Virtual FHI-aims Tutorial Series 2021
March 23 2022

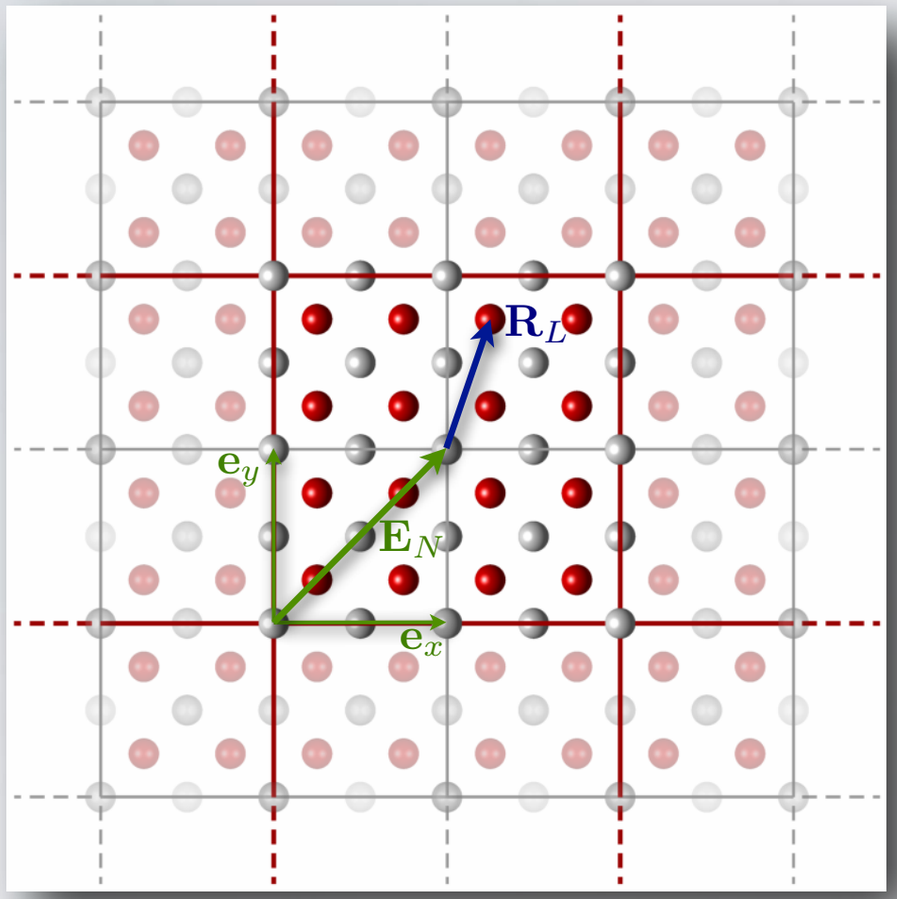
Phonons, electron-phonon coupling, heat and charge transport

Christian Carbogno

FRITZ-HABER-INSTITUT
MAX-PLANCK-GESELLSCHAFT

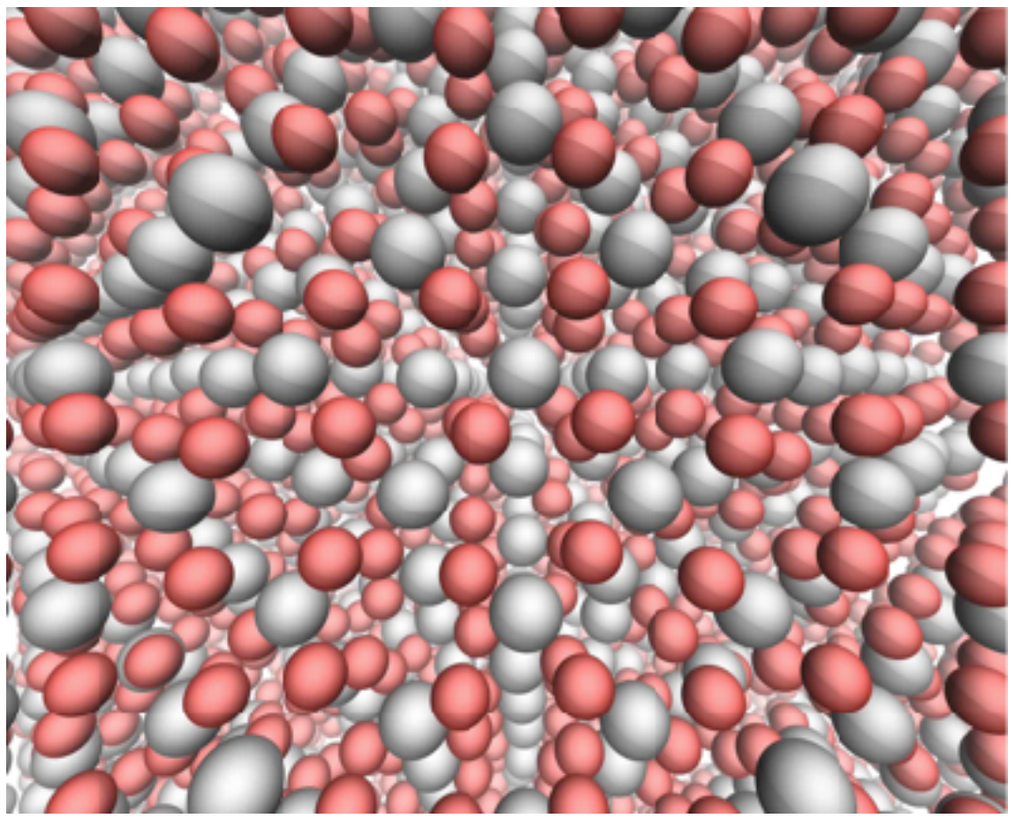
CRYSTALLINE SOLIDS

Idealized Crystal Structure



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

Real Materials



Everything moves!

Perfect periodicity disturbed!

FAILURES OF THE STATIC LATTICE MODEL

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

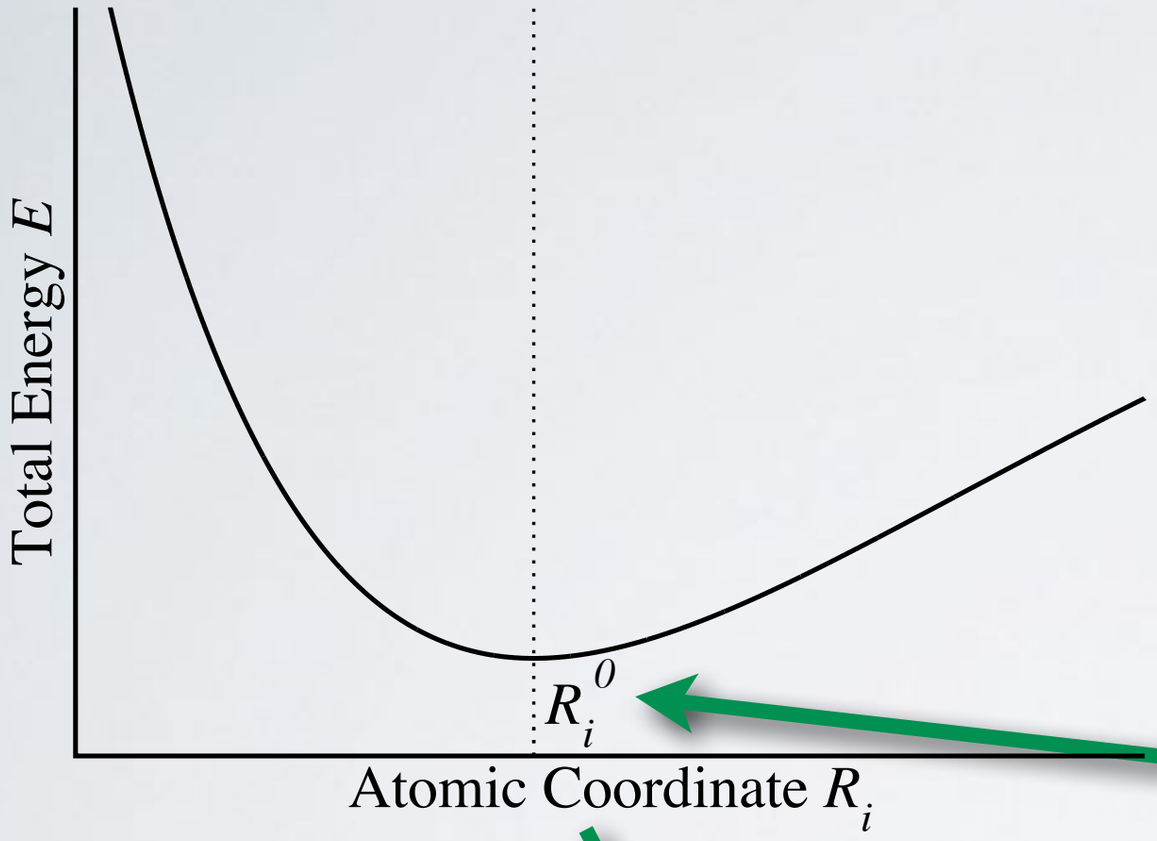
- **Inaccuracies** in the **equilibrium** properties at **0K**:
  Lattice Constants, Cohesive Energies, Elastic Constants,...

- **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:

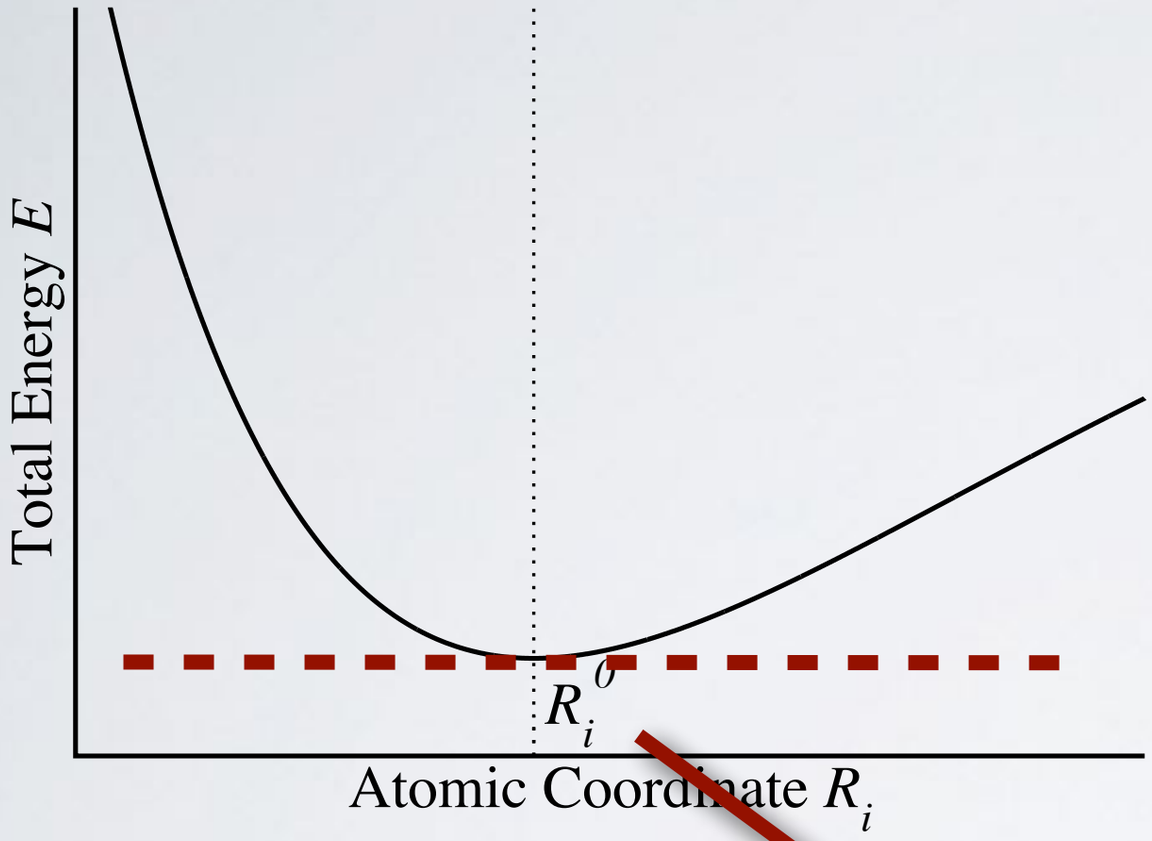
$$E = V\left(\mathbf{R}_1, \mathbf{R}_2, \cdots, \mathbf{R}_N\right)$$

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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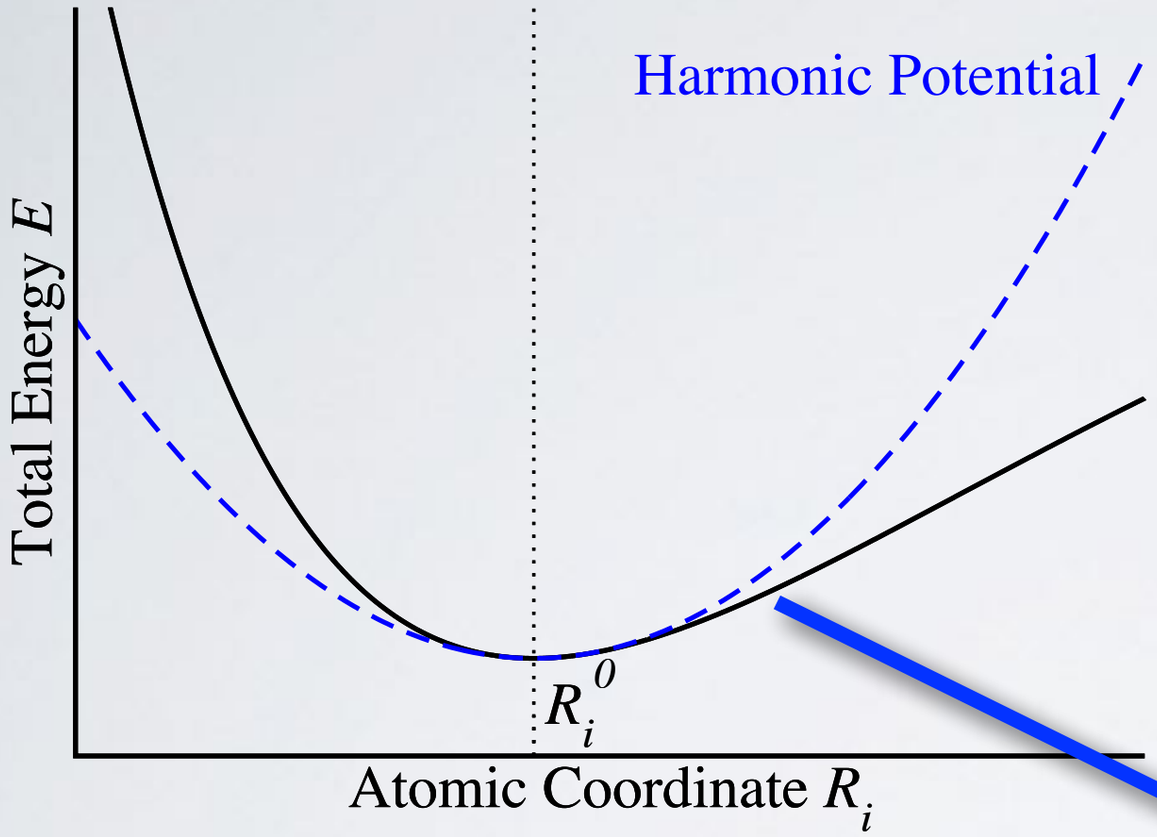
$$E\left(\{\mathbf{R}_0 + \Delta\mathbf{R}\}\right) \approx E\left(\{\mathbf{R}_0\}\right) + \sum_i \frac{\partial E}{\partial \mathbf{R}_i}\bigg|_{\mathbf{R}_0} \Delta\mathbf{R}_i + \cdots$$

Forces vanish at **R_0**

THE HARMONIC APPROXIMATION



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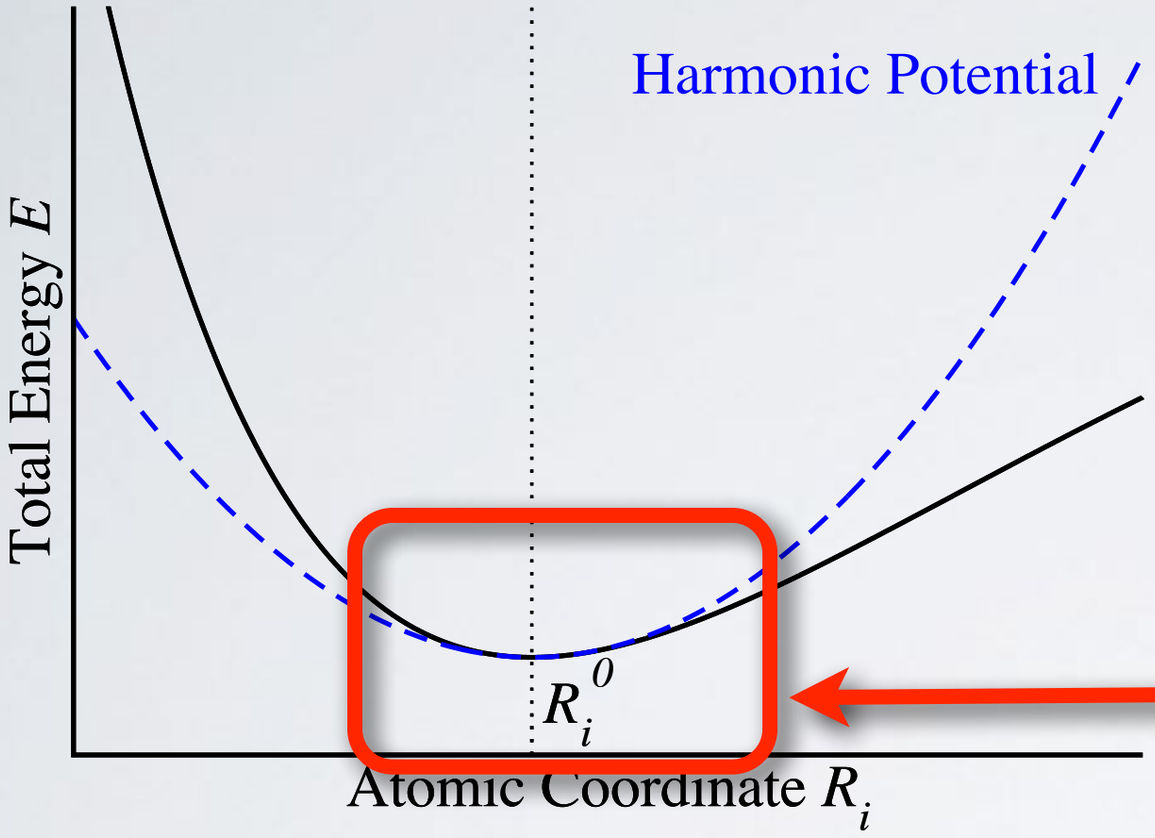
Hessian Φ_{ij}

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 $\boldsymbol{R^0}$!

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

THE HARMONIC APPROXIMATION

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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**
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Starting Point:
Kohn-Sham Equations

$$\hat{h}_{\mathrm{KS}}\psi_i = \left[\hat{t} + \hat{v}_{\mathrm{ext}}(r) + \hat{v}_{\mathrm{H}} + \hat{v}_{\mathrm{xc}}\right]\psi_i = \epsilon_i\psi_i$$

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First-order expansion of all relevant quantities with respect to a perturbation λ

$$\begin{aligned}
\hat{h}_{\mathrm{KS}}(\lambda) &= \hat{h}^{(0)}_{\mathrm{KS}} + \overbrace{\frac{d\hat{h}_{\mathrm{KS}}}{d\lambda}}^{\hat{h}^{(1)}_{\mathrm{KS}}}\Delta\lambda + \cdots \\
\psi_i(\lambda) &= \psi_i^{(0)} + \psi_i^{(1)}\Delta\lambda + \cdots \\
\varepsilon_i(\lambda) &= \varepsilon_i^{(0)} + \varepsilon_i^{(1)}\Delta\lambda + \cdots
\end{aligned}$$

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\end{aligned}$$

Solve: *Sternheimer Equation*

$$\hat{h}_{\mathrm{KS}}(\lambda)\,\psi_i(\lambda) = \varepsilon_i(\lambda)\psi_i(\lambda) \Rightarrow \left(\hat{h}^{(0)}_{\mathrm{KS}} - \varepsilon_i^{(0)}\right)\psi_i^{(1)} = -\left(\hat{h}^{(1)}_{\mathrm{KS}} - \epsilon_i^{(1)}\right)\psi_i^{(0)} + o(\lambda^2)$$

R.M. Sternheimer, *Phys. Rev.* **96** 951 (1954).

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Route A: *Density-functional Perturbation Theory* $\psi_i^{(1)} = \sum_l C_{il}\psi_l^{(0)}$

Route B: *Coupled-Perturbed Self-Consistent Field* $\psi_i^{(1)} = \sum_l C_{il}\varphi_l$

Additional Self-Concistency Cycle
required **per perturbation**!

Density-Functional Perturbation Theory

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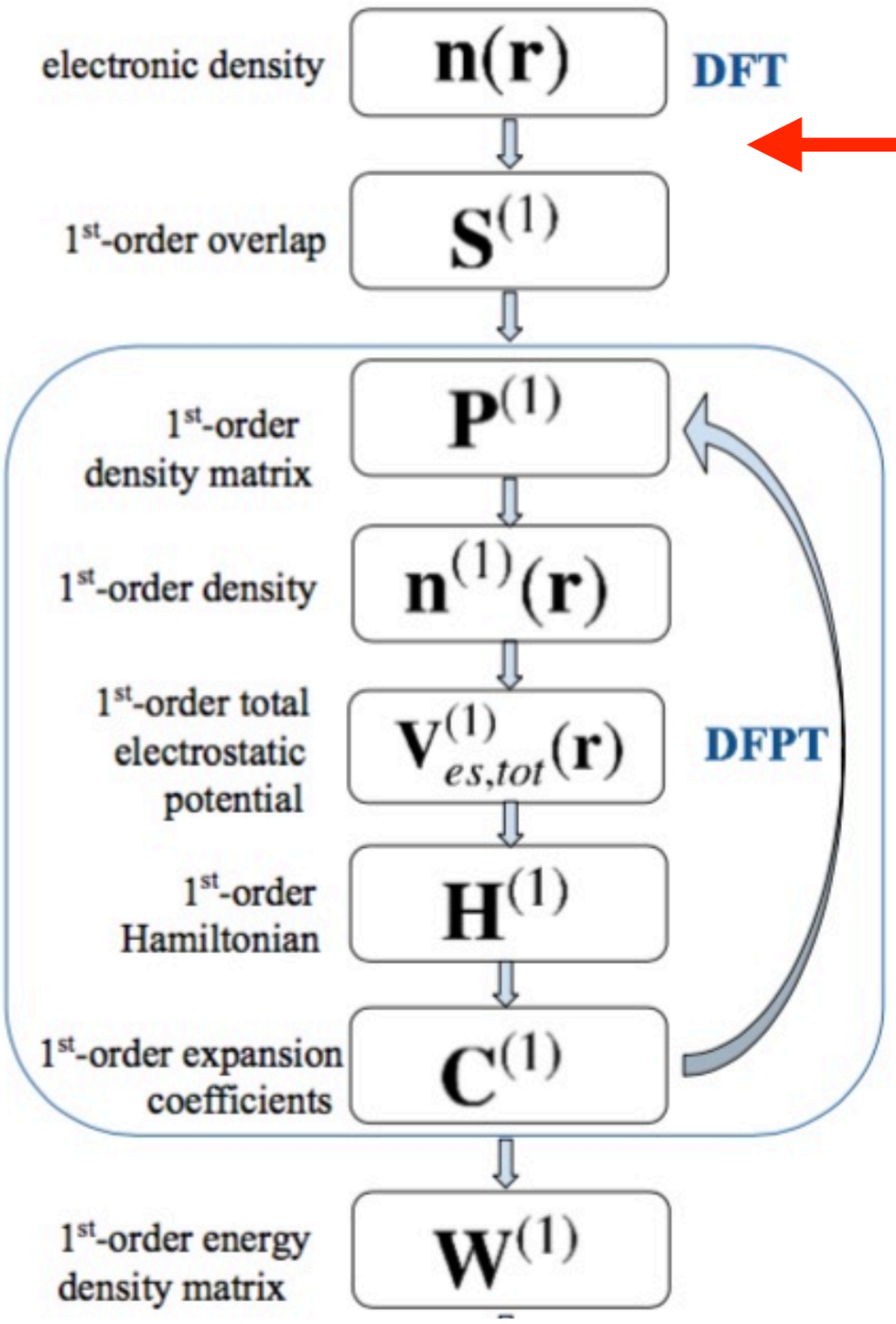
Normalization Conditions:

$$\left\langle \psi^{(0)}_i \middle| \psi^{(0)}_i \right\rangle = 1 \qquad \left\langle \psi^{(1)}_i \middle| \psi^{(0)}_i \right\rangle + \left\langle \psi^{(0)}_i \middle| \psi^{(1)}_i \right\rangle = 0$$

Phase Freedom: The phase of the perturbation can be freely chosen.

⇒ Extended Perturbations $\lambda(\mathbf{q})$ can be treated

in the unit cell!



Density Functional Theory:

density $n(\mathbf{r})$

Electric Field Perturbation Theory:

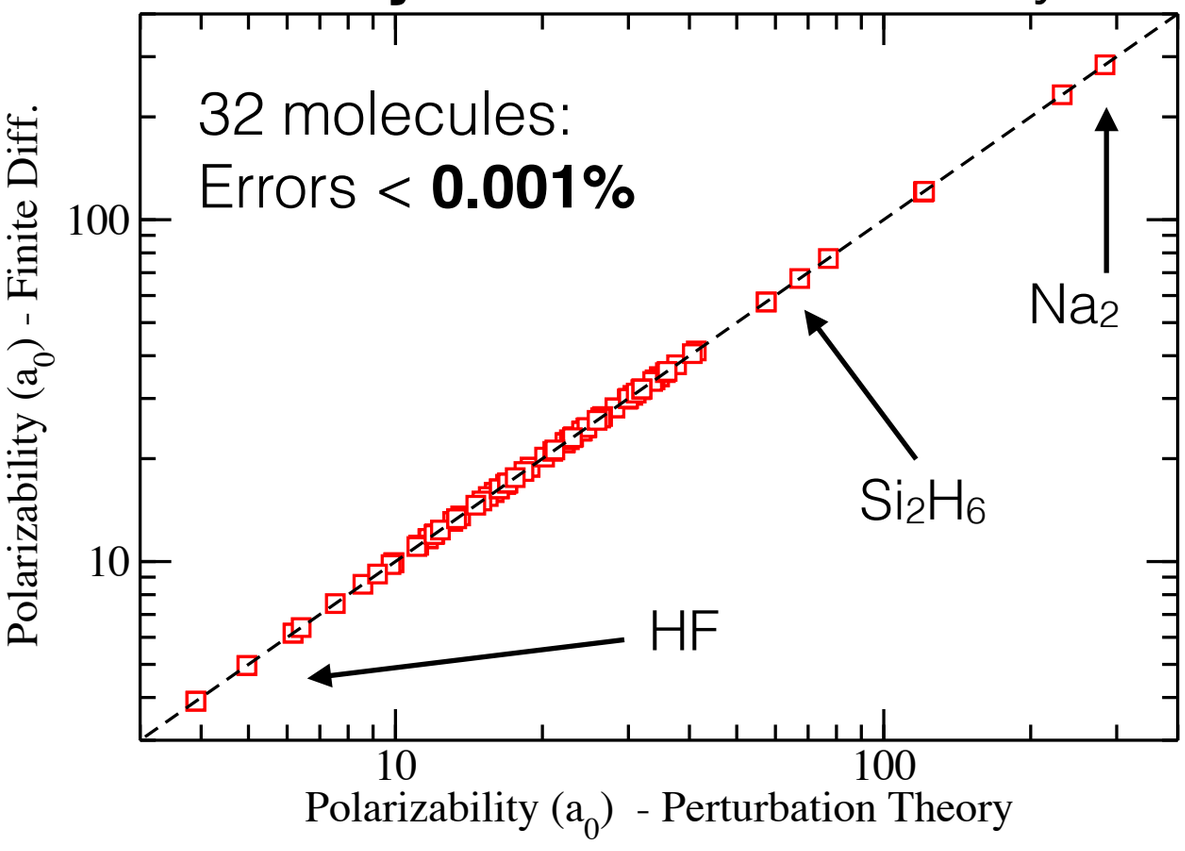
density response $dn(\mathbf{r})/d\mathbf{E}$

Polarizabilities & Dielectric Constants

Extensions: Response to Electric Fields

H. Shang, *et al.*, *New Journal of Physics* ***20***, *073040 (2018).*

Finite Systems: Polarizability



Validation:
Comparison **DFPT**
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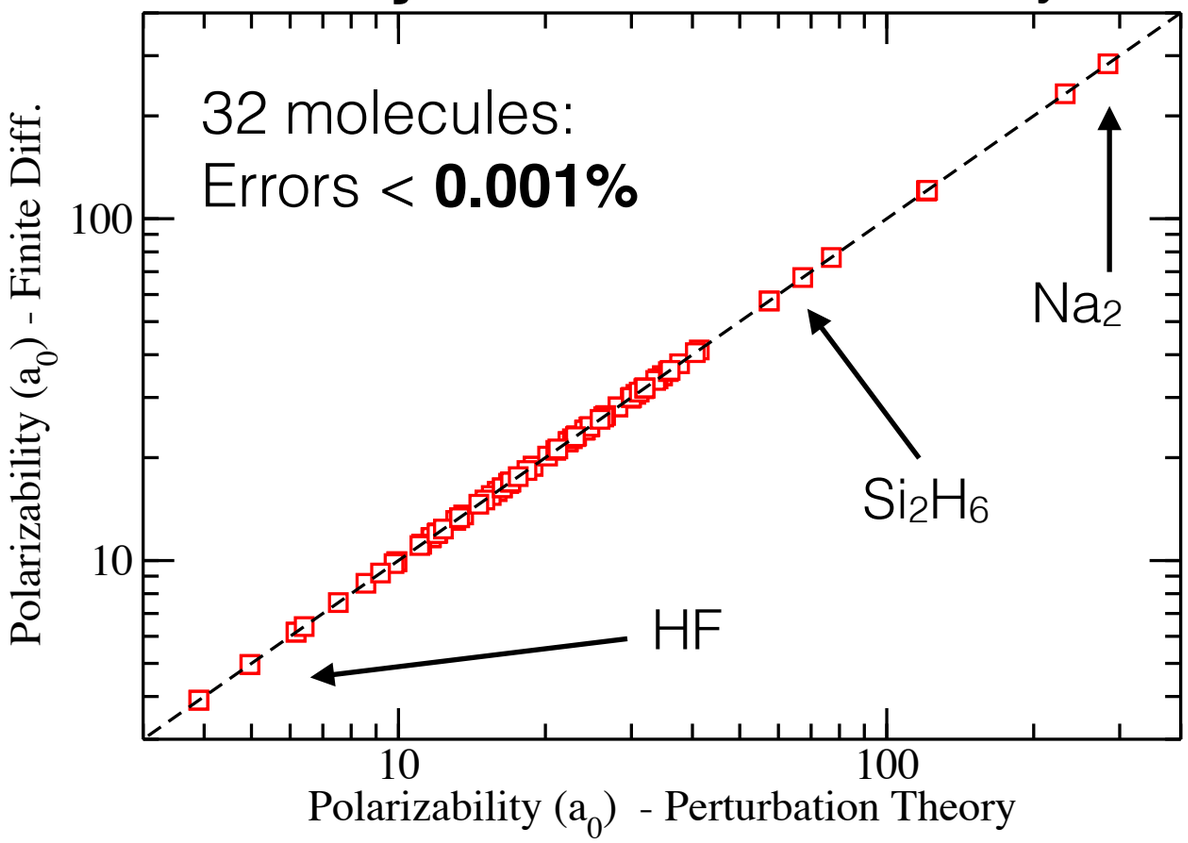

Periodic Systems: Dielectric Constant

	Exp.	this work (all electron) LDA	this work (all electron) PBE	Petousis *et al.*, 2016 PBE
Si	12.1	13.2	12.9	13.1
AlP	7.5	8.4	8.2	8.1
AlAs	8.2	9.5	9.5	9.5
AlSb	10.24	11.7	11.9	12.1
GaP	9.0	10.6	10.6	10.6

Theory Ref.: Petousis *et al.*, *Phys. Rev. B* **93**, 115151 (2016).

