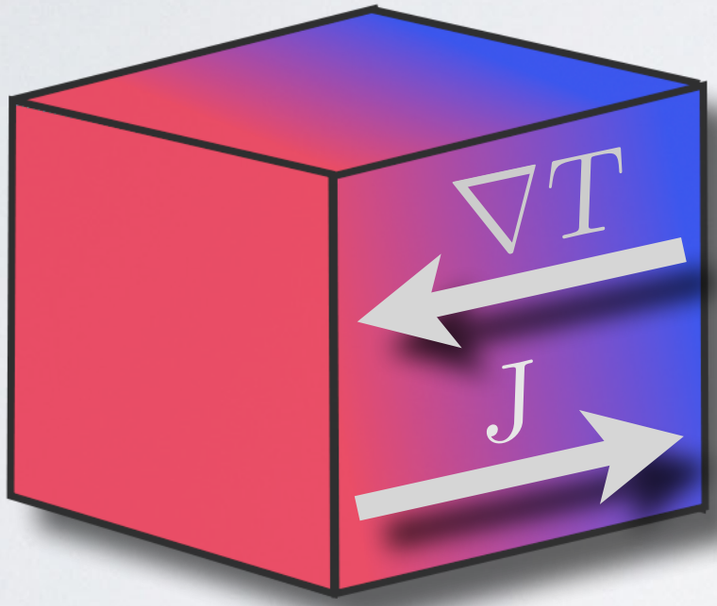
Fourier's Law:

$$\mathbf{J} = -\kappa \, \nabla T = -\alpha \, \rho \, c_V \, \nabla T$$

HEAT TRANSPORT

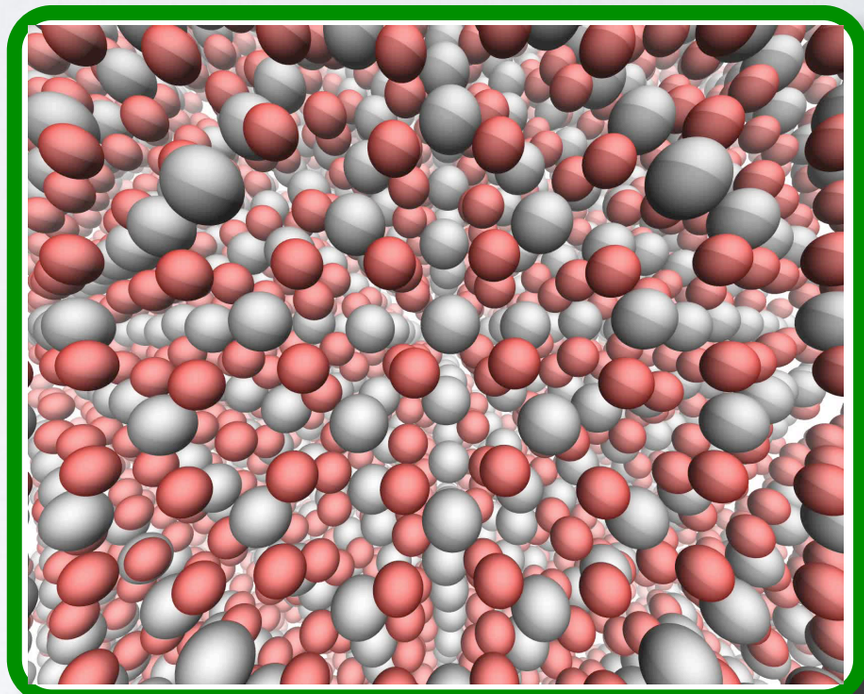
Macroscopic Effect:

$$\kappa = \cancel{\kappa_{\text{photon}}} + \cancel{\kappa_{\text{elec.}}} + \kappa_{\text{nucl.}}$$



Fourier's Law:

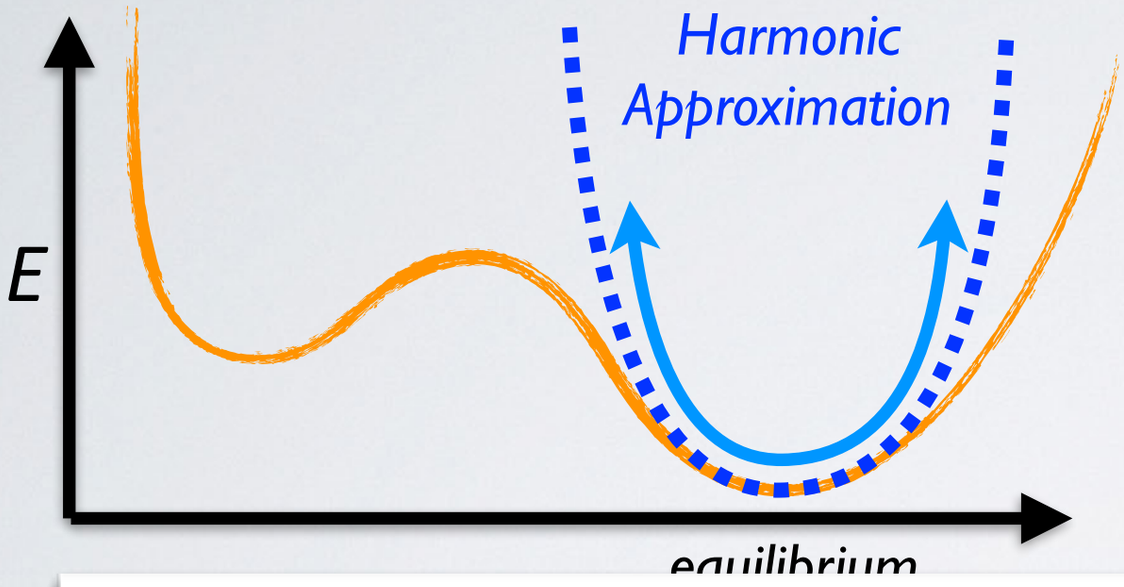
$$\mathbf{J} = -\kappa \, \nabla T = -\alpha \, \rho \, c_V \, \nabla T$$



Microscopic Mechanisms

Heat Transport Theory 101

Real Space Representation



Reciprocal Space Representation

Phonon (ω,q)

Decoupled Normal Modes

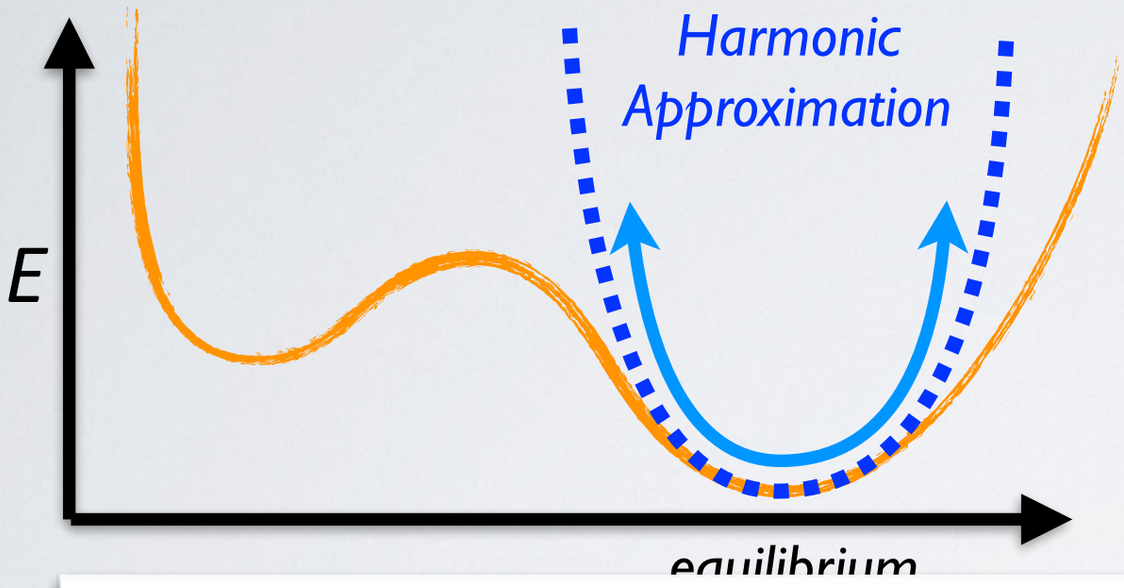
Infinite Phonon Lifetime

Harmonic Approximation:

Second order Taylor expansion of the **potential energy surface** around **equilibrium**

Heat Transport Theory 101

Real Space Representation



Decoupled Normal Modes

Reciprocal Space Representation

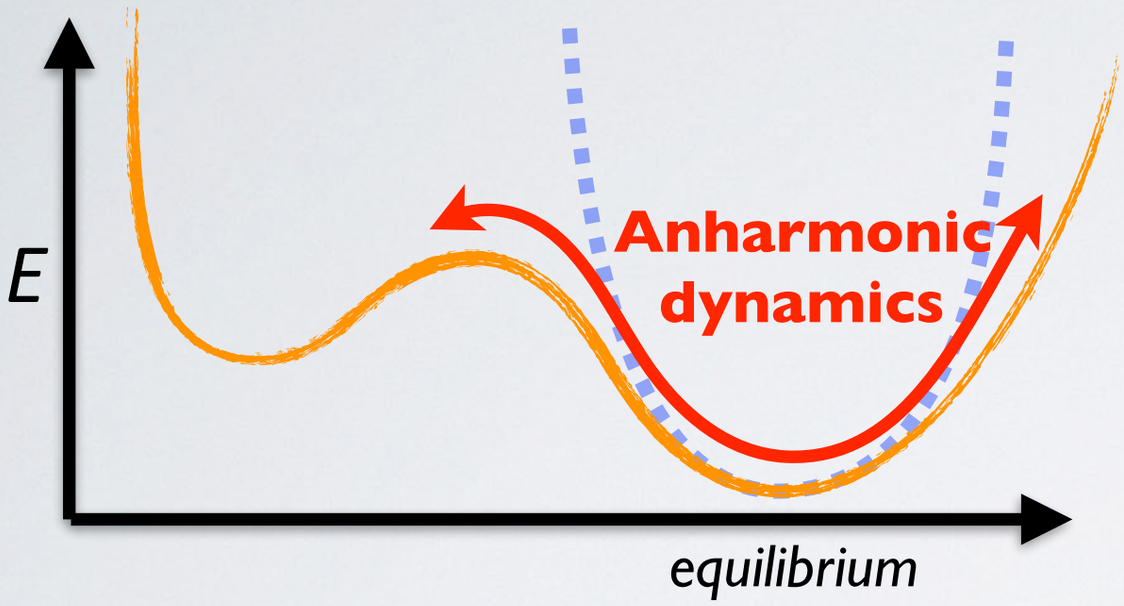
Phonon (ω,q)

Infinite Phonon Lifetime

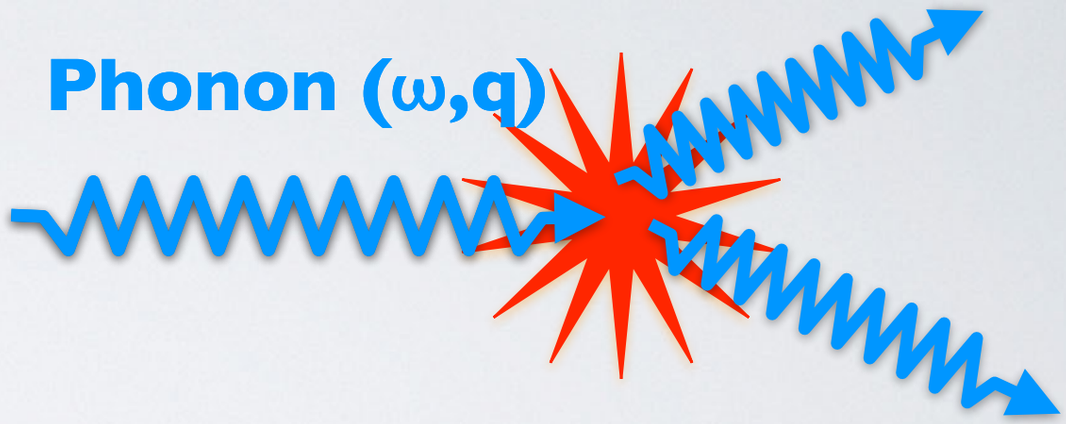
Infinite thermal conductivity!