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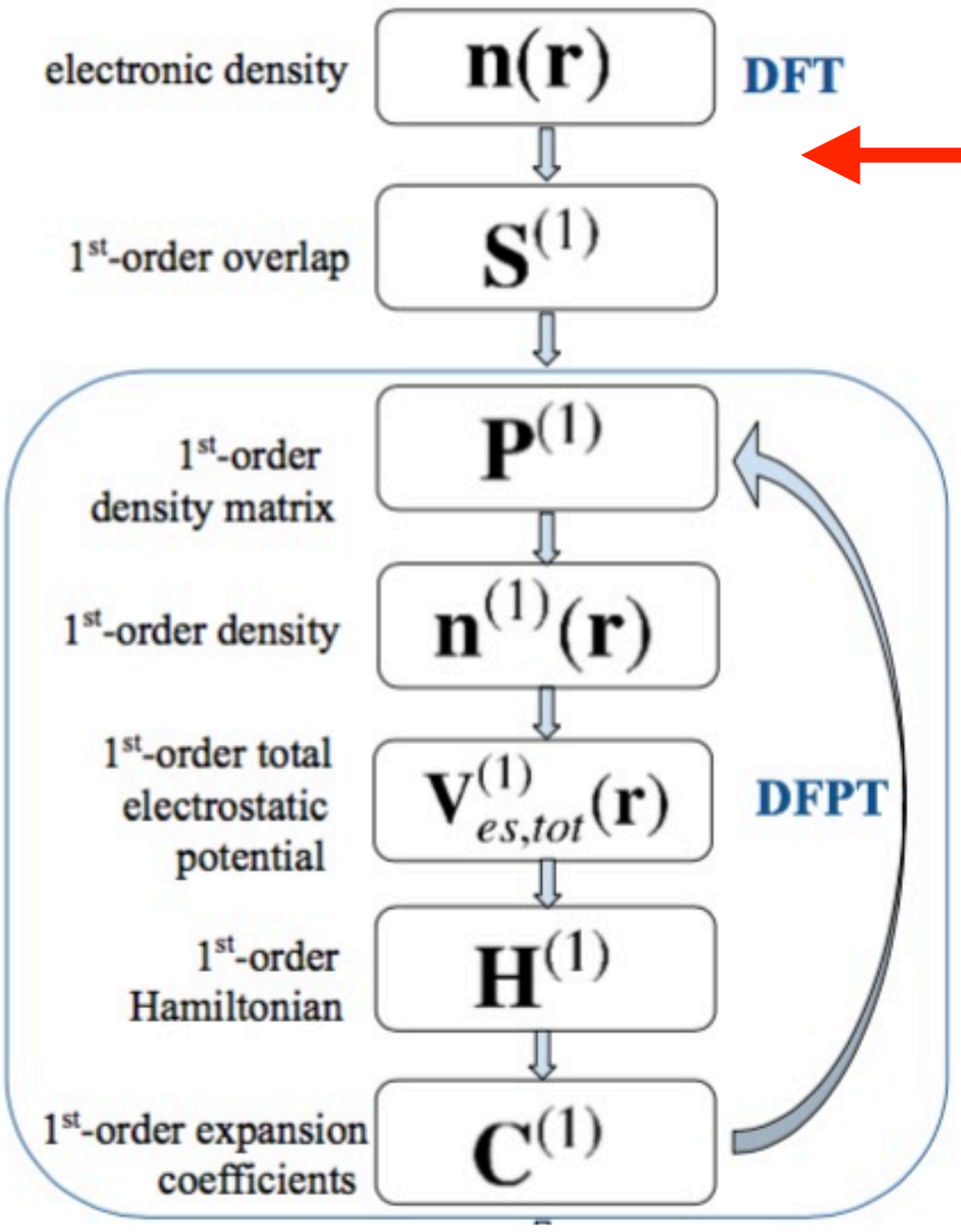
Validation:
Comparison **DFPT** with **exp.**/**theo.** literature

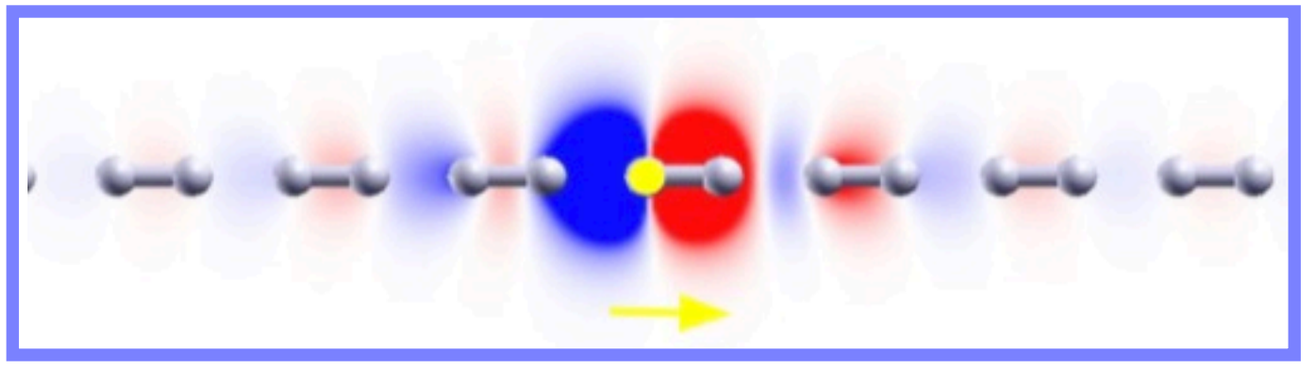


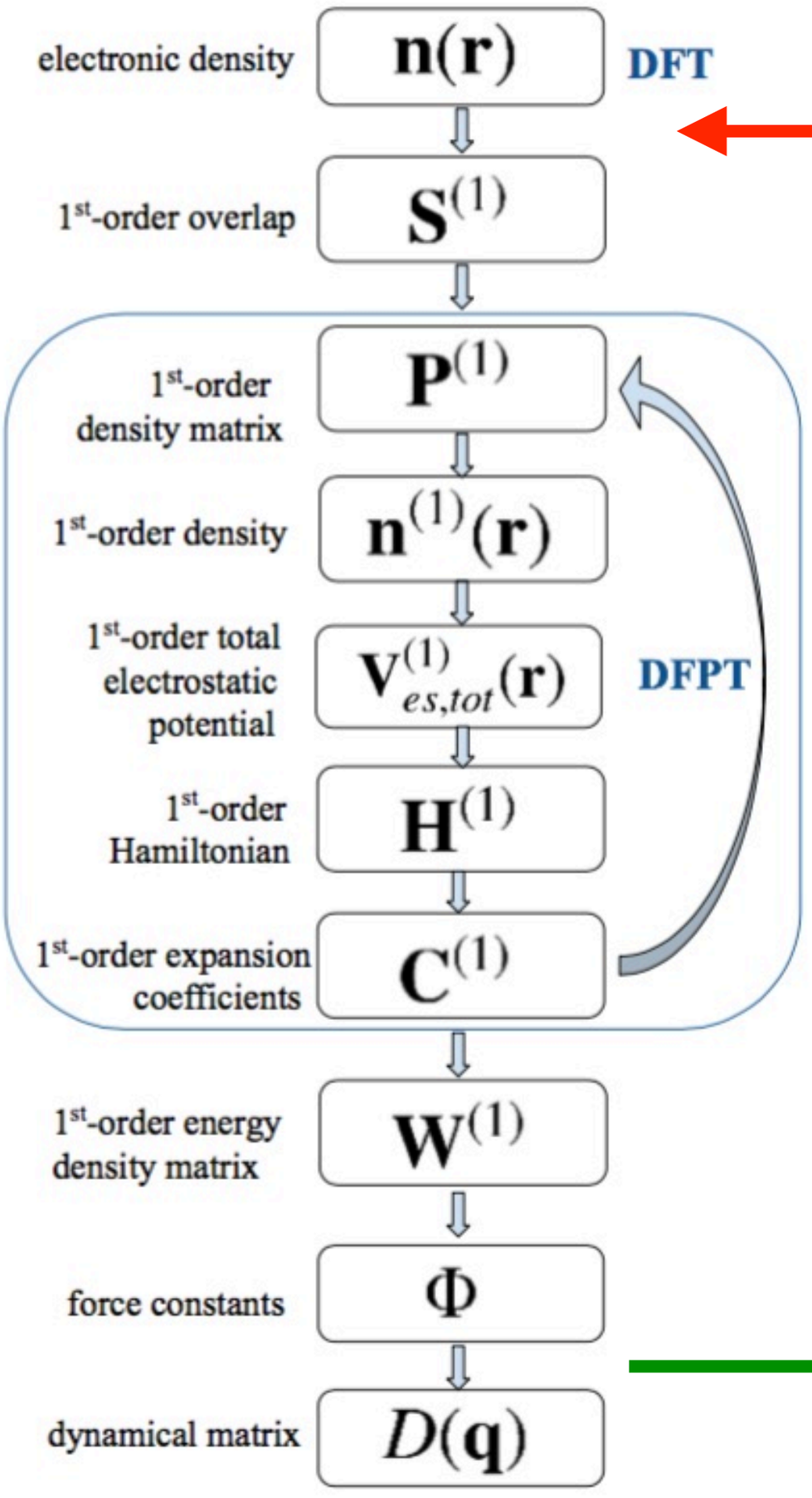
Density Functional Theory:

*density n(**r**)*

Density Functional Perturbation Theory:

density response $dn(\mathbf{r})/d\mathbf{R}_I$





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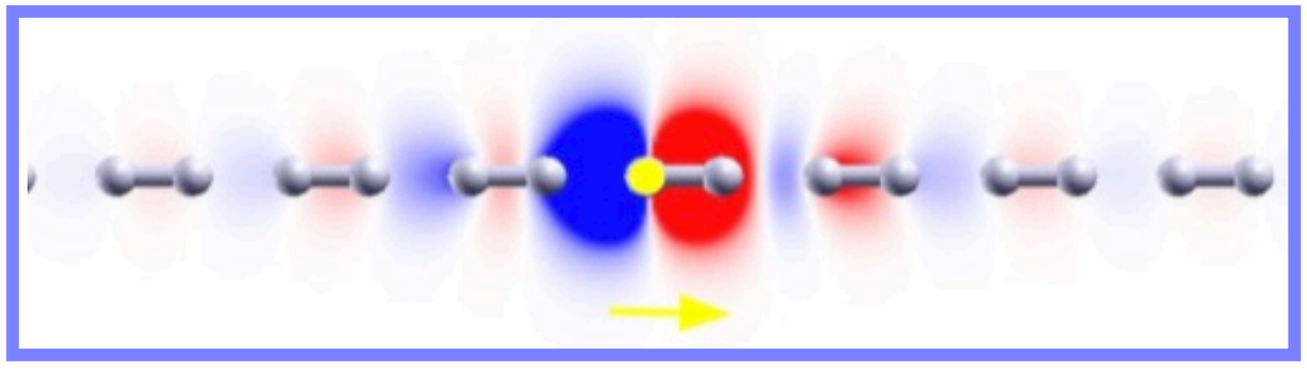
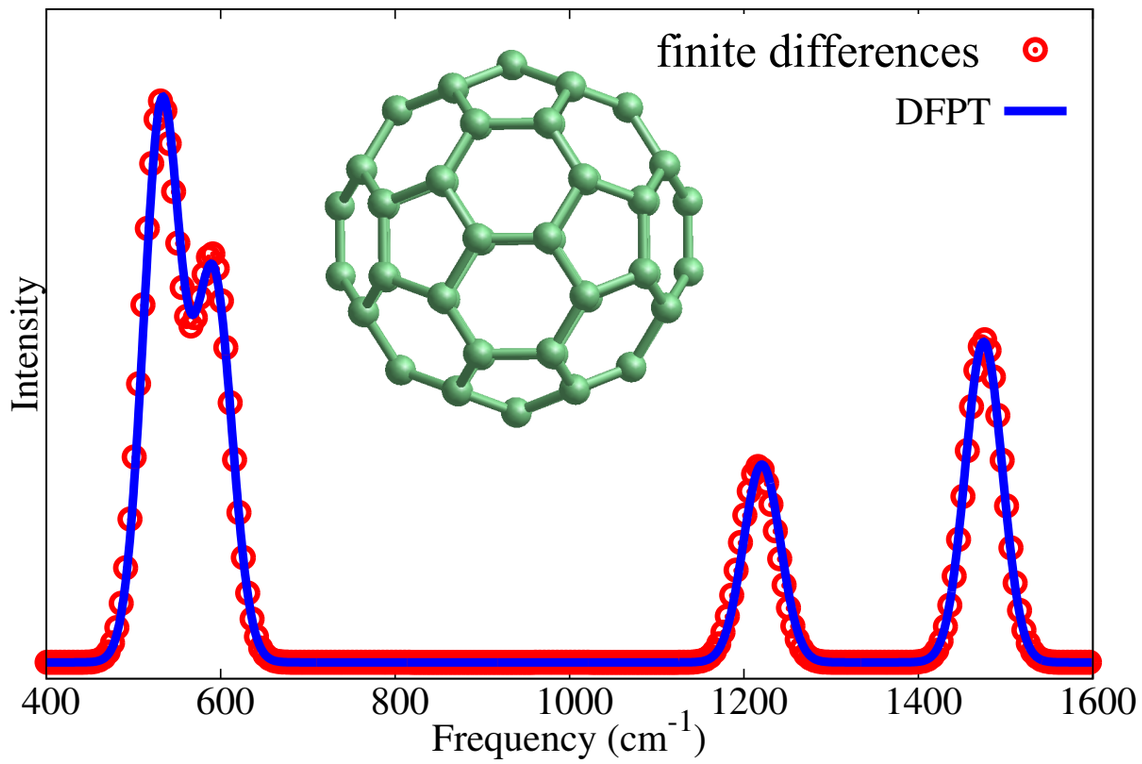


All phonon properties!

DF-Perturbation Theory in *FHI-aims*

H. Shang, C. Carbogno, P. Rinke, and M. Scheffler, Comp. Phys. Comm. ***215****, 26 (2017).*

Finite Systems: C_{60}



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Comparison **DFPT** and **finite differences** for vibrational properties

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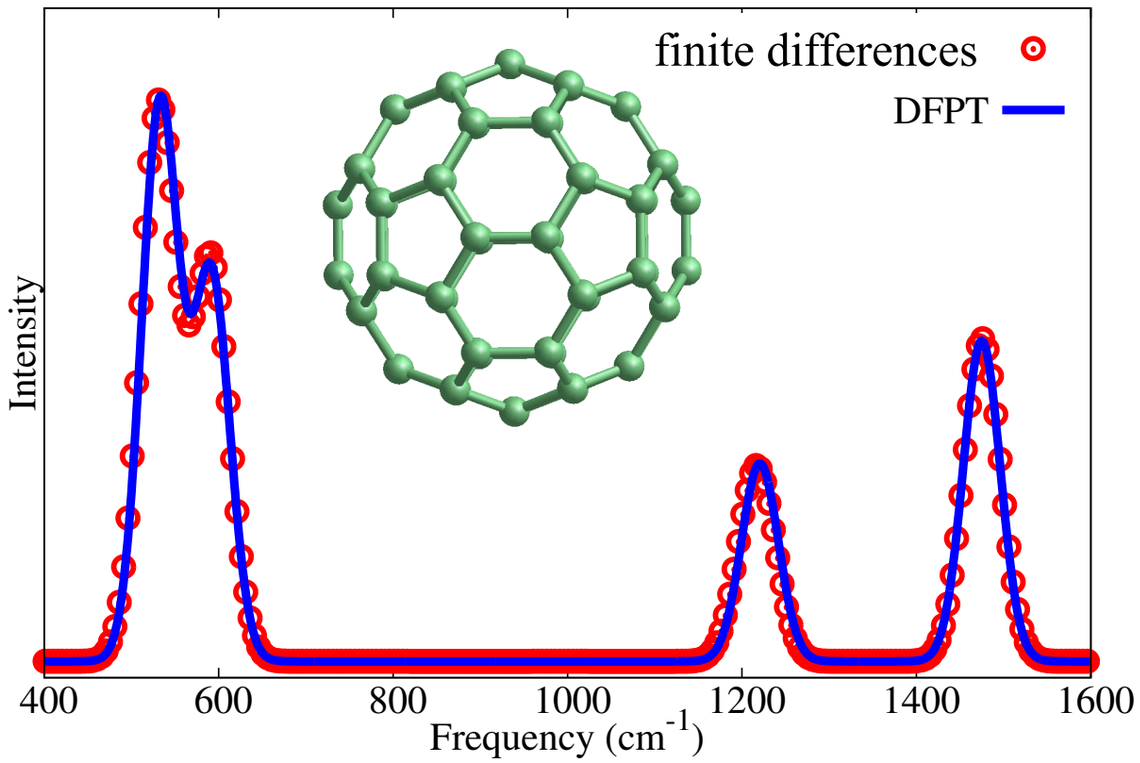
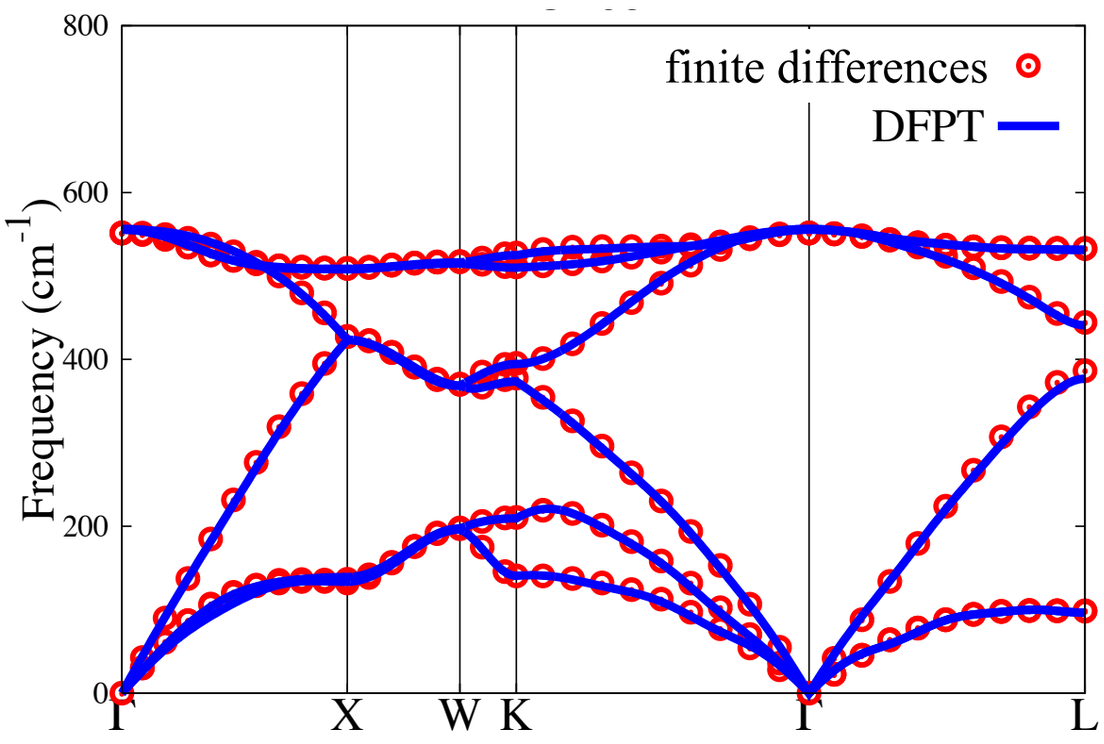


Periodic Systems: Silicon



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Static Equilibrium Energy from DFT

Hessian Φ_{ij}

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

`FHI-vibes & phonopy`

F. Knoop *et al.*, *J. Open Source Softw.* **5**, 2671 (2020).
A. Togo, F. Oba, and I. Tanaka, *Phys. Rev. B* **78**, 134106 (2008).

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  K. Kunc, and R. M. Martin, *Phys. Rev. Lett.* **48**, 406 (1982) &
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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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\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}$$

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: $9N^2$

...in Crystalline Solids:

N ... Number of atoms

⇓

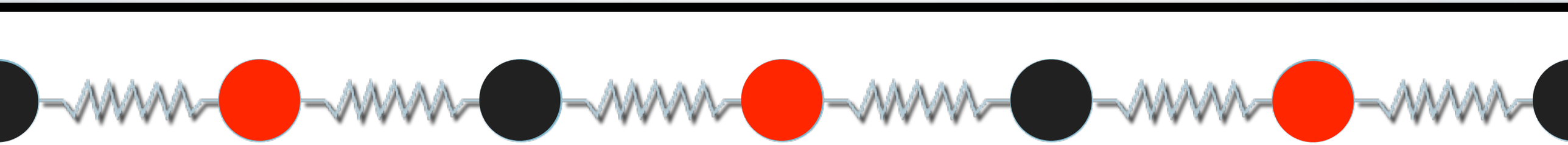
Degrees of Freedom: ***3N***

Dimension of Hessian: $9N^2$

BUT:

$$N \to \infty$$

PERIODIC BOUNDARY CONDITIONS

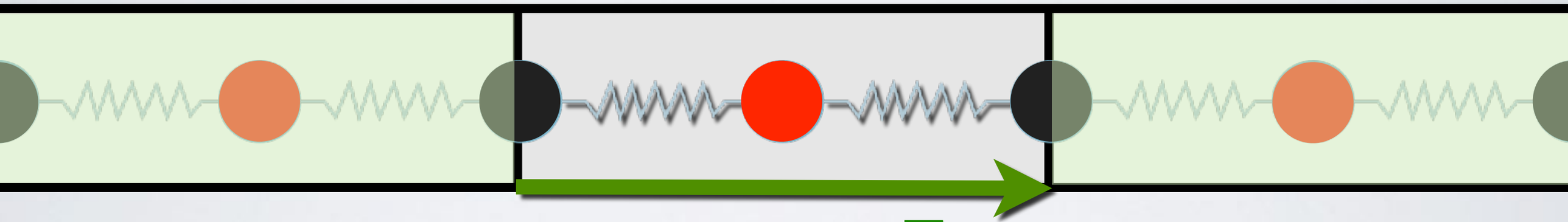


PERIODIC BOUNDARY CONDITIONS

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

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

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

Fourier Transform

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

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)

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

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

VIBRATIONS IN A CRYSTAL 101

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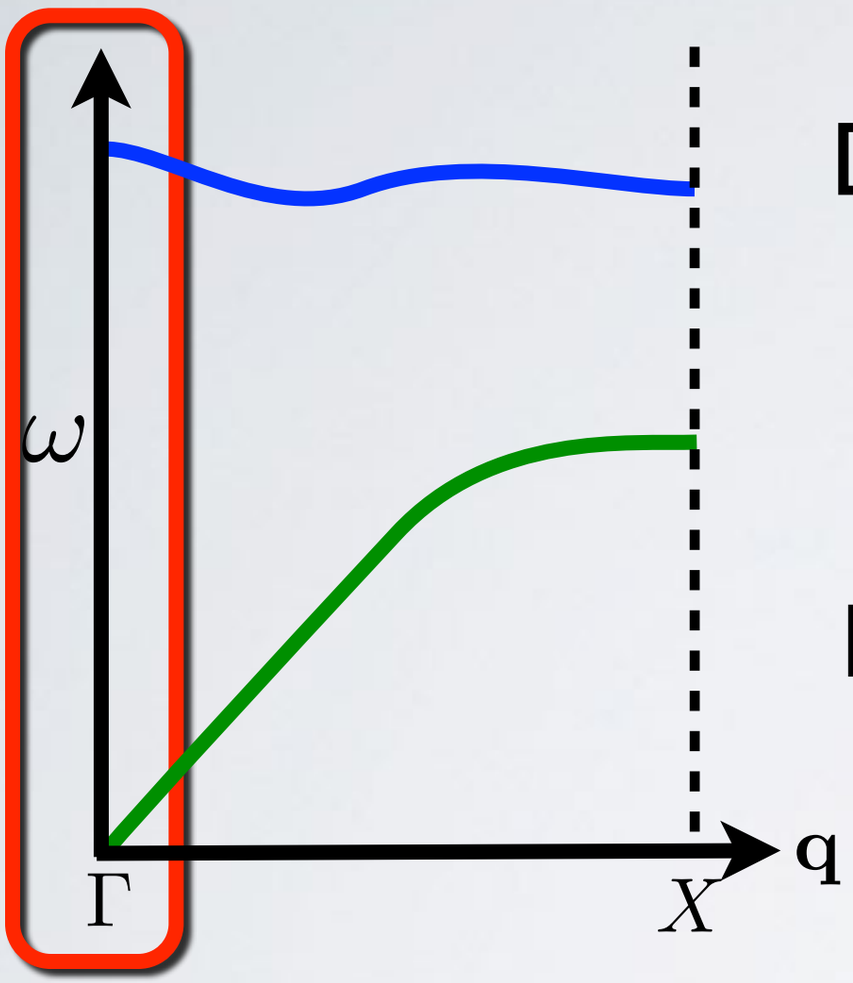

Dynamical matrix:

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

$= 1$

Eigenvalue problem:

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

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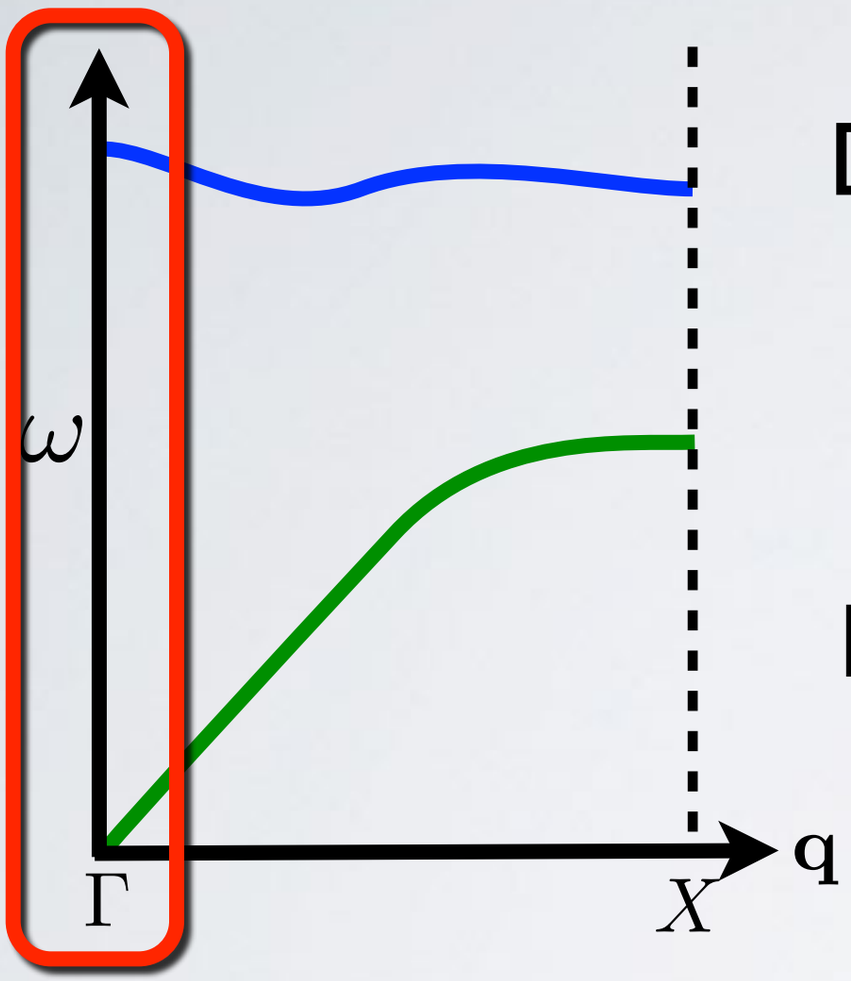

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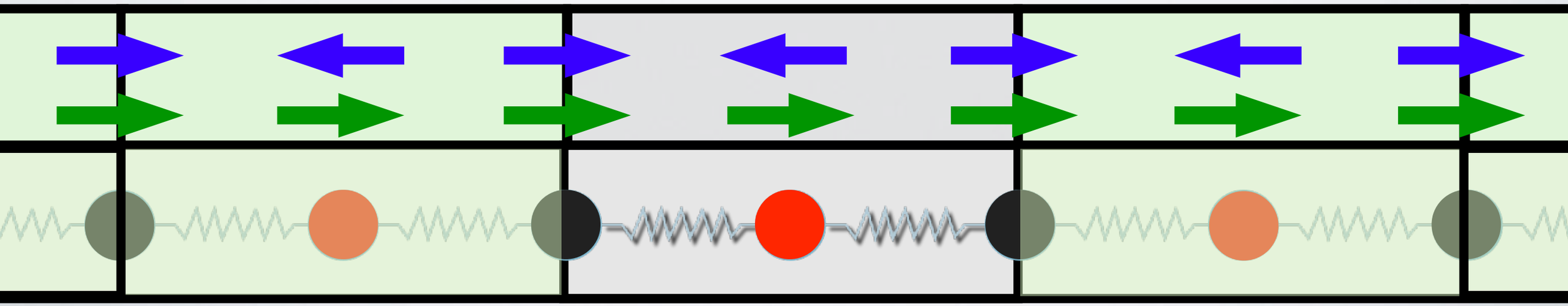

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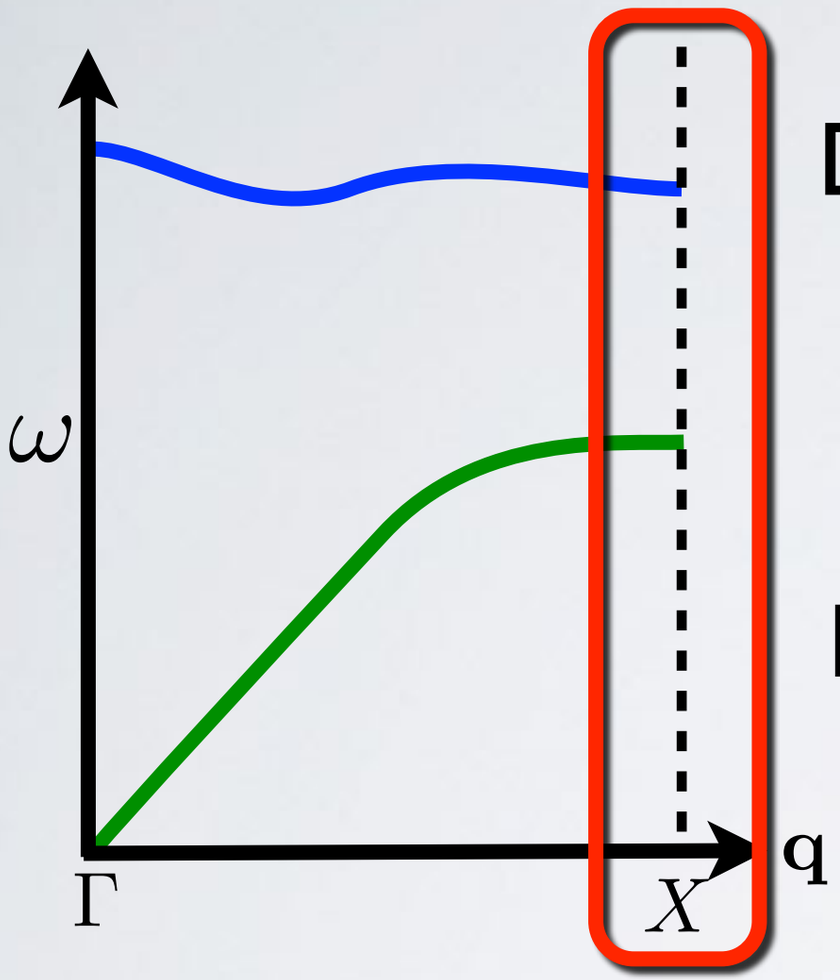