Heat Transport Theory 101

Real Space Representation



Reciprocal Space Representation



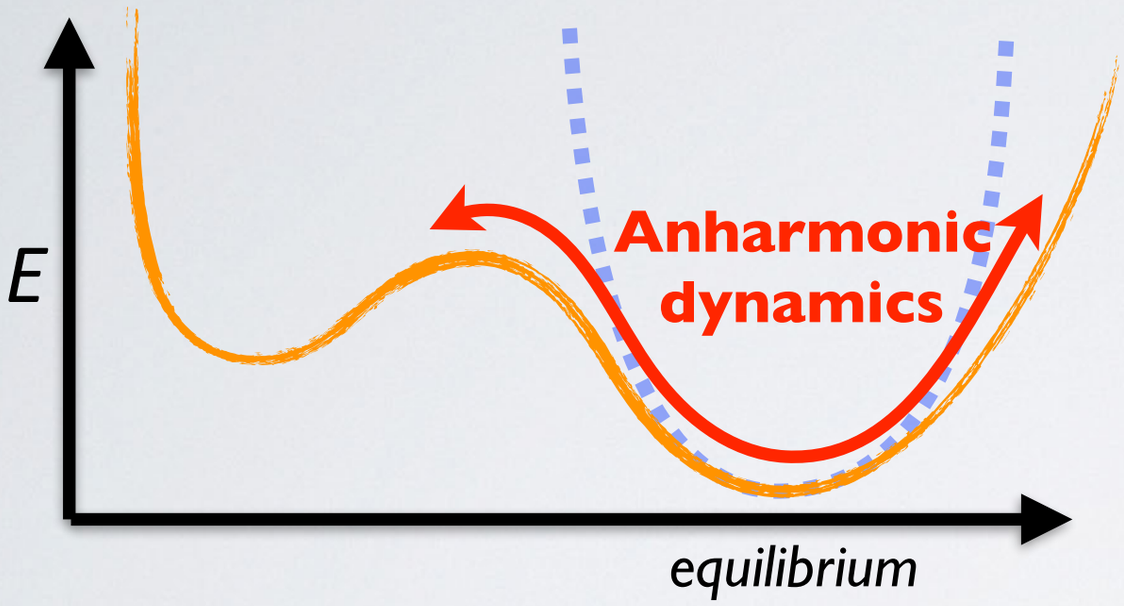
Anharmonicity

Electron-Phonon Coupling

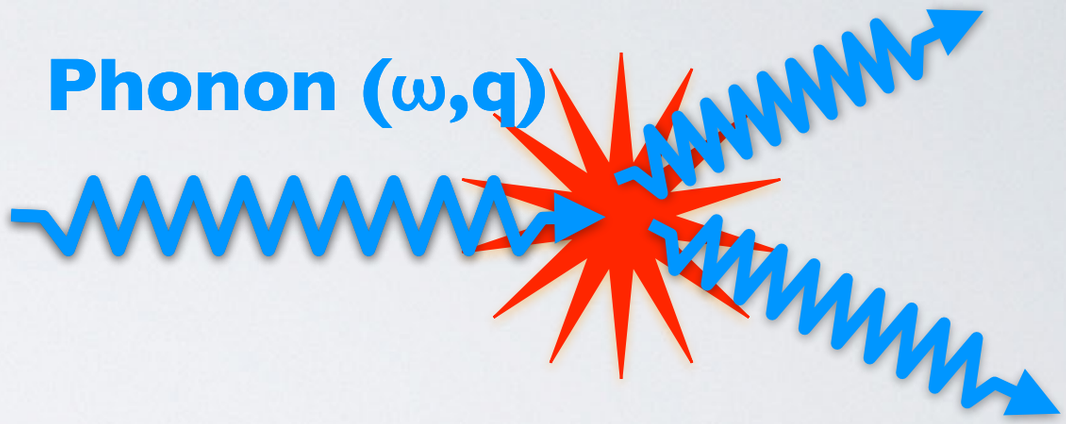
Phonon Scattering

Heat Transport Theory 101

Real Space Representation



Reciprocal Space Representation



Anharmonicity

Electron-Phonon Coupling

Phonon Scattering

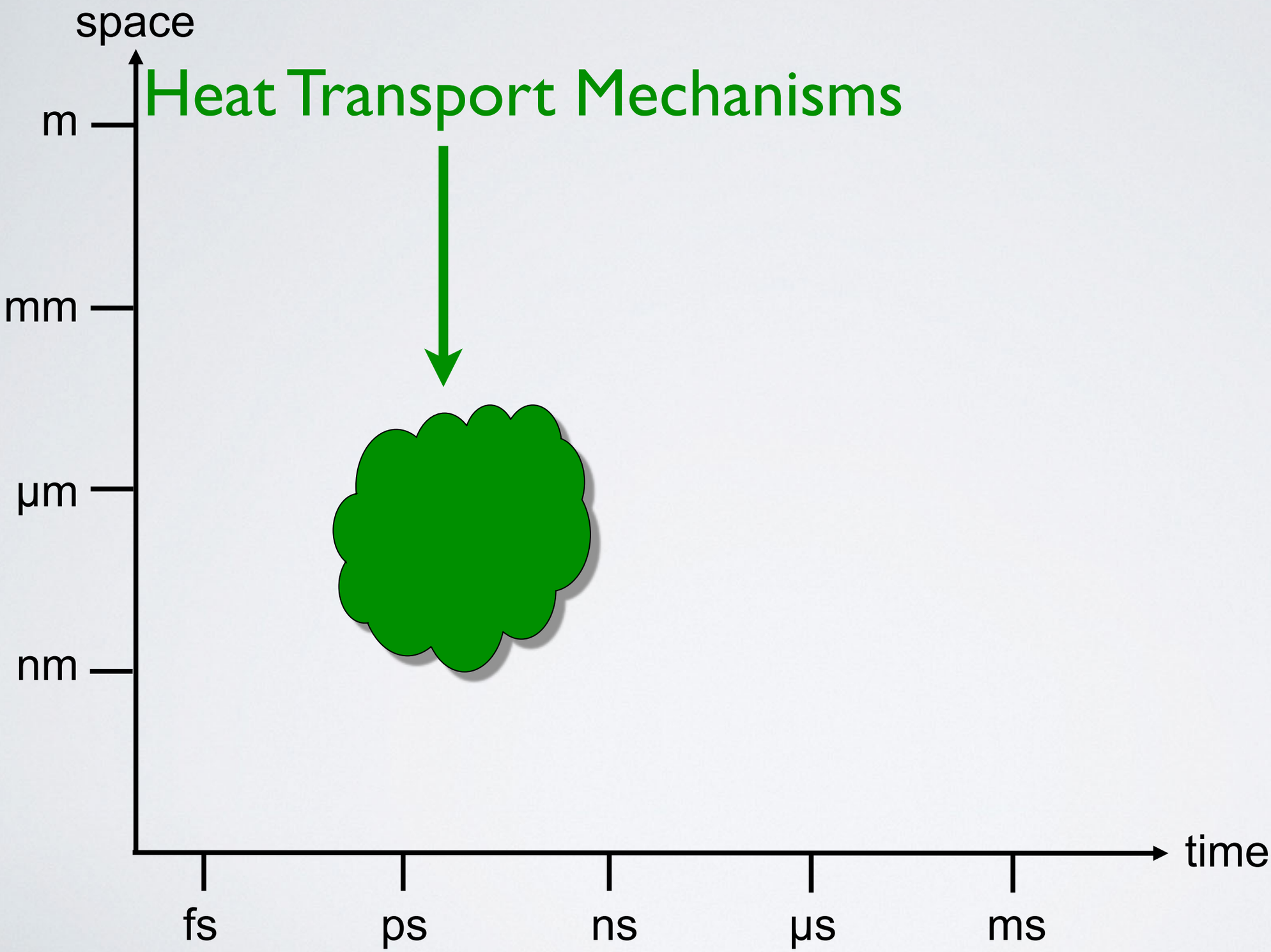
Theory Toolbox

Molecular Dynamics

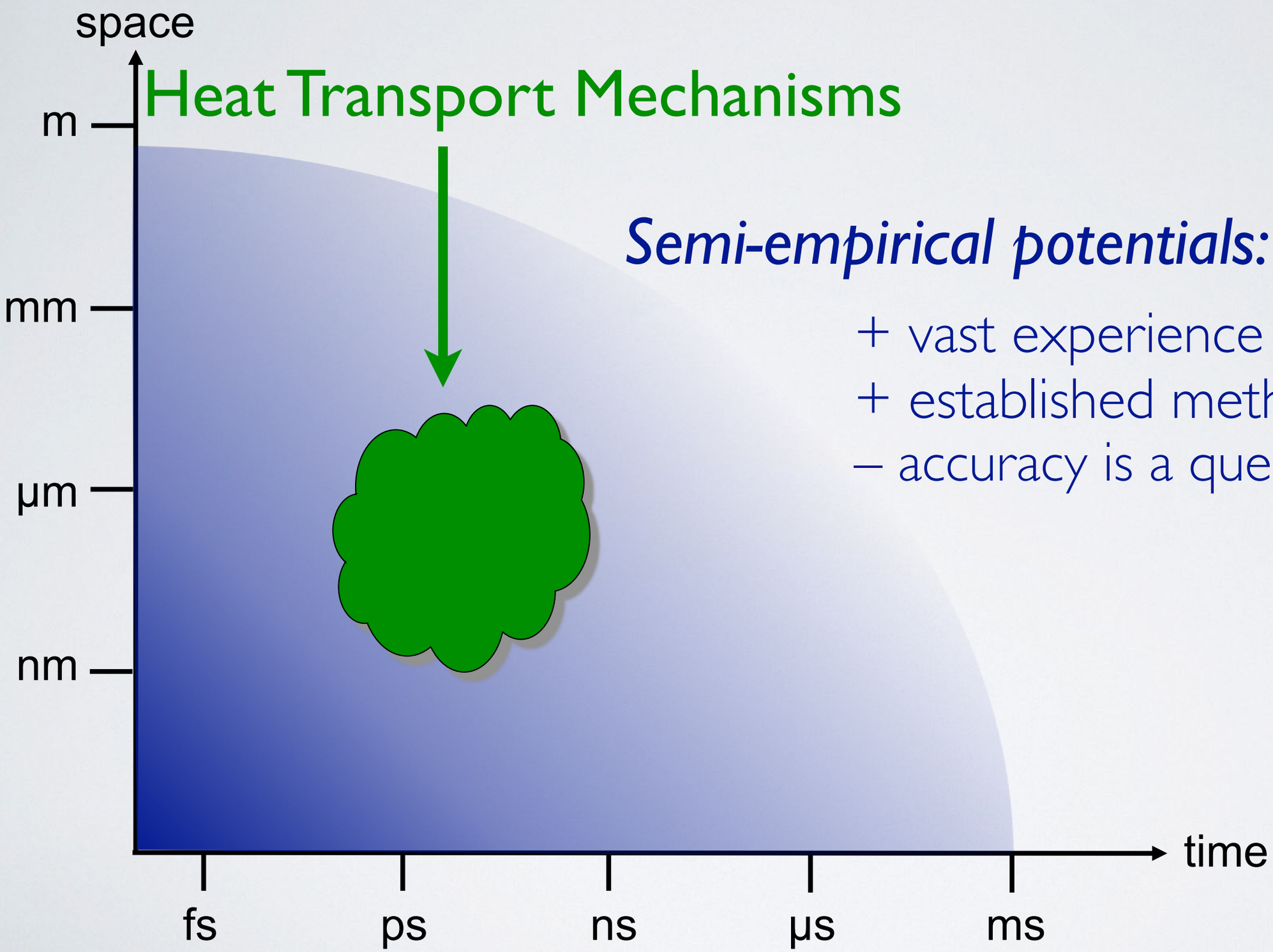
Electronic Structure Theory

Perturbation Theory

TIME AND LENGTH SCALES



TIME AND LENGTH SCALES



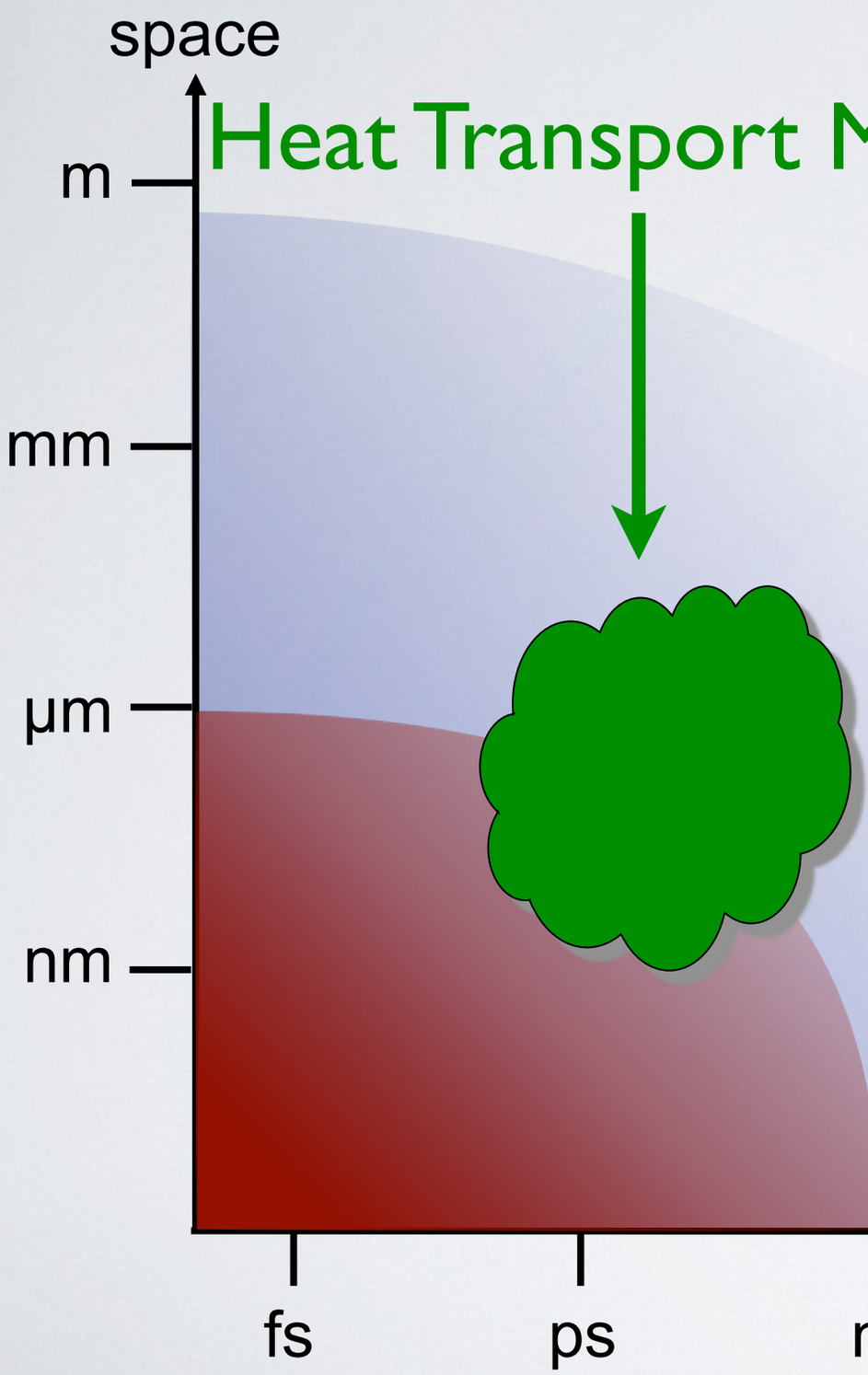
Semi-empirical potentials:

\+ vast experience

\+ established methodologies

– accuracy is a question

TIME AND LENGTH SCALES



Semi-empirical potentials:

\+ vast experience

\+ established methodologies

– accuracy is a question

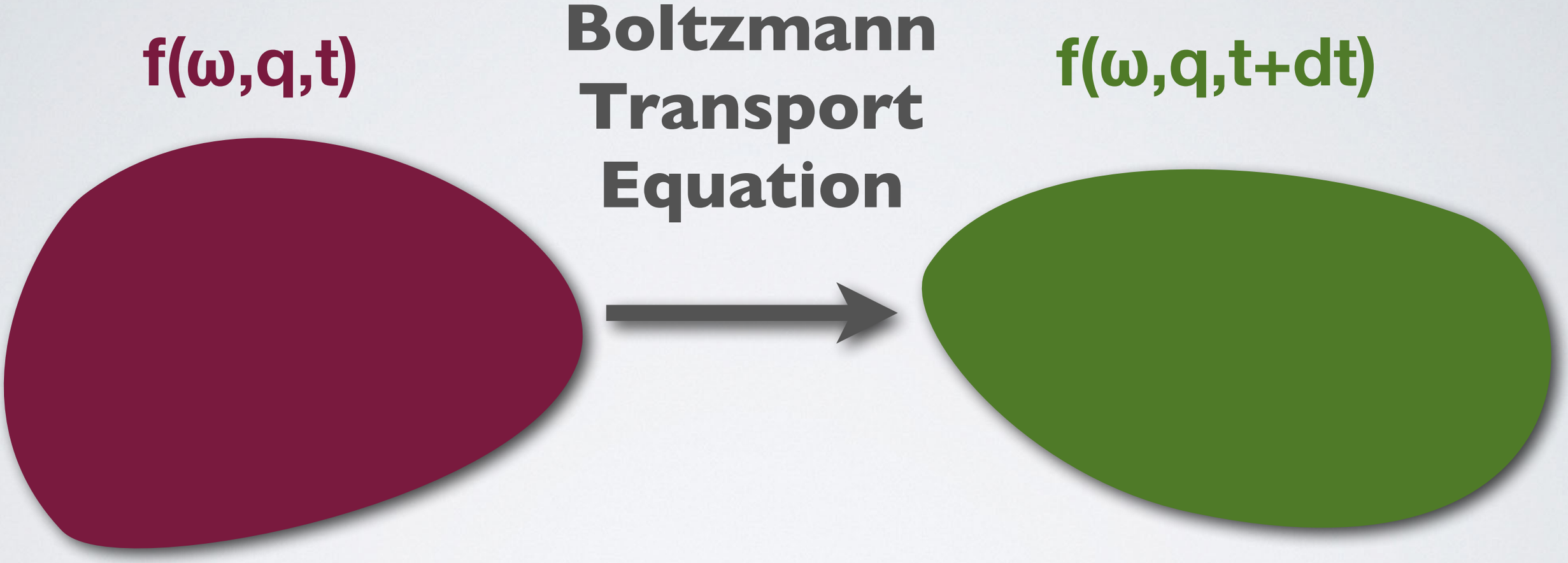
First-principles approaches:

\+ more accurate interactions

– limited time and length scales

BOLTZMANN TRANSPORT EQUATION

R. Peierls, *Ann. Phys.* **395**,1055 (1929).
D. A. Broido *et al.*, *Appl. Phys. Lett.* **91**, 231922 (2007).



Boltzmann-Peierls-Transport-Equation describes the evolution of the **phonon** phase space distribution **f(ω,q,t)**.

(A) BOLTZMANN TRANSPORT EQUATION

R. Peierls, *Ann. Phys.* **395**,1055 (1929).
D. A. Broido *et al.*, *Appl. Phys. Lett.* **91**, 231922 (2007).

Single-mode relaxation time approximation

$$\kappa \sim \sum_s v_s^2 \, \omega_s^2 \, n_s(n_s+1) \, \tau_s$$

Group velocity — **Frequency** — **Equilibrium population** — **phonon lifetime**

Harmonic phonon theory

?

Phonon Lifetimes from First Principles

- from **Density Functional Perturbation Theory**
  D. A. Broido *et al., Appl. Phys. Lett.* **91**, 231922 (2007).
  J. Garg *et al., Phys. Rev. Lett.* **106**, 045901 (2011).

- from **fitting** the **forces** in ***ab initio MD***
  K. Esfarjani, and H. T. Stokes, *Phys. Rev. B* **77**, 144112 (2008).

- from **fitting** the **phonon line width** determined via ***ab initio MD***
  N. De Koker, *Phys. Rev. Lett.* **103**, 125902 (2009).

All these approaches give very **accurate** results for **good thermal conductors** at **low** temperatures.

Results are **questionable** at high levels of **anharmonicity**!

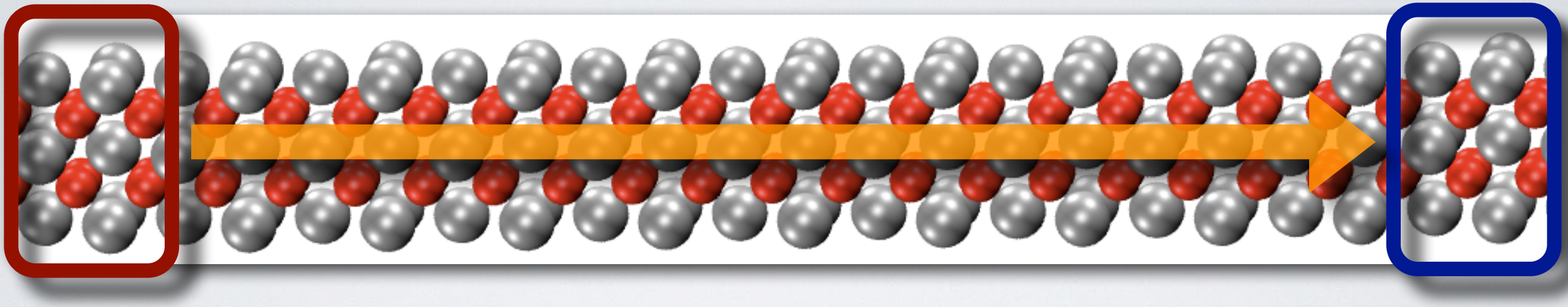
FIRST-PRINCIPLES APPROACHES

	Order of interaction	Validity & Applicability	Finite Size Effects	Disorder
Boltzmann-Transport Eq.	~$\mathcal{O}(r^3)$	low T	Minute	Parameter
Non-Equilib. MD				
Green-Kubo MD				

Boltzmann-Transport-Eq. gives **very accurate** results for **perfect crystals** at **low temperatures**.

NON-EQUILIBRIUM MD

S. Stackhouse, L. Stixrude, and B. B. Karki, *Phys. Rev. Lett.* **104**, 208501(2010).



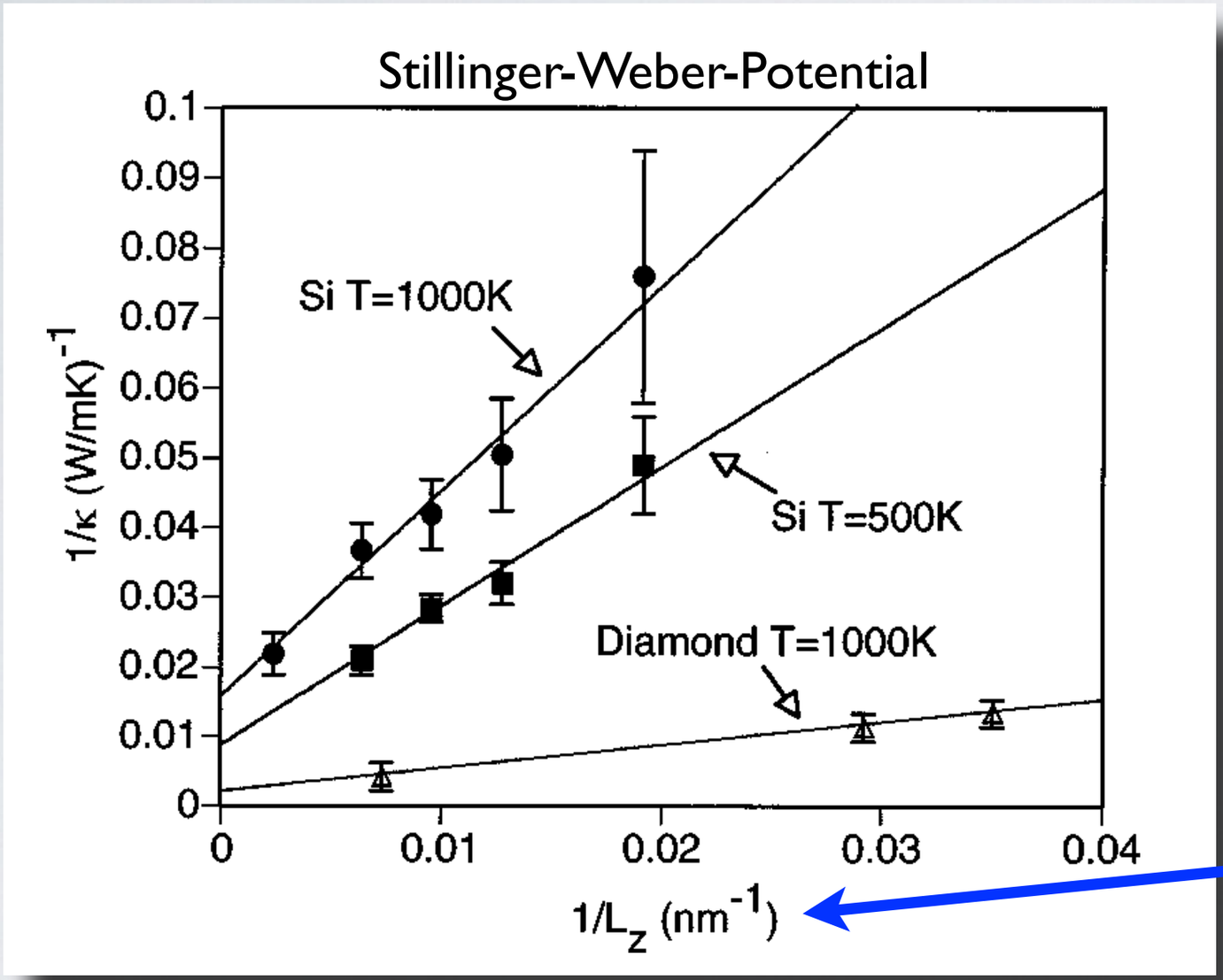
heat source → • Temperature gradient ∇T • Stationary heat flux **J** → **heat sink**

⇓

Thermal conductivity can be calculated by applying Fourier‘ s Law.

$$\mathbf{J} = -\kappa \nabla T$$

FINITE SIZE EFFECTS



Finite Size Corrections

$$\frac{1}{\kappa} \sim \left(\frac{1}{l_\infty} + \frac{4}{L_z} \right)$$

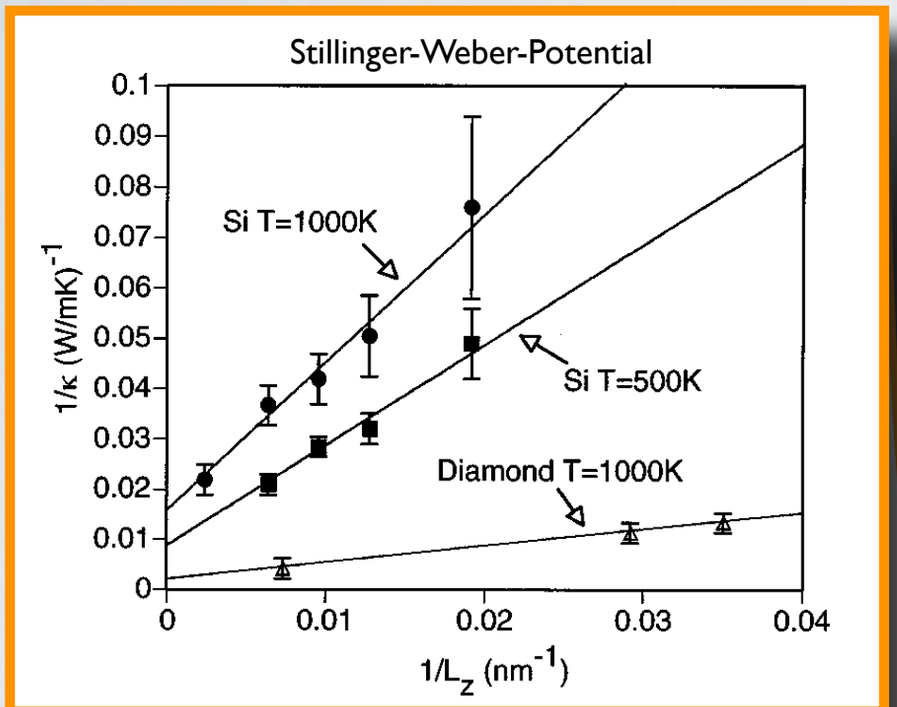
mean free path

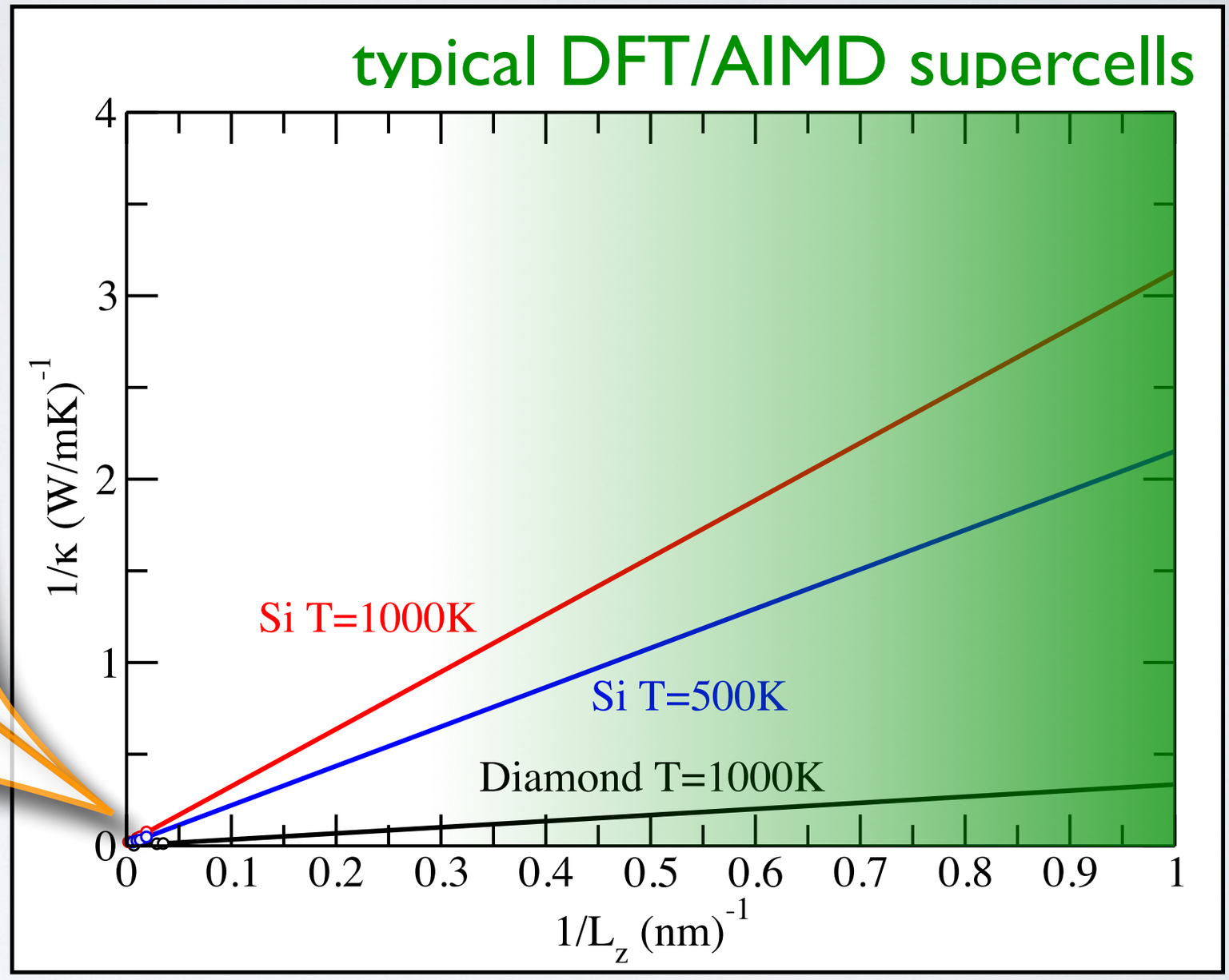
supercell length

P. Schelling, S. Phillpot, and P. Keblinski,
Phys. Rev. B **65**, 144306 (2002).

FINITE SIZE EFFECTS

P. Schelling, S. Phillpot, and P. Keblinski,
Phys. Rev. B **65**, 144306 (2002).

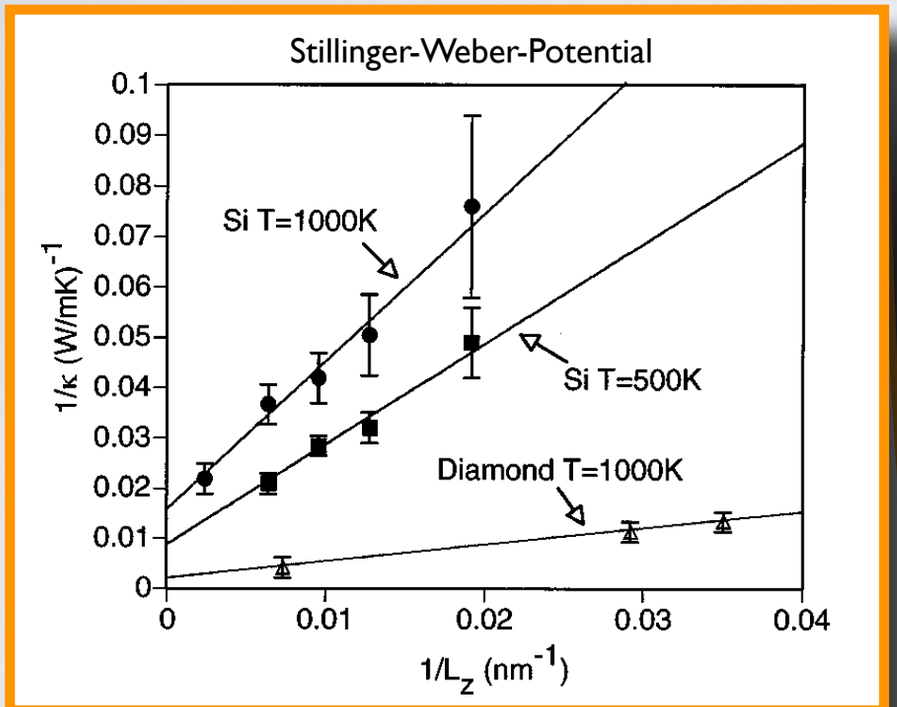


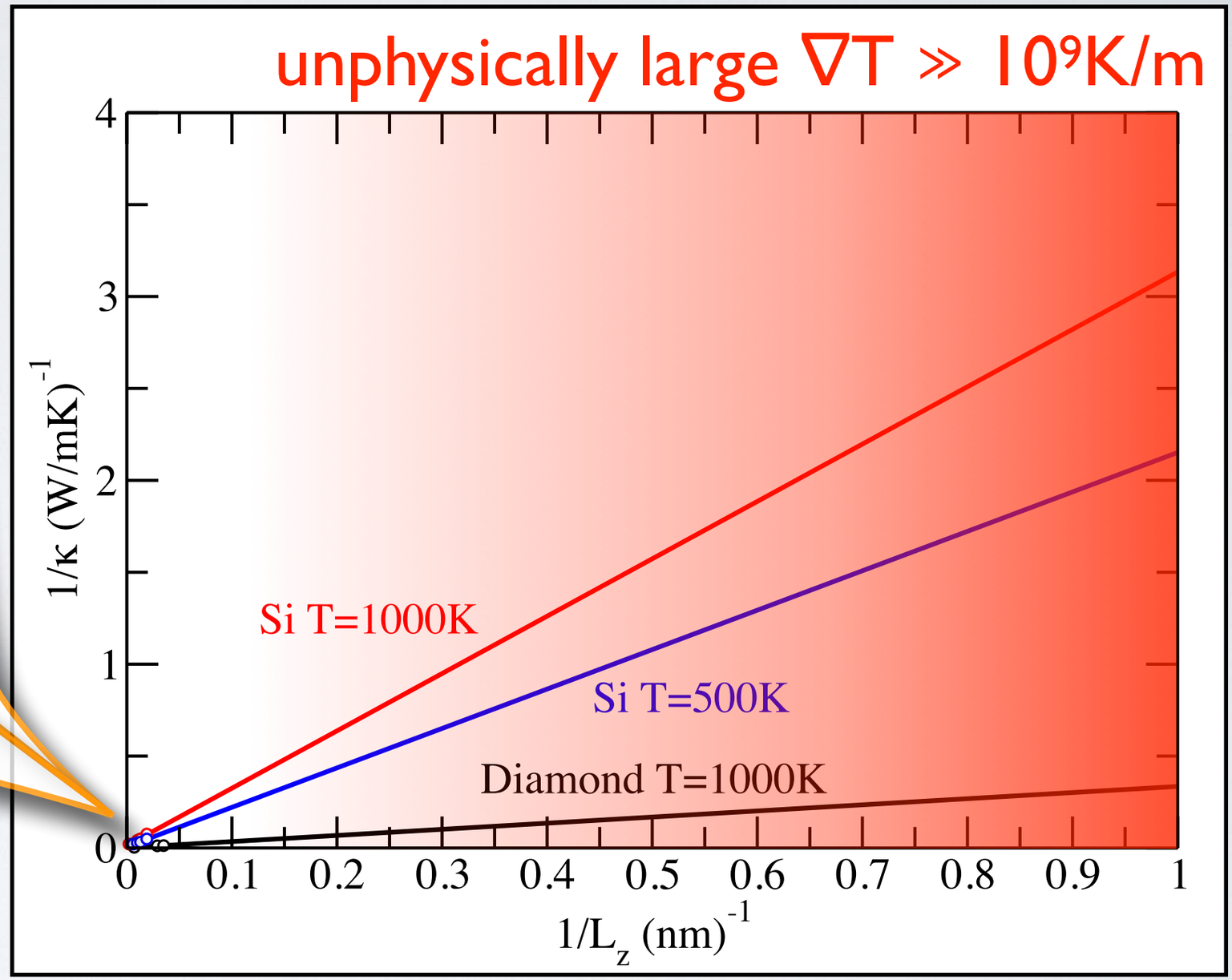


Non-equilibrium MD exhibits strong finite-size artifacts
in supercells typically accessible within DFT/AIMD.

FINITE SIZE EFFECTS

P. Schelling, S. Phillpot, and P. Keblinski,
Phys. Rev. B **65**, 144306 (2002).





Non-equilibrium MD can suffer from non-linear artifacts
in supercells typically accessible within DFT/AIMD.

FIRST-PRINCIPLES APPROACHES

	Order of interaction	Validity & Applicability	Finite Size Effects	Disorder
Boltzmann-Transport Eq.	~$\mathcal{O}(r^3)$	low T	Minute	Parameter
Non-Equilib. MD	Full	all T	Huge	as in supercell
Green-Kubo MD				

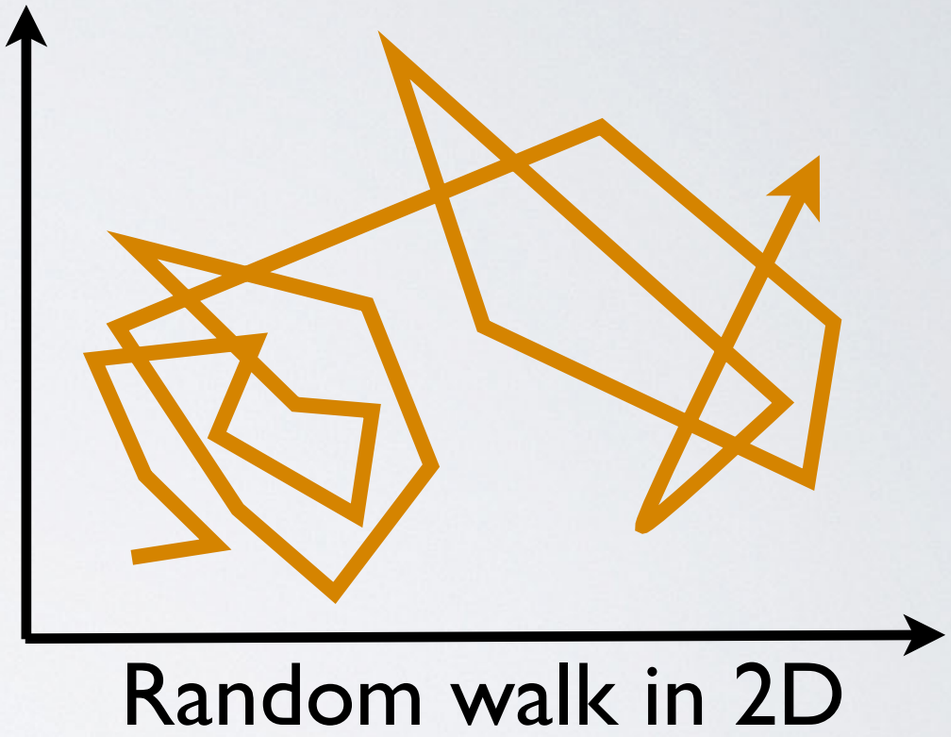
Non-Equilibrium MD approaches are **in principle exact**,
in **DFT** however **prohibitively costly** to converge **accurately**.

FLUCTUATION-DISSIPATION THEOREM

Brownian Motion:

A. Einstein, *Ann. Phys.* **322**, 549 (1905).

The erratic motion of the particles
is closely related to
frictional force under perturbation.



The **fluctuations of the forces** in thermodynamic **equilibrium** is related to the **generalized resistance** in **non-equilibrium** for linear dissipative systems.

H. B. Callen, and T. A. Welton, *Phys. Rev.* **83**, 34 (1951).

GREEN-KUBO METHOD

R. Kubo, M. Yokota, and S. Nakajima, *J. Phys. Soc. Japan* **12**, 1203 (1957).

Fluctuation-Dissipation Theorem

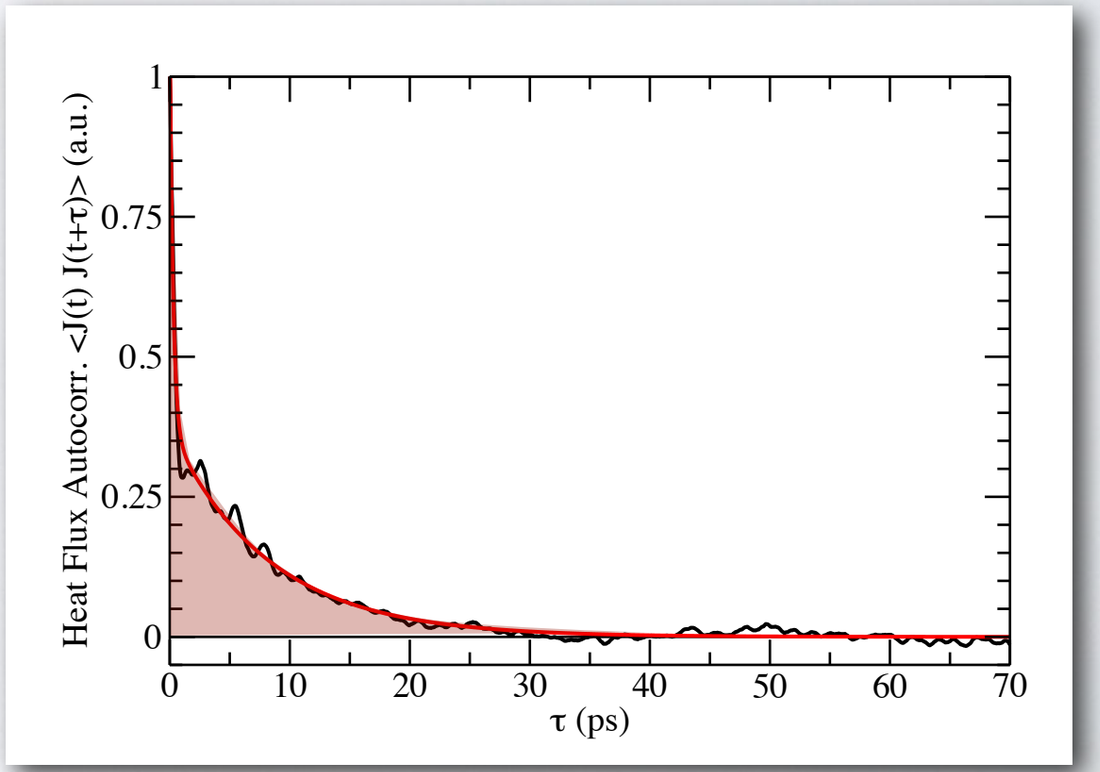
Simulations of the **thermodynamic equilibrium**

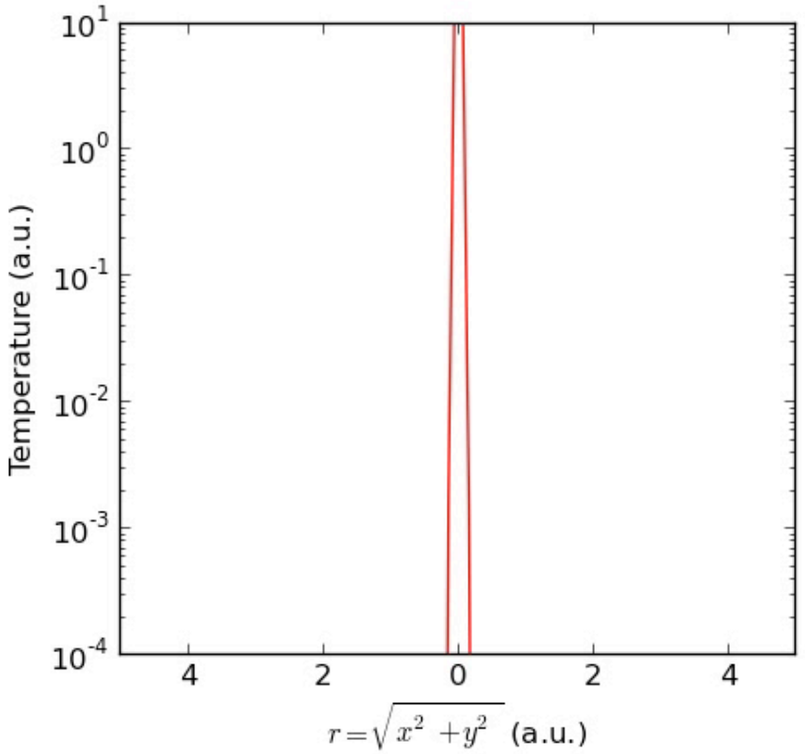
⇓ ⇓ ⇓

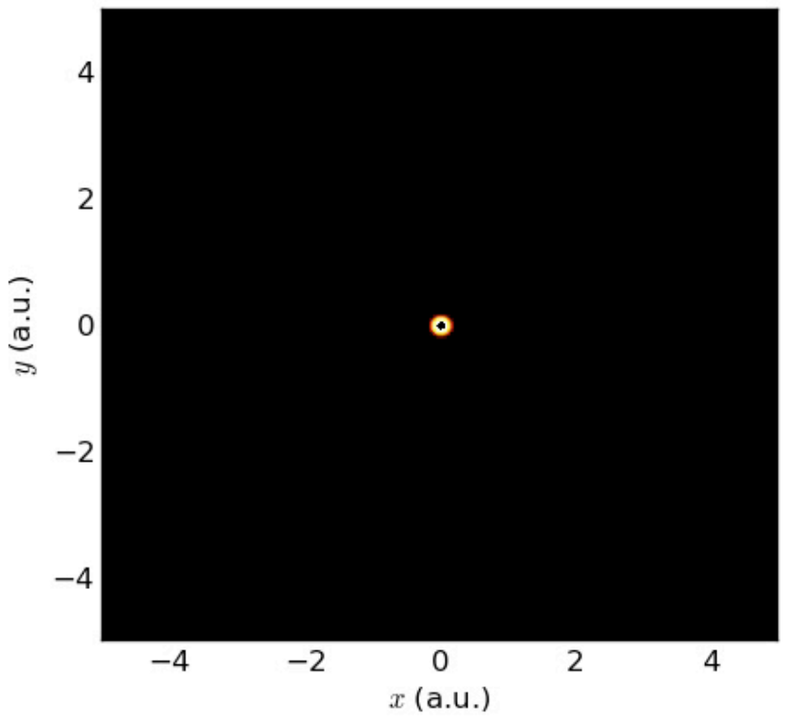
Information about **non-equilibrium processes**

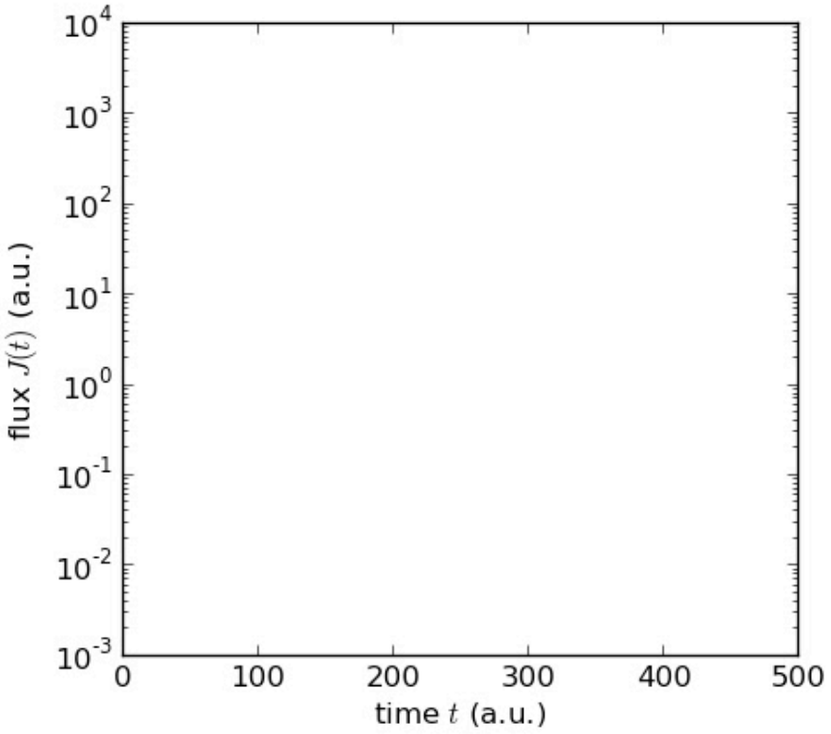
$$\kappa \sim \int_0^\infty d\tau \left\langle \mathbf{J}(0)\, \mathbf{J}(\tau) \right\rangle_{eq}$$

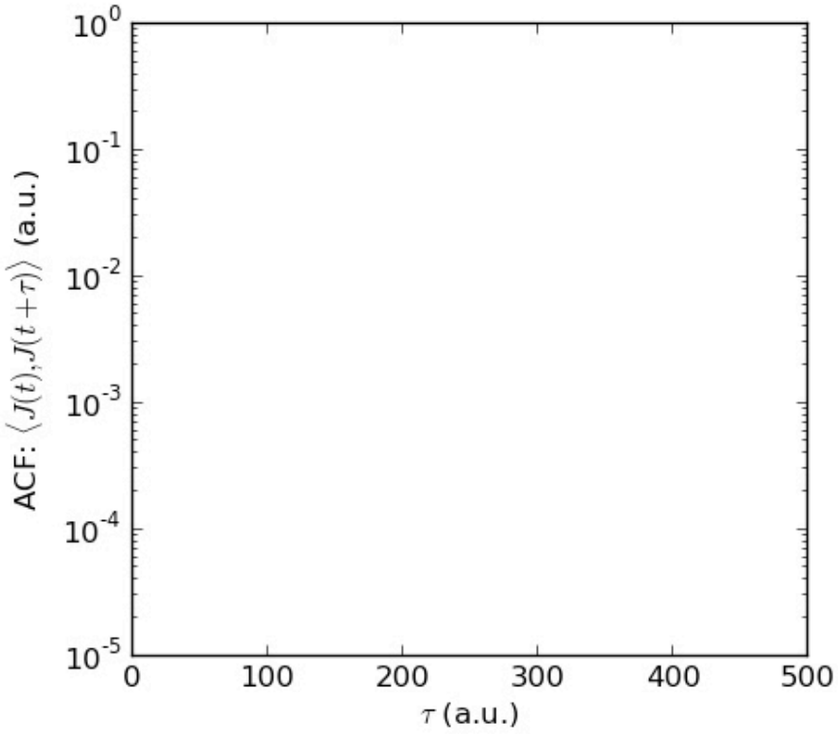
The **thermal conductivity** is related to the **autocorrelation function** of the **heat flux**