Dynamical matrix:

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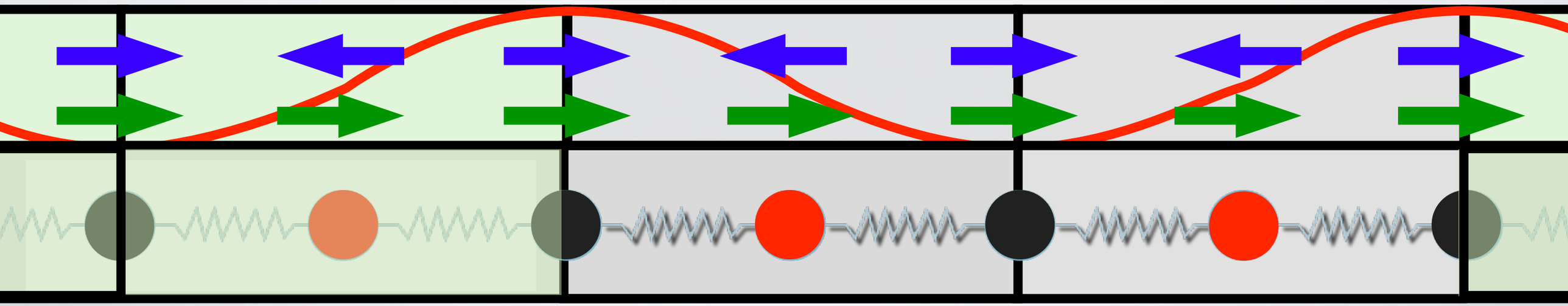
Eigenvalue problem:

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



VIBRATIONS IN A CRYSTAL 101

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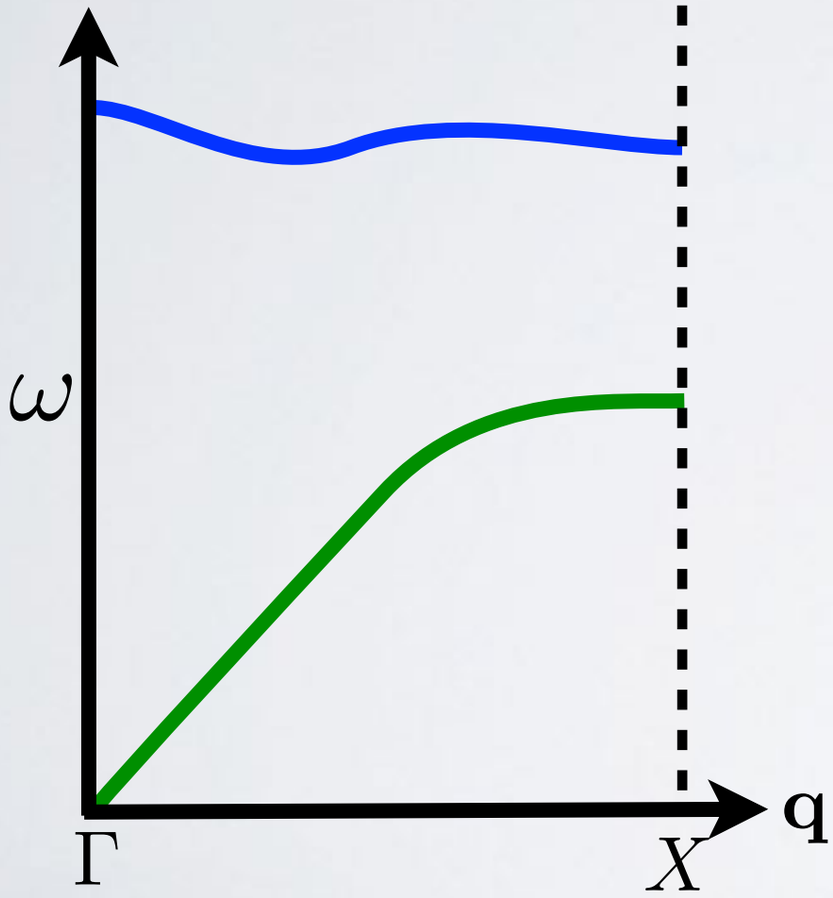
a

For N_p atoms in the unit cell there are:



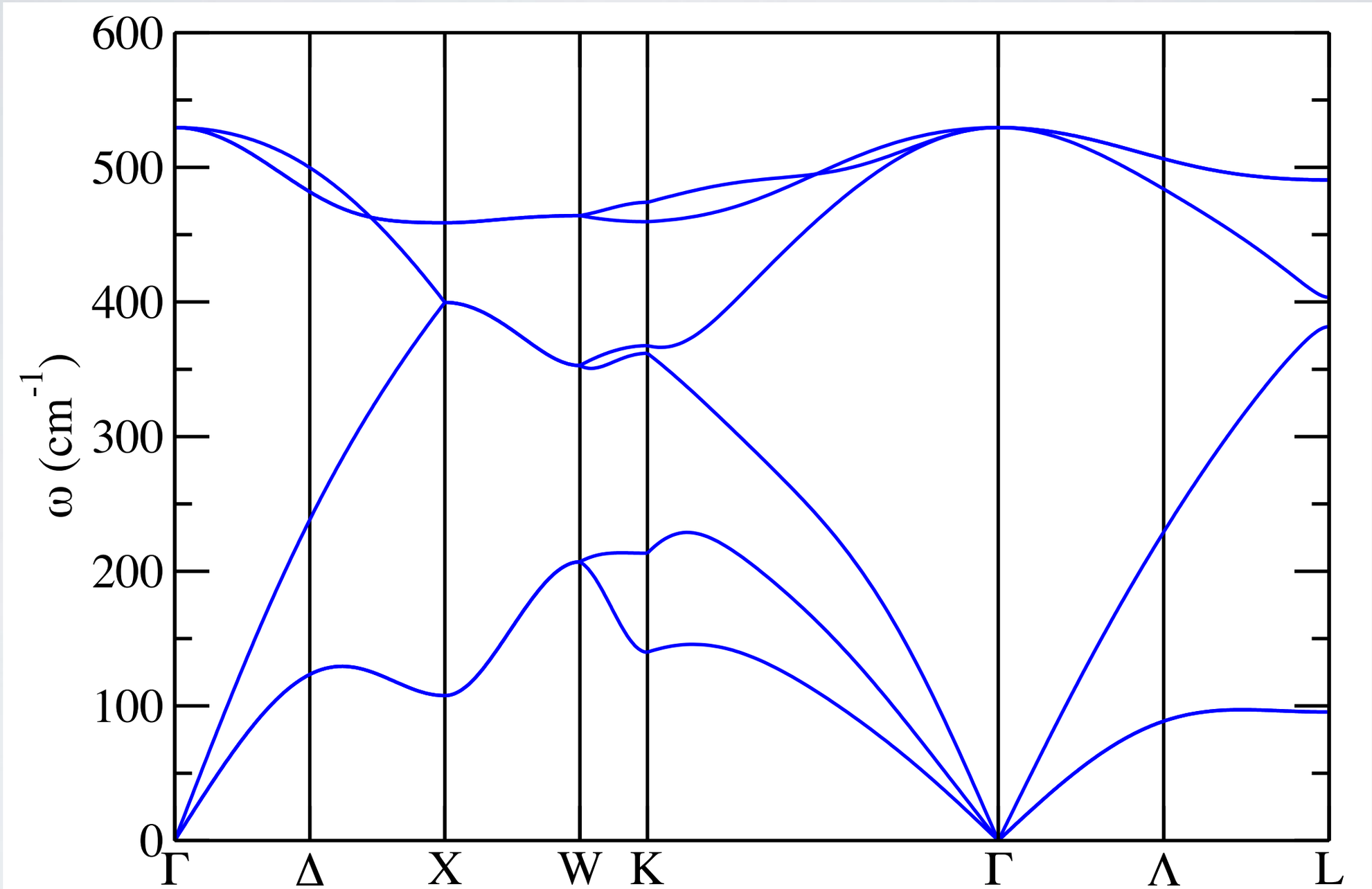
3 Acoustic modes:

- 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

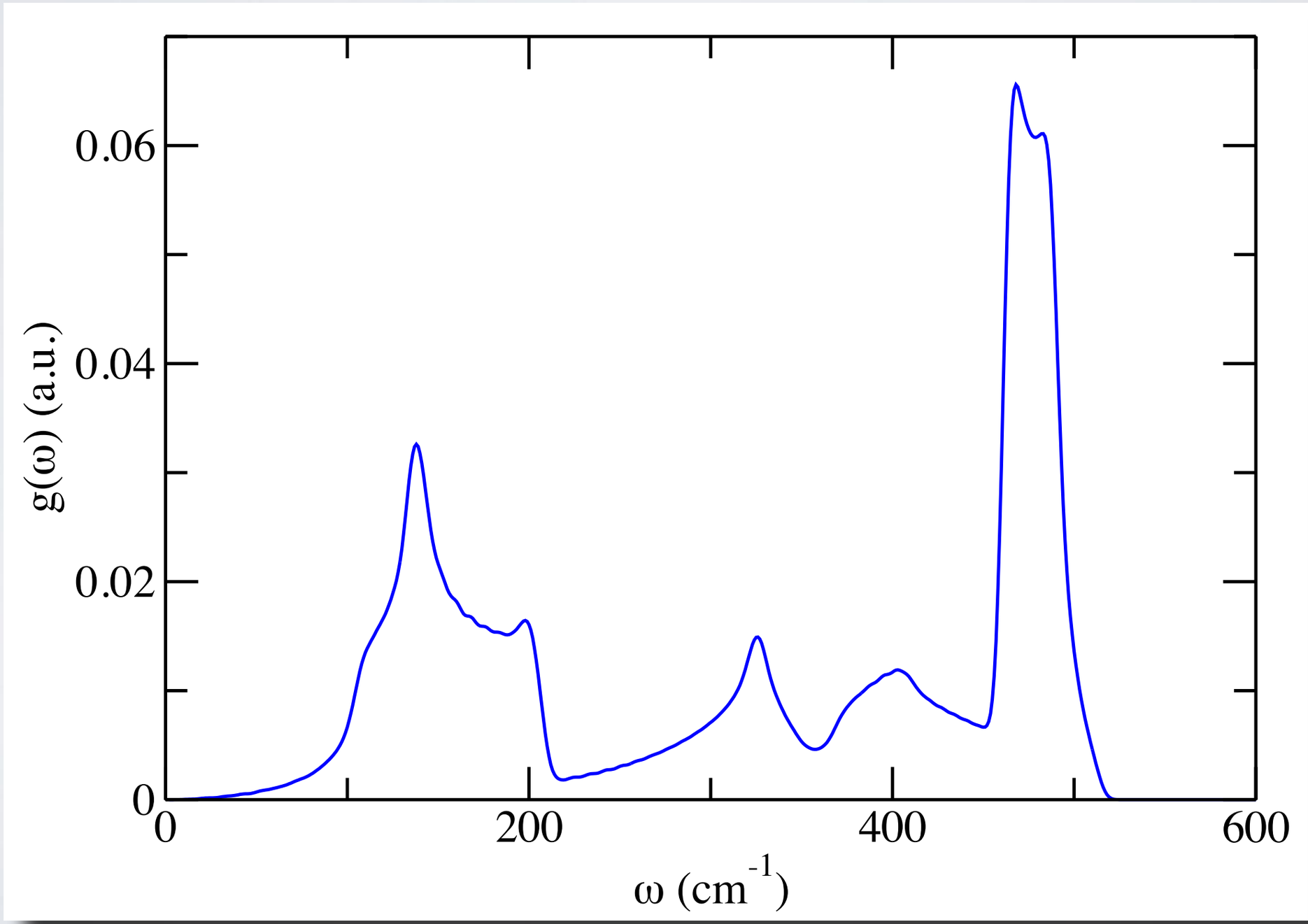
VIBRATIONAL BAND STRUCTURE



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

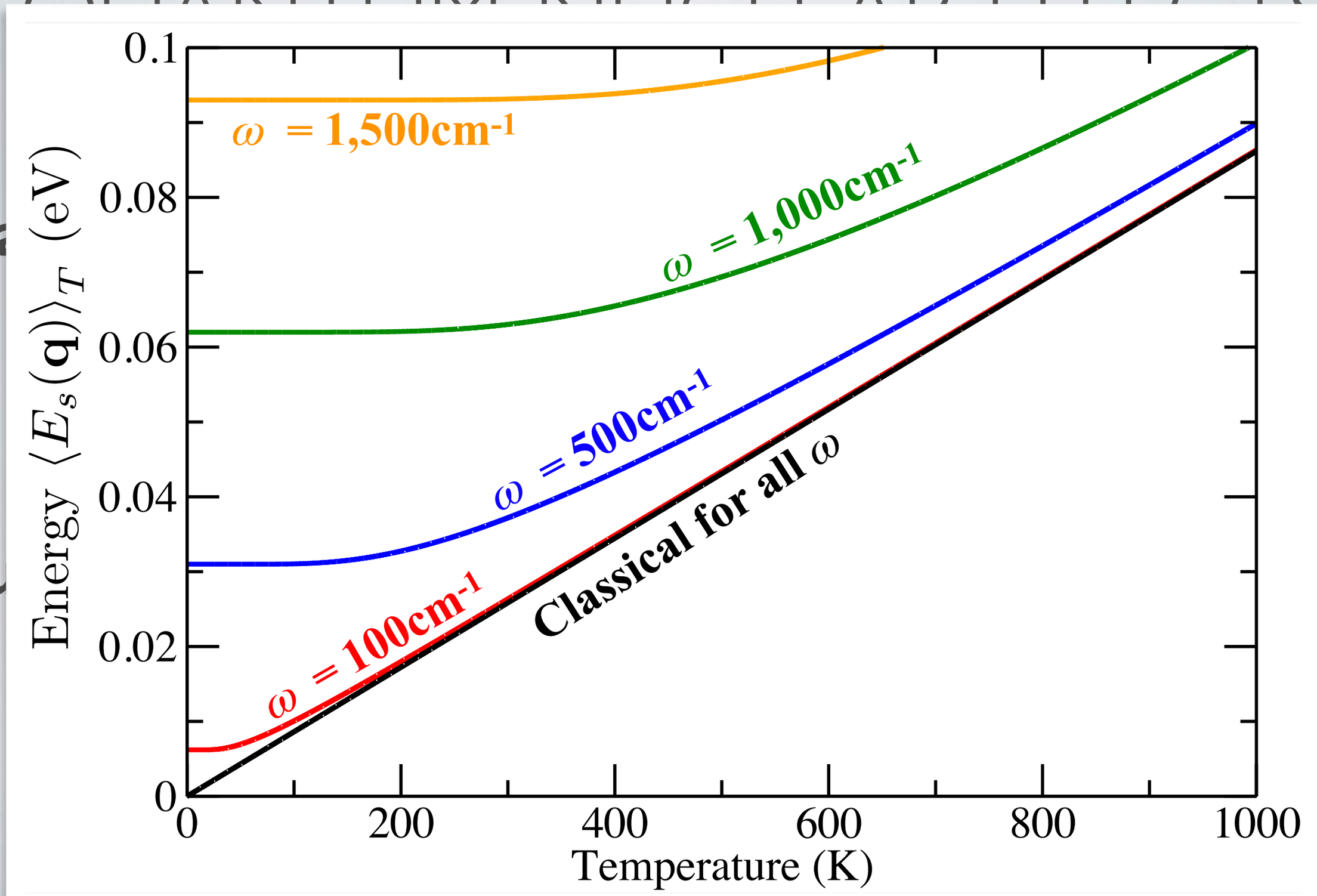
$$\langle E_s(\mathbf{q}, T)\rangle = \hbar\omega_s(\mathbf{q}) \left(n_{\mathrm{BE}}(\omega_s(\mathbf{q}), T)) + \frac{1}{2} \right)$$

ATTENTION:

QUANTUM NUCLEAR EFFECTS

Cla

Qu



THE HARMONIC FREE ENERGY

$$F^{ha}(T) = E(\{\mathbf{R}_0\})$$

Static Equilibrium Energy

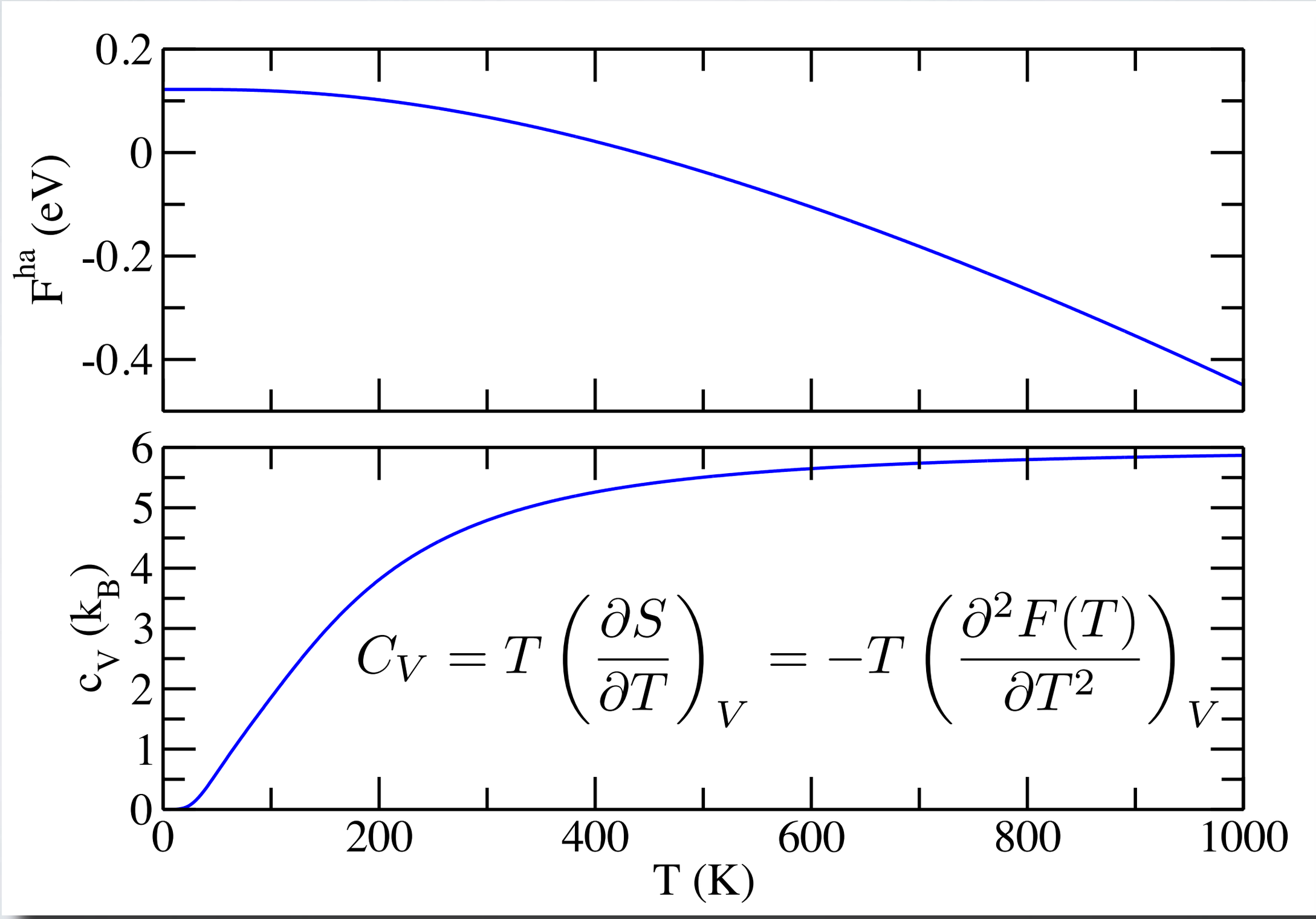
$$+ \int d\omega\ g(\omega) \frac{\hbar\omega}{2}$$

Zero-point vibration

$$+ \int d\omega\ g(\omega)\ k_B T \ln\left(1 - e^{\left(-\frac{\hbar\omega}{k_B T}\right)}\right)$$

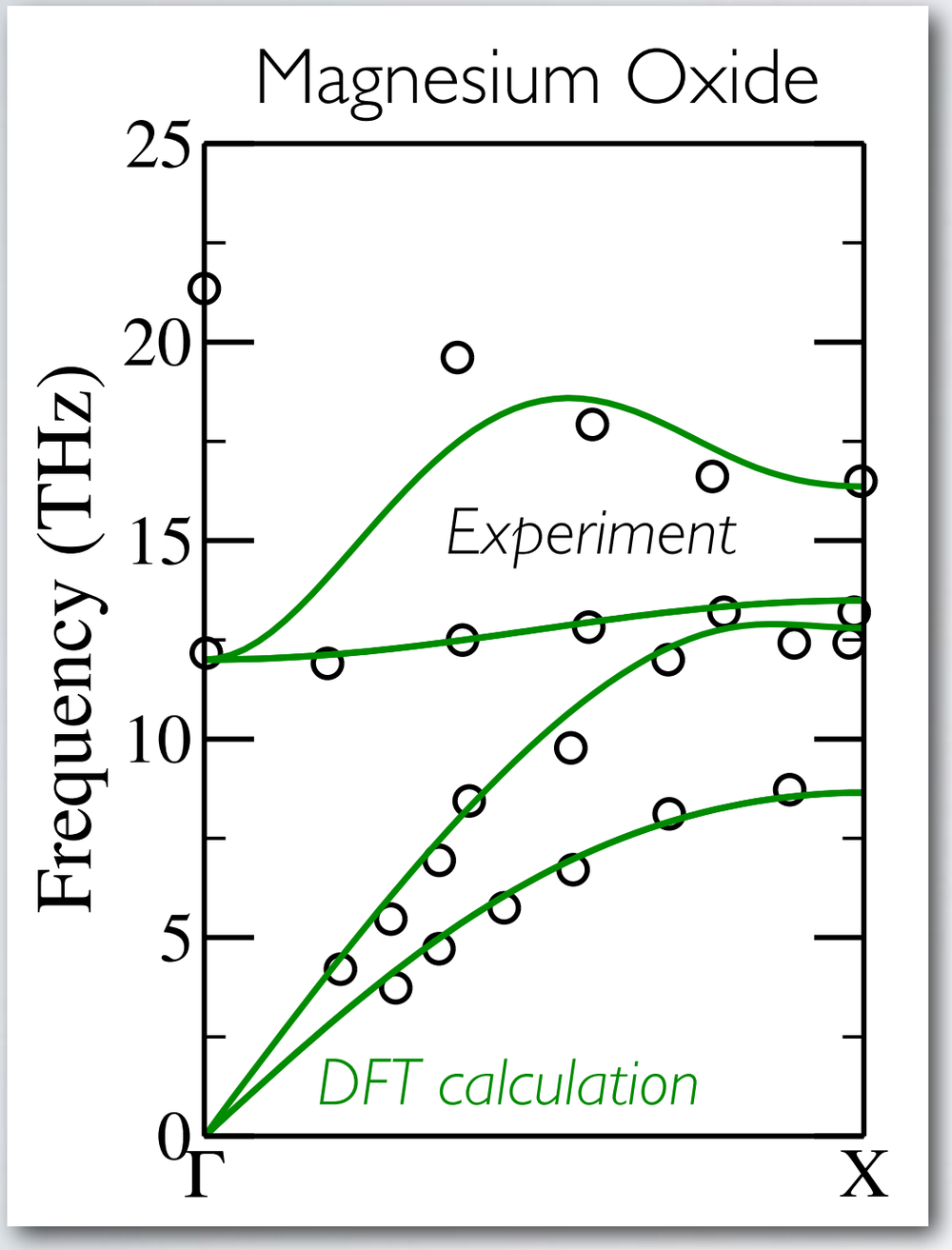
Thermally induced vibrations

FREE ENERGY AND HEAT CAPACITY



POLAR CRYSTALS

P. Giannozzi, S. Degironcoli, P. Pavone, and S. Baroni, *Phys. Rev. B* **43**, 7231 (1991)
X. Gonze, and C. Lee, *Phys. Rev. B* **55**, 10355 (1997)



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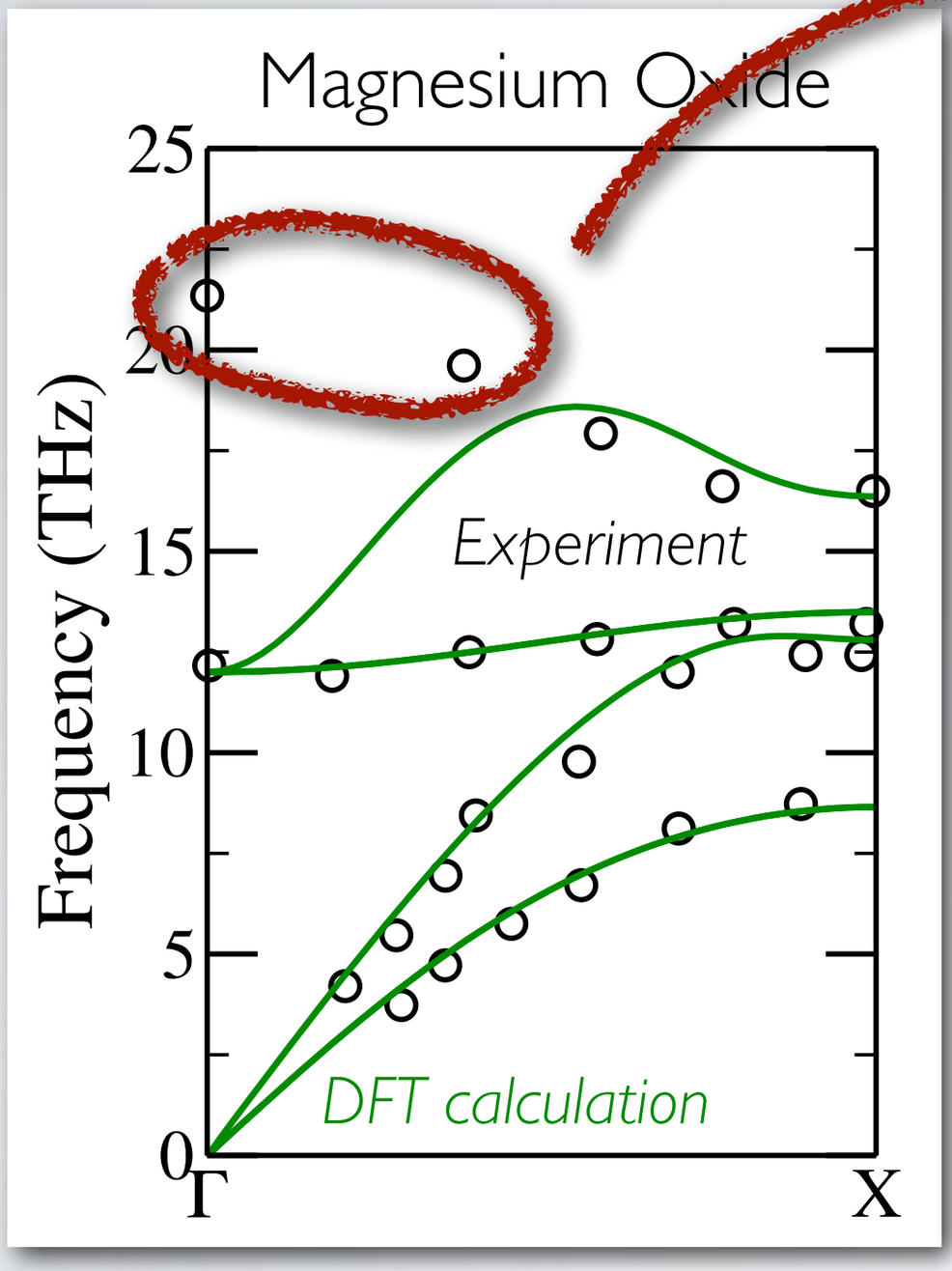
What is wrong here?



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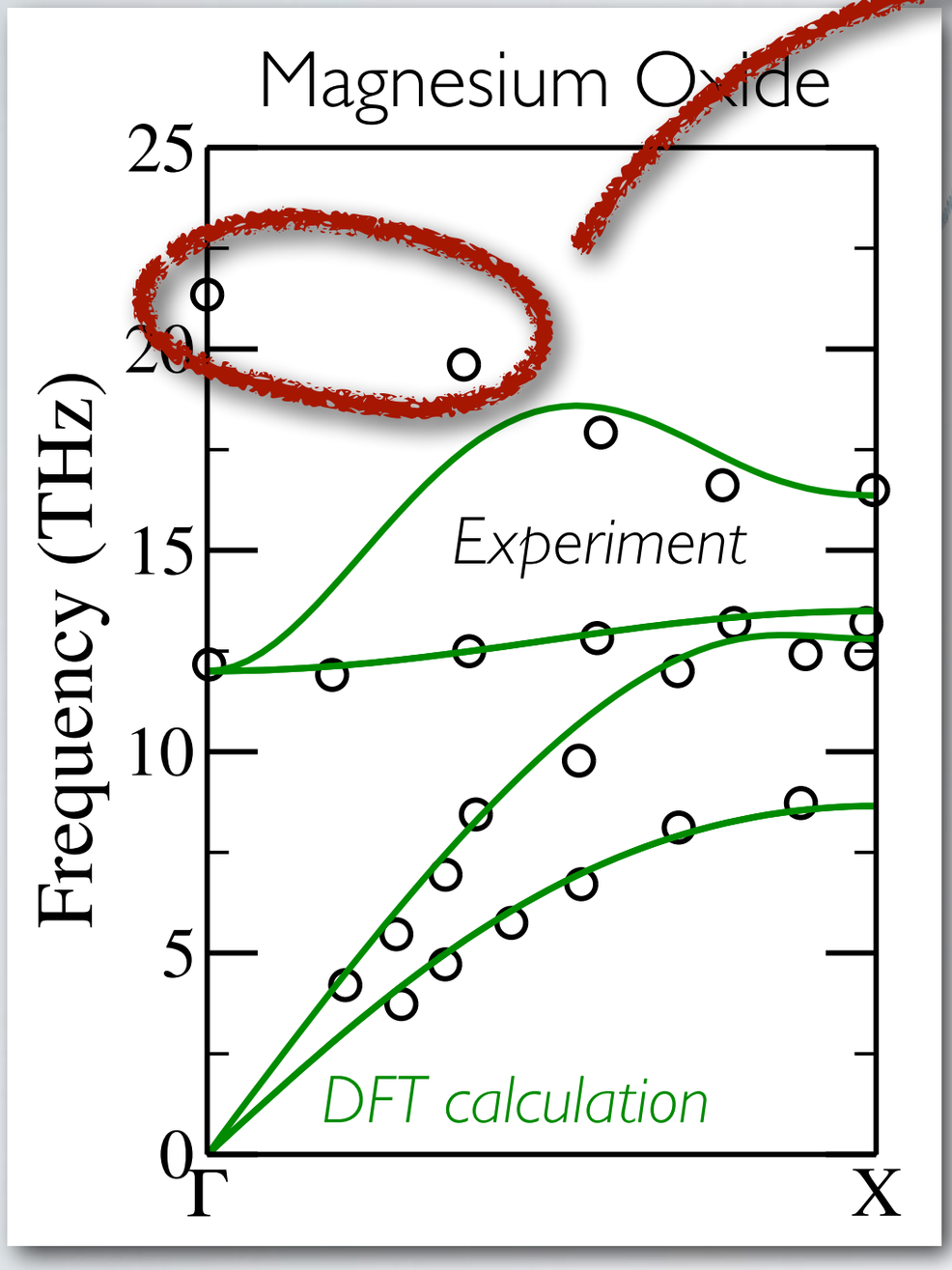

Exp: M. J. L. Sangster, G. Peckham, and D. H. Saunderson, J. Phys. C **3**, 1026 (1970).

What is wrong here?

When *charged* atoms are *displaced*, a **weak, long-ranged** dipole field is induced.

In the **short-range** ($q \gg 0$) this interaction is clouded by all other forces.

In the **long-range** ($q \approx 0$) this interaction becomes **significant**.