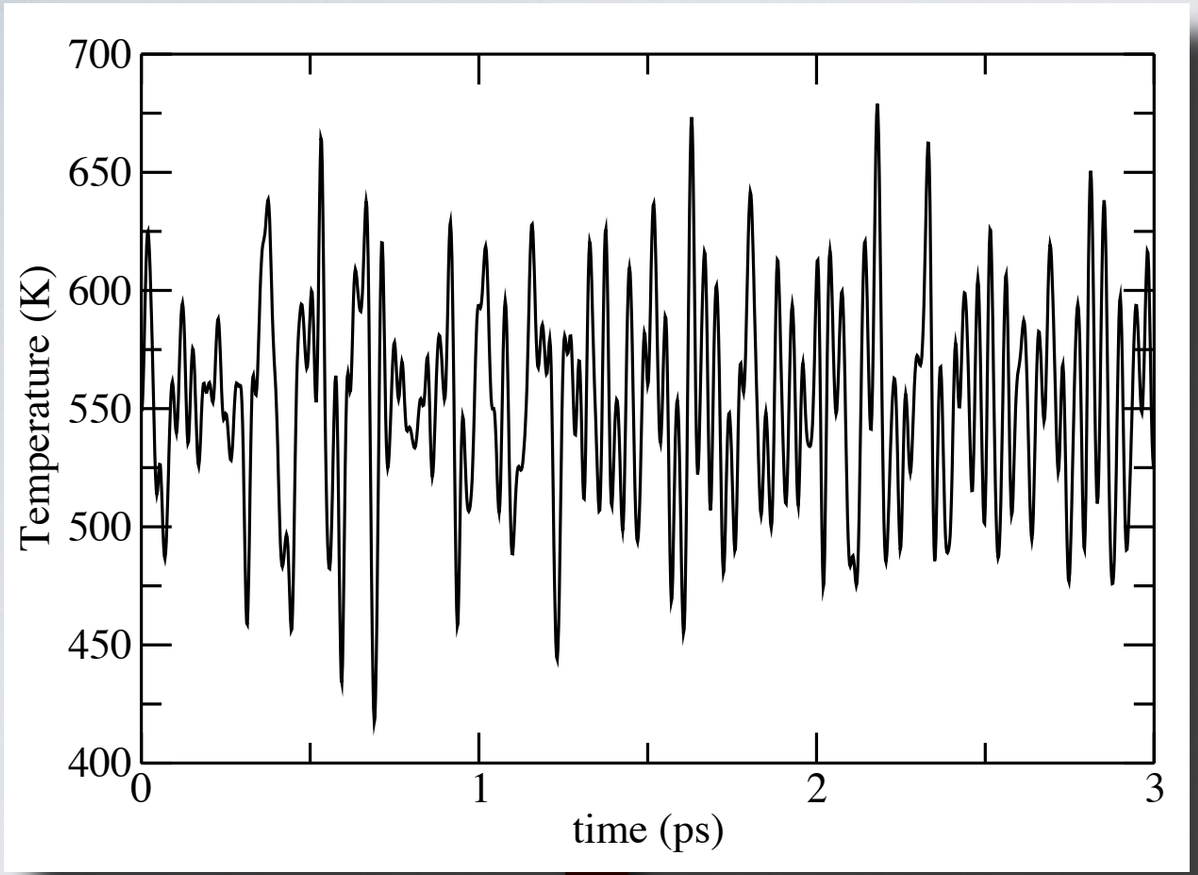


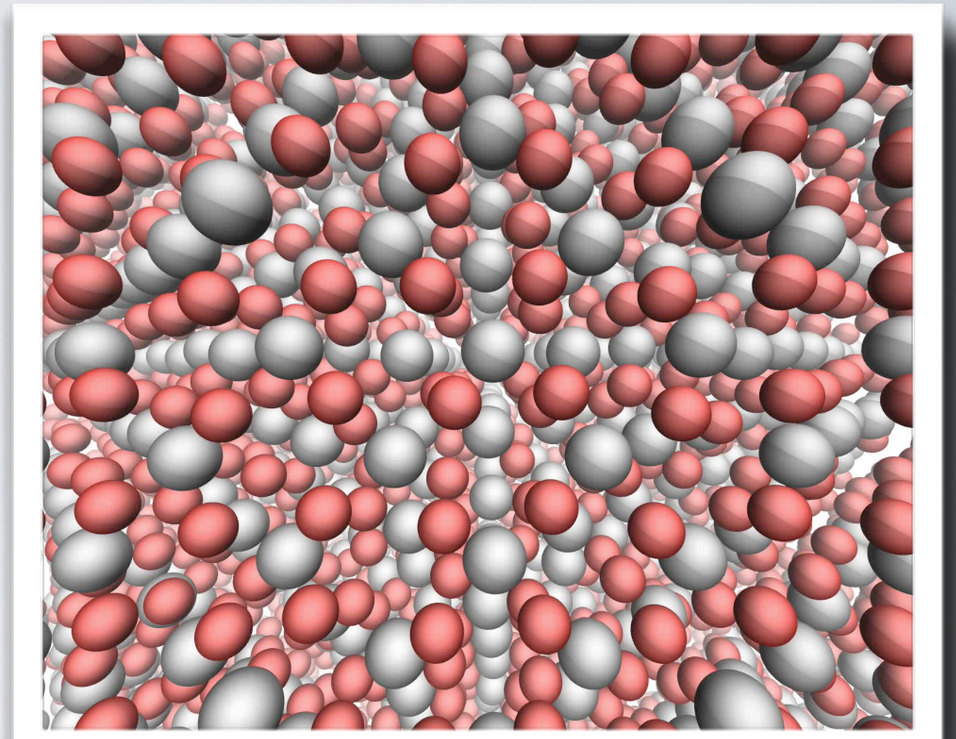


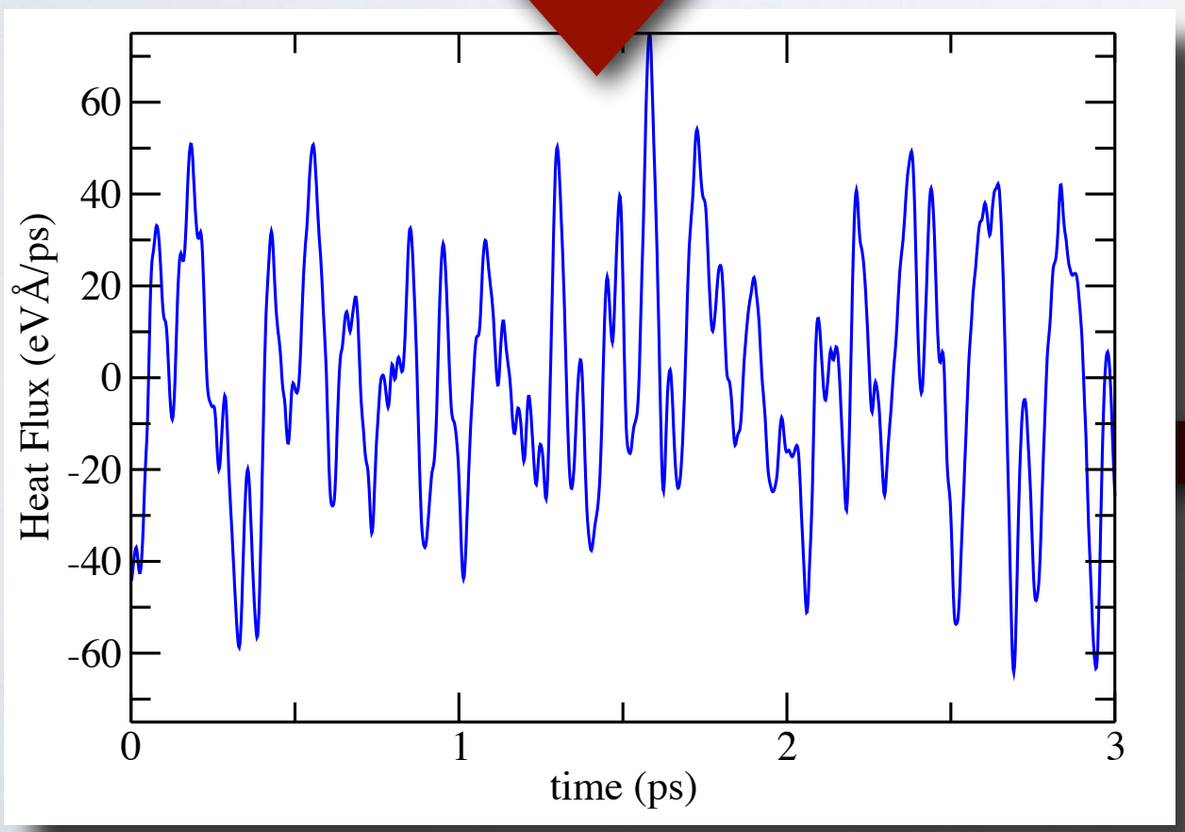


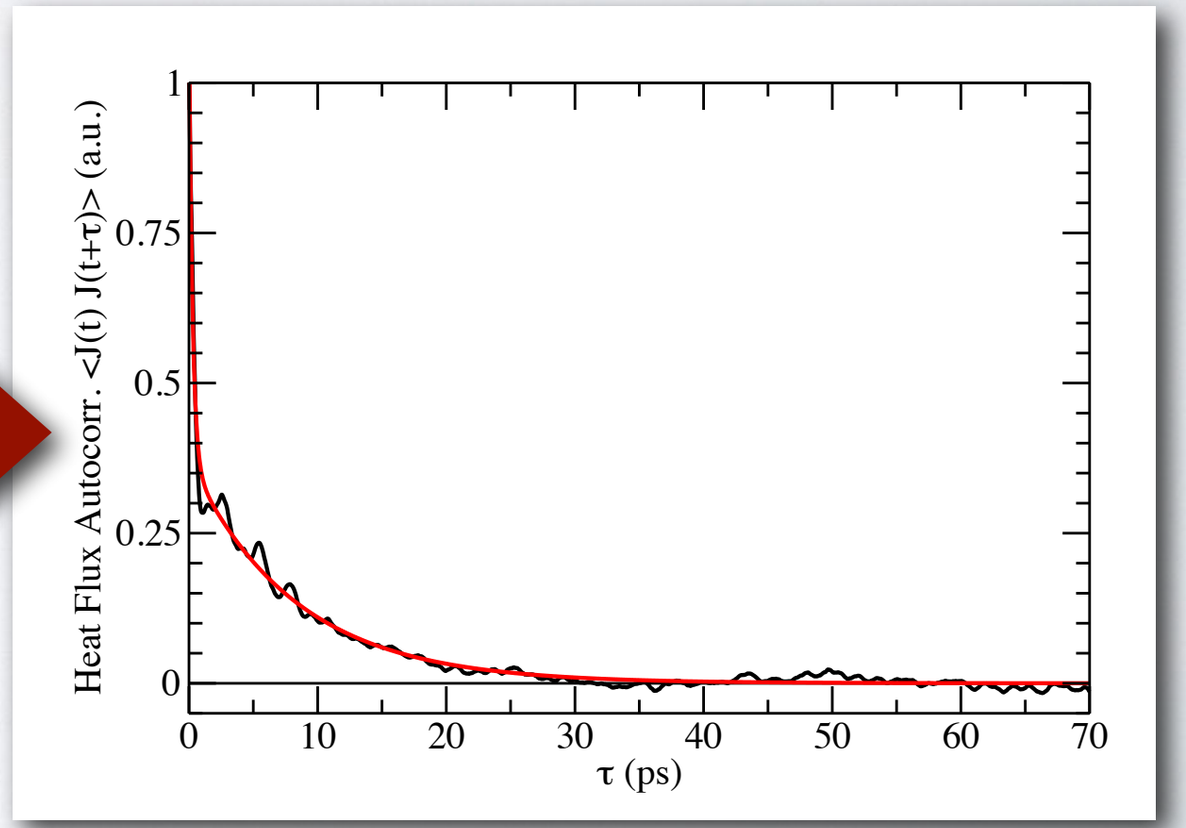


$$T(\mathbf{r}, t) = \frac{1}{(4\pi\kappa t)^{3/2}} \exp\left(-\frac{\mathbf{r}^2}{4\kappa t}\right) \quad \Rightarrow \quad \int \langle J(t), J(t+\tau) \rangle \, d\tau \quad \sim \kappa$$


700
650
600
550
500
450
400
Temperature (K)
0
1
2
3
time (ps)




60
40
20
0
-20
-40
-60
Heat Flux (eVÅ/ps)
0
1
2
3
time (ps)


1
0.75
0.5
0.25
0
Heat Flux Autocorr. <J(t) J(t+τ)> (a.u.)
0
10
20
30
40
50
60
70
τ (ps)

THE ATOMISTIC HEAT FLUX

E. Helfand, *Phys. Rev.* **119**, 1 (1960).

Continuity Equation:

$$\frac{\partial E(\mathbf{r})}{\partial t} + \nabla \cdot \mathbf{j}(\mathbf{r}) = 0 \qquad \mathbf{J}(t) = \int \mathbf{j}(\mathbf{r})\, \mathbf{dr}$$

Energy decomposition

$$E(\mathbf{r}) = \sum_I E_I \, \delta(\mathbf{r} - \mathbf{R}_I) \quad \Rrightarrow \quad \mathbf{J}(t) = \frac{d}{dt}\left(\sum_I \mathbf{R}_I E_I\right)$$

Heat flux

Correct heat flux definition requires a **decomposition** of the **energy**, which **is not unique** by definition.

THE ATOMISTIC HEAT FLUX

E. Helfand, *Phys. Rev.* **119**, 1 (1960).

Same problem in first-principles formulation:

$$E(\mathbf{r}) = \int \varepsilon(\mathbf{r}')\delta(\mathbf{r}-\mathbf{r}')\,d\mathbf{r}' \quad \Rightarrow\!\Rightarrow \quad \mathbf{J}(t) = \frac{d}{dt}\left(\int \mathbf{r}\,\varepsilon(\mathbf{r})\,d\mathbf{r}\right)$$

First-principles **energy densities**
are **not** gauge-independent.

N. Chetty and R. Martin, *Phys. Rev. B* **45**, 6074 (1992).
A. Marcolongo, P. Umari, and S. Baroni, *Nat. Phys.* **12**, 80 (2016).
L. Ercole, *et al.*, *J Low Temp Phys* **185**, 79 (2016).

decomposition of the energy,
which **is not unique** by definition.

THE VIRIAL HEAT FLUX

R. J. Hardy, *Phys. Rev.* **132**,168 (1963).

Helfands' Heat Flux ***Hardys' Heat Flux***

$$\mathbf{J}(t) = \frac{d}{dt}\left(\sum_I \mathbf{R}_I\, E_I\right) = \sum_I \mathbf{V}_I E_I + \sum_I \mathbf{R}_I \dot{E}_I$$

~~***Convective Heat Flux***~~

Liquids & Gases:

⇛ use **energy density**

A. Marcolongo, P. Umari, and S. Baroni, *Nat. Phys.* **12**, 80 (2016).

Virial Heat Flux:

- **Unique:**
  Does **not** depend on **partitioning**
- Describes **phonon** transports
- **Well-defined** for **classical** potentials
- **Well-defined**
  in ***first-principles*** **frameworks**

DEFINING THE VIRIAL HEAT FLUX

R. J. Hardy, *Phys. Rev.* **132**,168 (1963).

kinetic + potential energy

$$E_I = T_I + U_I \quad \Rrightarrow$$

kinetic energy

potential energy

$$\dot{E}_I = \mathbf{F}_I \cdot \dot{\mathbf{R}}_I + \sum_J (\nabla_{\mathbf{R}_J} U_I) \cdot \dot{\mathbf{R}}_J$$

$$\mathbf{J}(t) = \sum_I \mathbf{R}_I \dot{E}_I$$

$$\mathbf{J}(t) = \frac{1}{V}\left(\sum_I \mathbf{R}_I(\mathbf{F}_I \cdot \dot{\mathbf{R}}_I) + \sum_{I,J} \mathbf{R}_I\,(\nabla_{\mathbf{R}_J} U_I) \cdot \dot{\mathbf{R}}_J)\right)$$

$$= \frac{1}{V}\sum_{I,J}(\mathbf{R}_J - \mathbf{R}_I)(\nabla_{\mathbf{R}_J} U_I) : \dot{\mathbf{R}}_I \quad ???$$

$\Rrightarrow$ Heat flux does **not** depend on **absolute** positions.

WHAT ABOUT FIRST-PRINCIPLES?

C. Carbogno, R. Ramprasad, and M. Scheffler, *Phys. Rev. Lett.* **118**, 175901 (2017).

$$\mathbf{J}(t) = \sum_I \mathbf{R}_I \dot{E}_I$$

$$\Downarrow$$

This is the *virial* of atom *I*, i.e., its contribution to the *internal stress* $\boldsymbol{\sigma}_I$ of the system.

Kinetic energy of the **nuclei**

Nuclear Coulomb repulsion

Nuclear-Electronic Coulomb attraction

$$\mathbf{J}(t) = \frac{1}{V}\sum_I Z_I \left(\sum_J Z_J \frac{(\mathbf{R}_I - \mathbf{R}_J)(\mathbf{R}_I - \mathbf{R}_J)}{|\mathbf{R}_I - \mathbf{R}_J|^3} - \int n(\mathbf{r}) \frac{(\mathbf{r} - \mathbf{R}_I)(\mathbf{r} - \mathbf{R}_I)}{|\mathbf{r} - \mathbf{R}_I|^3} d\mathbf{r} \right) \cdot \dot{\mathbf{R}}_I$$

$\Rightarrow$ **Unique** and **well-defined!**

ALL-ELECTRON FORMALISM FOR TOTAL ENERGY STRAIN DERIVATIVES

F. Knuth, C. Carbogno, V. Atalla, V. Blum, and M. Scheffler, *Comp. Phys. Comm.* **190**, 33 (2015).

Formulas for analytical stress

$$\sigma_{ij} = \sigma_{ij}^{\mathrm{HF}} + \sigma_{ij}^{\mathrm{MP}} + \sigma_{ij}^{\mathrm{Pulay}} + \sigma_{ij}^{\mathrm{kin}} + \sigma_{ij}^{\mathrm{Jac}}.$$

$$\sigma_{ij}^{\mathrm{HF}} = \frac{1}{2V} \sum_{\alpha,\beta\neq\alpha} \frac{\partial v_{\beta}^{\mathrm{es,tot}}(|\mathbf{R}_\alpha - \mathbf{R}_\beta|)}{\partial R_i^\alpha} (\mathbf{R}_\alpha - \mathbf{R}_\beta)_j$$

$$\sigma_{ij}^{\mathrm{MP}} = \frac{1}{V} \sum_{\alpha} \int_{\mathrm{UC}} \mathrm{d}\mathbf{r} \left[n(\mathbf{r}) - \frac{1}{2} n_{\mathrm{MP}}(\mathbf{r}) \right] \frac{\partial v_{\alpha}^{\mathrm{es,tot}}(|\mathbf{r} - \mathbf{R}_\alpha|)}{\partial r_i} (\mathbf{r} - \mathbf{R}_\alpha)_j$$

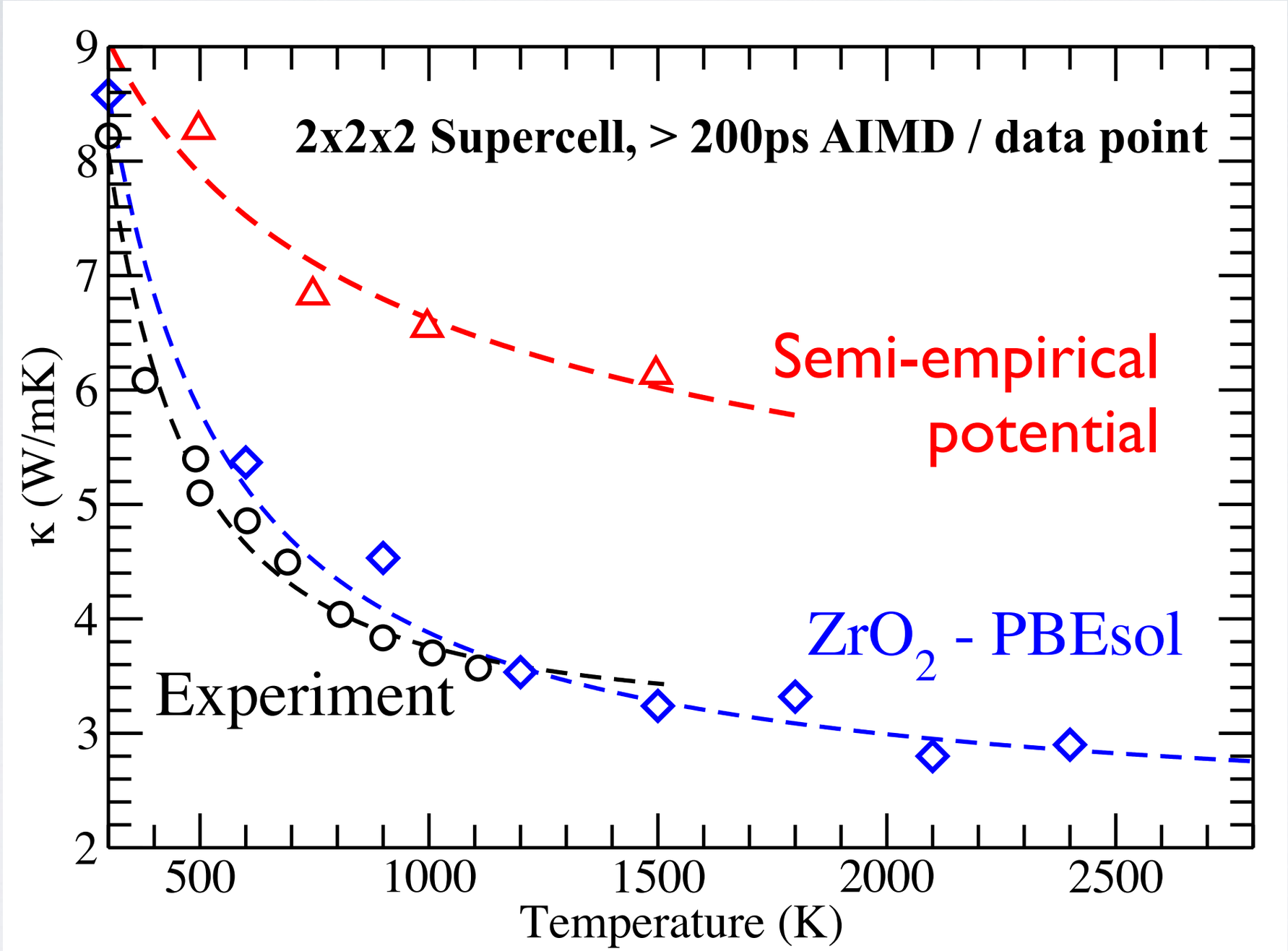
$$- \frac{1}{2V} \sum_{\alpha} \int_{\mathrm{UC}} \mathrm{d}\mathbf{r} \frac{\partial n_{\alpha}^{\mathrm{MP}}(\mathbf{r} - \mathbf{R}_\alpha)}{\partial r_i} (\mathbf{r} - \mathbf{R}_\alpha)_j v_{\mathrm{es,tot}}(\mathbf{r})$$

$$\sigma_{ij}^{\mathrm{Pulay}} = \frac{2}{V} \sum_{k} \sum_{\alpha, l(\alpha)} \sum_{\beta, m(\beta)} f_k c_{kl} c_{km} \int_{\mathrm{UC}} \mathrm{d}\mathbf{r} \frac{\partial \varphi_l(\mathbf{r} - \mathbf{R}_\alpha)}{\partial r_i} (\mathbf{r} - \mathbf{R}_\alpha)_j \left[\hat{h}_{\mathrm{KS}} - \varepsilon_k \right] \varphi_m(\mathbf{r} - \mathbf{R}_\beta)$$

$$\sigma_{ij}^{\mathrm{kin}} = \frac{1}{V} \sum_{k} \sum_{\alpha, l(\alpha)} \sum_{\beta, m(\beta)} f_k c_{kl} c_{km} \int_{\mathrm{UC}} \mathrm{d}\mathbf{r}\, \varphi_l(\mathbf{r} - \mathbf{R}_\alpha)(\mathbf{r} - \mathbf{R}_\alpha)_j \left[\frac{\partial}{\partial r_i} \frac{\partial}{\partial r_j} \varphi_m(\mathbf{r} - \mathbf{R}_\beta) \right]$$

$$\sigma_{ij}^{\mathrm{Jac}} = \frac{1}{V} \delta_{ij} \left[E_{\mathrm{xc}}[n] - \int \mathrm{d}\mathbf{r}\, n(\mathbf{r}) v_{\mathrm{xc}}(\mathbf{r}) - \frac{1}{2} \int \mathrm{d}\mathbf{r}\, n_{\mathrm{MP}}(\mathbf{r}) v_{\mathrm{es,tot}}(\mathbf{r}) \right]$$