POLAR CRYSTALS

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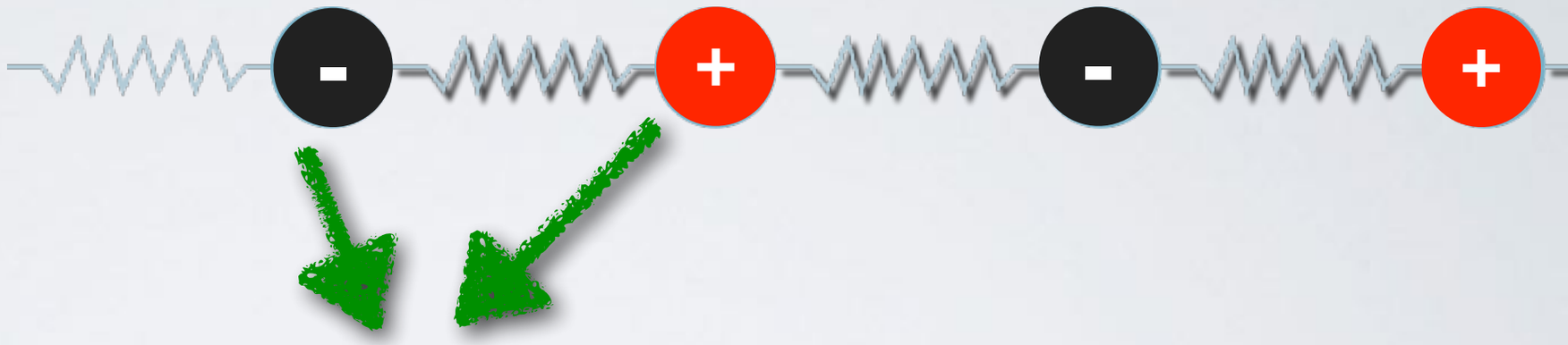
X. Gonze, and C. Lee, *Phys. Rev. B* **55**, 10355 (1997)

How to account for it?



(a) Calculate *Born Effective Charges* $\mathbf{Z_i^*}$, i.e., the **derivative** of the **polarisation**.

(b) Calculate *dielectric constant* ε_∞, i.e, how the electric field is **screened**.

(c) Add the **additional** interaction.

$$\mathbf{D}\left(jj'\right) \rightarrow \mathbf{D}\left(jj'\right) + \frac{1}{\sqrt{M_j M_{j'}}} \frac{4\pi}{\Omega_0} \frac{\left[\mathbf{q}\cdot\mathbf{Z}_j^*\right]\left[\mathbf{q}\cdot\mathbf{Z}_{j'}^*\right]}{\mathbf{q}\cdot\varepsilon^\infty\cdot\mathbf{q}}$$

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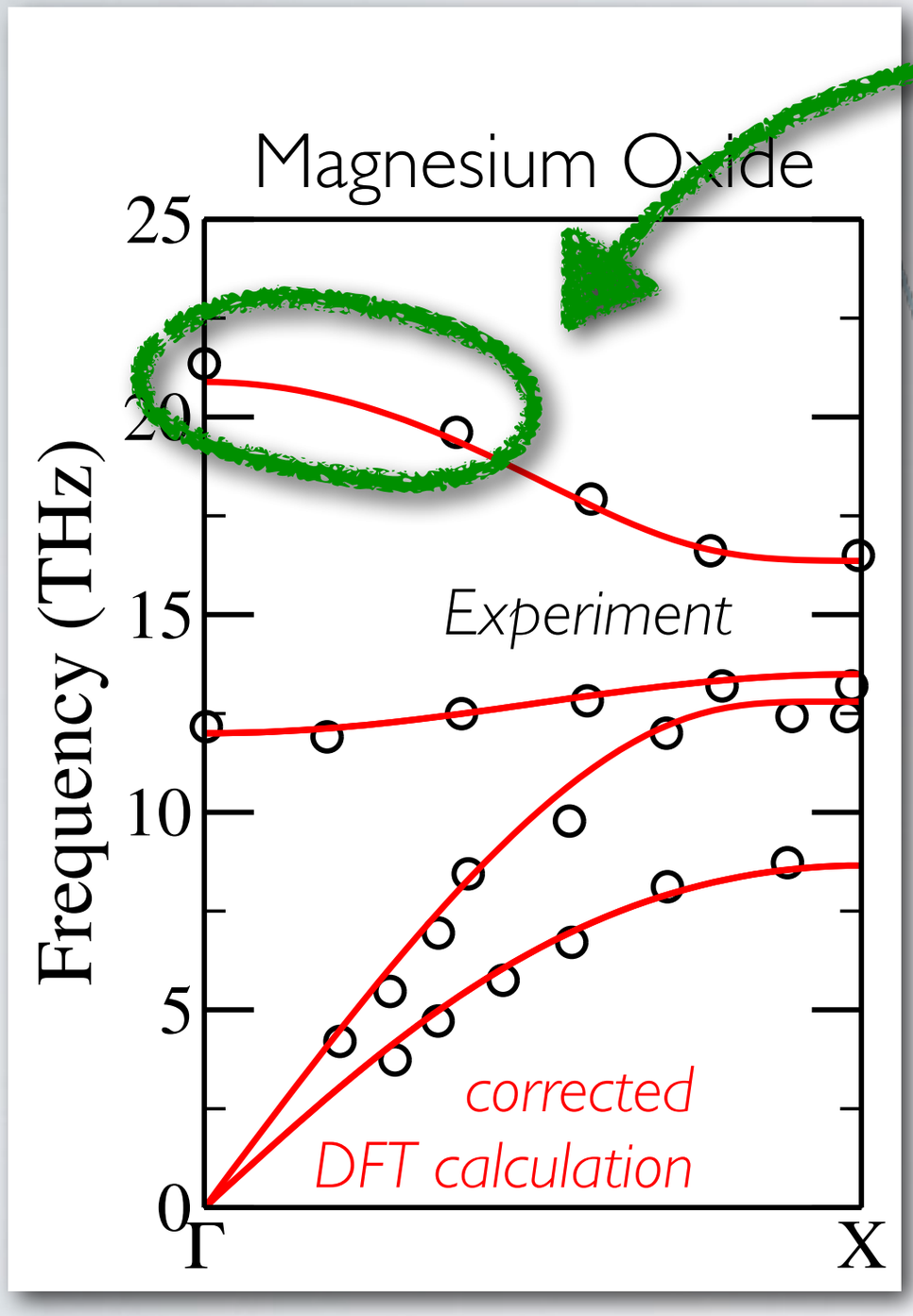

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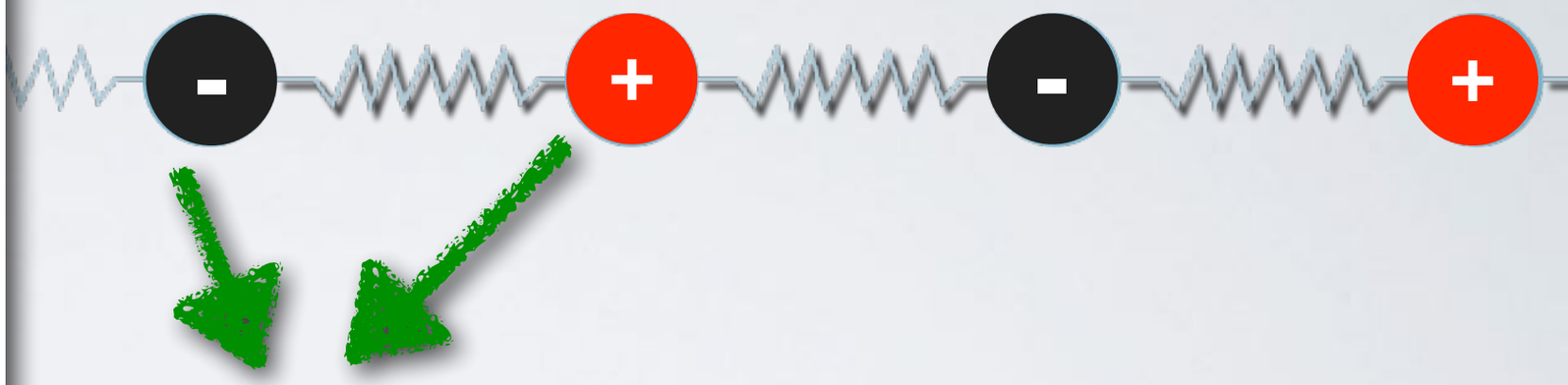

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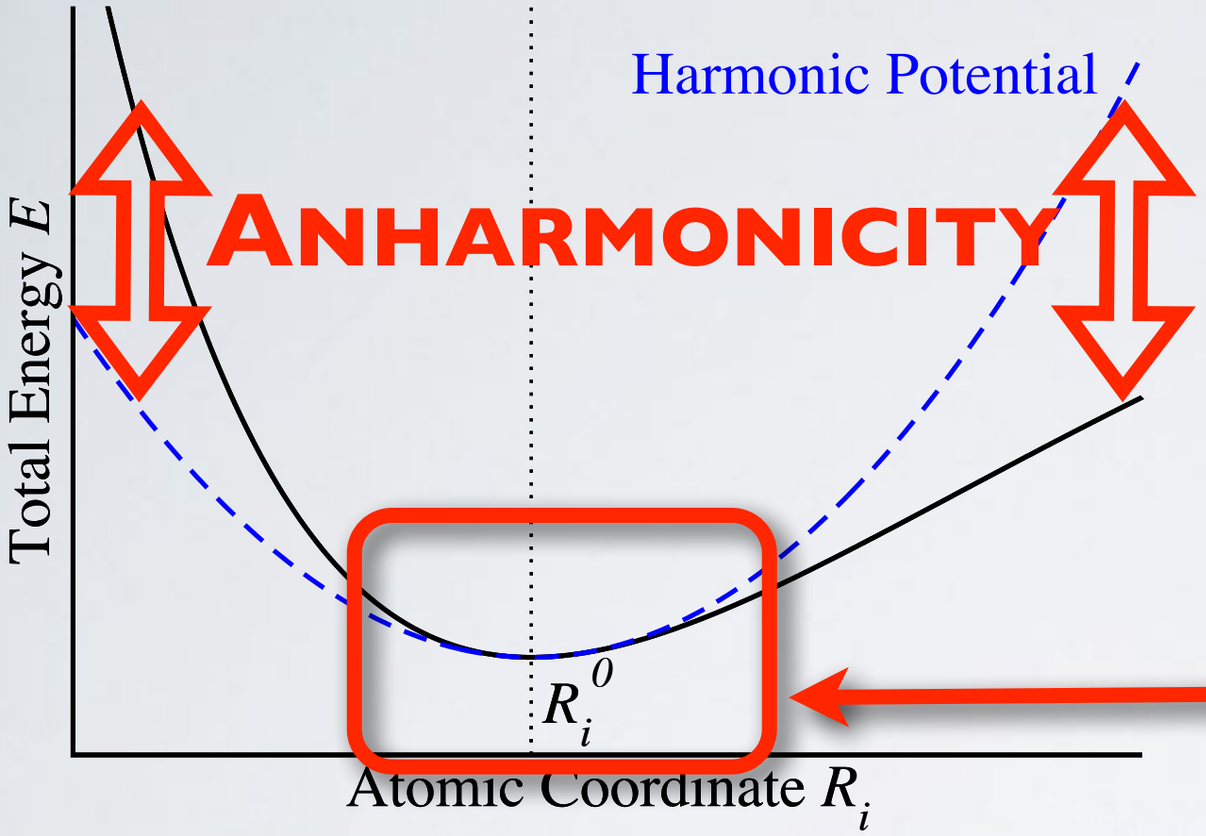
II. ANHARMONICITY

THE HARMONIC APPROXIMATION

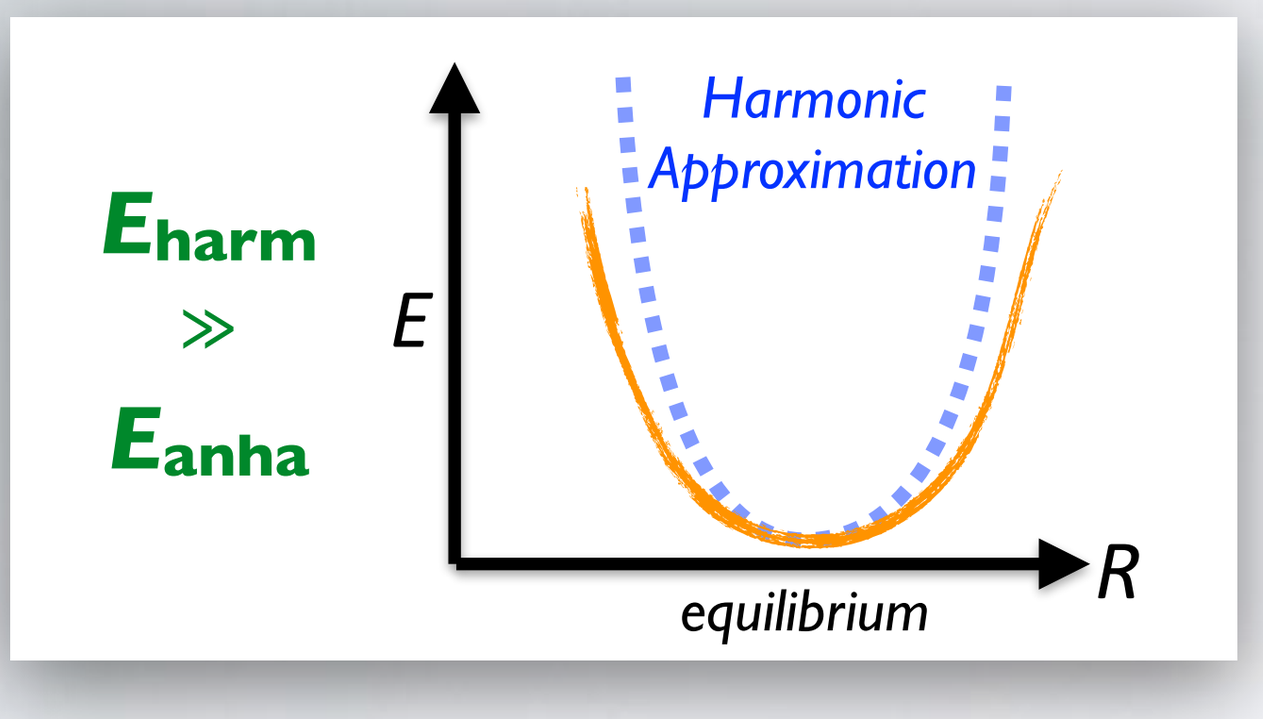


WARNING:

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

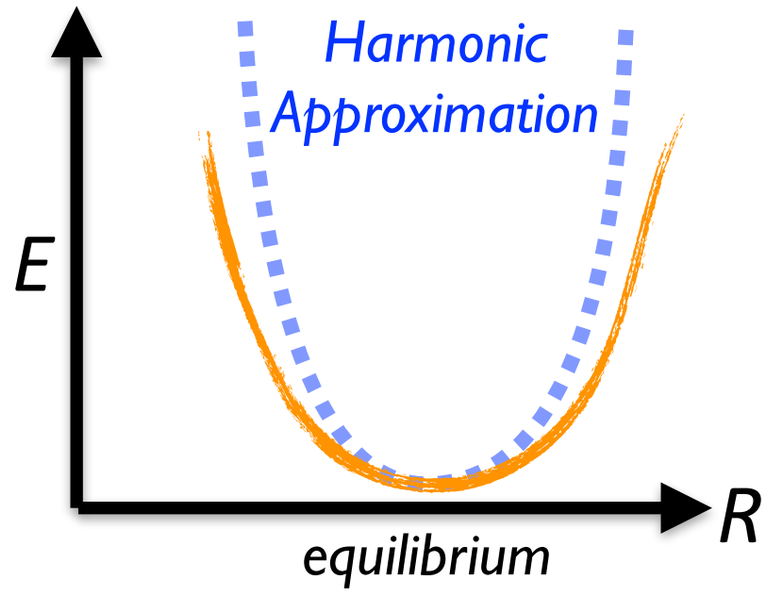
At elevated temperatures the harmonic approximation becomes increasingly **inaccurate** – and often **terribly misleading**!

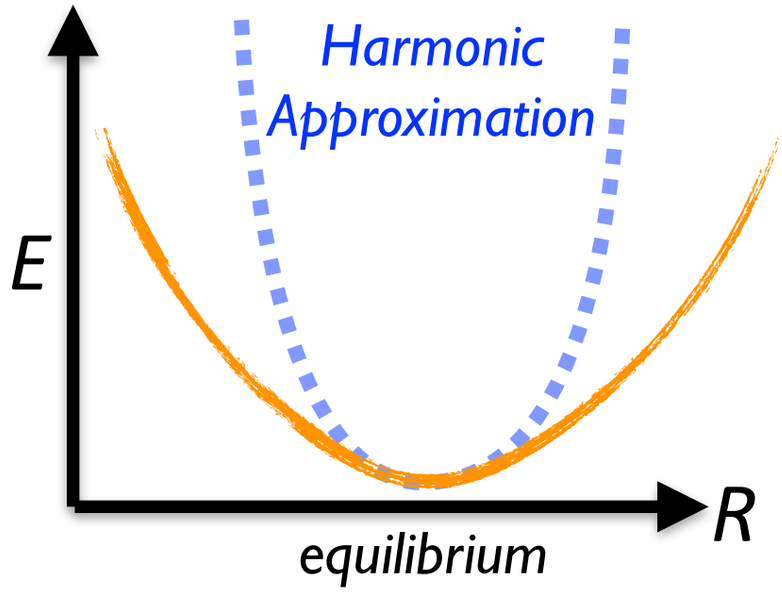
What is Anharmonicity?



What is Anharmonicity?

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





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

What is Anharmonicity?

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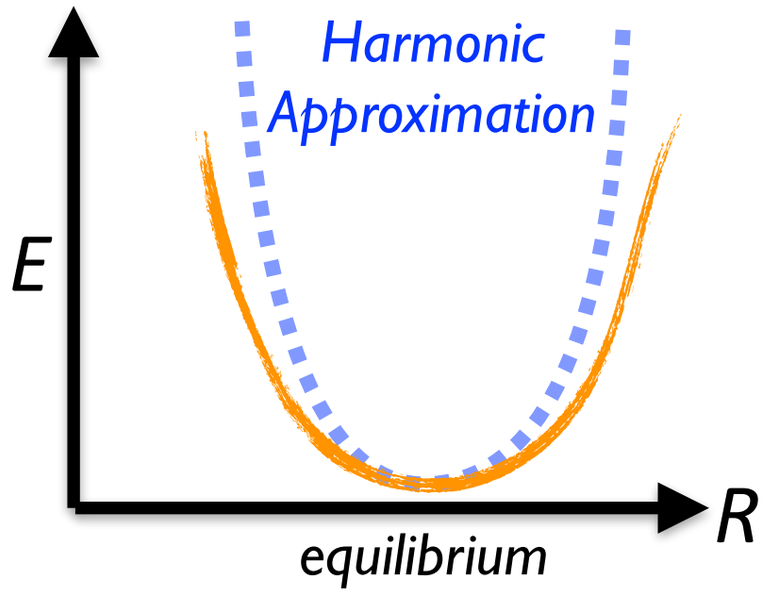
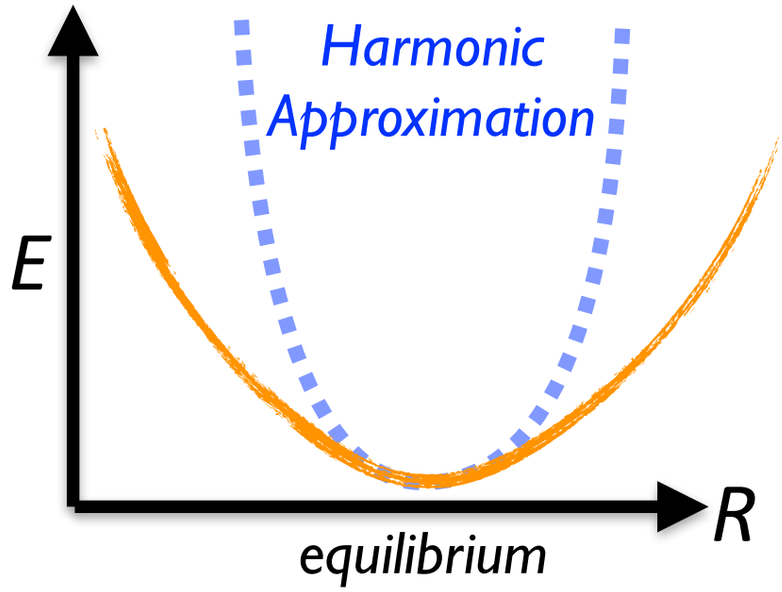
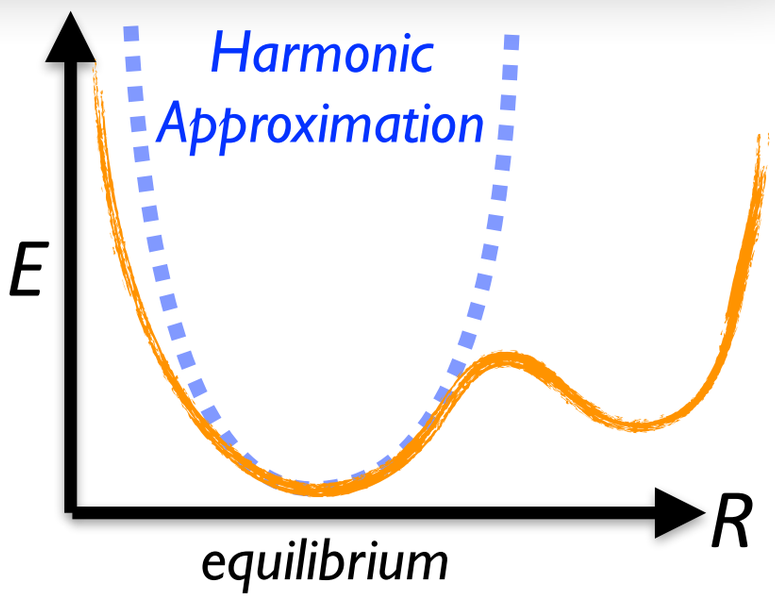




$E_{harm} \approx E_{anha}$

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



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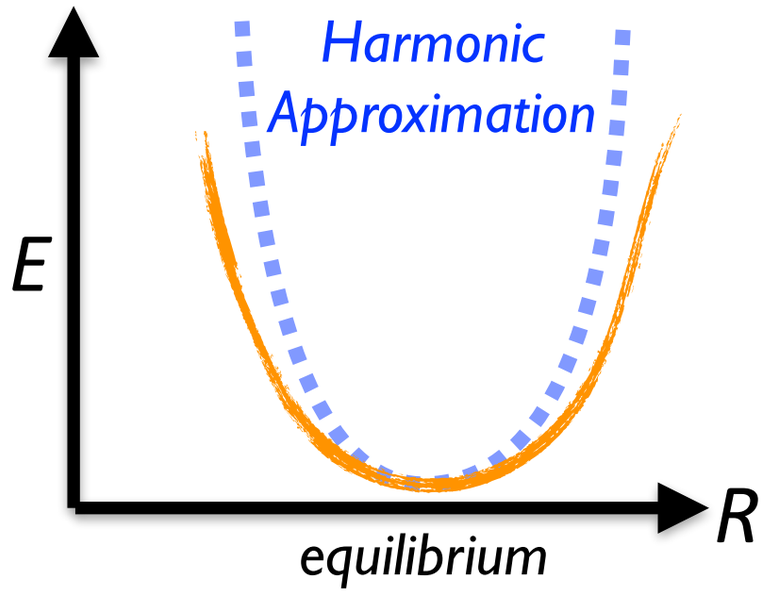

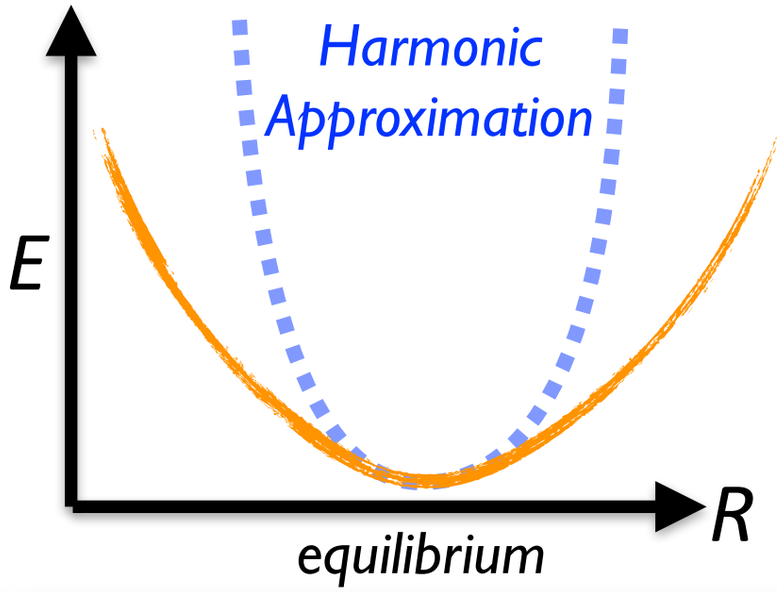

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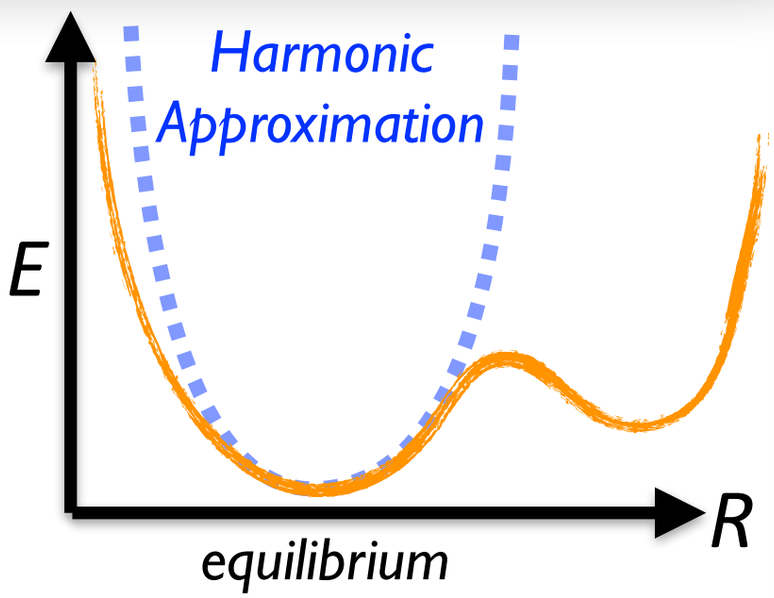
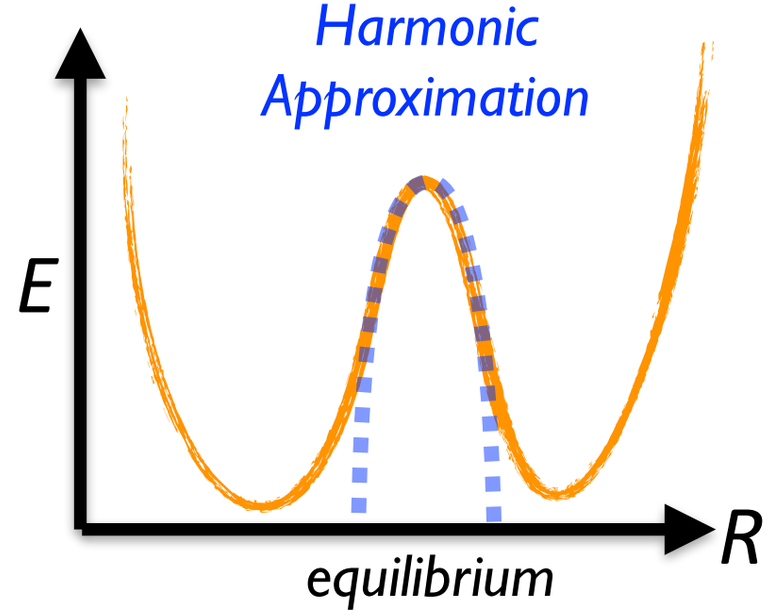
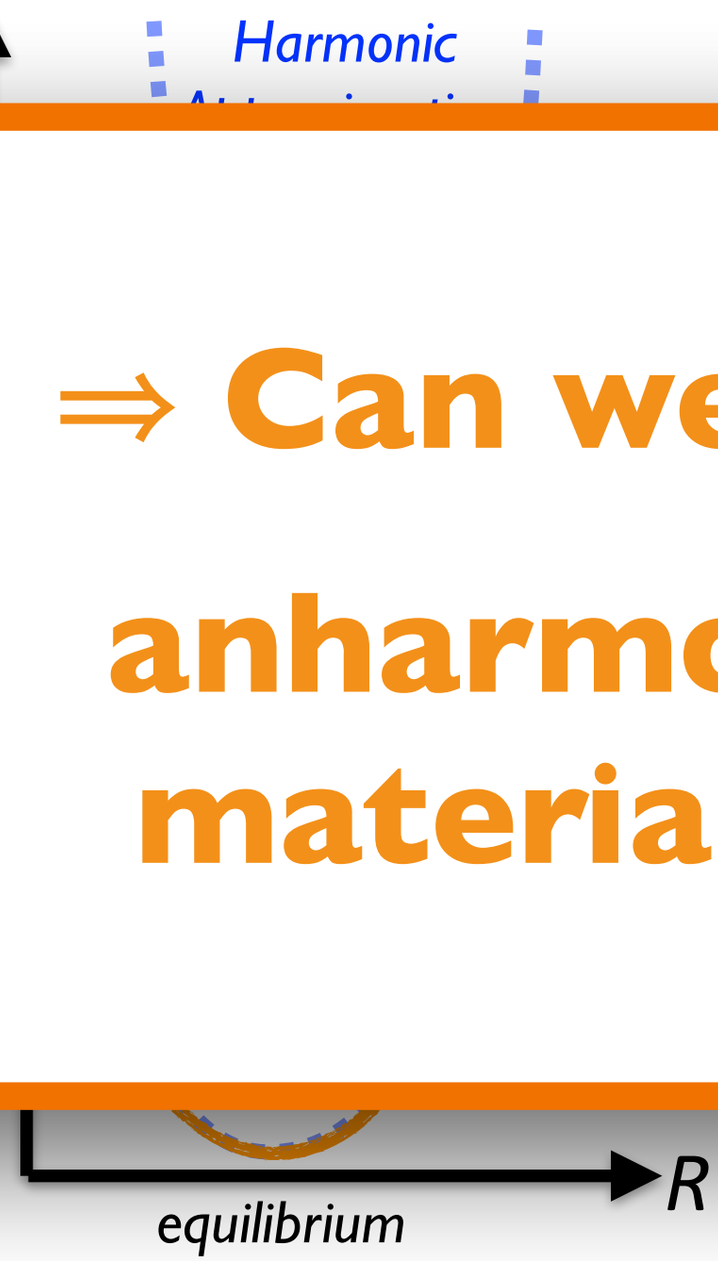




$E_{harm} = ?$

What is Anharmonicity?

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



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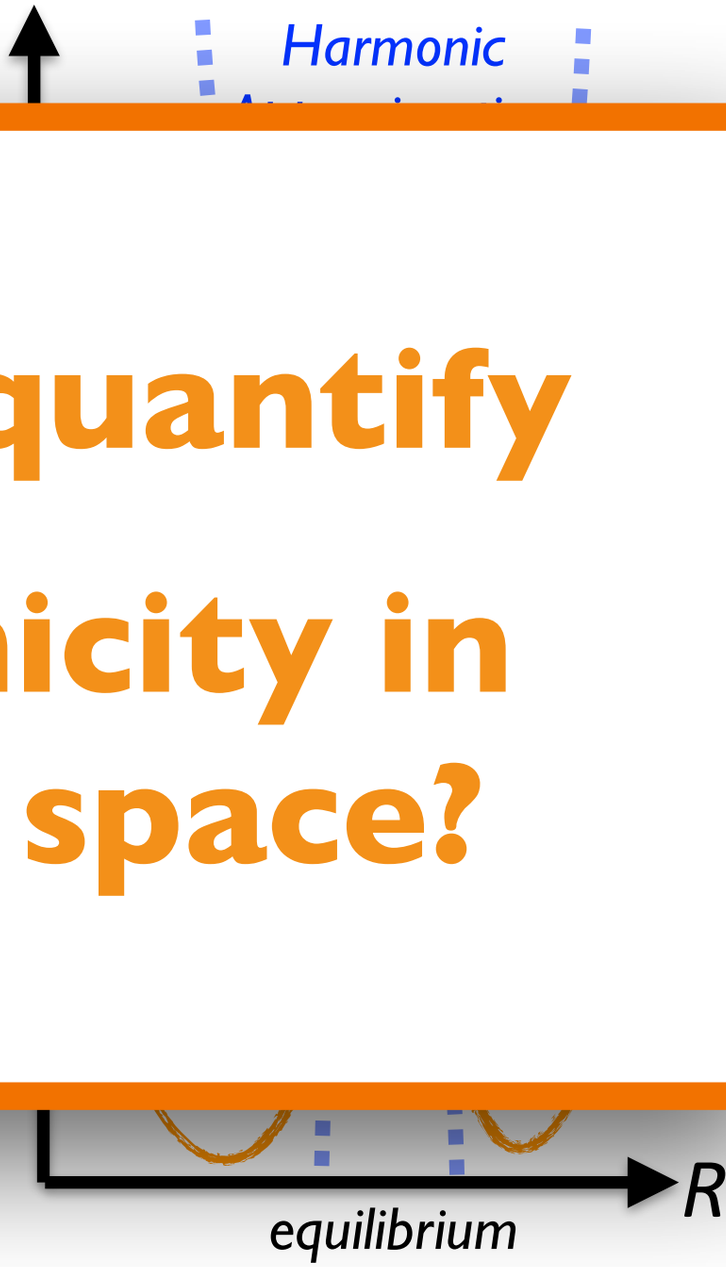


$E_{harm} \ll E_{anha}$

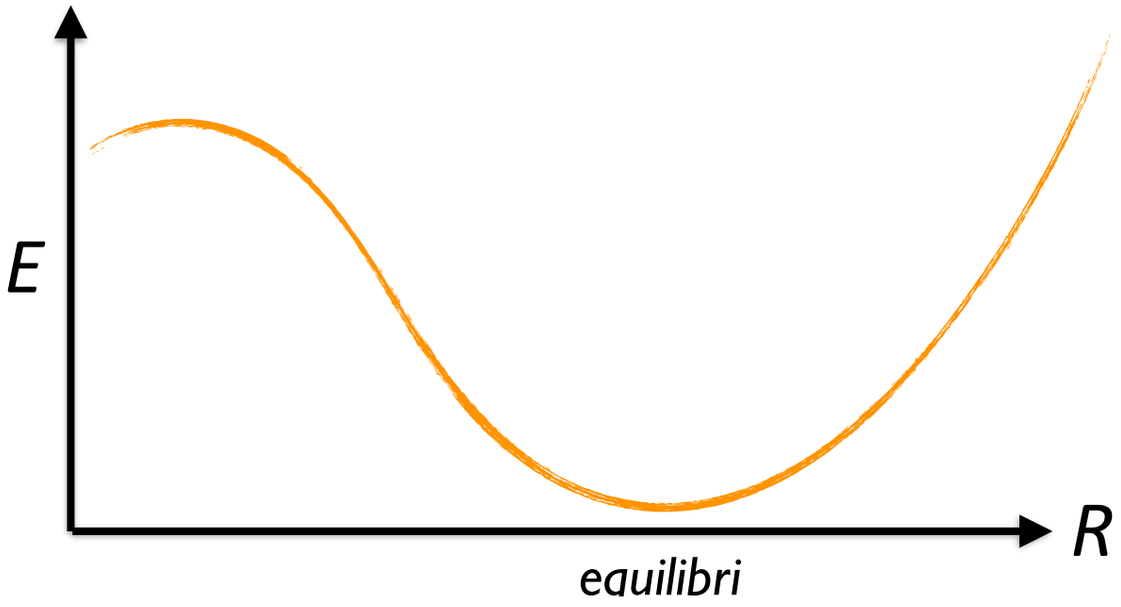
$E_{harm} = ?$

⇒ Can we quantify anharmonicity in materials space?

Anharmonicity Quantification

How do E_{harm} and $E_{anha} = E_{DFT}$ compare in different materials?

F. Knoop, T. A. R. Purcell, M. Scheffler, and C. Carbogno, *Phys. Rev. Mater.* **4**, 083809 (2020).



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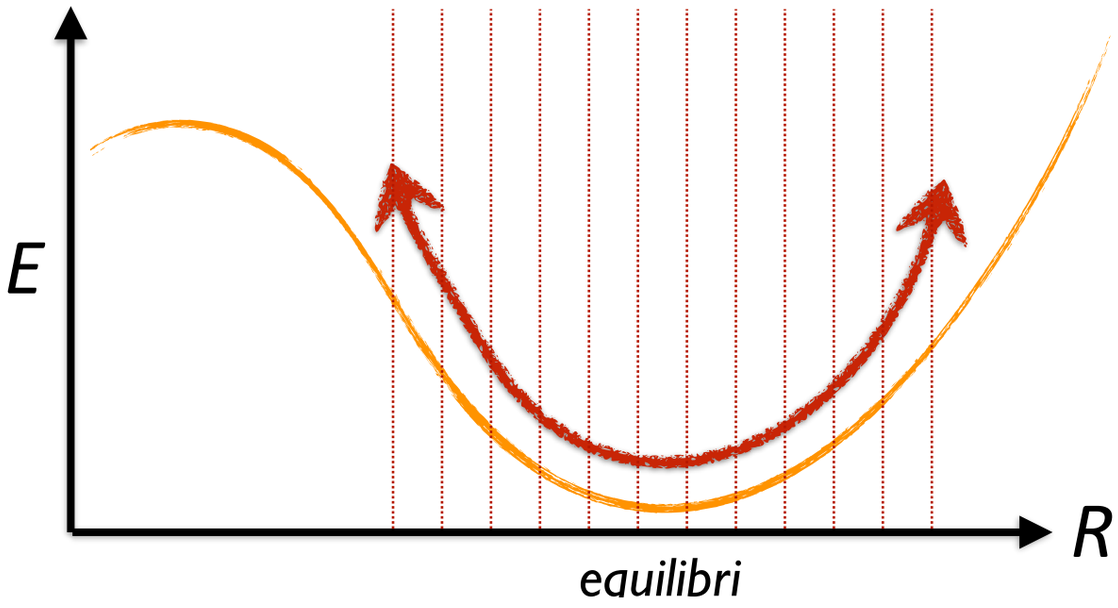

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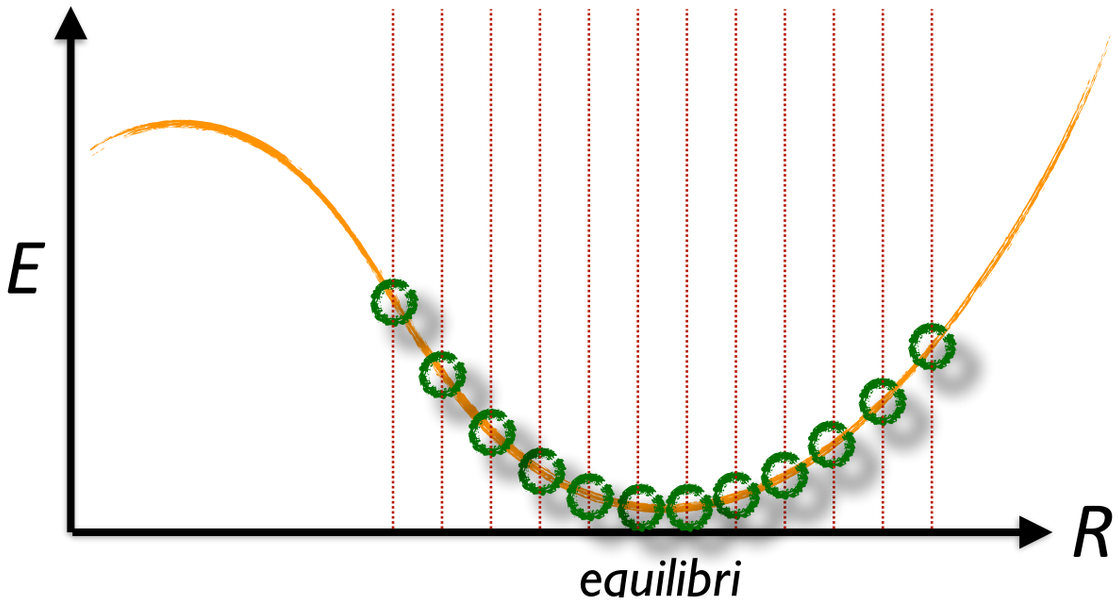
1) Run *ab initio* MD simulations to obtain anharmonic trajectories $\boldsymbol{R}_I^{DFT}(t)$.

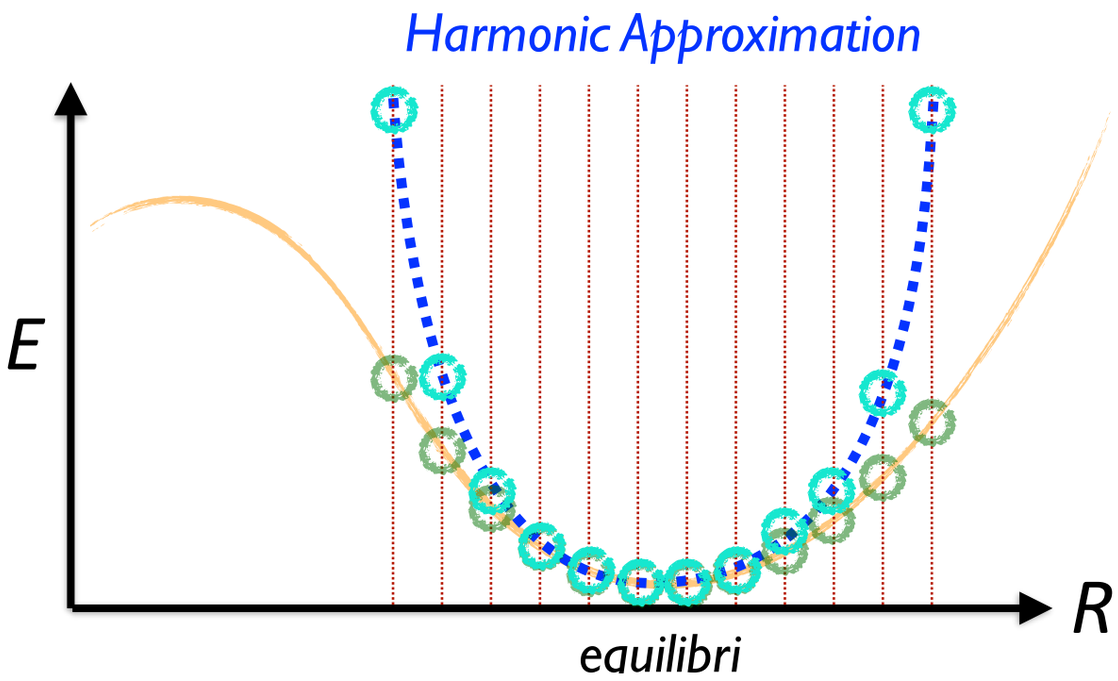
2) Store the potential energies $E^{DFT}(t)$ observed along $\boldsymbol{R}_I^{DFT}(t)$.



Anharmonicity Quantification

How do E_{harm} and $E_{anha} = E_{DFT}$ compare in different materials?

F. Knoop, T. A. R. Purcell, M. Scheffler, and C. Carbogno, *Phys. Rev. Mater.* **4**, 083809 (2020).



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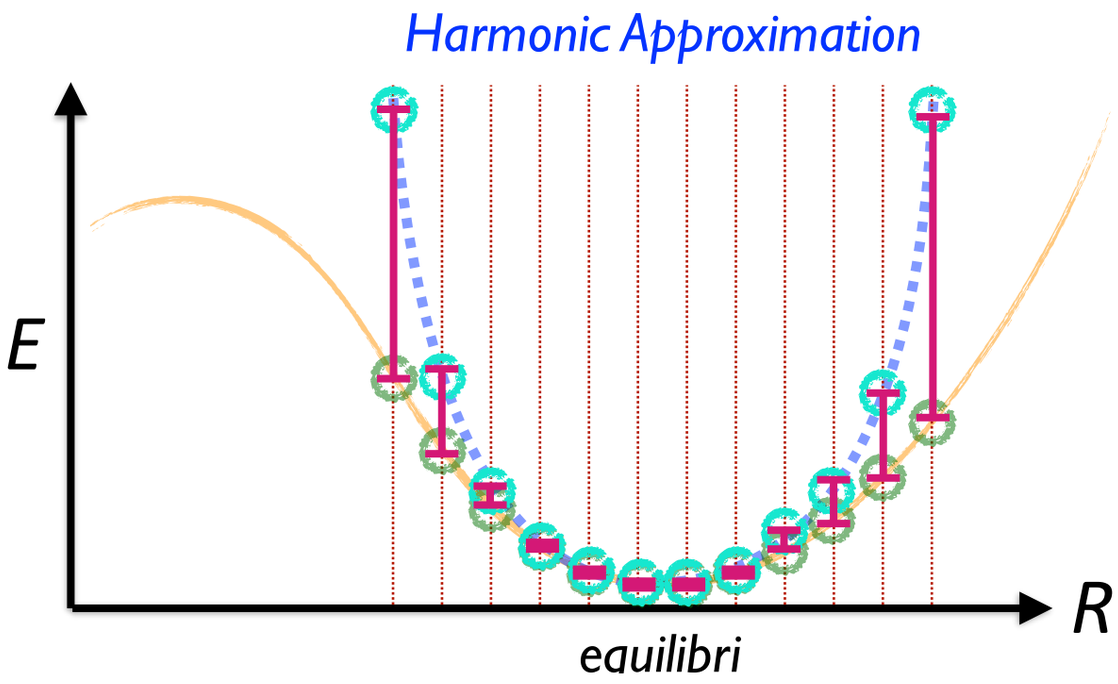

1) Run *ab initio* MD simulations to obtain anharmonic trajectories $\boldsymbol{R}_I^{DFT}(t)$.

2) Store the potential energies $E^{DFT}(t)$ observed along $\boldsymbol{R}_I^{DFT}(t)$.

3) Evaluate which potential energies $E^{harm}(t)$ the *harmonic approximation* would predict along $\boldsymbol{R}_I^{DFT}(t)$.

4) The difference $E^{harm}(t)$ - $E^{DFT}(t)$ quantifies the strength of anharmonic effects.

Anharmonicity Quantification

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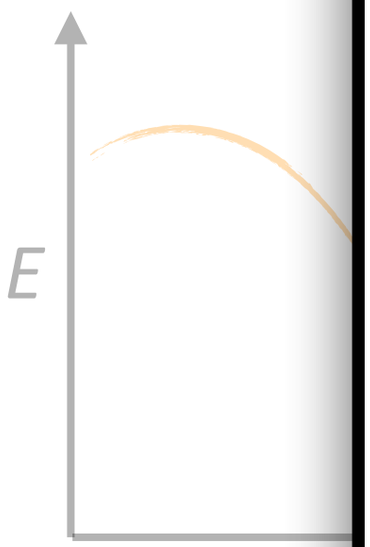

In practice,
it is beneficial to work with
harmonic $\mathbf{F}_I^{harm}(t)$ and
anharmonic forces $\mathbf{F}_I^{DFT}(t)$,
since this allows for
an atom-specific resolution
of anharmonic effects.

Anharmonicity Quantification

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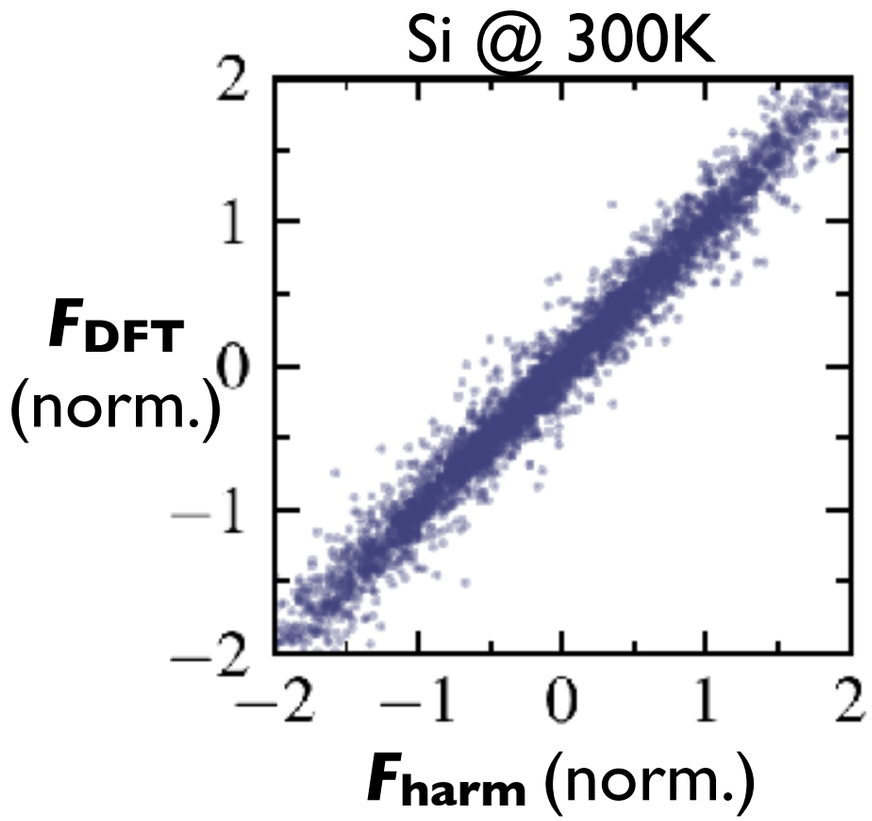

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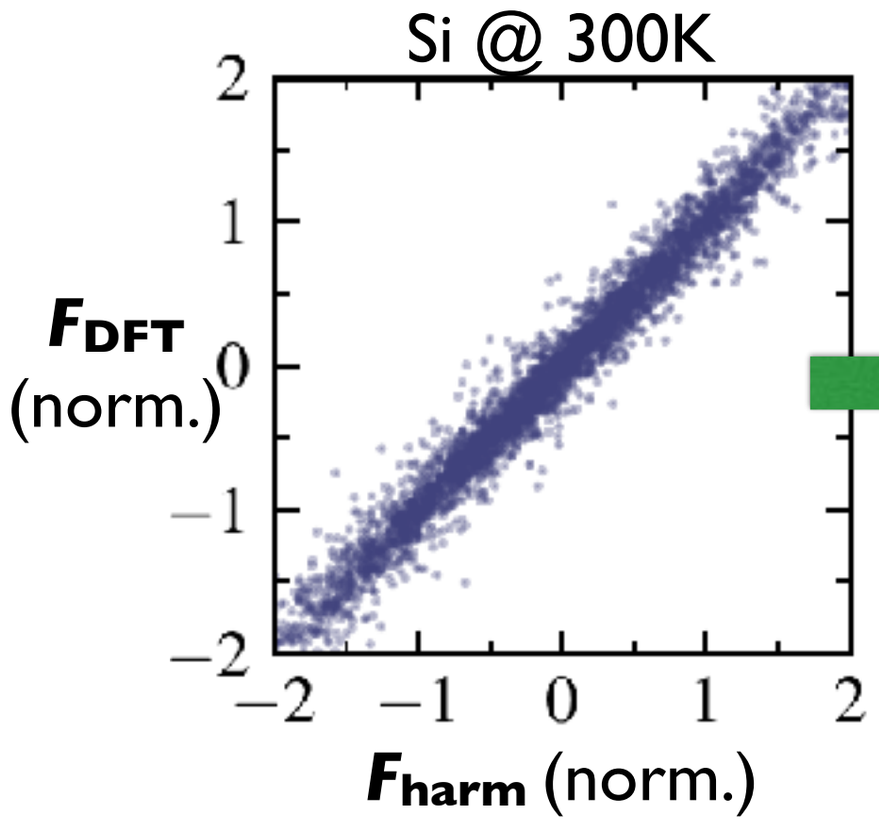

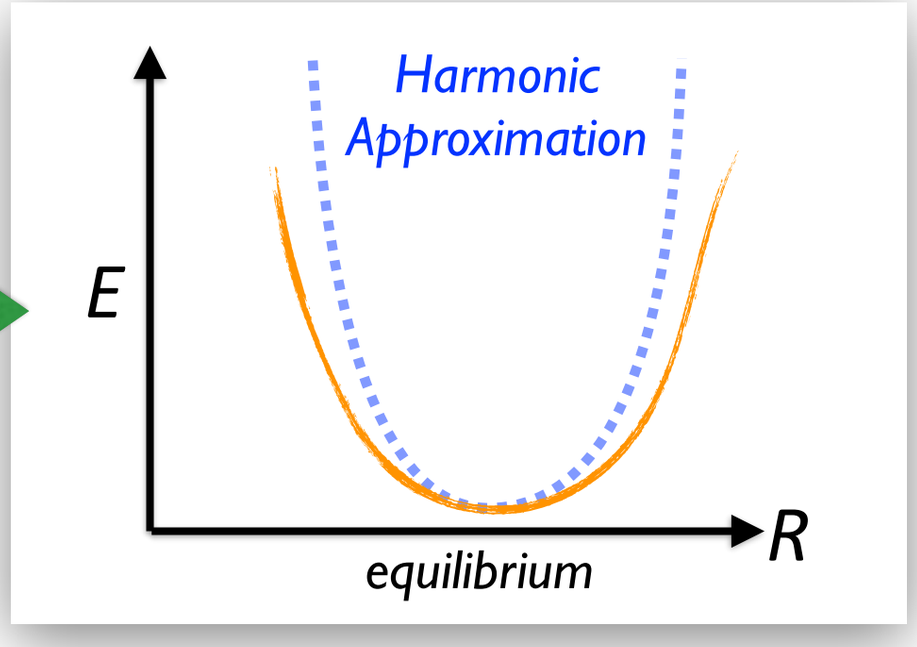

$E_{harm} \gg E_{anha}$

Anharmonicity Quantification

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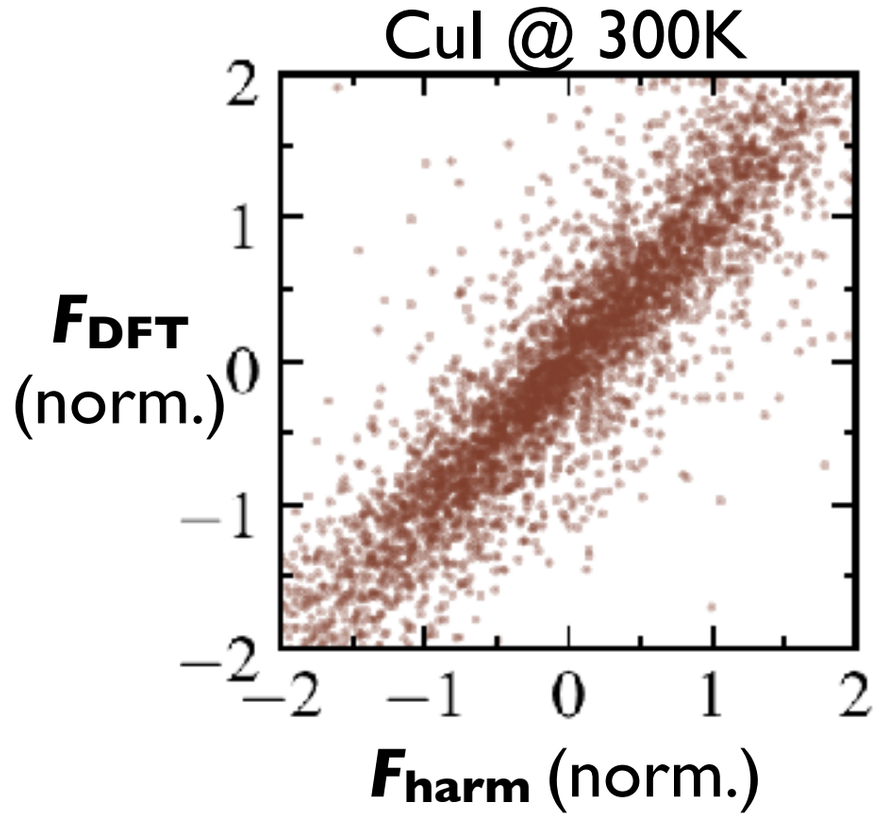

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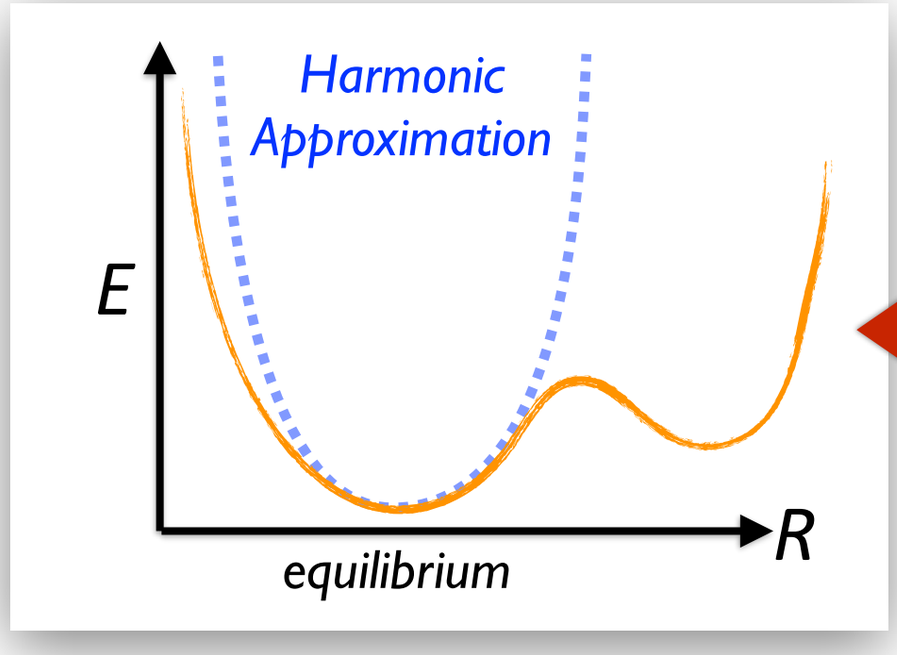
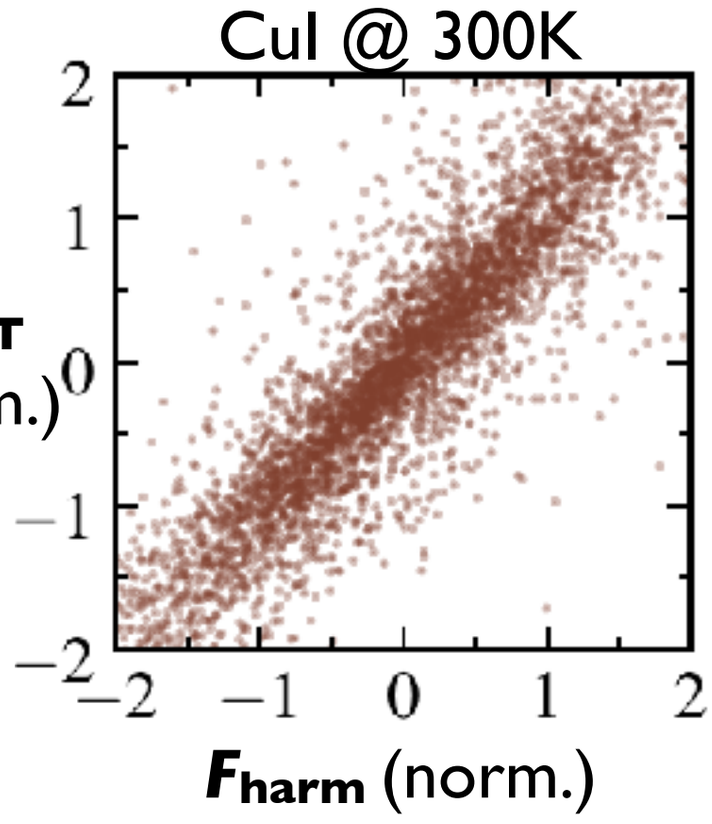


$E_{harm} \ll E_{anha}$

F_{DFT} (norm.)