APPLICATION TO ZIRCONIA



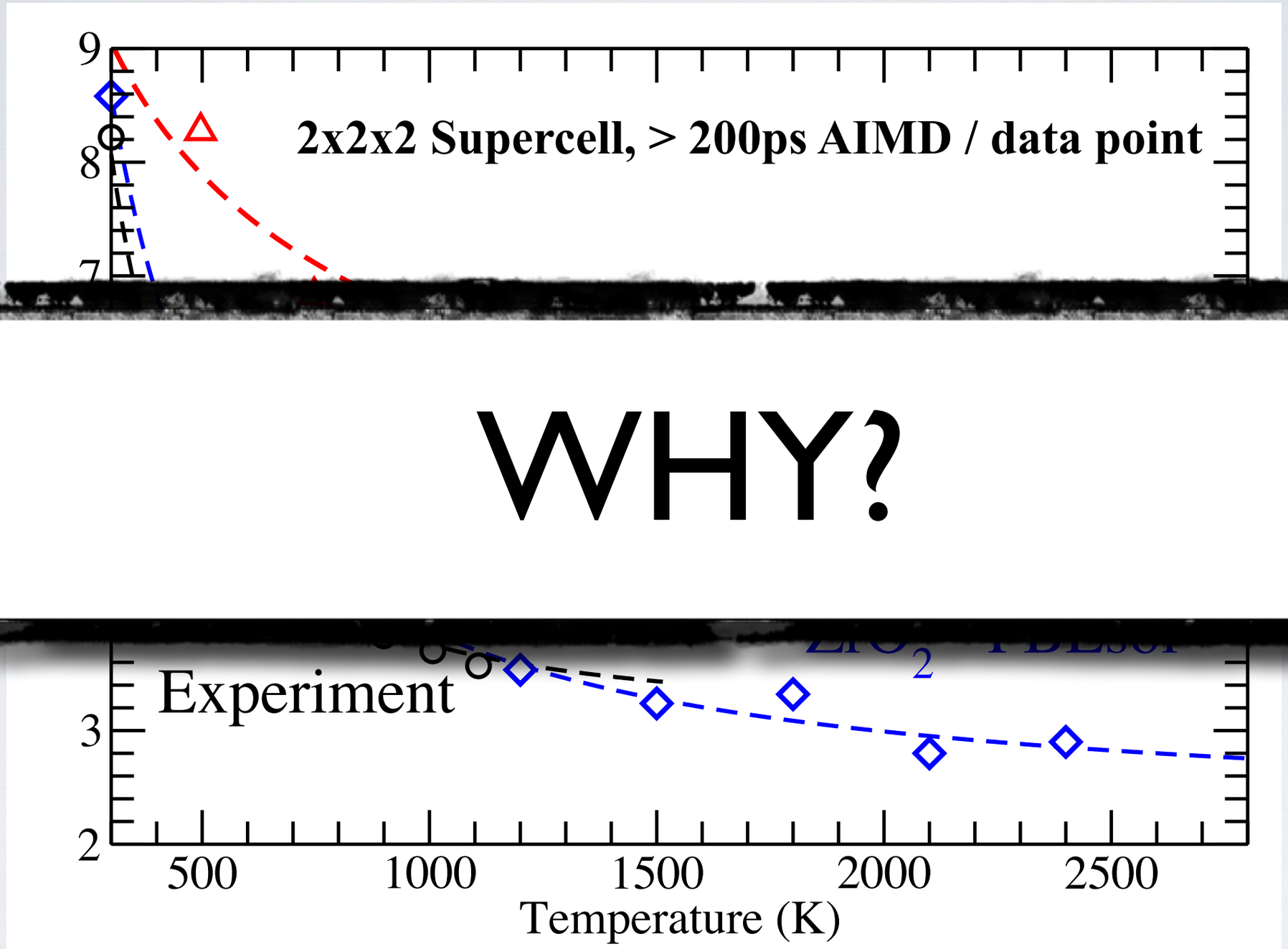
Experiment:

J.-F. Bisson *et al.*, *J. Am. Cer. Soc.* **83**, 1993 (2000).
G. E. Youngblood *et al.*, *J. Am. Cer. Soc.* **71**, 255 (1988).
S. Raghavan *et al.*, *Scripta Materialia* **39,** 1119 (1998).

Semi-empirical MD:

P. K. Schelling, and S. R. Phillpot,
J. Am. Cer. Soc. **84**, 2997 (2001).

APPLICATION TO ZIRCONIA



WHY?

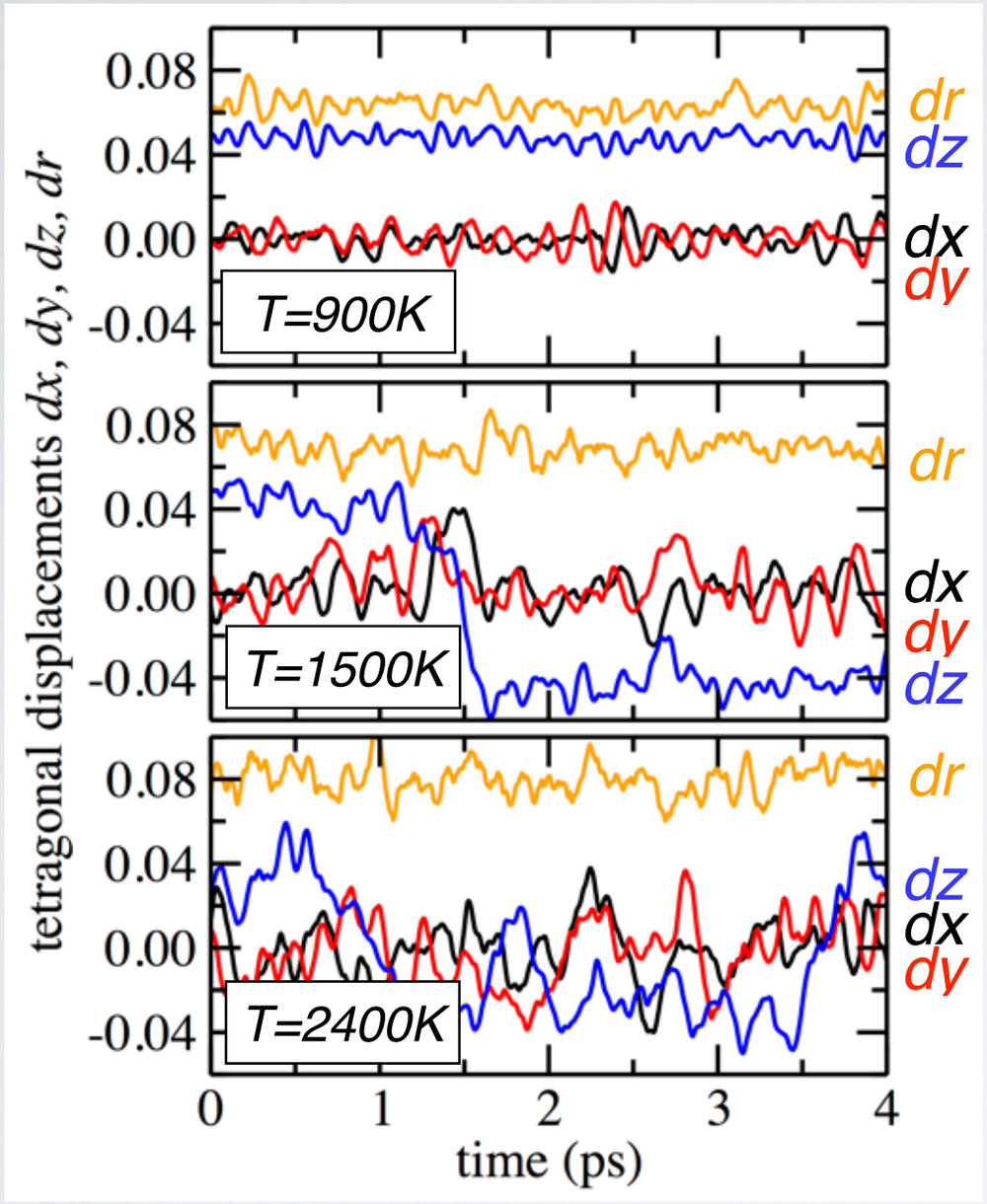
Experiment:

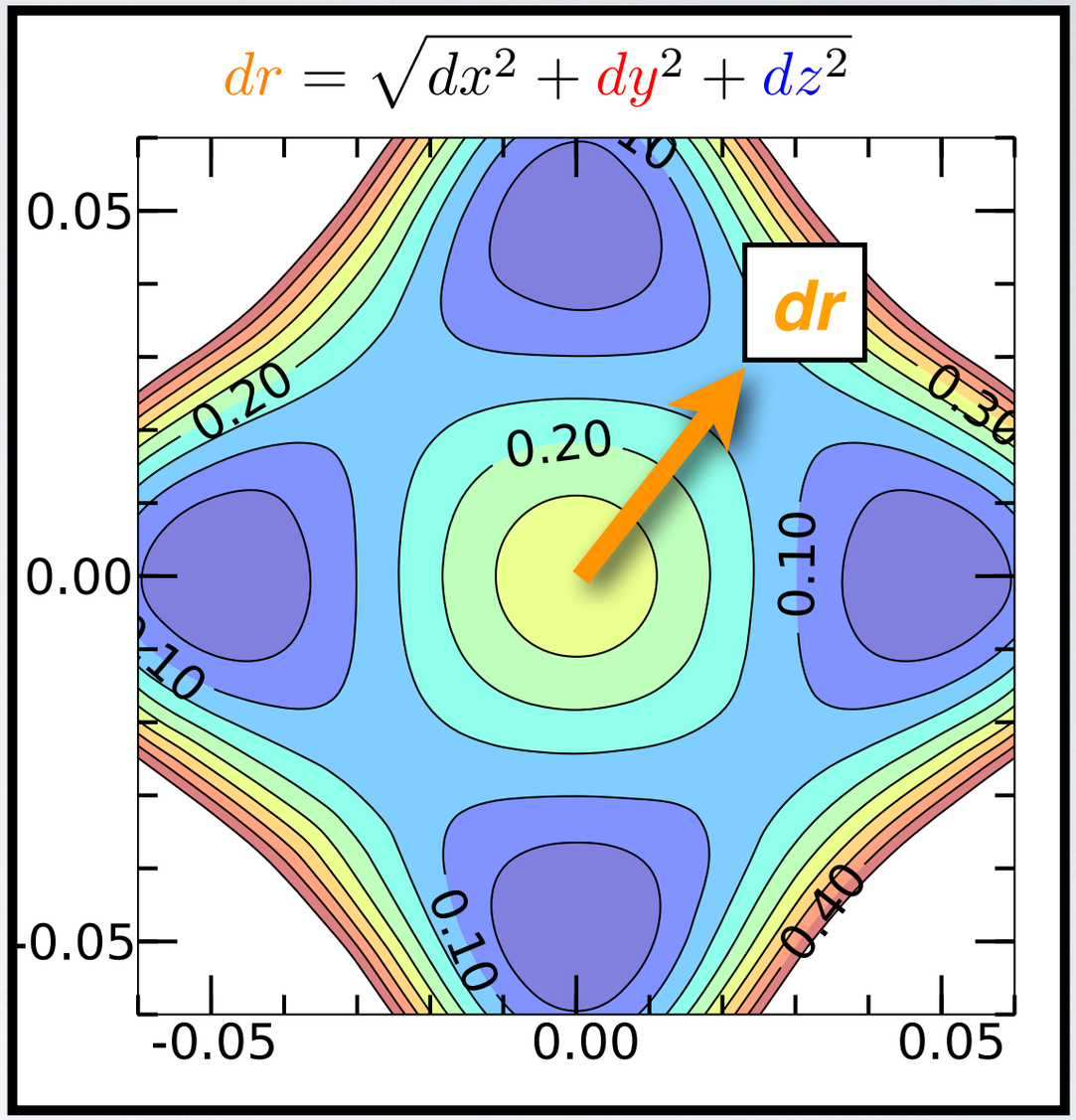
J.-F. Bisson *et al.*, *J. Am. Cer. Soc.* **83**, 1993 (2000).
G. E. Youngblood *et al.*, *J. Am. Cer. Soc.* **71**, 255 (1988).
S. Raghavan *et al.*, *Scripta Materialia* **39,** 1119 (1998).

Semi-empirical MD:

P. K. Schelling, and S. R. Phillpot,
J. Am. Cer. Soc. **84**, 2997 (2001).

Ab initio MD Evidence

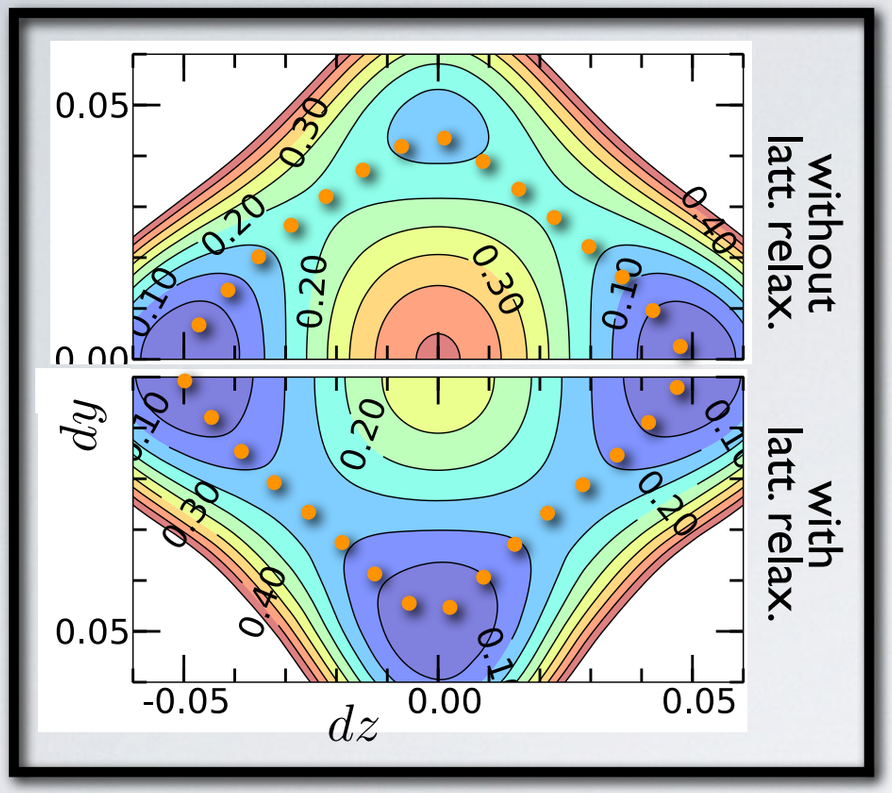




Distance ***dr*** finite at **all** temperatures!

⇒**Switches** are an **intrinsic feature** of the dynamics.

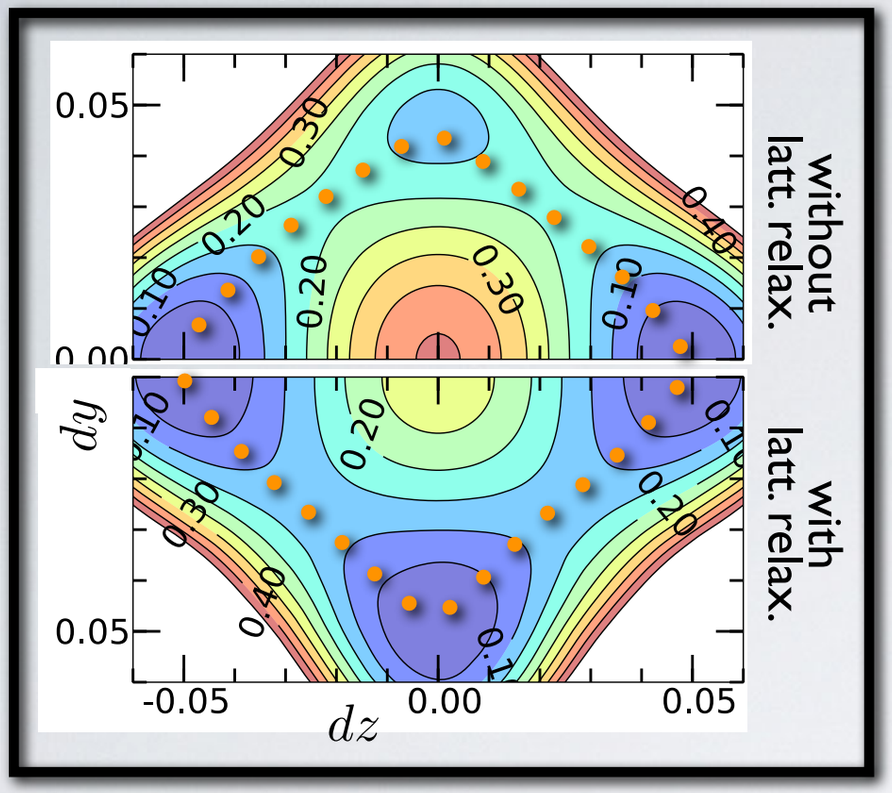
pristine ZrO_2



$E_{barrier}$

140 / 70 meV

pristine ZrO_2

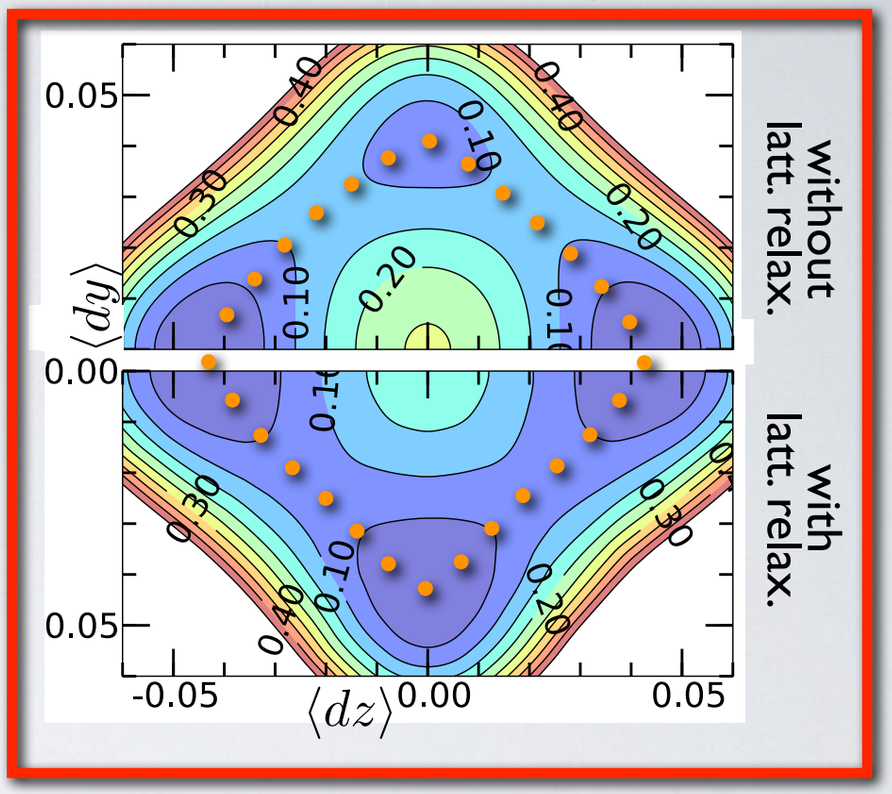


$E_{barrier}$

140 / 70 meV

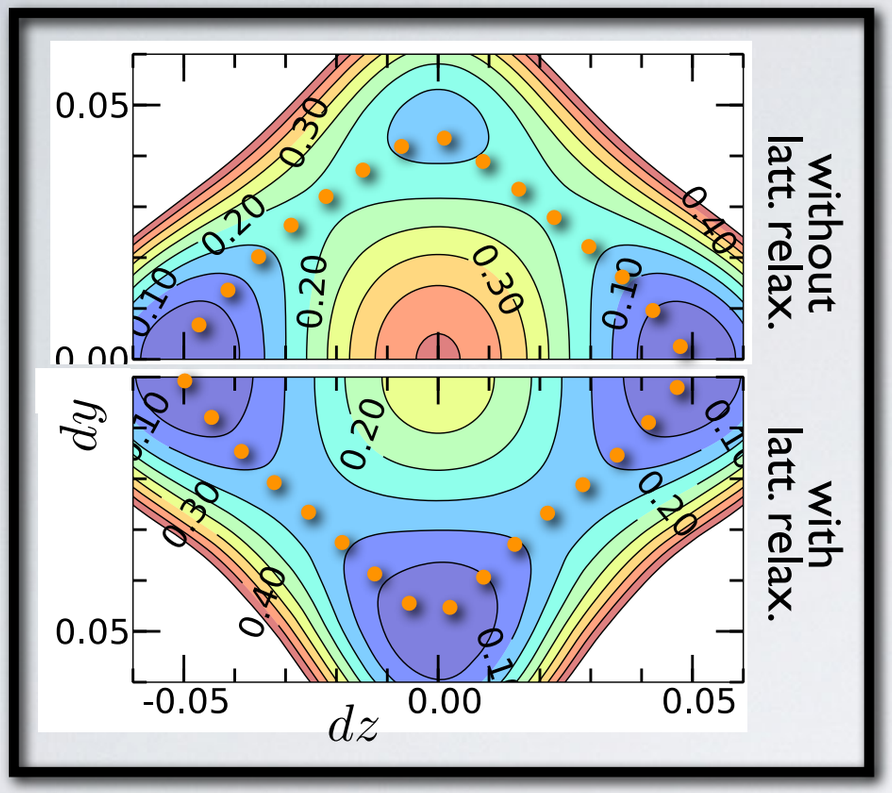
80 / 40 meV

6.25 mol-% $ZrO_{1.5}$ doped ZrO_2



Vacancies **reduce** the barrier
but **retain** the topology!

pristine ZrO_2



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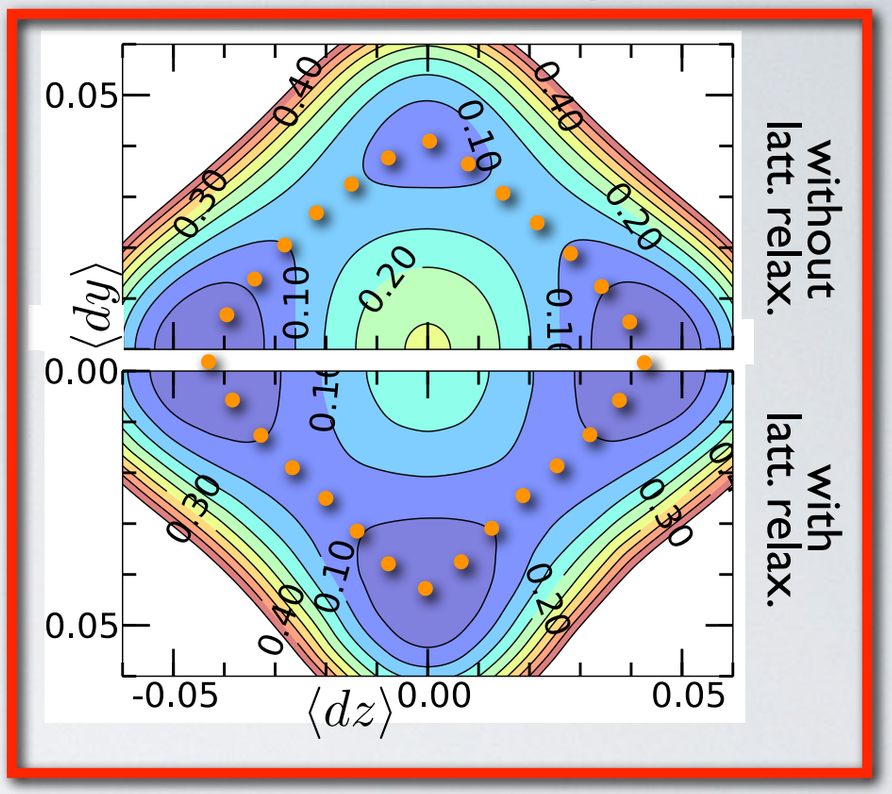
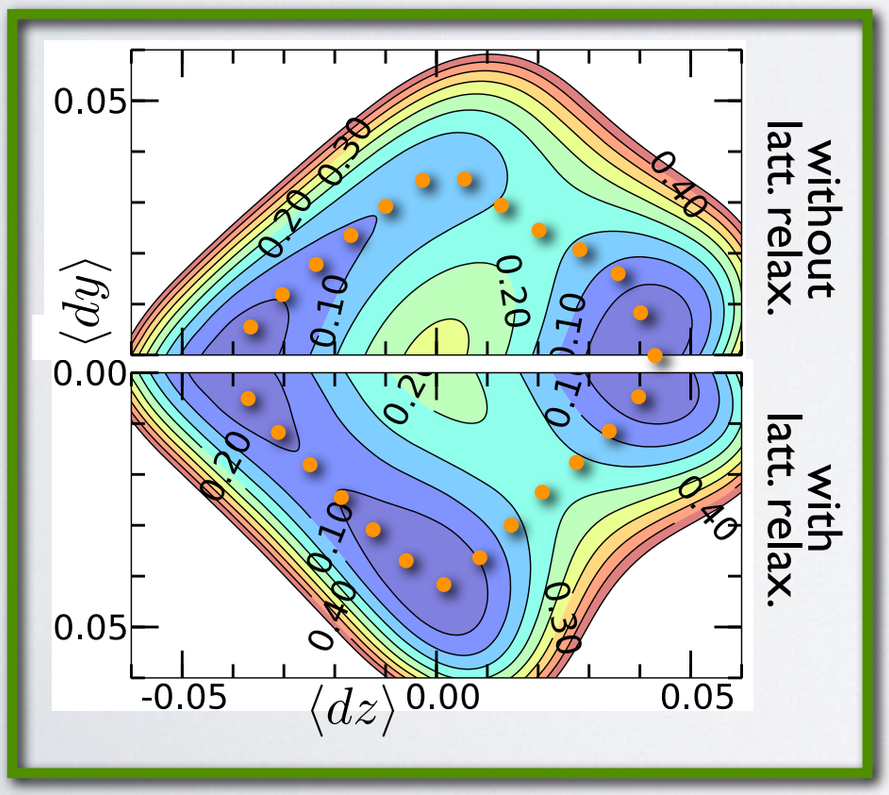


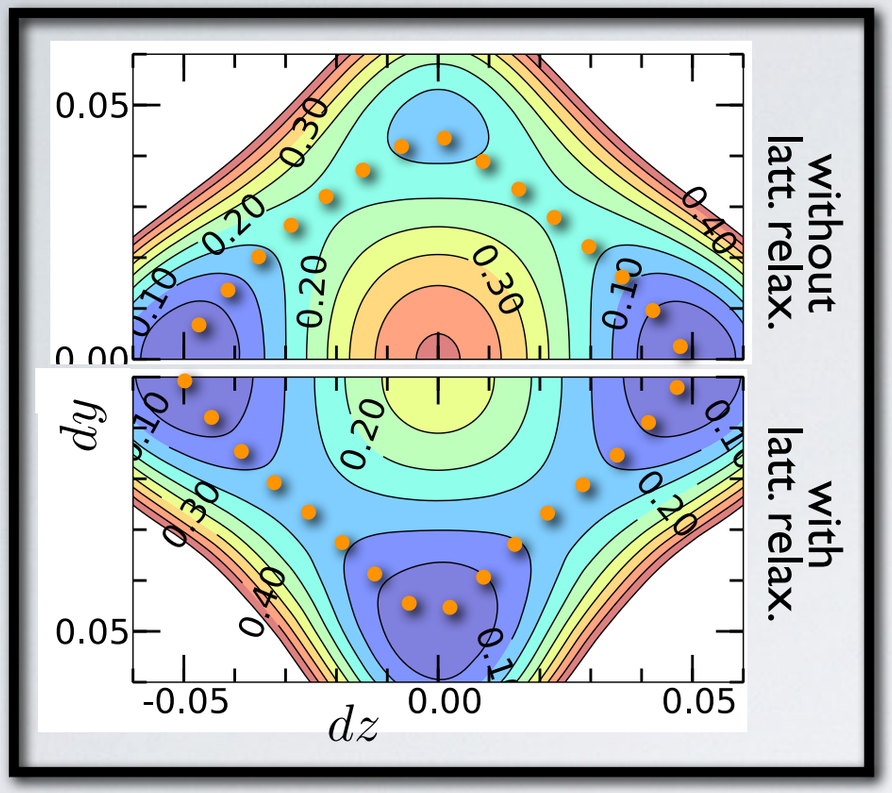


6.25 mol-% $YO_{1.5}$ doped ZrO_2

80 / 30 meV

Y cations **affect** the topology,
but **not** the barriers!

pristine ZrO_2

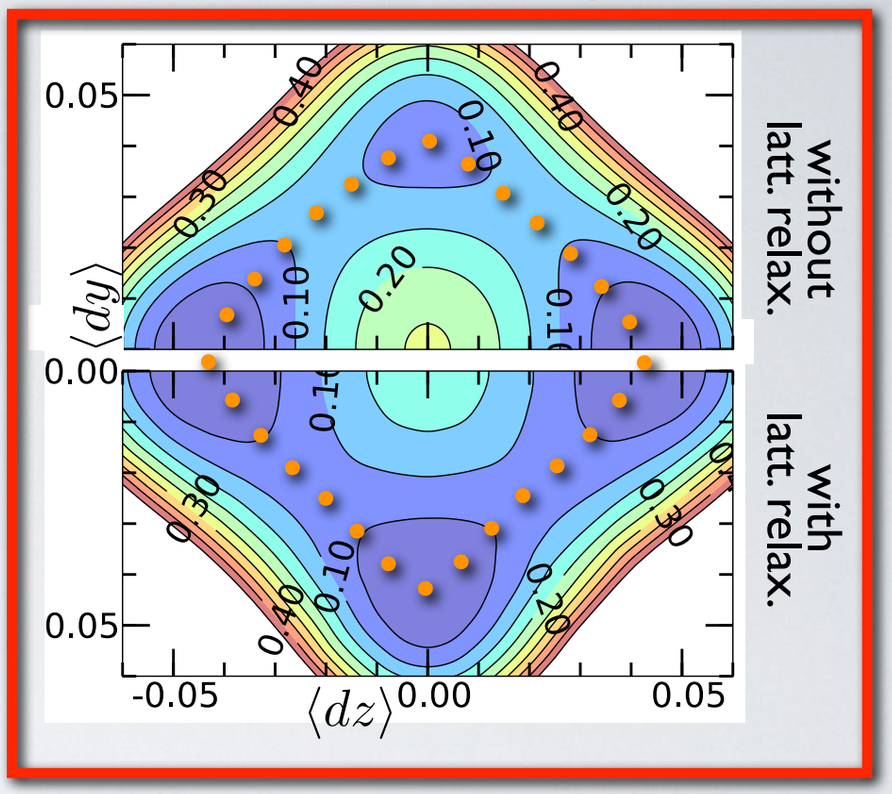


$E_{barrier}$

140 / 70 meV

80 / 40 meV

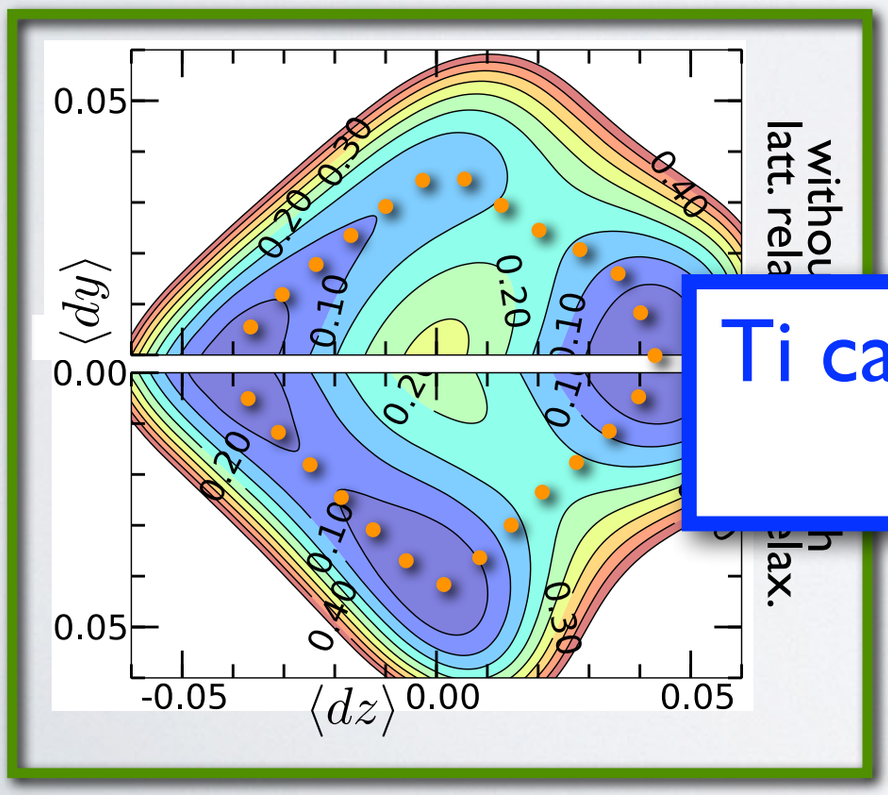
6.25 mol-% $ZrO_{1.5}$ doped ZrO_2



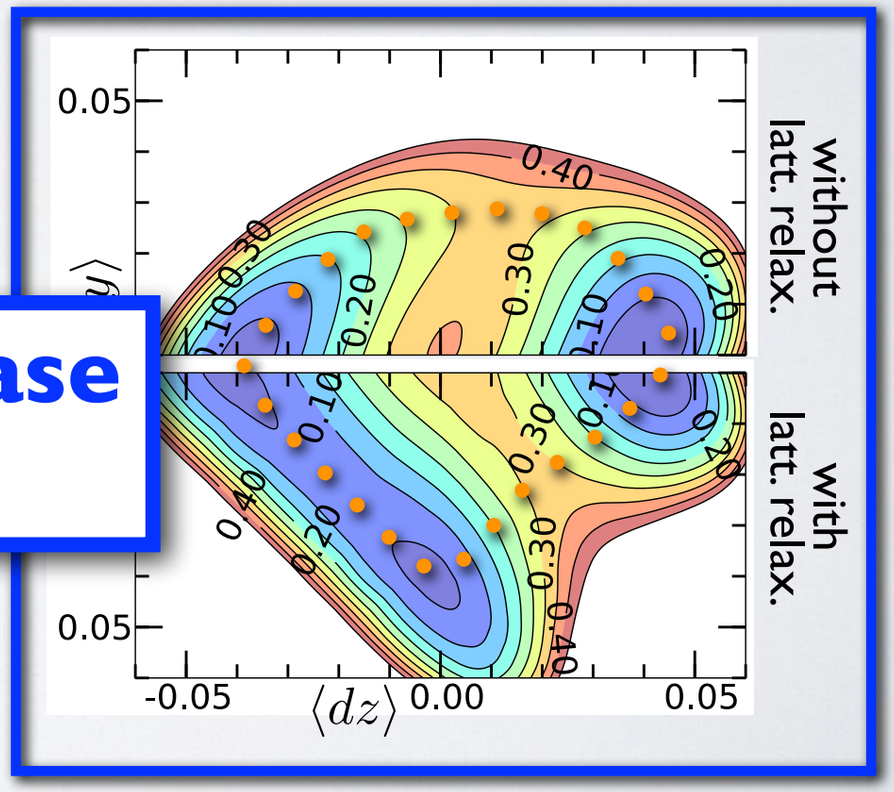
80 / 30 meV

Ti cations even **increase** the barriers!

160 / 100 meV



6.25 mol-% $YO_{1.5}$ doped ZrO_2



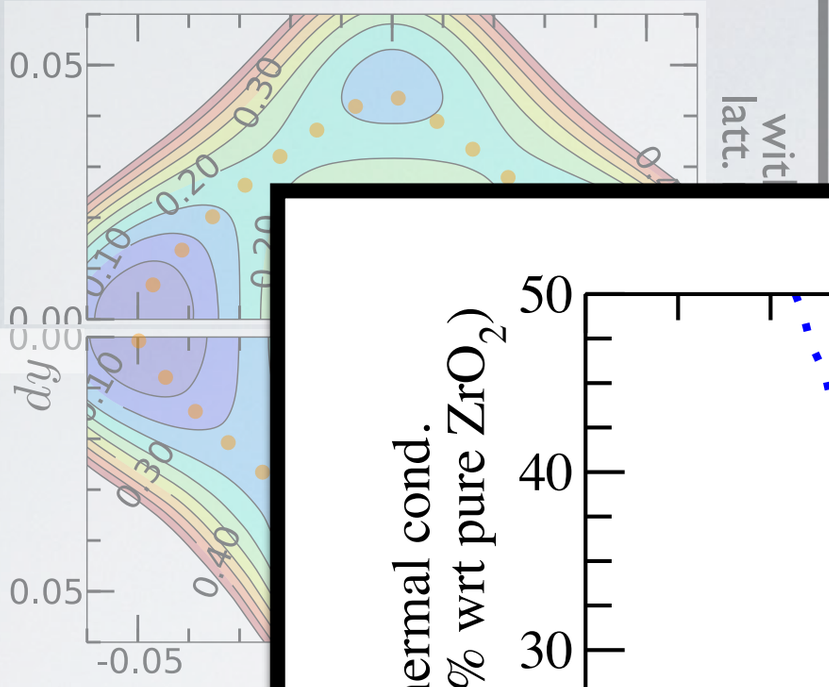
6.25 mol-% $YO_{1.5}$ + 3.125 mol-% TiO_2 doped ZrO_2

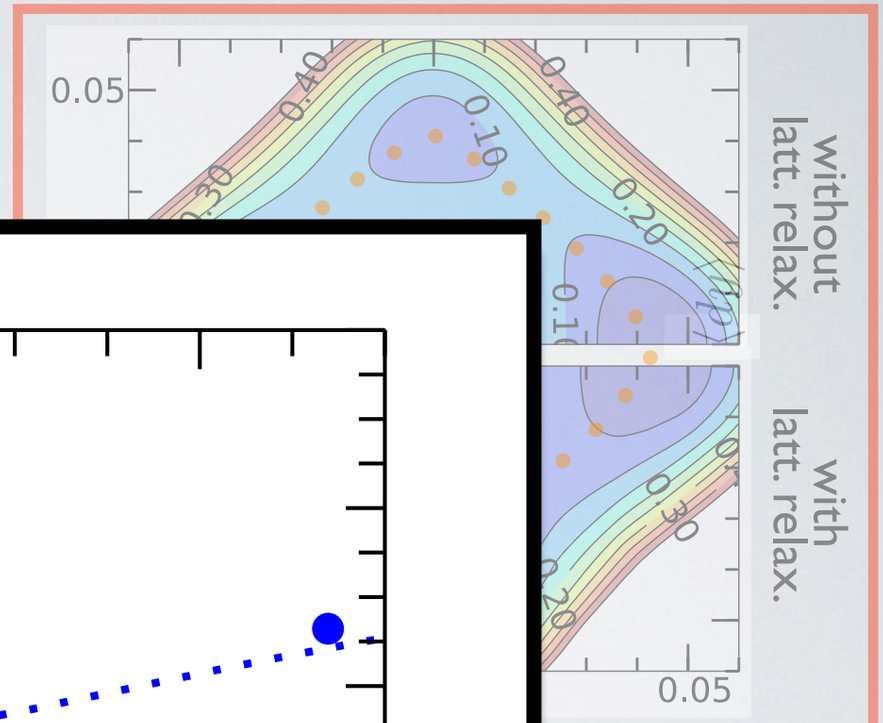
pristine ZrO_2

$E_{barrier}$

140 / 70 meV

6.25 mol-% $ZrO_{1.5}$ doped ZrO_2



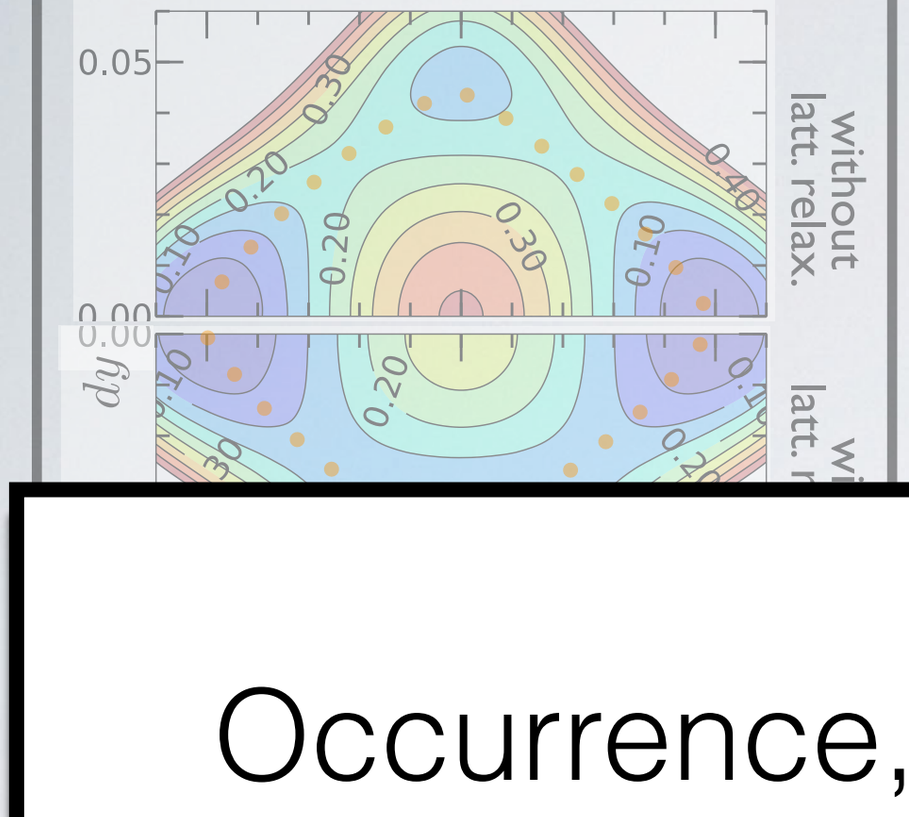


160 / 100 meV

6.25 mol-% $YO_{1.5}$ doped ZrO_2

6.25 mol-% $YO_{1.5}$ + 3.125 mol-% TiO_2 doped ZrO_2

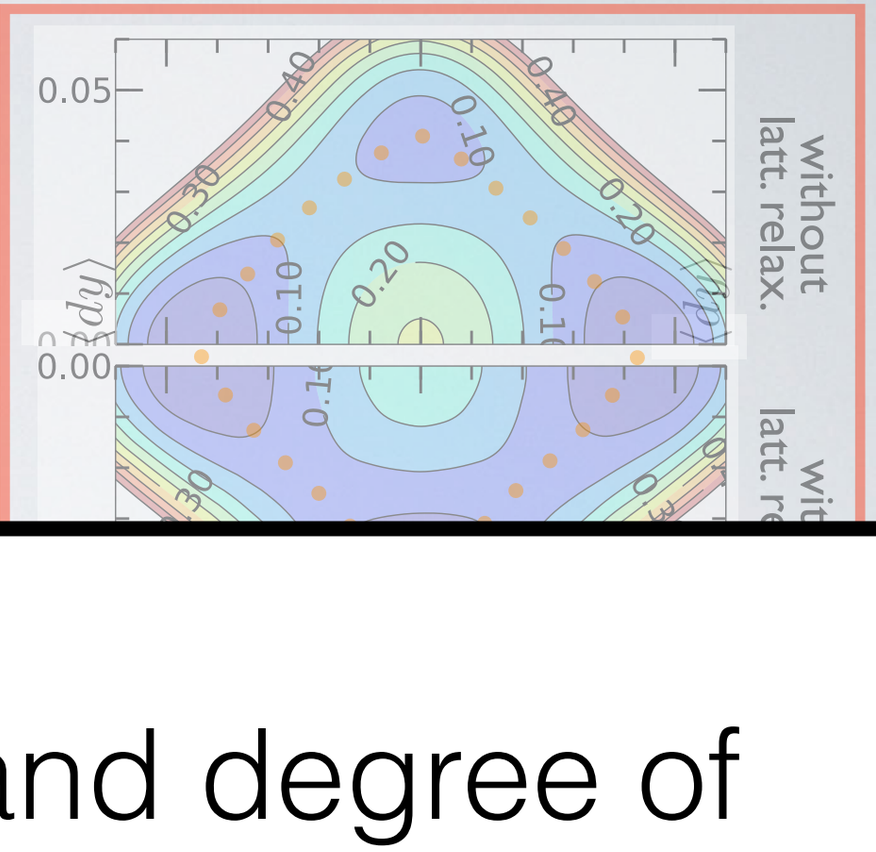
pristine ZrO_2



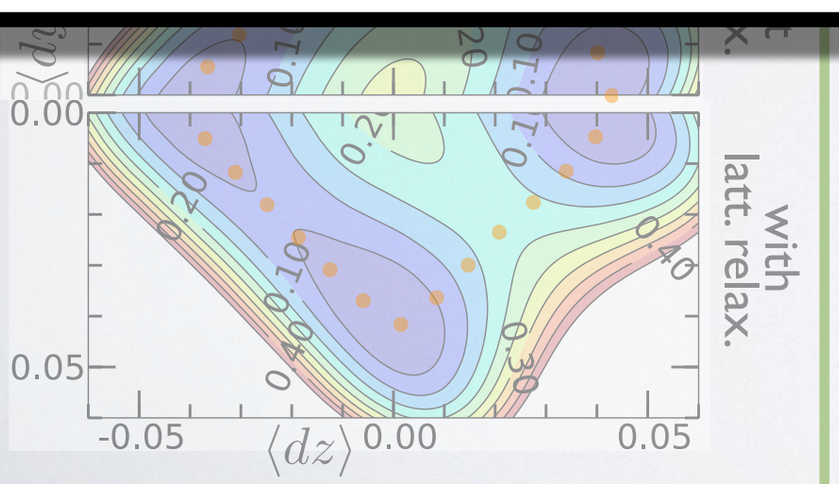
$E_{barrier}$

140 / 70 meV

6.25 mol-% $ZrO_{1.5}$ doped ZrO_2

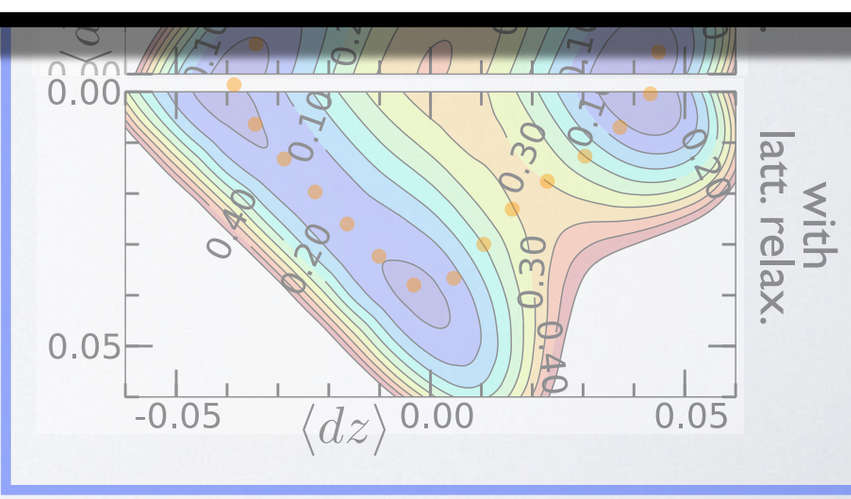


Occurrence, character and degree of anharmonicity can be tailored by doping!