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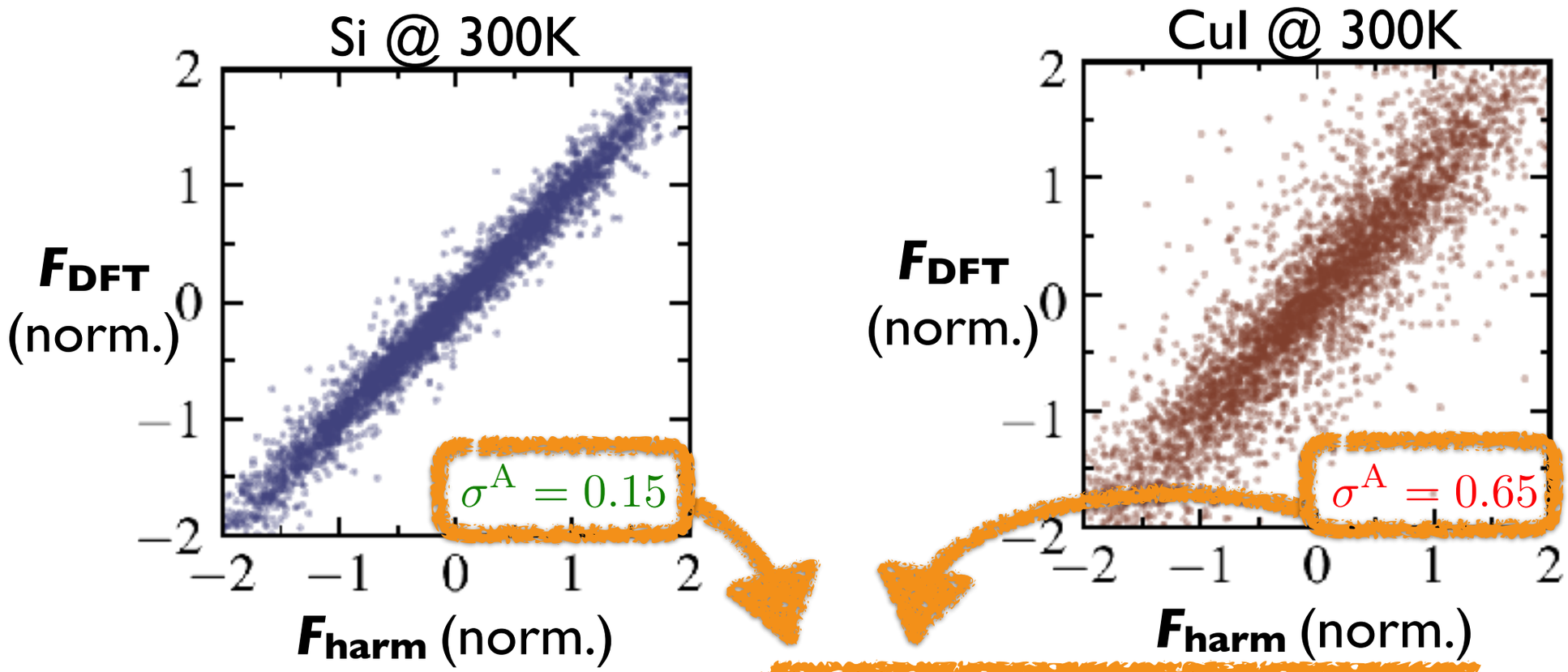

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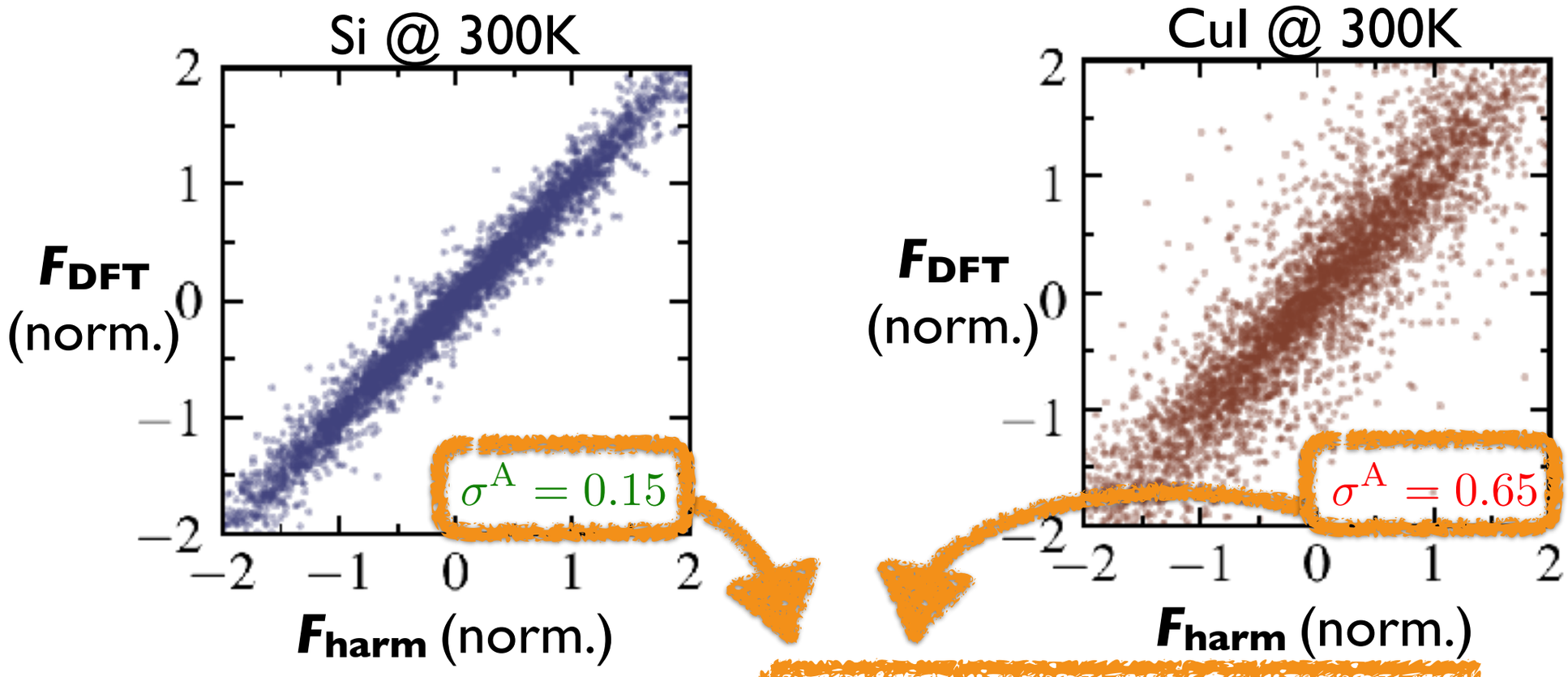


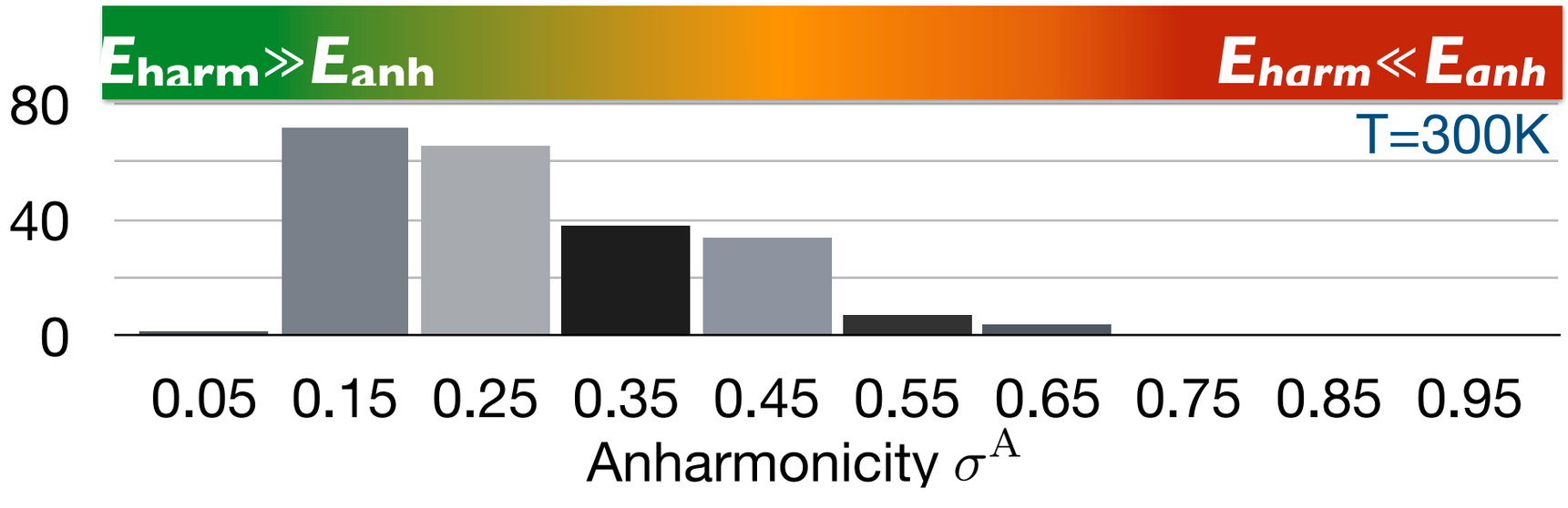
$$\sigma^{\mathrm{A}}(T) = \sqrt{\frac{\sum_{I,\alpha} \left\langle \left(F^{\mathrm{DFT}}_{I,\alpha} - F^{\mathrm{harm}}_{I,\alpha} \right)^2 \right\rangle_T}{\sum_{I,\alpha} \left\langle \left(F^{\mathrm{DFT}}_{I,\alpha} \right)^2 \right\rangle_T}}$$

In Simpler Words:

How much do anharmonic effects contribute to the forces on average?

Anharmonicity Quantification across Material Space

F. Knoop, T. A. R. Purcell, M. Scheffler, and C. Carbogno, *Phys. Rev. Mater.* **4**, 083809 (2020).



200+ Material Test Set:

- 97 Rock salt
- 67 Zincblende
- 45 Wurtzite
- 10 Perovskites

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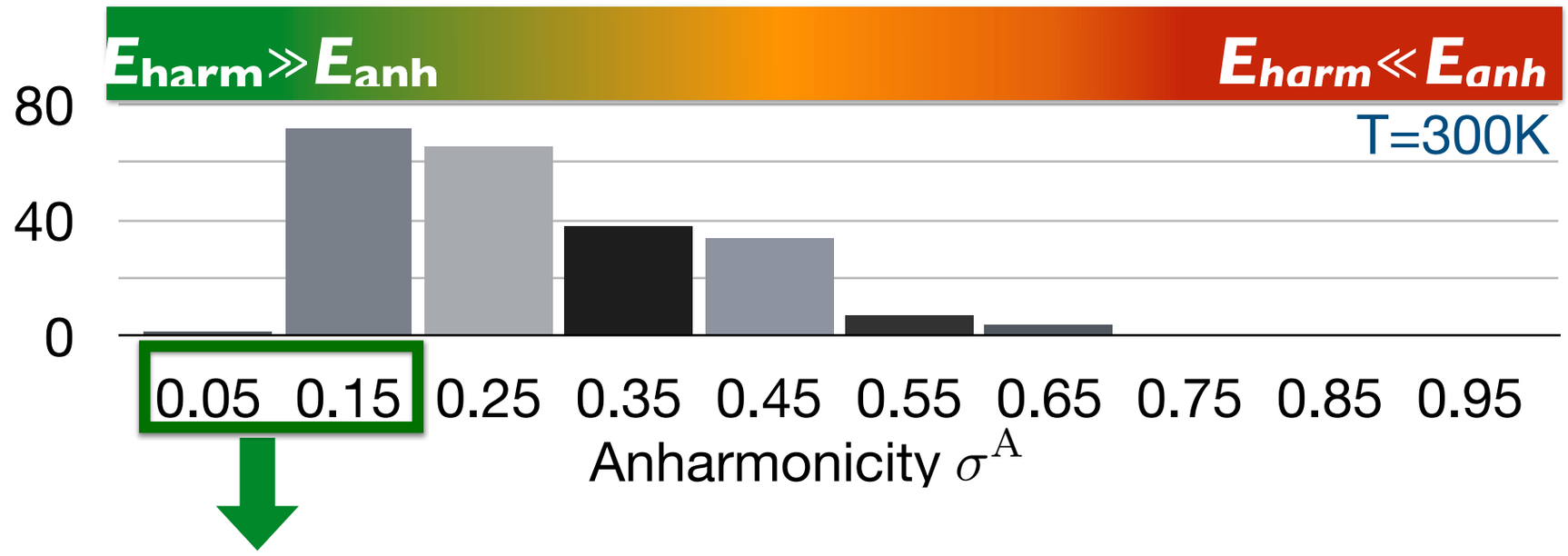

At **300K**, many materials indeed behave **almost perfectly harmonically**.

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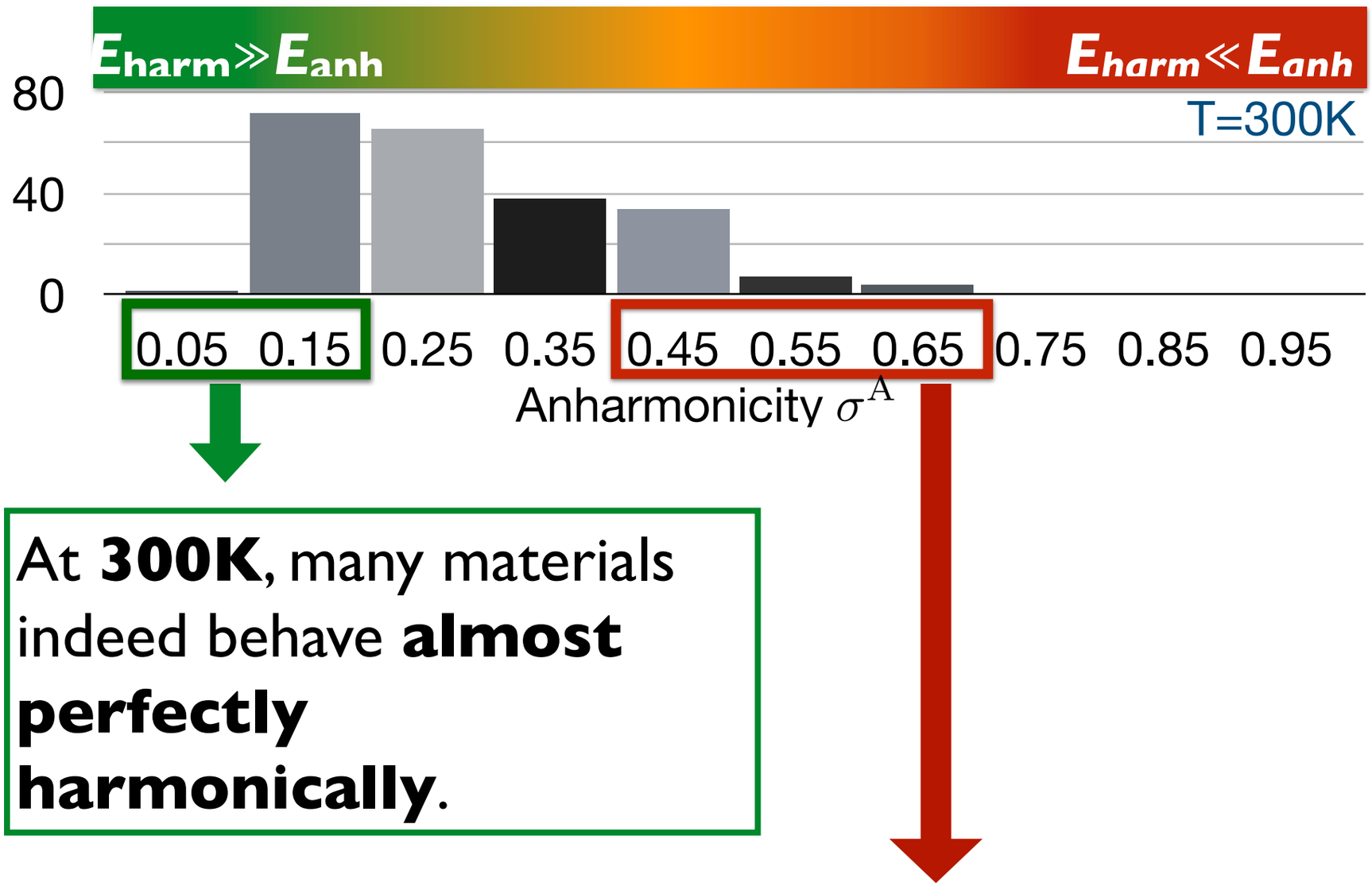

At **300K**, many materials indeed behave **almost perfectly harmonically**.

But even at **300K**, there are systems that exhibit a **strongly anharmonic** dynamics.

200+ Material Test Set:

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Anharmonicity Quantification across Material Space

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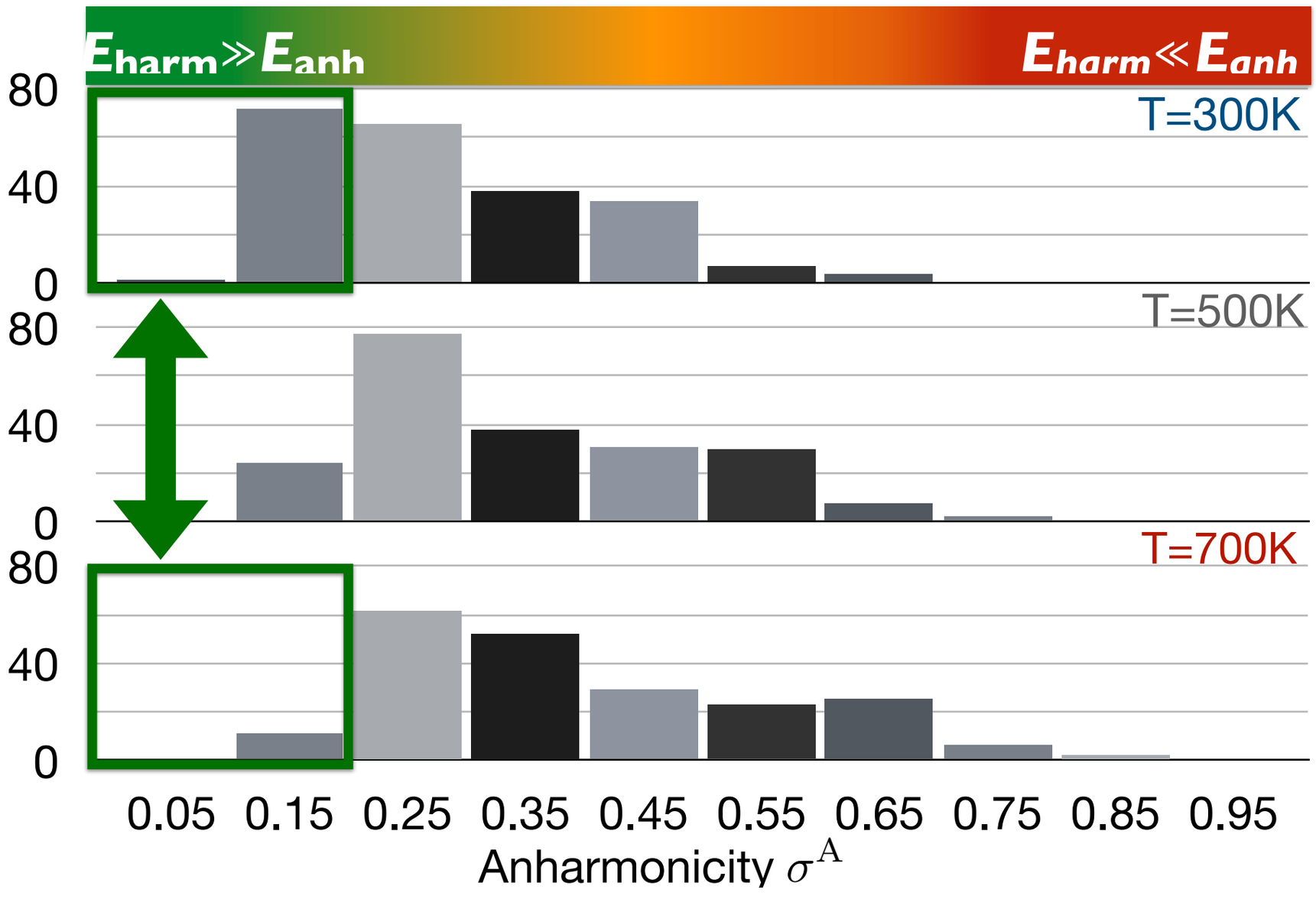

At 700K, only <35% of the materials are **almost perfectly harmonic.**

200+ Material Test Set:

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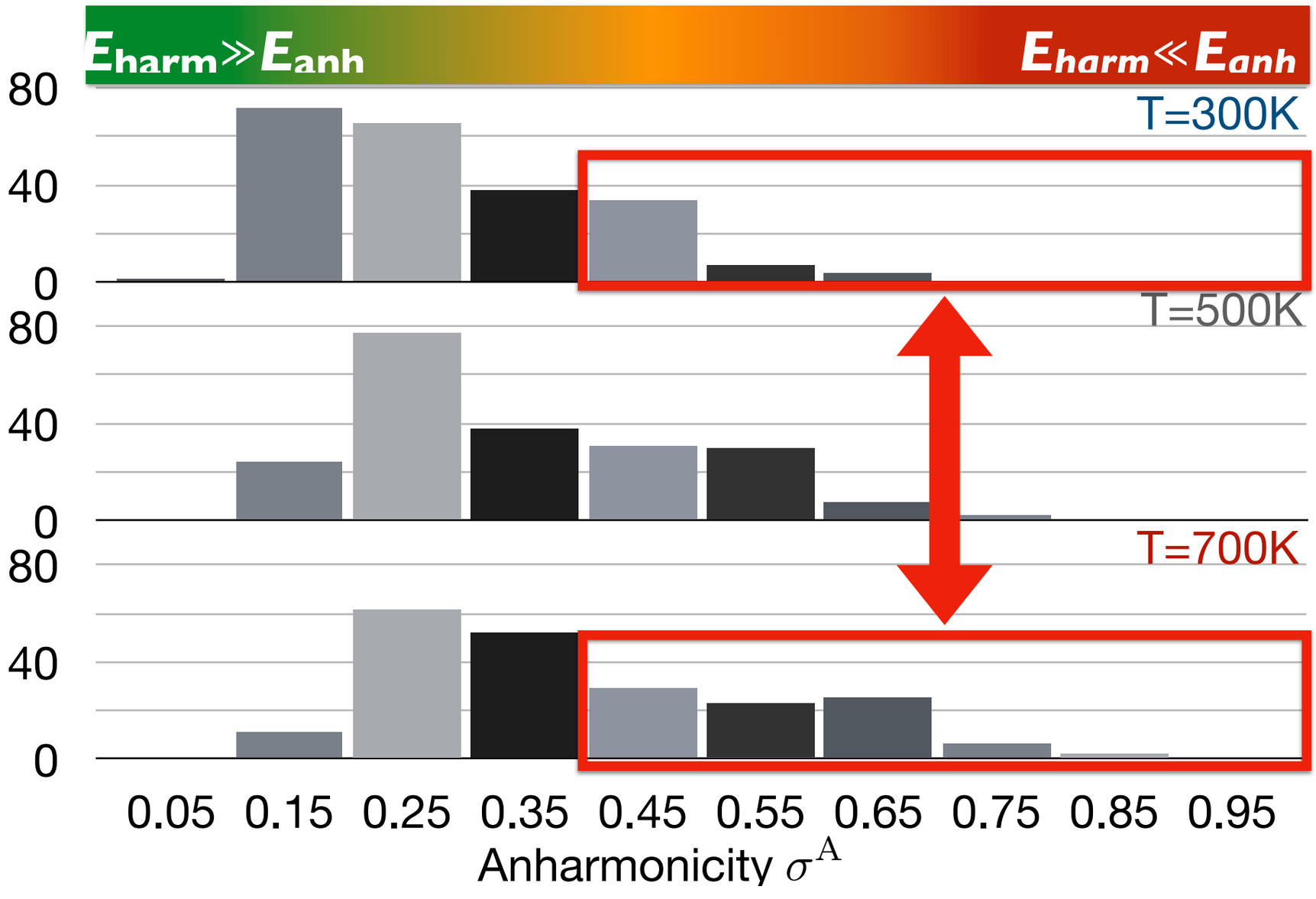

At **700K**, already **>40%** of the materials exhibit **strong anharmonic effects.**

200+ Material Test Set:

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Anharmonicity Quantification across Material Space

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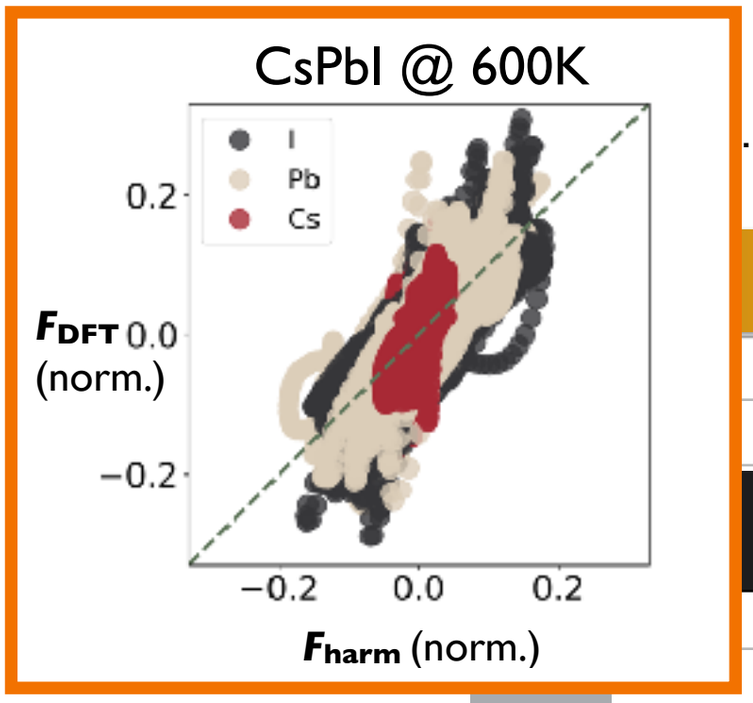

At **all** temperatures, **complex materials** exhibit **stronger anharmonic effects.**

200+ Material Test Set:

- 97 Rock salt
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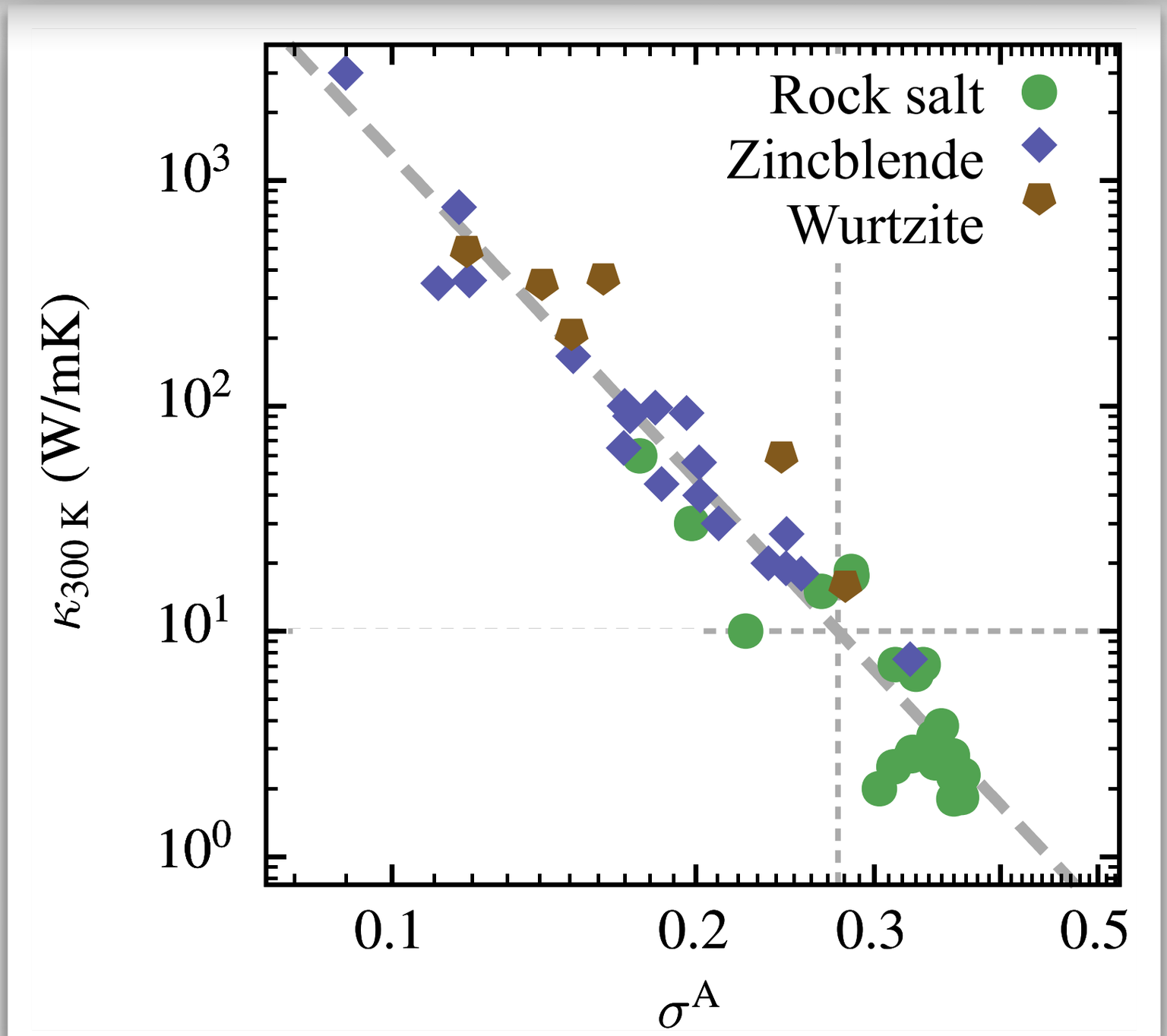
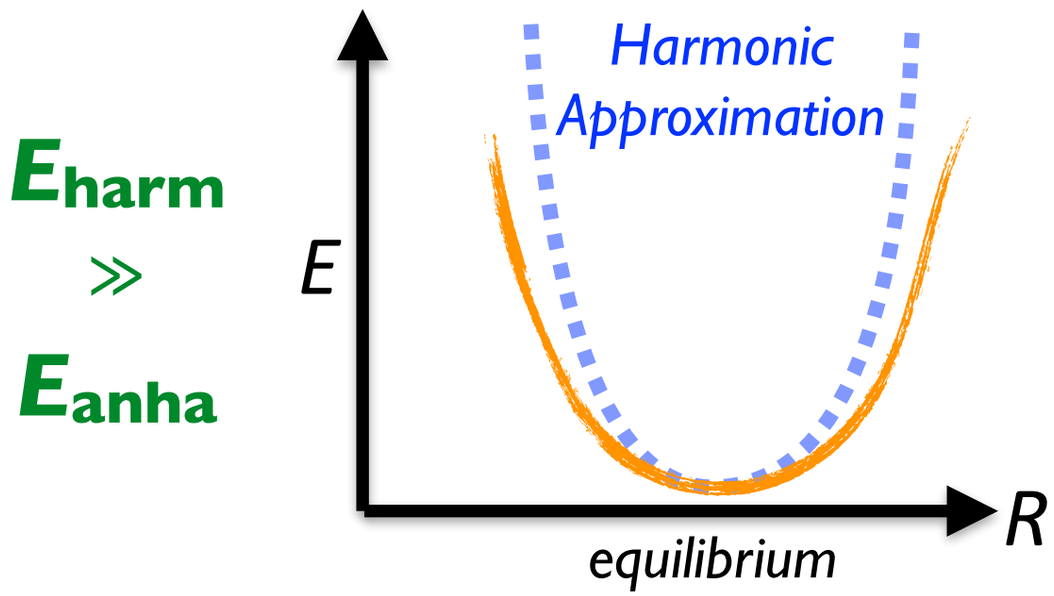
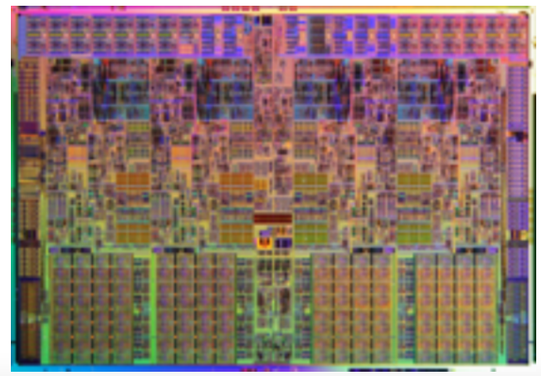
- 45 Wurtzite
- 10 Perovskites

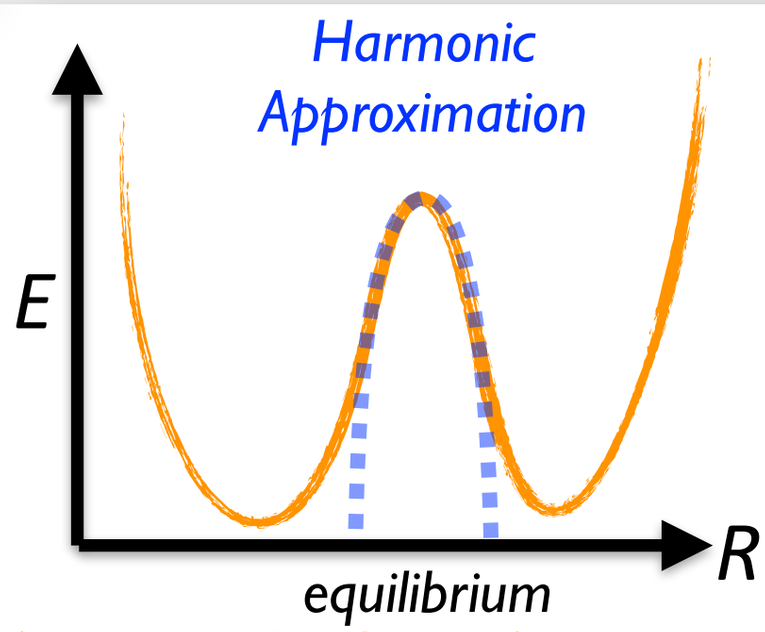
The *anharmonicity* shows a **promising correlation** with *experimental thermal conductivities*.