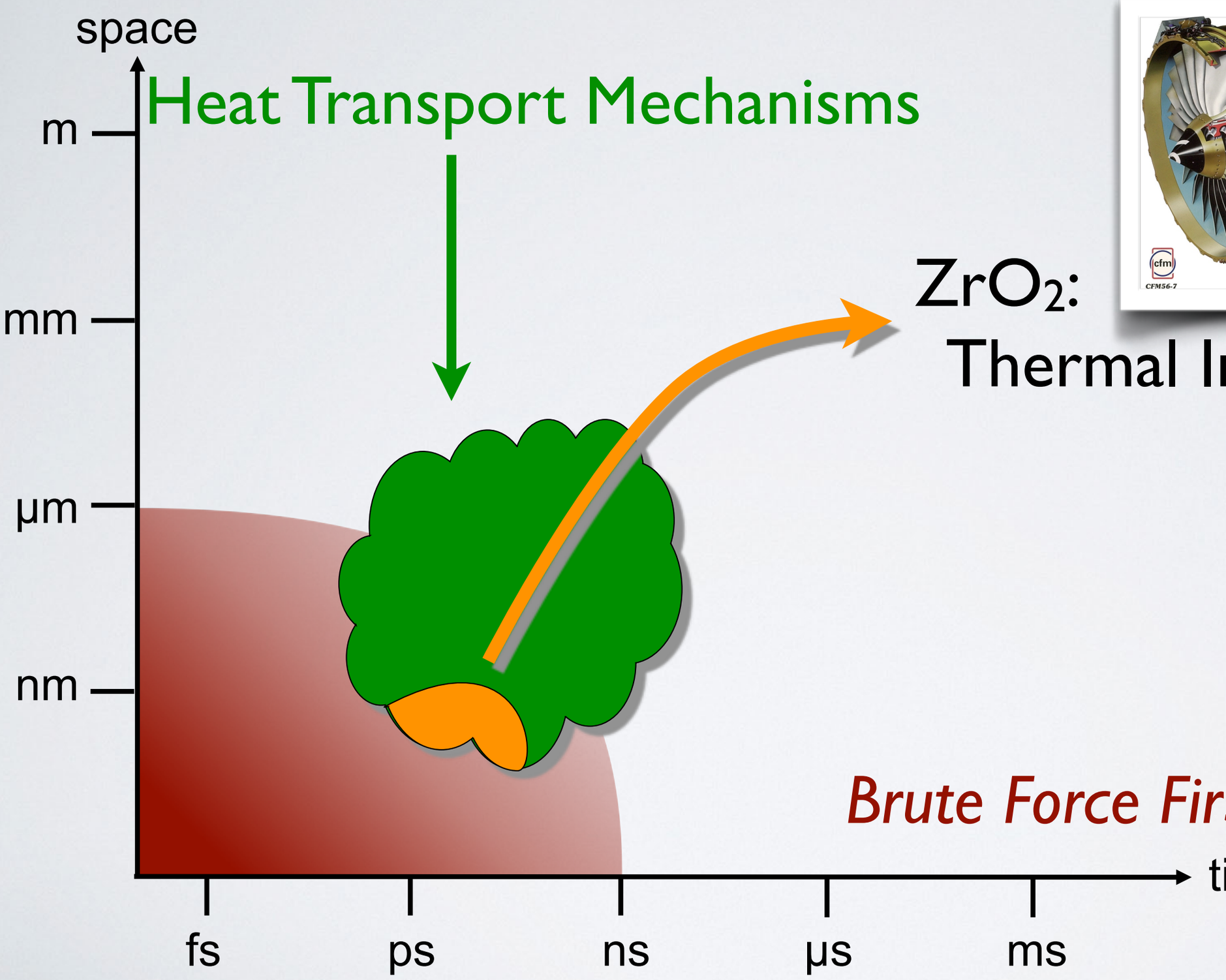
6.25 mol-% $YO_{1.5}$ doped ZrO_2

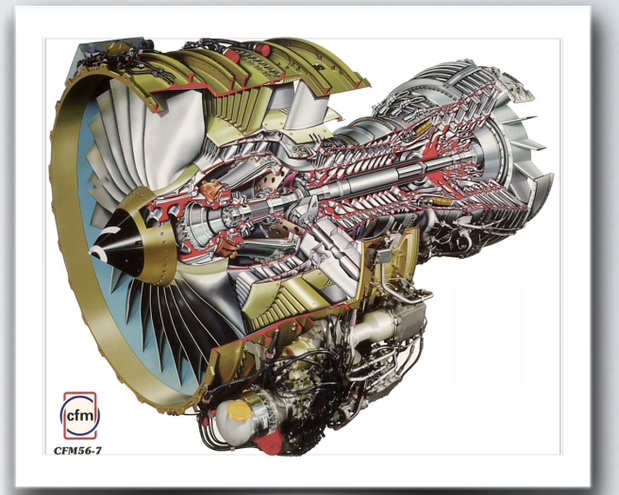
160 / 100 meV



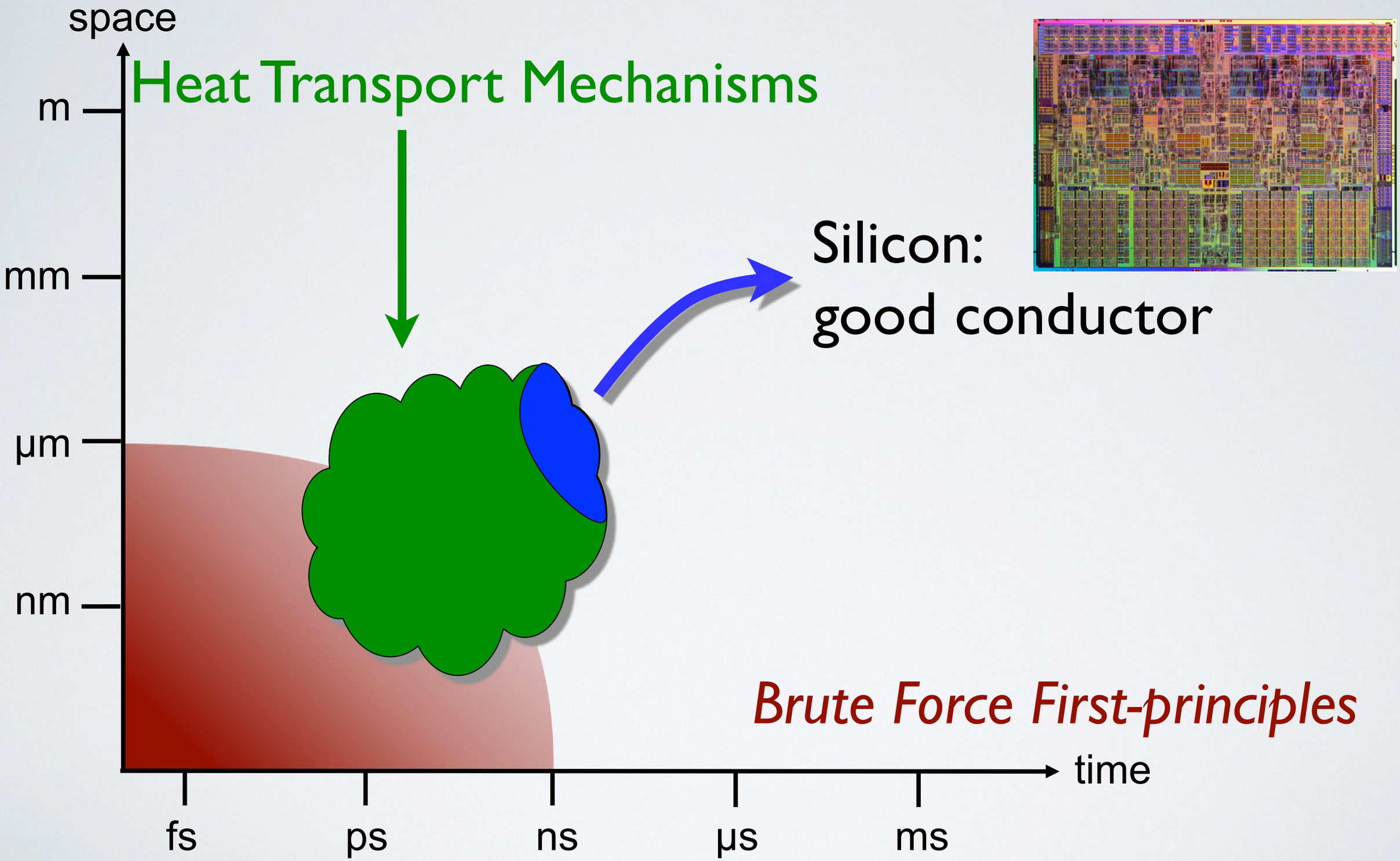
6.25 mol-% $YO_{1.5}$ + 3.125 mol-% TiO_2 doped ZrO_2

TIME AND LENGTH SCALES



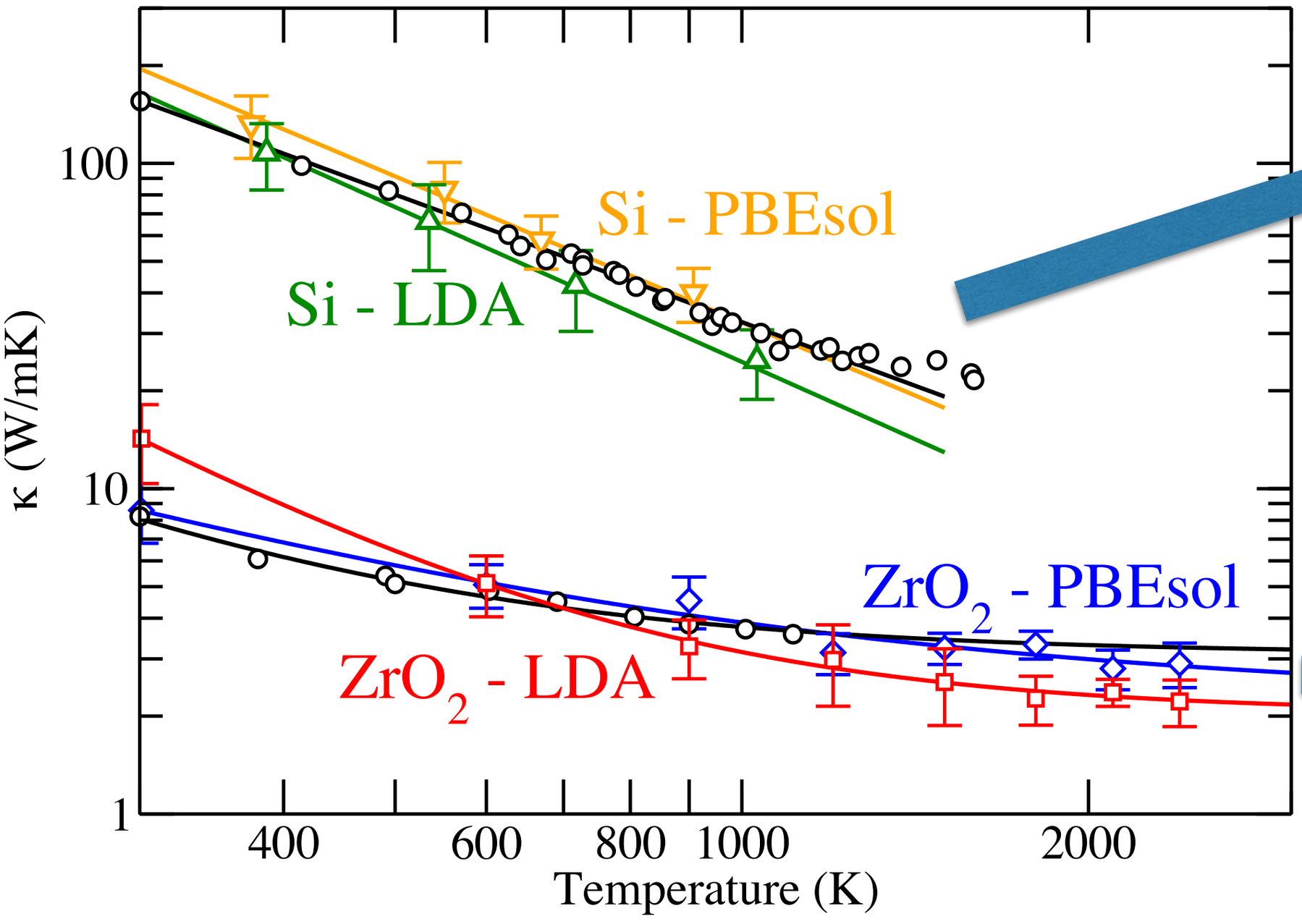


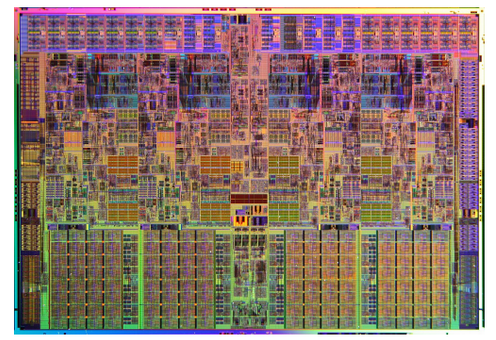
TIME AND LENGTH SCALES



APPLICATION TO SILICON AND ZIRCONIA

C. Carbogno, R. Ramprasad, and M. Scheffler, *Phys. Rev. Lett.* **118**, 175901 (2017).





Accurate computation of the thermal conductivities in solids achievable from first principles.

FIRST-PRINCIPLES APPROACHES

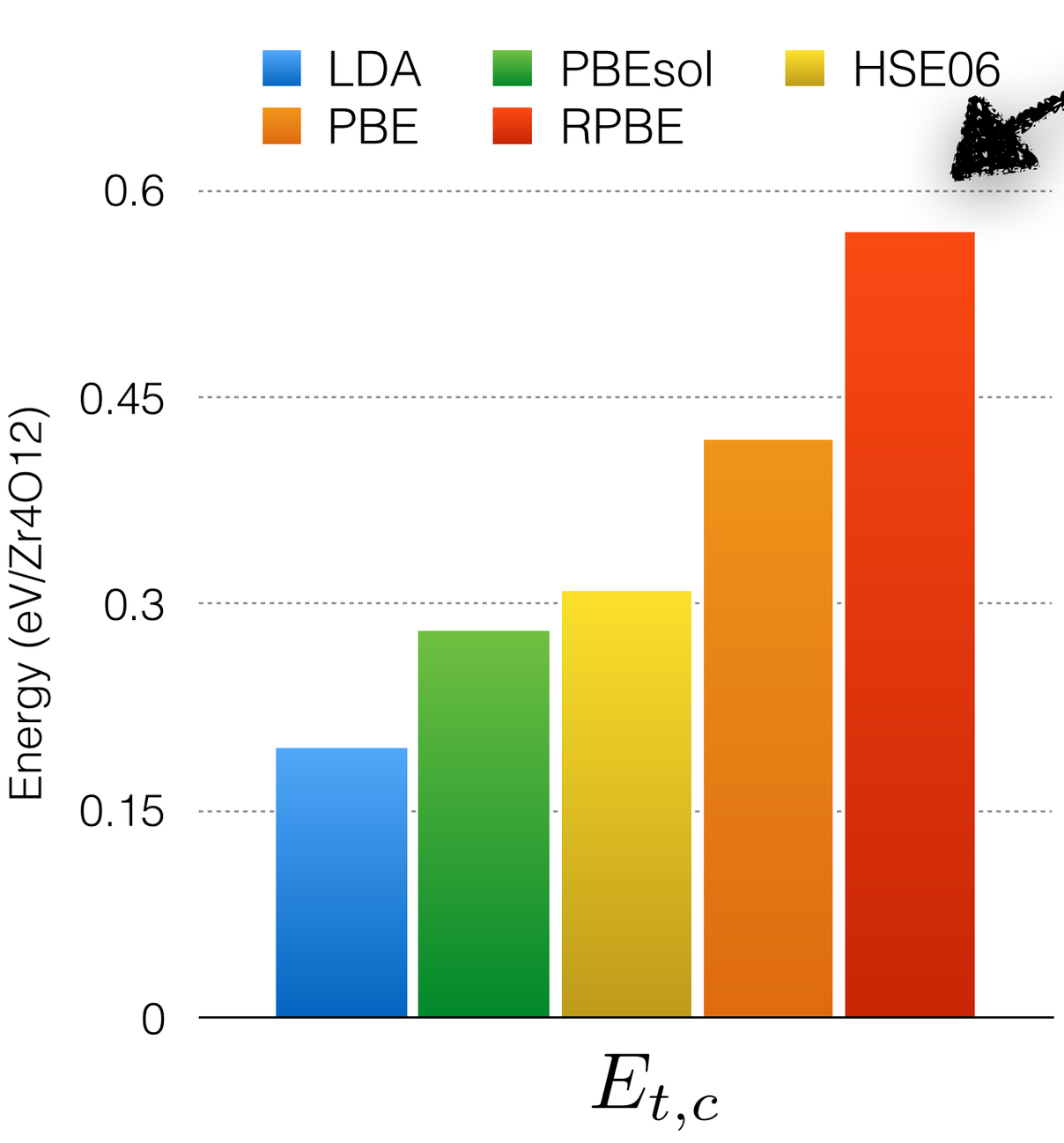
	Order of interaction	Validity & Applicability	Finite Size Effects	Disorder
Boltzmann-Transport Eq.	~$\mathcal{O}(r^3)$	low T	Minute	Parameter
Non-Equilib. MD	Full	all T	Huge	as in supercell
Green-Kubo MD	Full	all T	Small	as in supercell

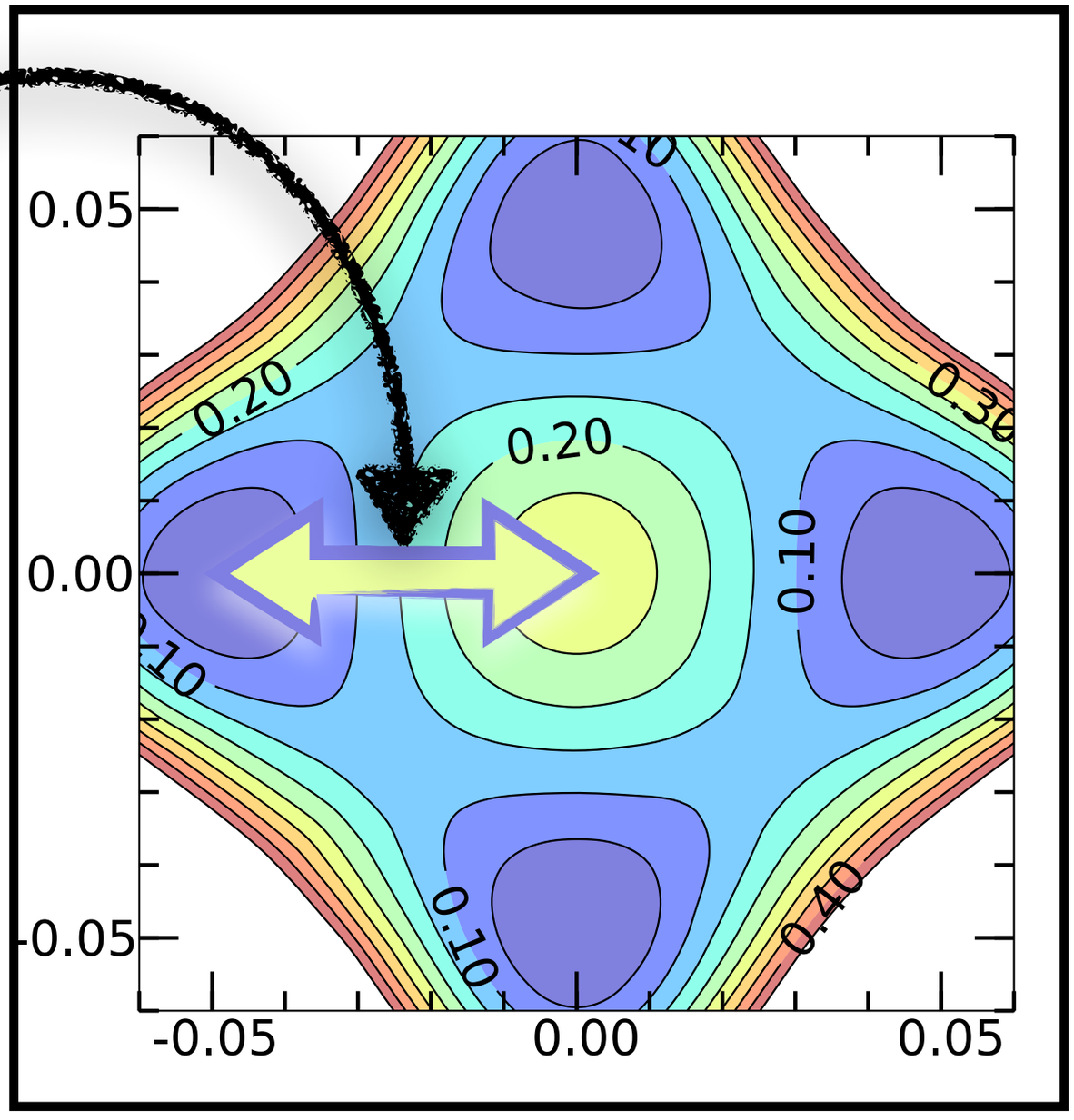
Ab initio **Green-Kubo** approach allows the **accurate** and **predictive** computation of **lattice thermal conductivities** κ at **arbitrarily high temperatures**!