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

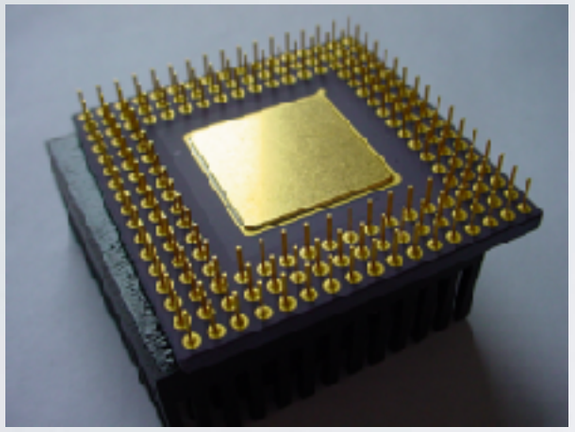




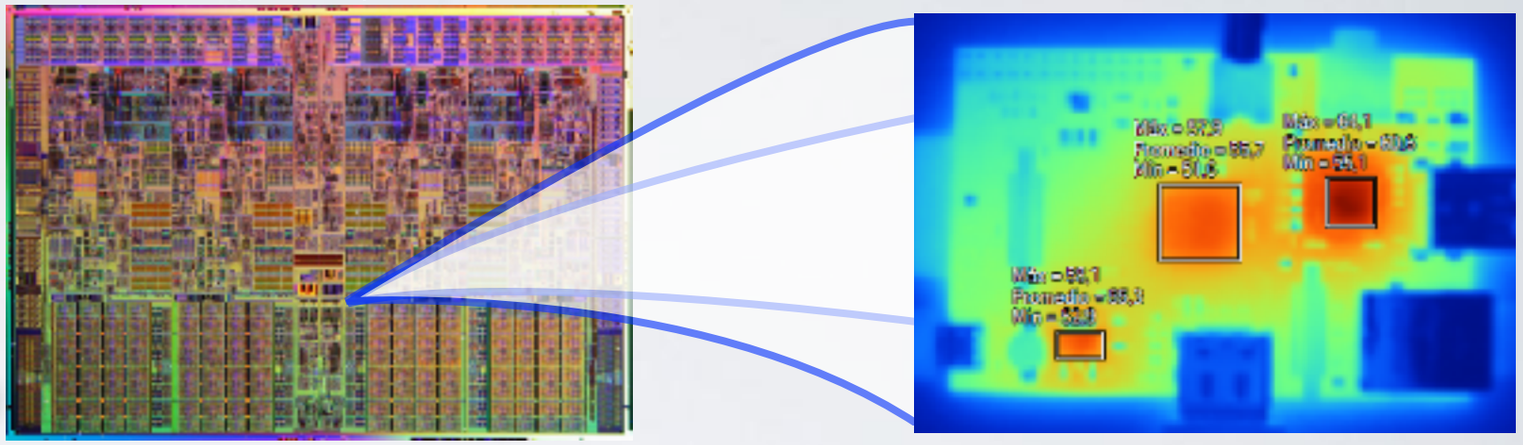
E_{harm} = ?

Semiconductor Technology

486 (1995): 10^6 Trans.



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

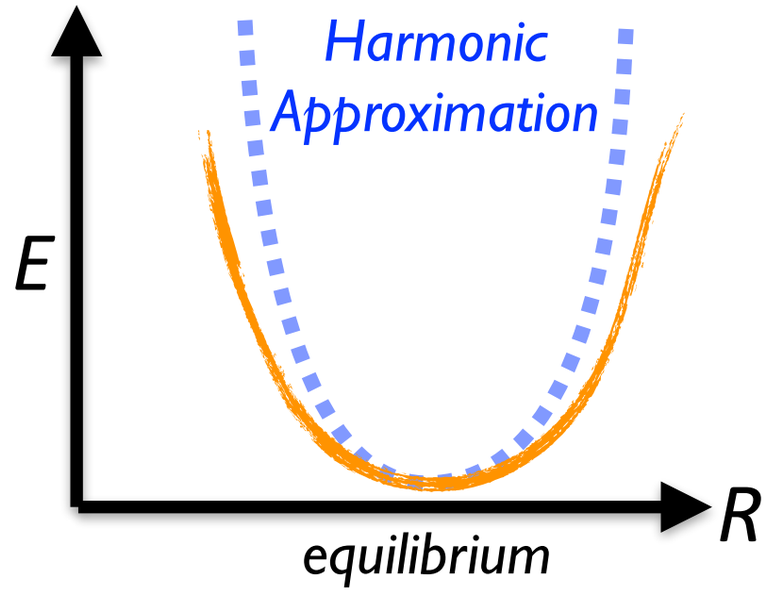


Miniaturization has lead to **enormous** transistor densities

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.

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



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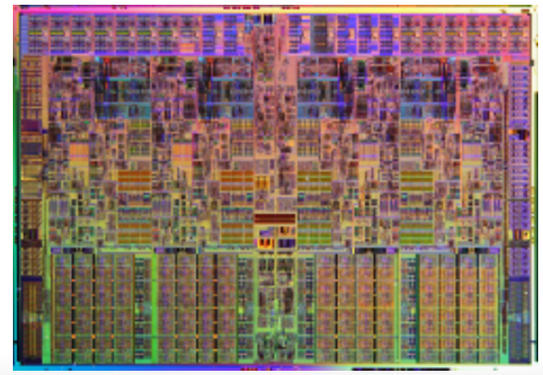
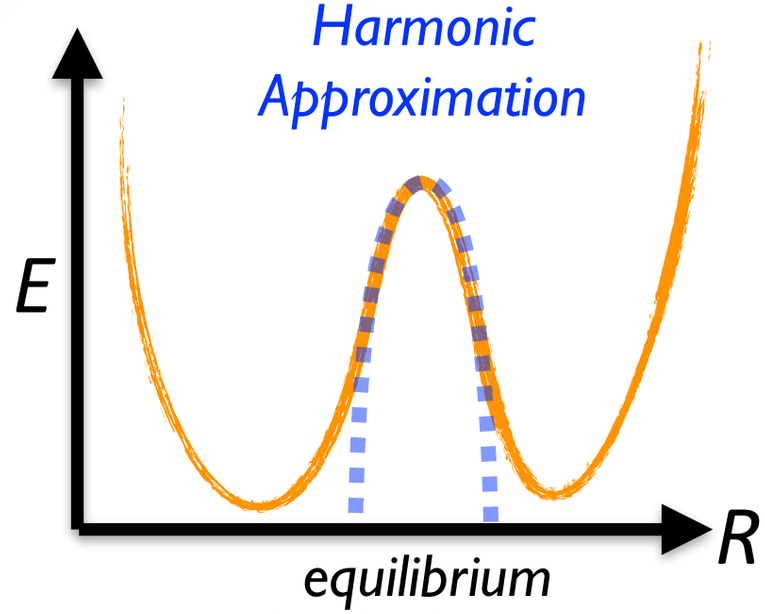


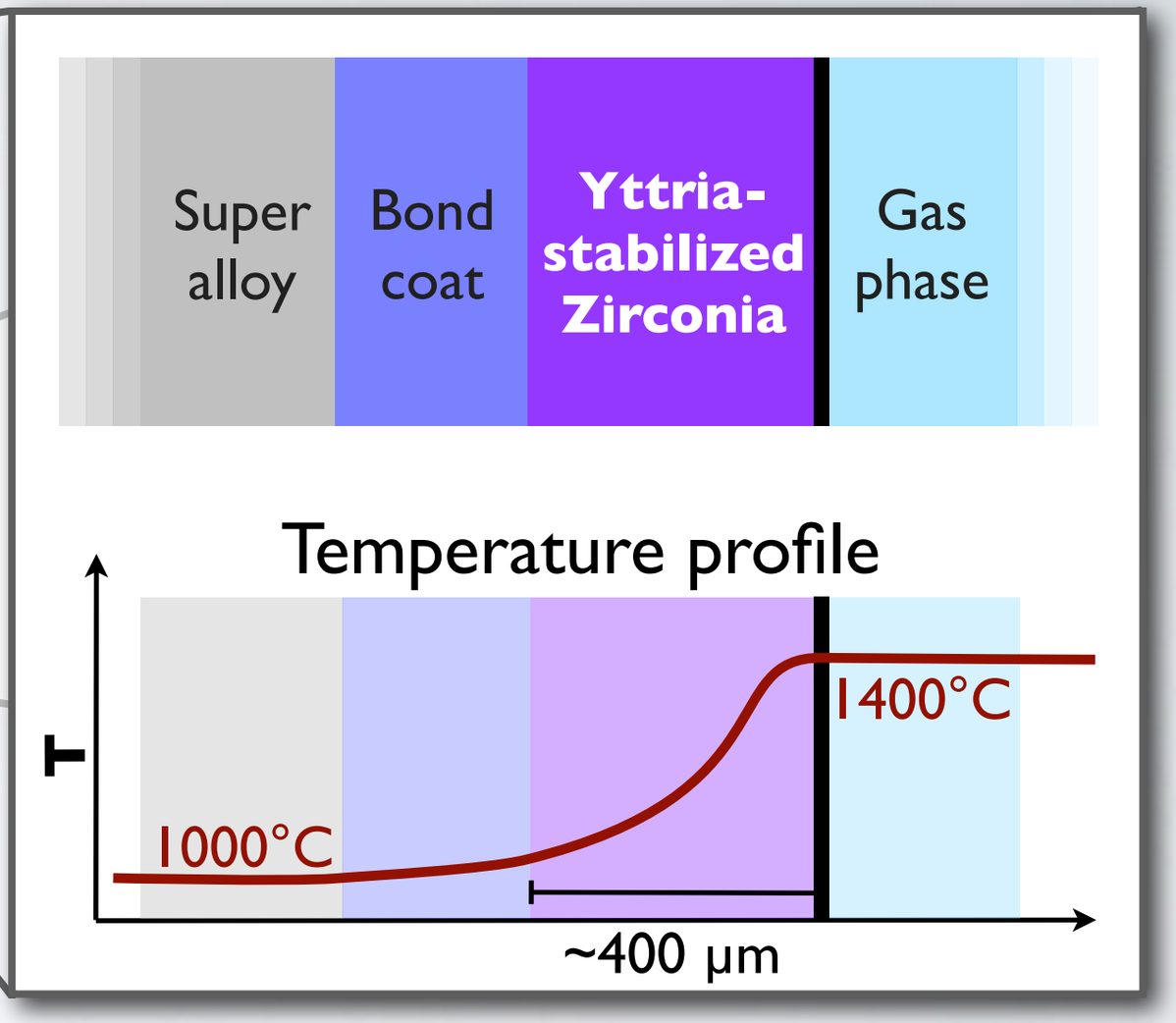
ZrO_2: Thermal conductivity **minute** (~3 W/mK)



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!

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ZrO_2: Thermal conductivity

minute (~3 W/mK)

Suppress heat transport even further!

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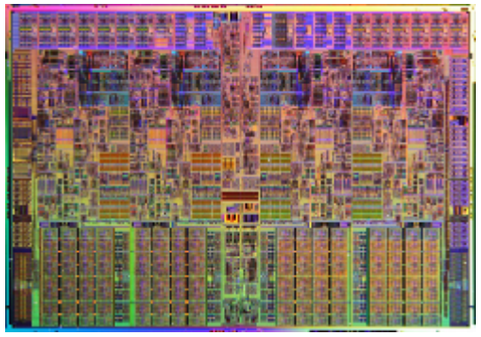

Boost heat transport even further!

TECHNOLOGICAL EDGE CASES

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Suppress heat transport even further!

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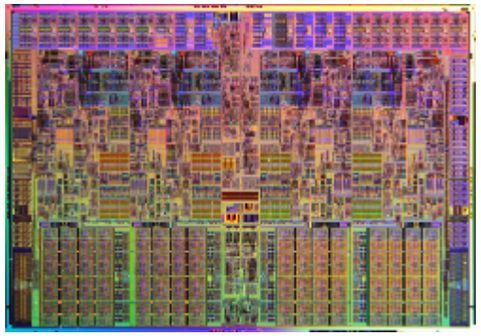


Boost heat transport even further!

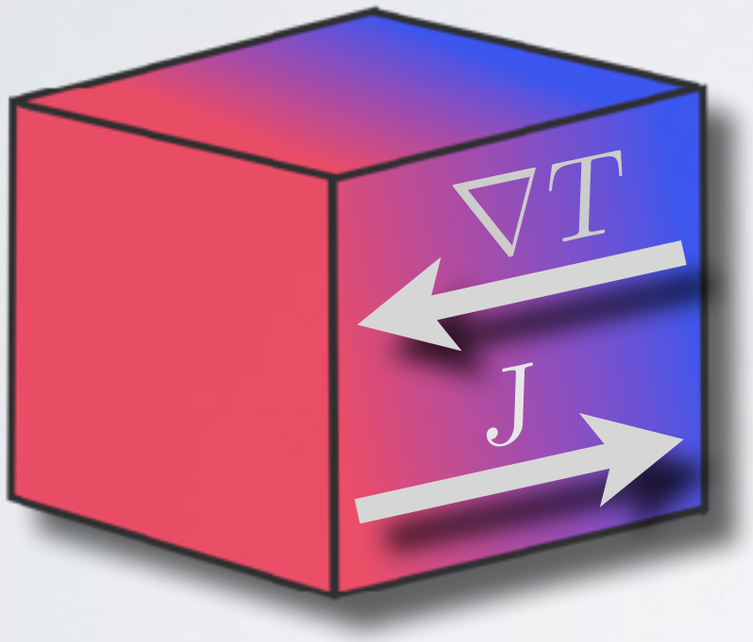
First Principles Theory

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

III. HEAT TRANSPORT

HEAT TRANSPORT

Macroscopic Effect:



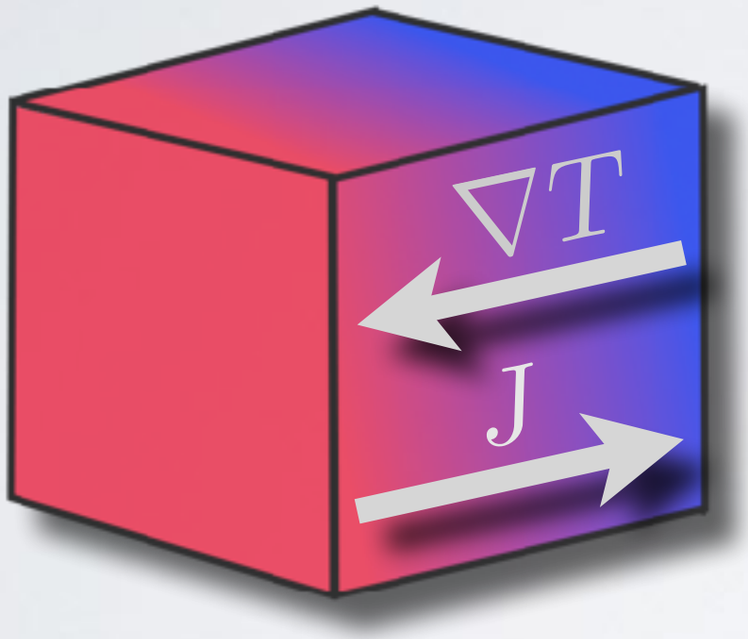
Fourier‘s Law:

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

HEAT TRANSPORT

Macroscopic Effect:

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



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HEAT TRANSPORT

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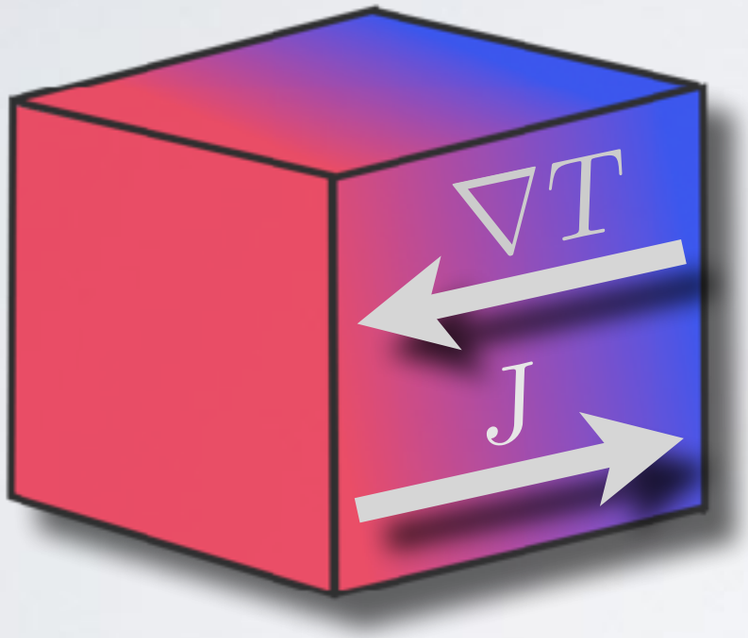

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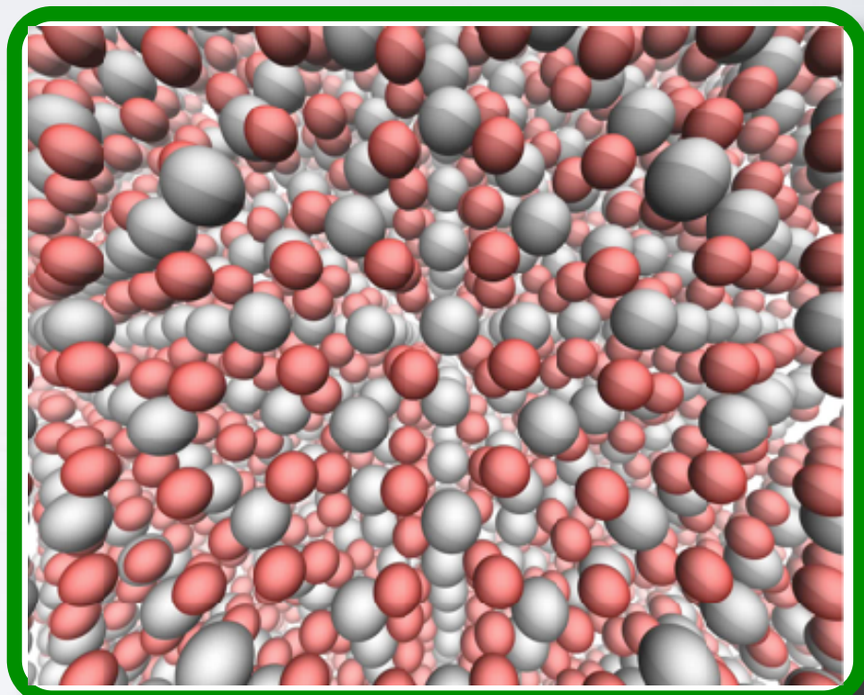
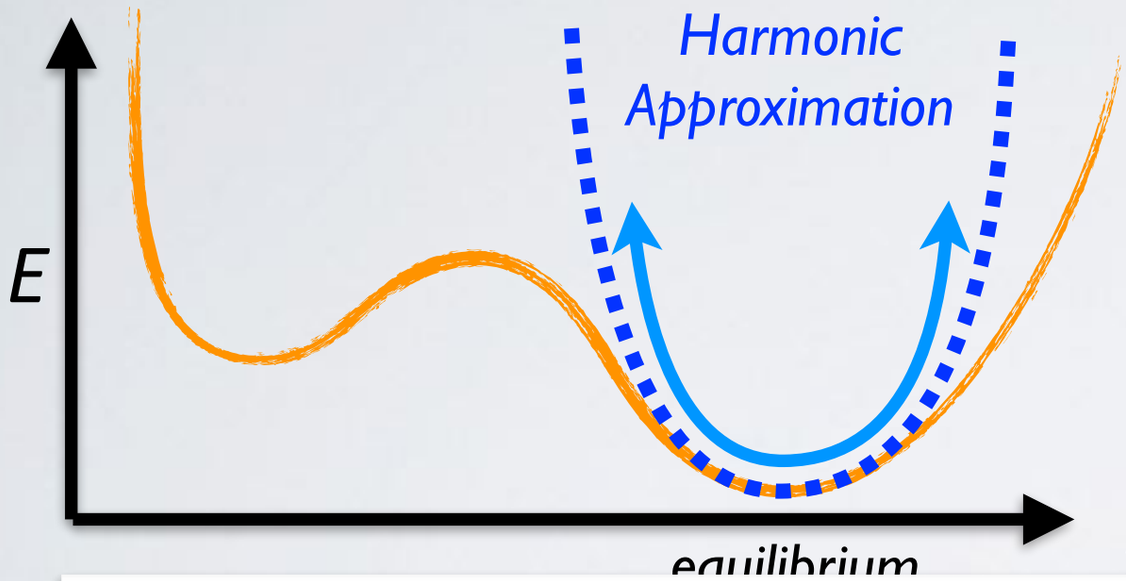


Microscopic Mechanisms

Heat Transport Theory 101

Real Space Representation



Reciprocal Space Representation

Phonon (ω,q)

Decoupled Normal Modes

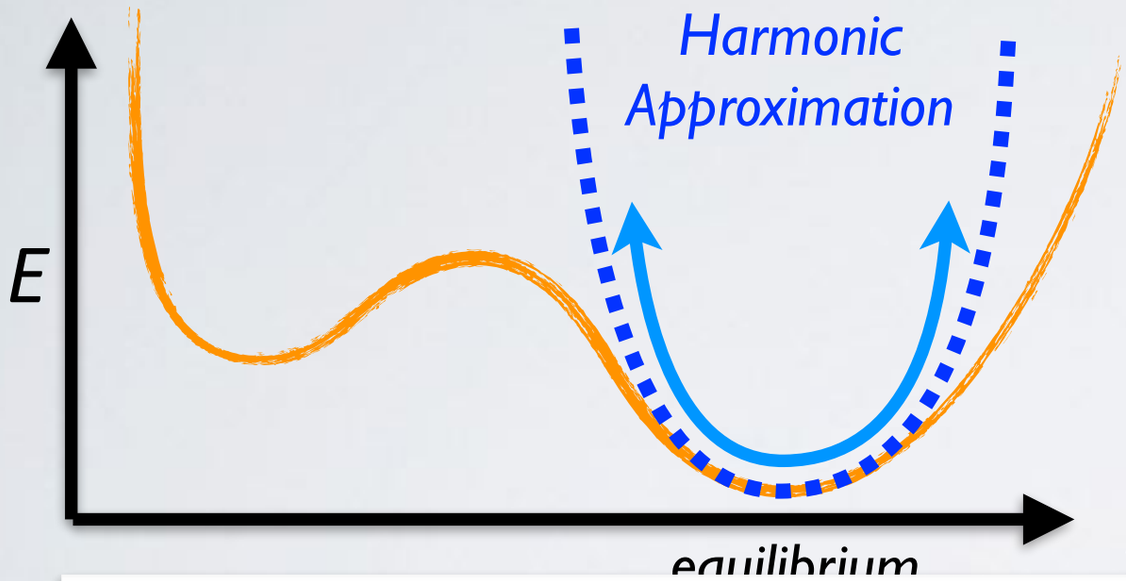
Infinite Phonon Lifetime

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

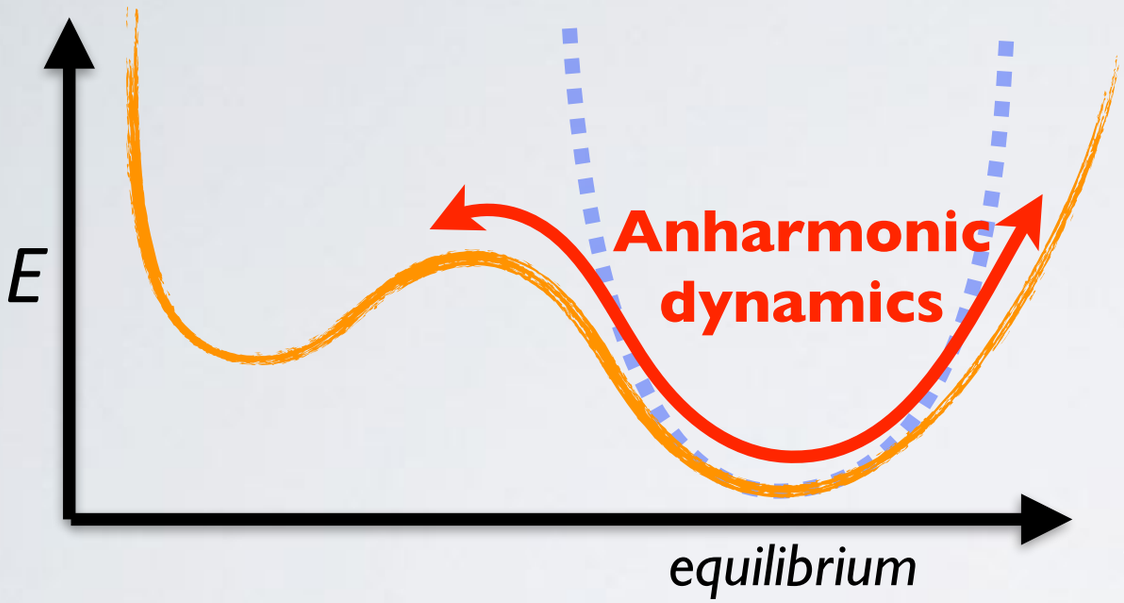
Phonon (ω,q)

Infinite Phonon Lifetime

Infinite thermal conductivity!

Heat Transport Theory 101

Real Space Representation



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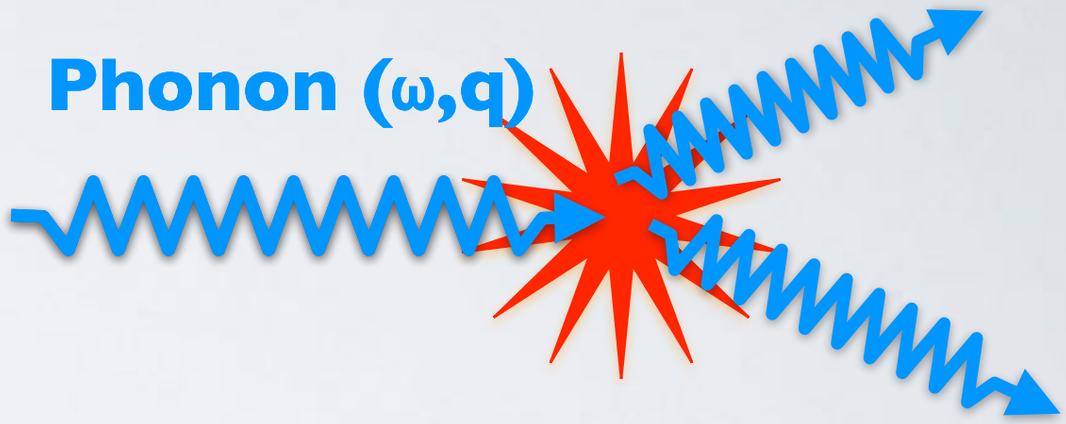


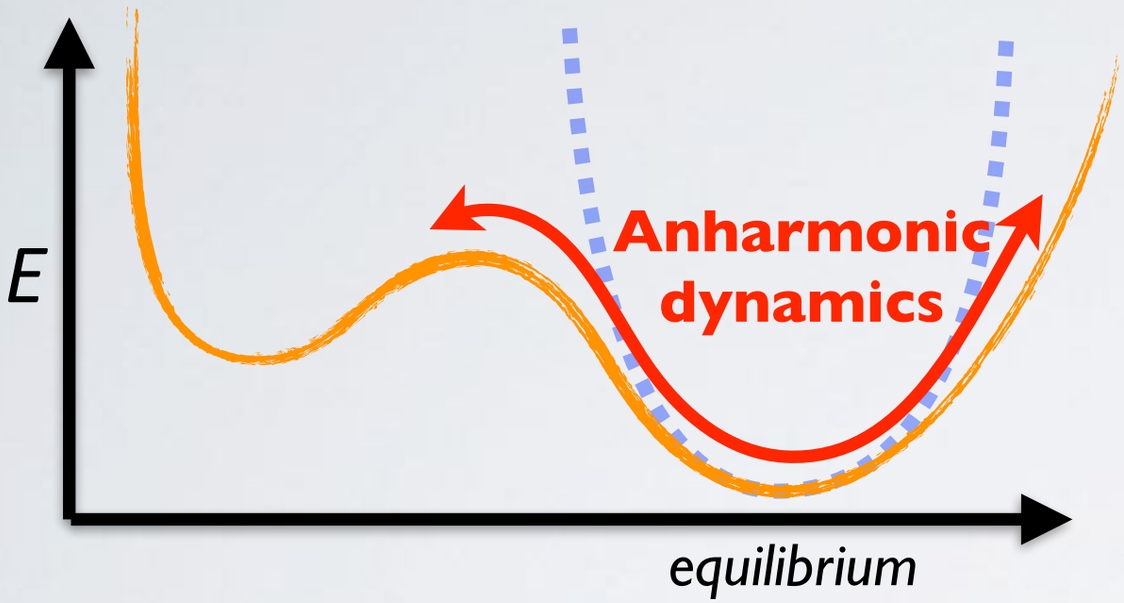
Anharmonicity

Electron-Phonon Coupling

Phonon Scattering

Heat Transport Theory 101

Real Space Representation



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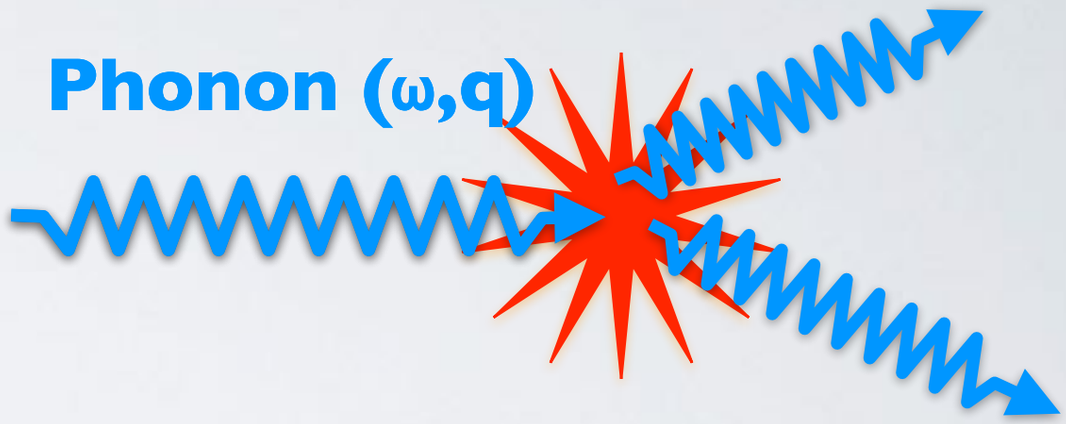