IV. ONE LAST WORD OF CAUTION…

WHAT ABOUT THE FUNCTIONAL?

C. Carbogno, C. G. Levi, C. G. Van de Walle, and M. Scheffler, PRB **90**, 144109 (2014).





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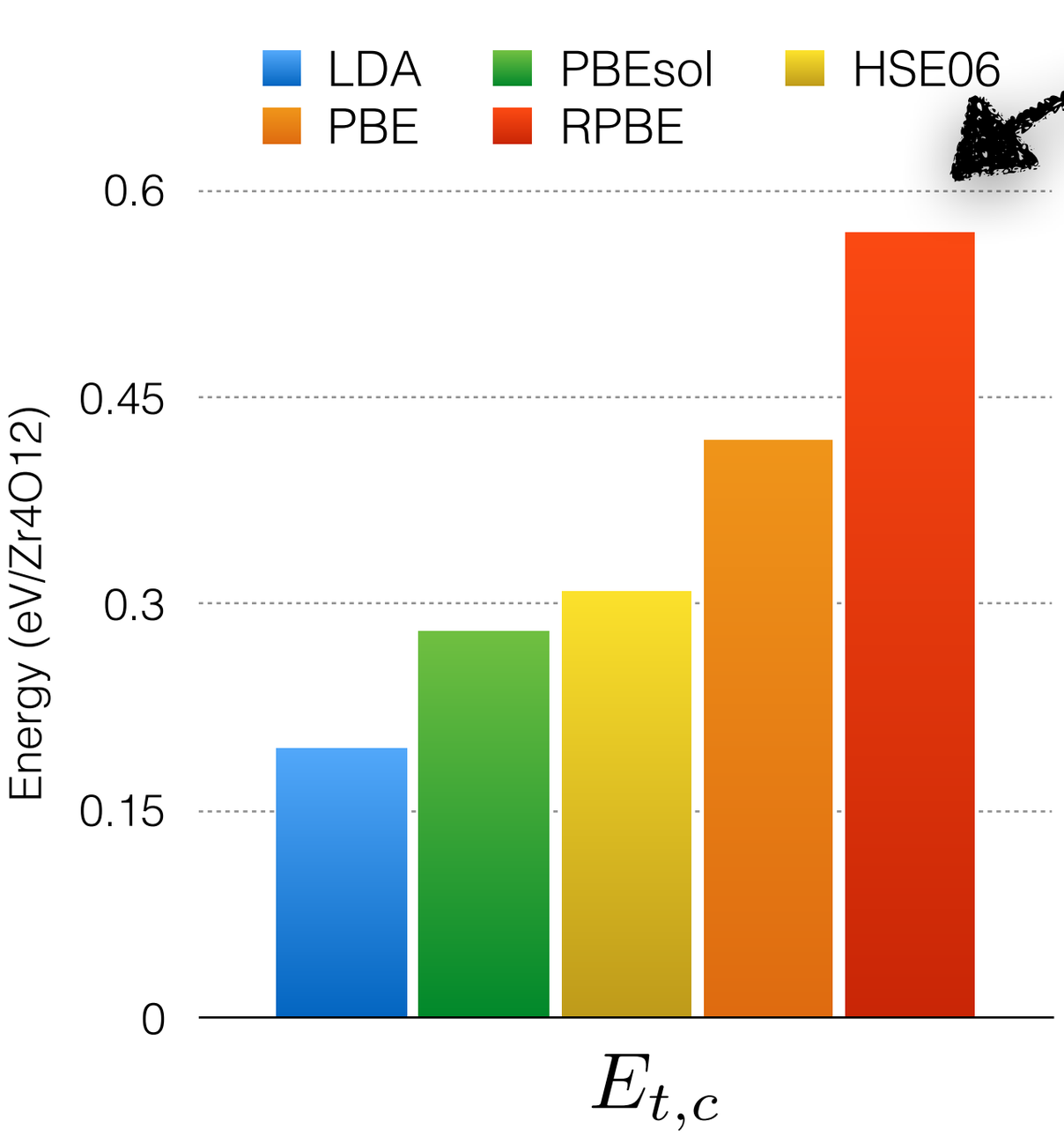
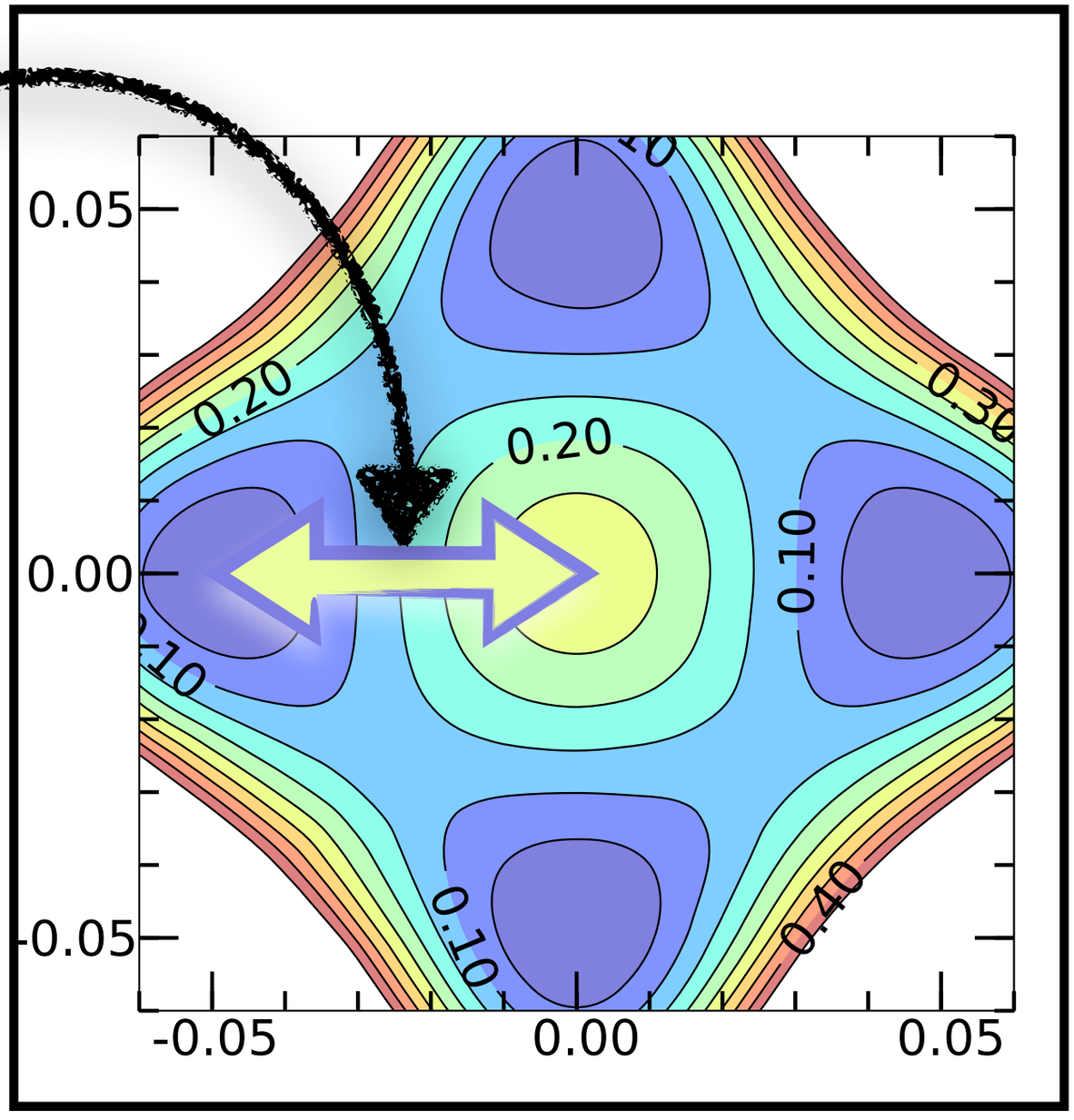


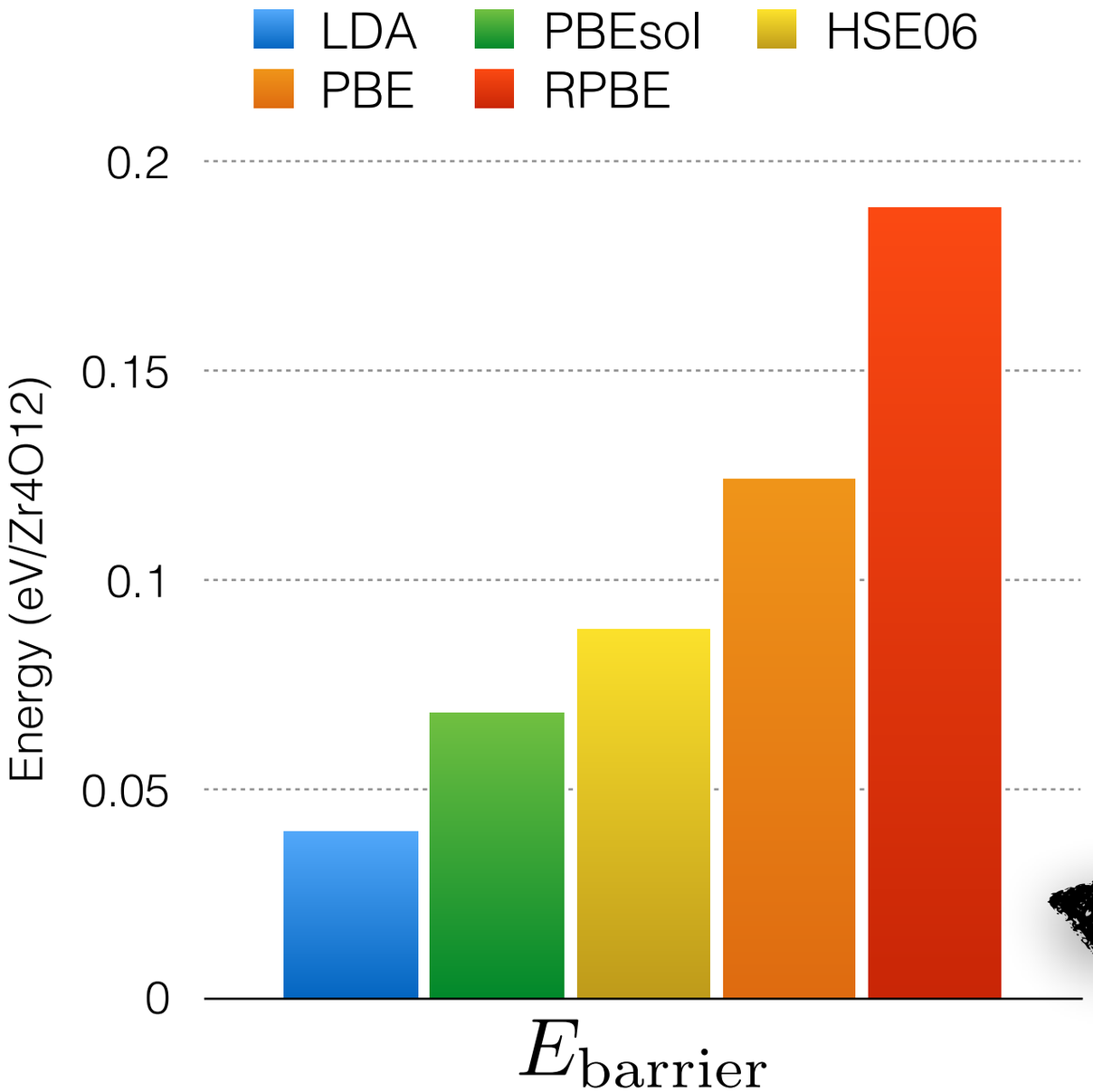


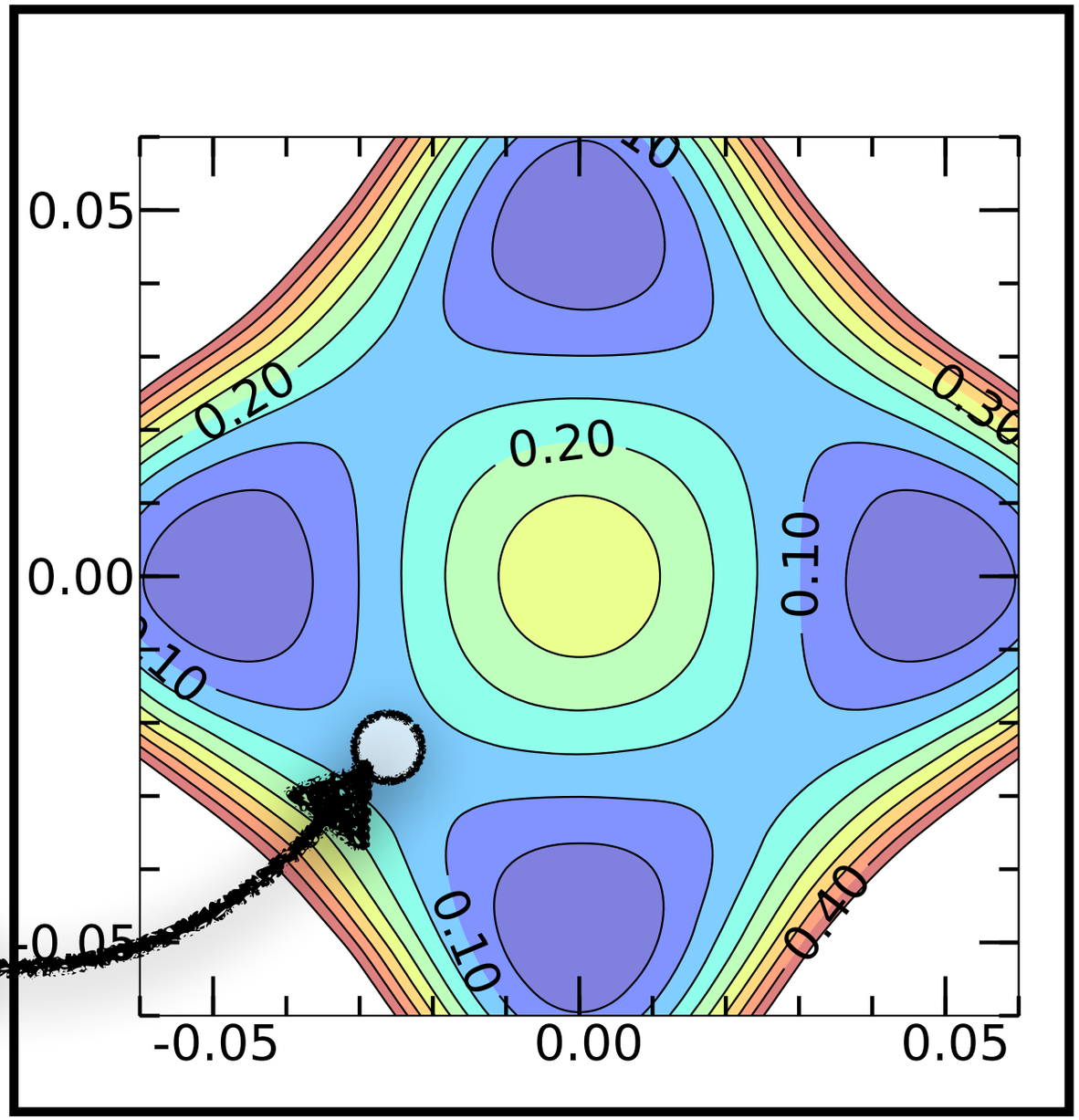
HSE06 value recently validated by *Diffusion Monte Carlo*.

H. Shin, *et al.*, *Phys. Rev. Materials* **2**, 075001 (2018).

WHAT ABOUT THE FUNCTIONAL?

C. Carbogno, C. G. Levi, C. G. Van de Walle, and M. Scheffler, PRB **90**, 144109 (2014).

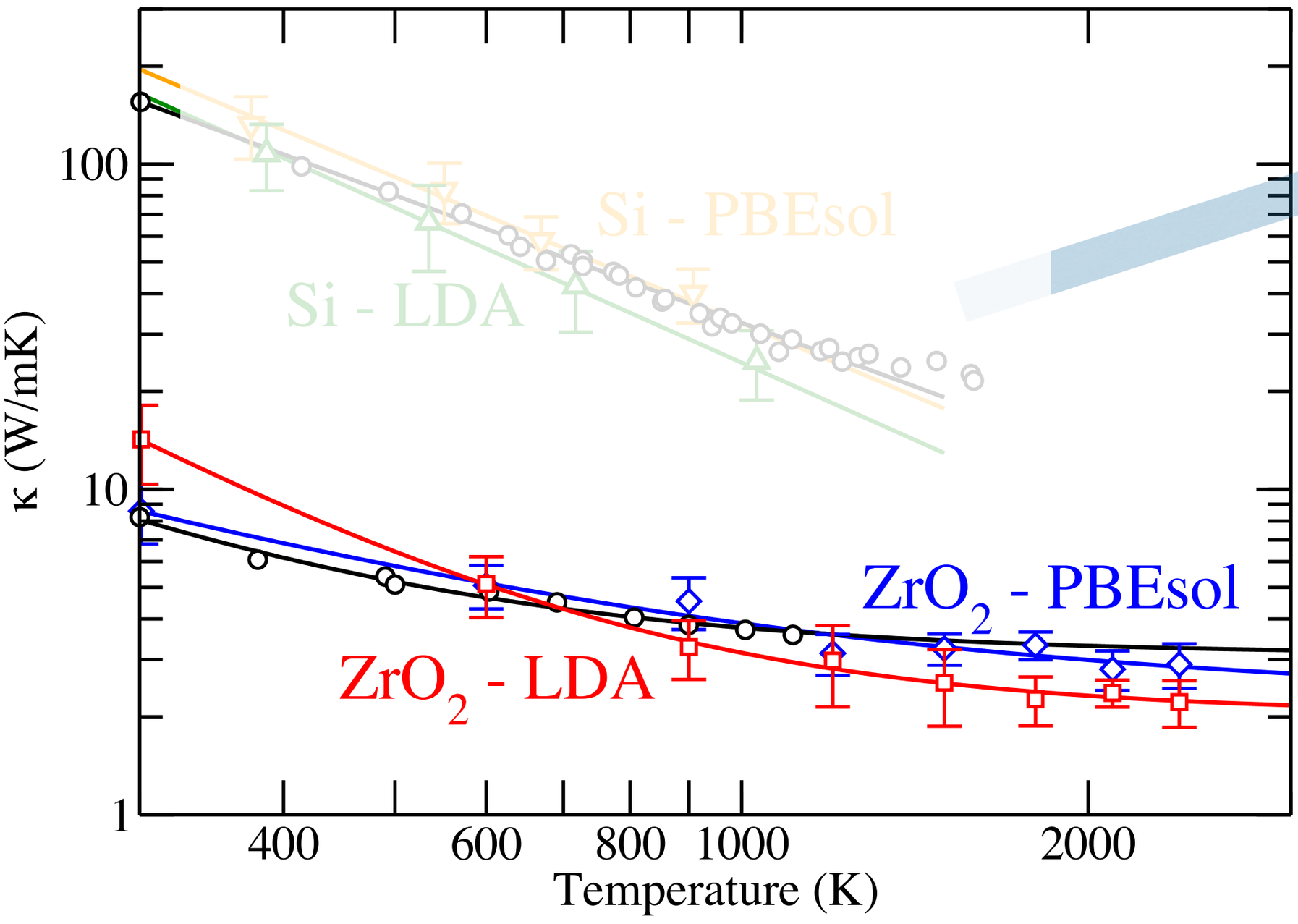


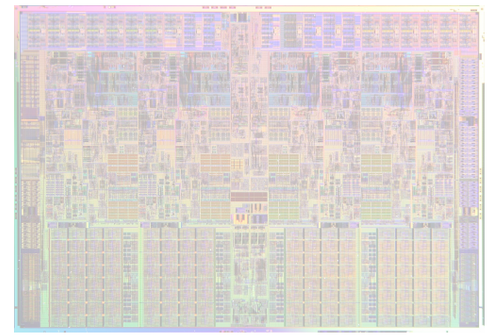


Different Functionals change the degree of anharmonicity, since bond-breaking is involved!

APPLICATION TO SILICON AND ZIRCONIA

C. Carbogno, R. Ramprasad, and M. Scheffler, *Phys. Rev. Lett.* **118**, 175901 (2017).





Correct choice of xc-functional can be critical…

Carlos G. Levi

Chris Van de Walle

MATERIALS
UC Santa Barbara

University of Connecticut

Rampi Ramprasad