Anharmonicity

Electron-Phonon Coupling

Phonon Scattering

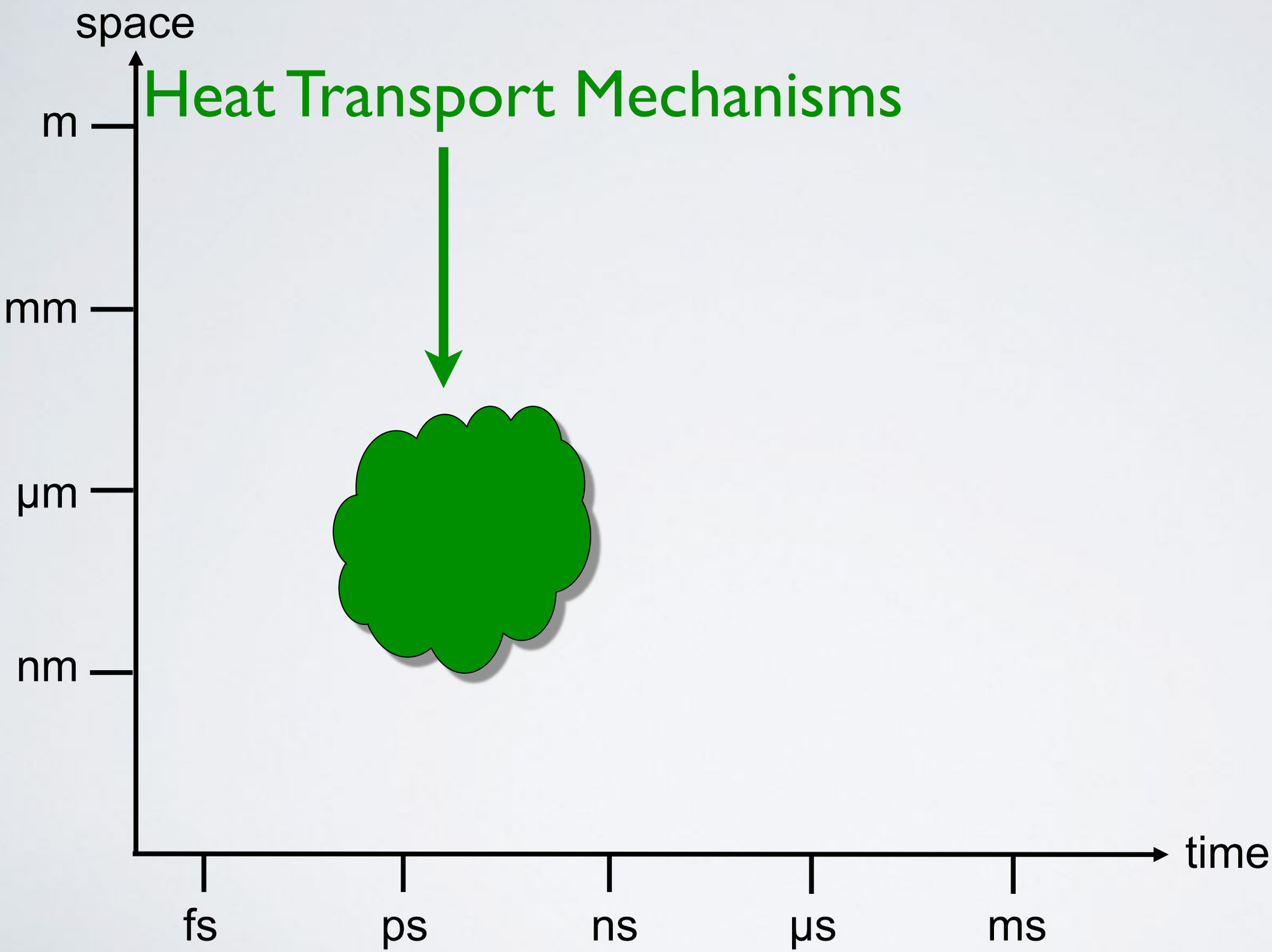
Theory Toolbox

Molecular Dynamics

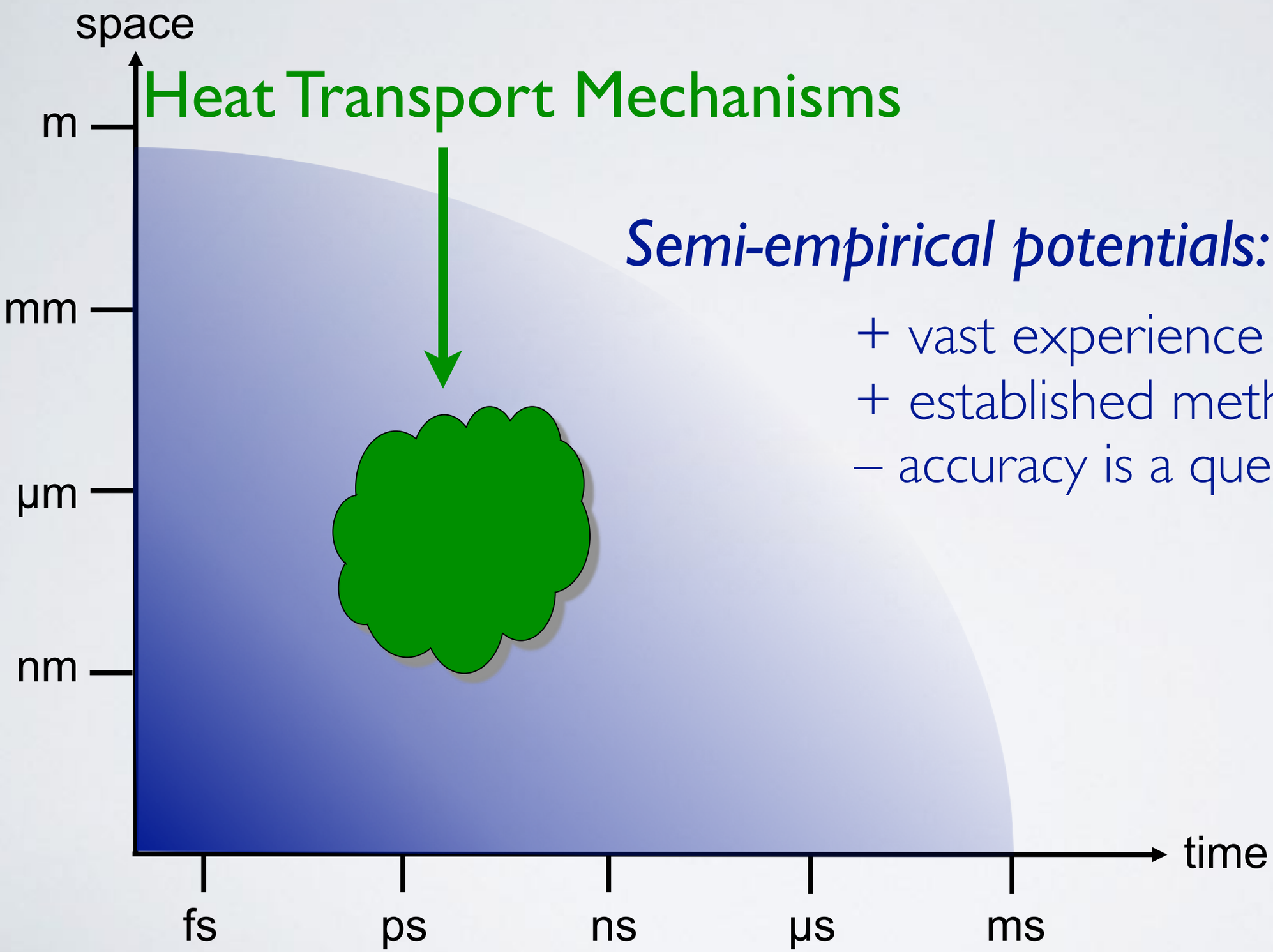
Electronic Structure Theory

Perturbation Theory

TIME AND LENGTH SCALES



TIME AND LENGTH SCALES



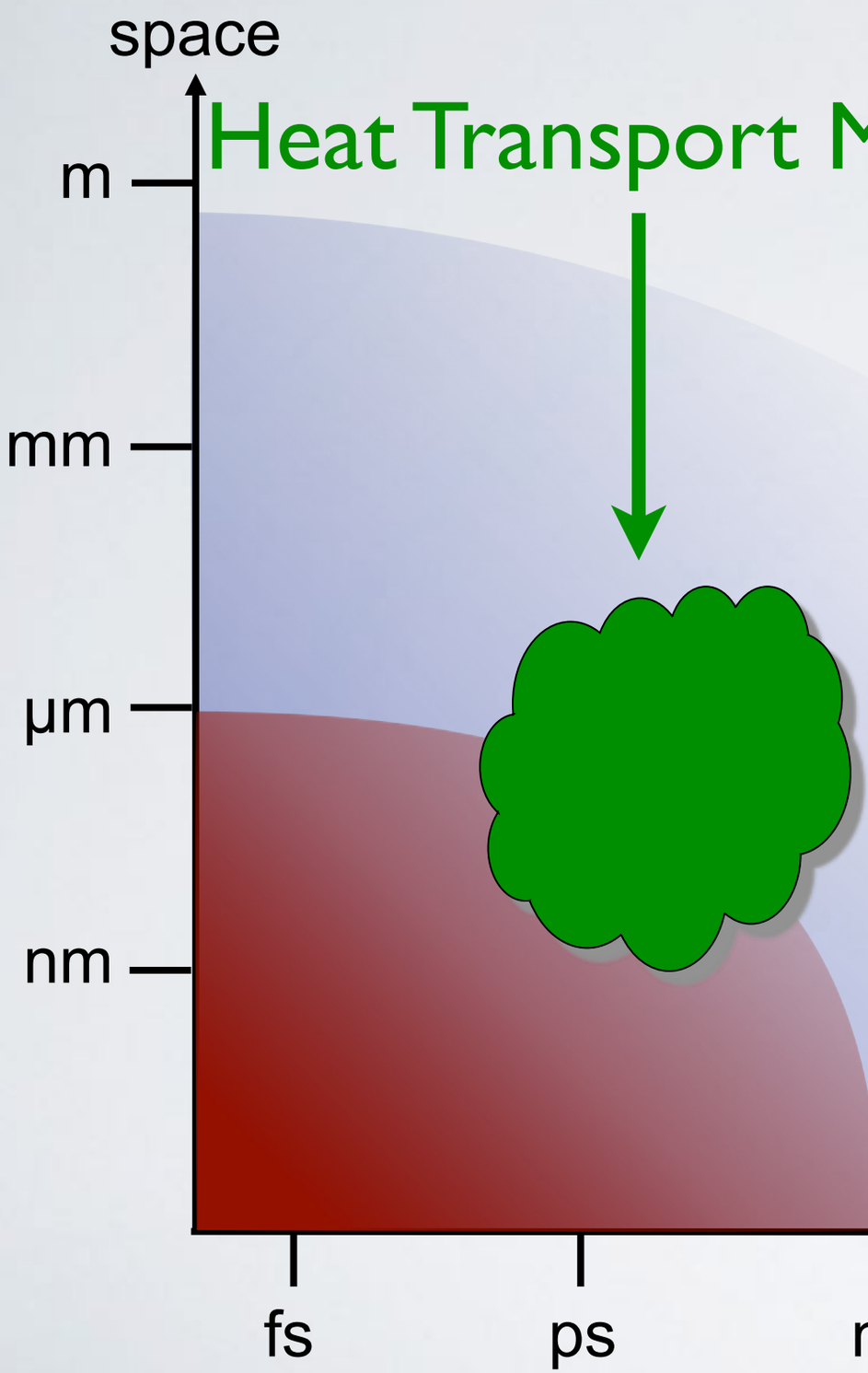
Semi-empirical potentials:

\+ vast experience

\+ established methodologies

– accuracy is a question

TIME AND LENGTH SCALES



Semi-empirical potentials:

\+ vast experience

\+ established methodologies

– accuracy is a question

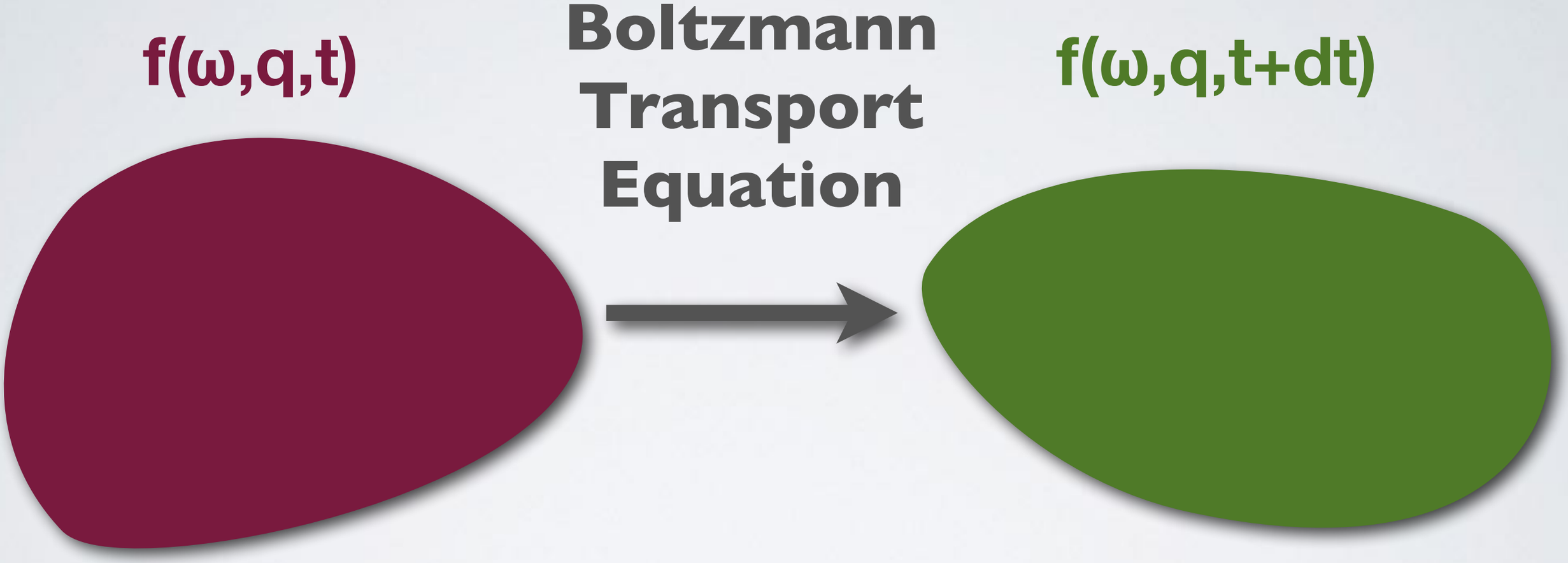
First-principles approaches:

\+ 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).

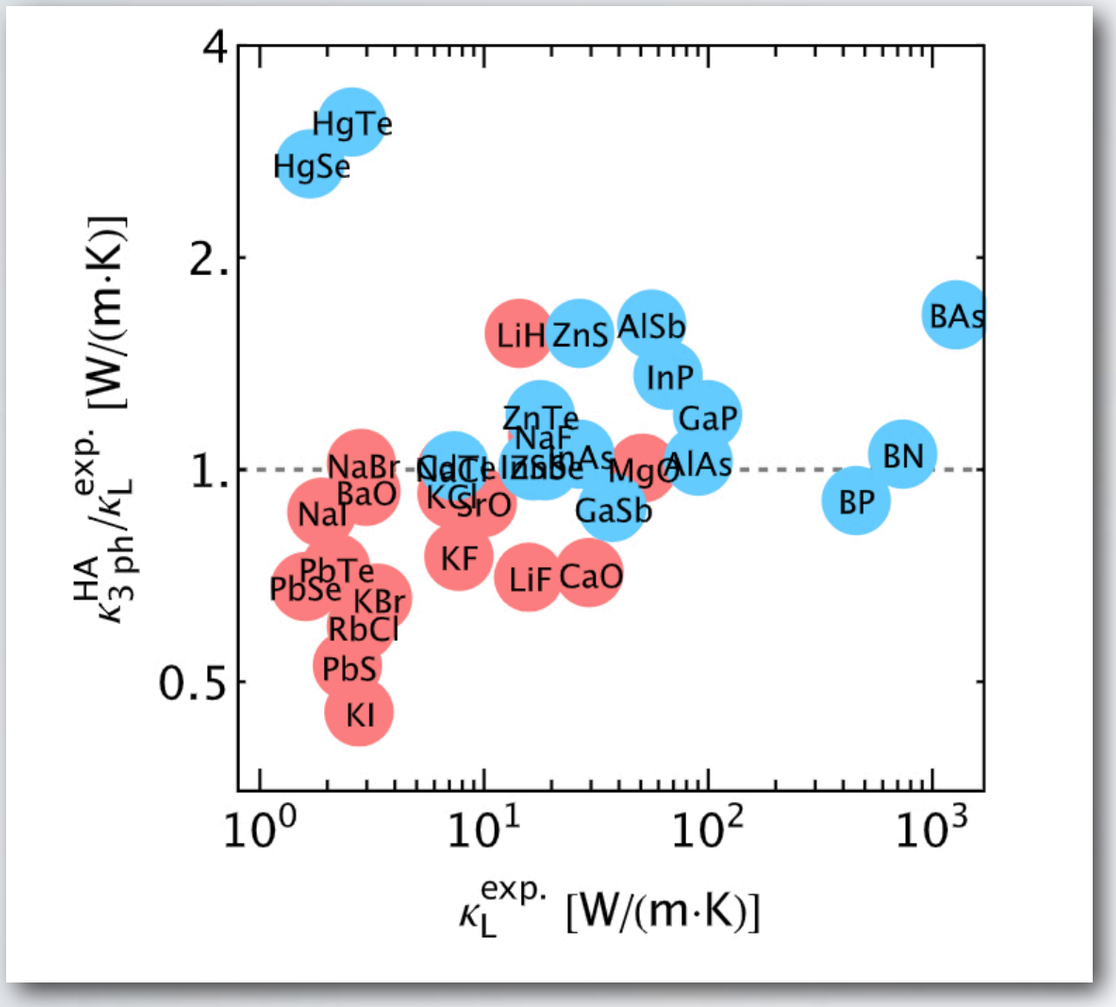
All these approaches give very **accurate** results for **good thermal conductors** at **low** temperatures.

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

Improving the Accuracy of Perturbative Calculations

Y. Xia *et al*., Physical Review X **10**, 041029 (2020).

3rd-order expansion



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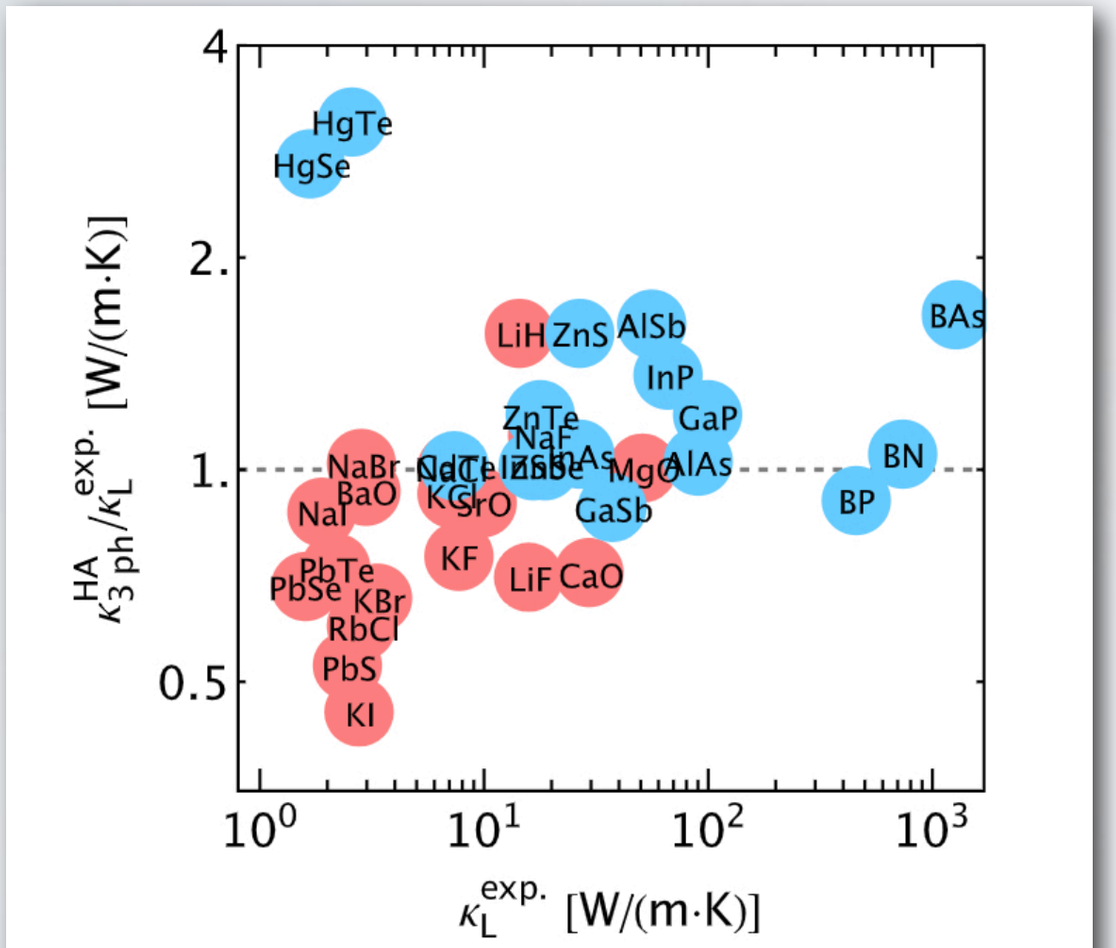
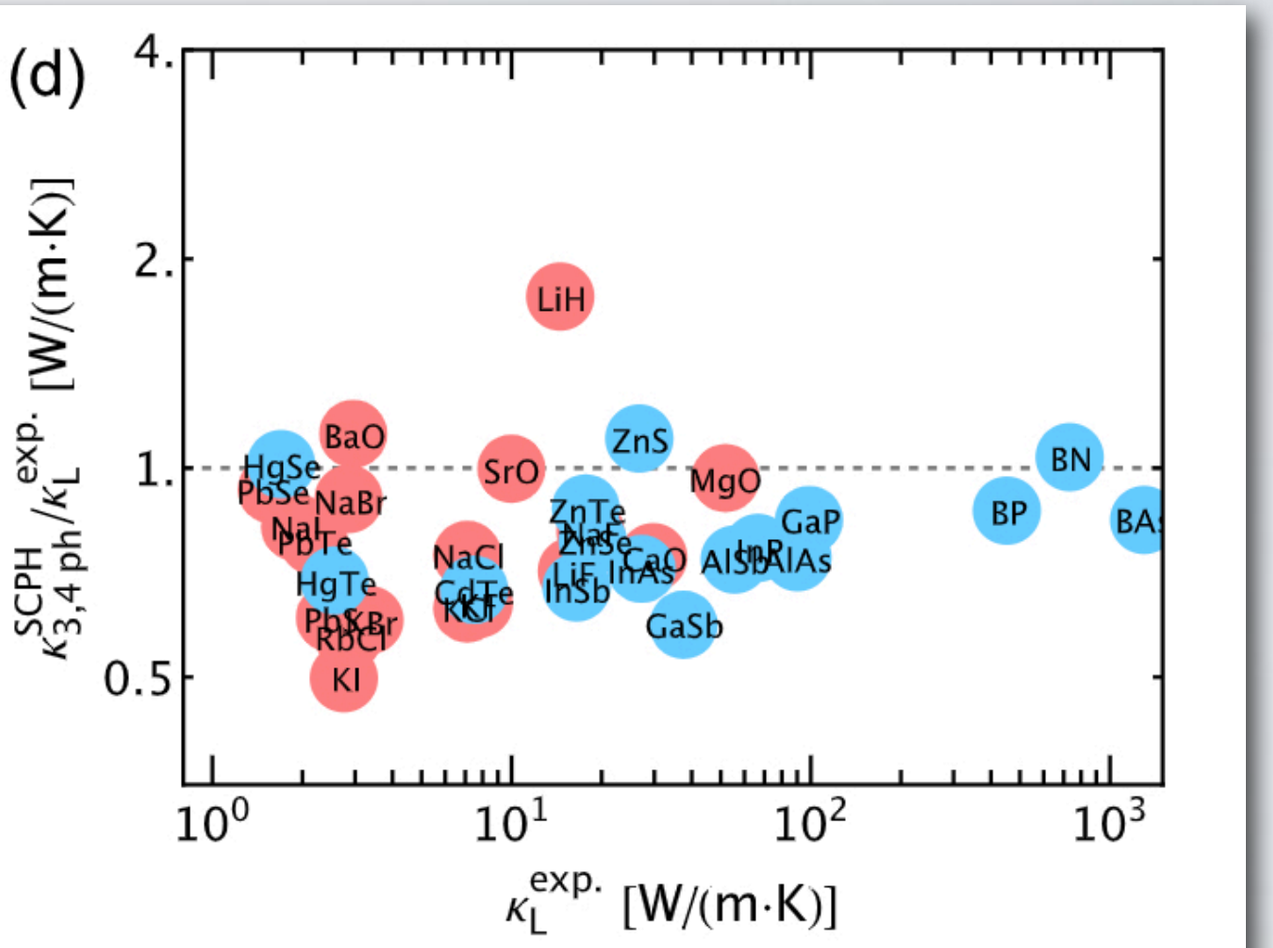


4th-order expansion + effective higher orders



FIRST-PRINCIPLES APPROACHES

	Order of interaction	Validity & Applicability	Finite Size Effects	Disorder
Boltzmann-Transport Eq.	$\sim\mathcal{O}(r^{3\text{-}4})$	weak anharmonic effects	Minute	Parameter
Green-Kubo MD				

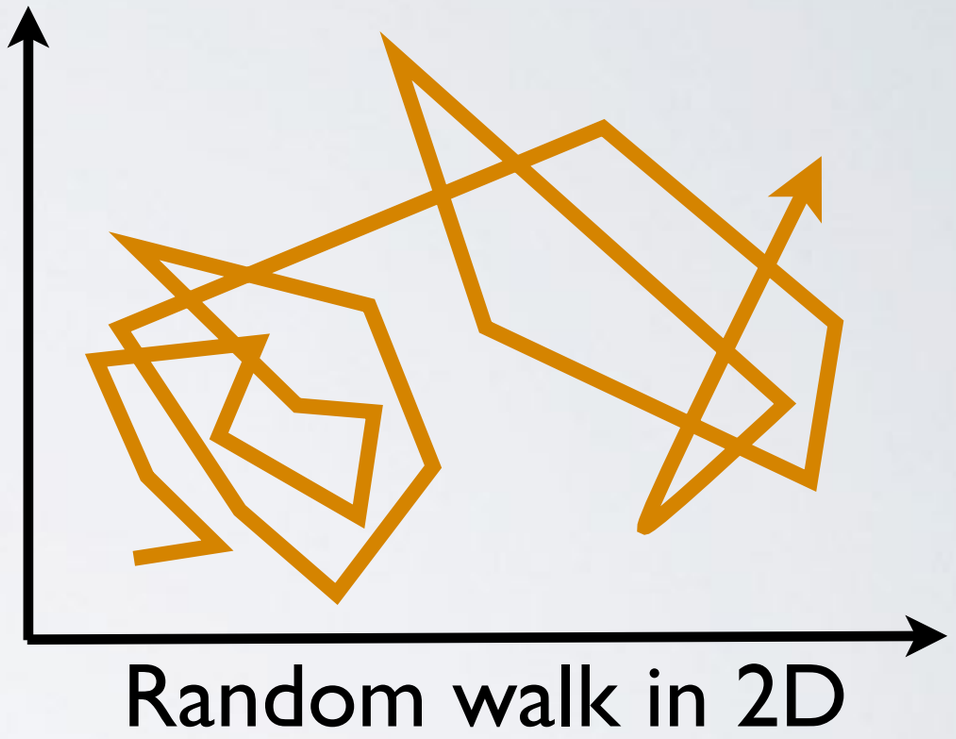
Boltzmann-Transport-Eq. gives **very accurate** results for **perfect crystals** at **low temperatures**.

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

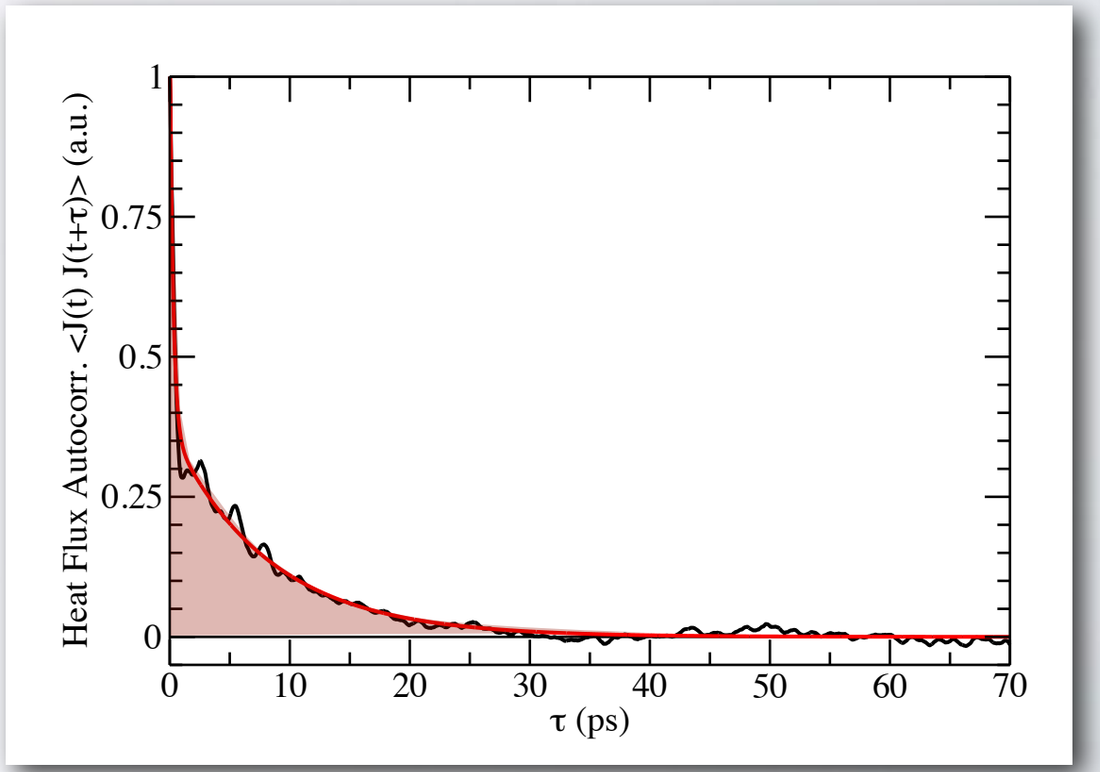
Simulations of the **thermodynamic equilibrium**

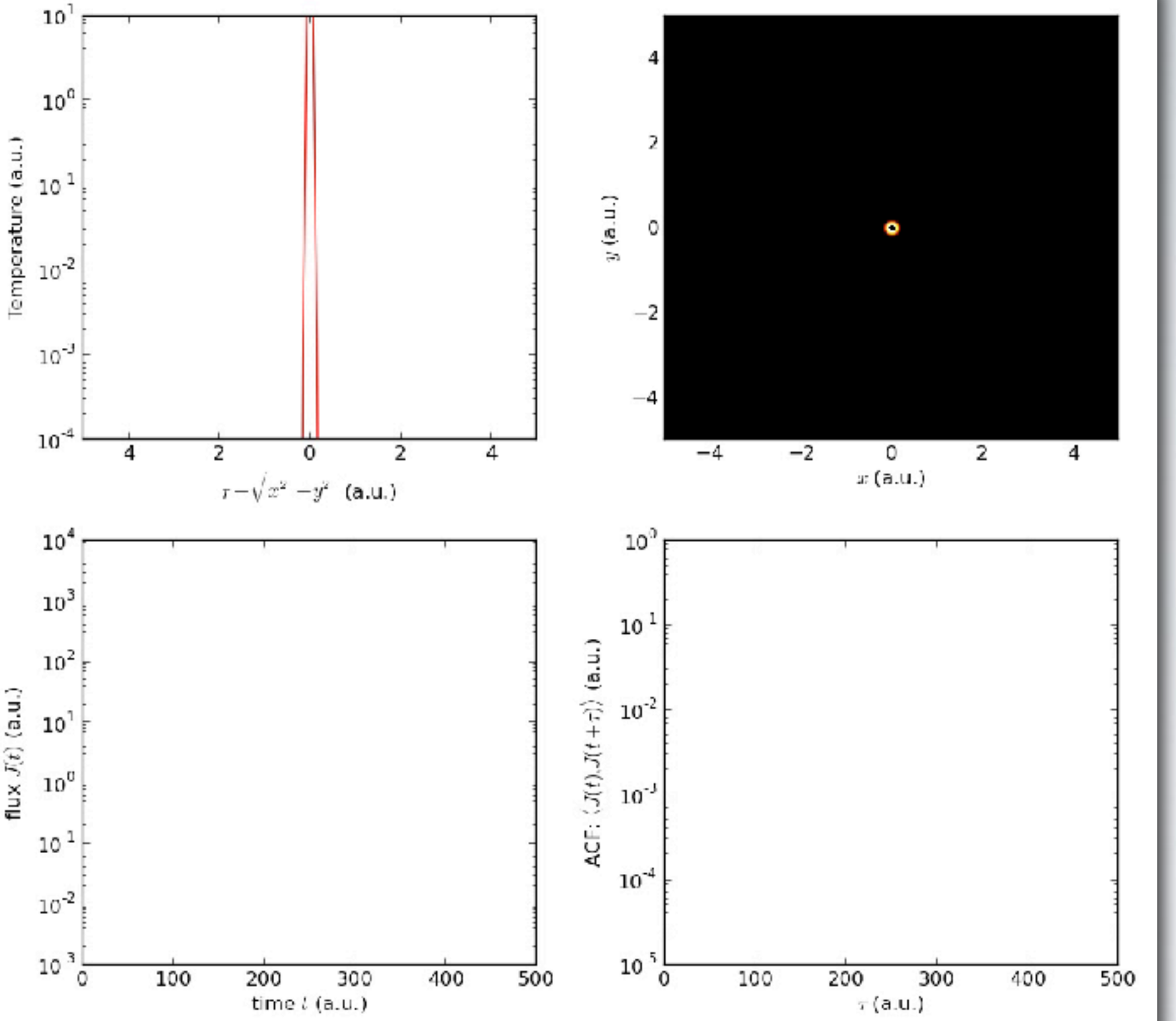
⇓ ⇓ ⇓

Information about **non-equilibrium processes**

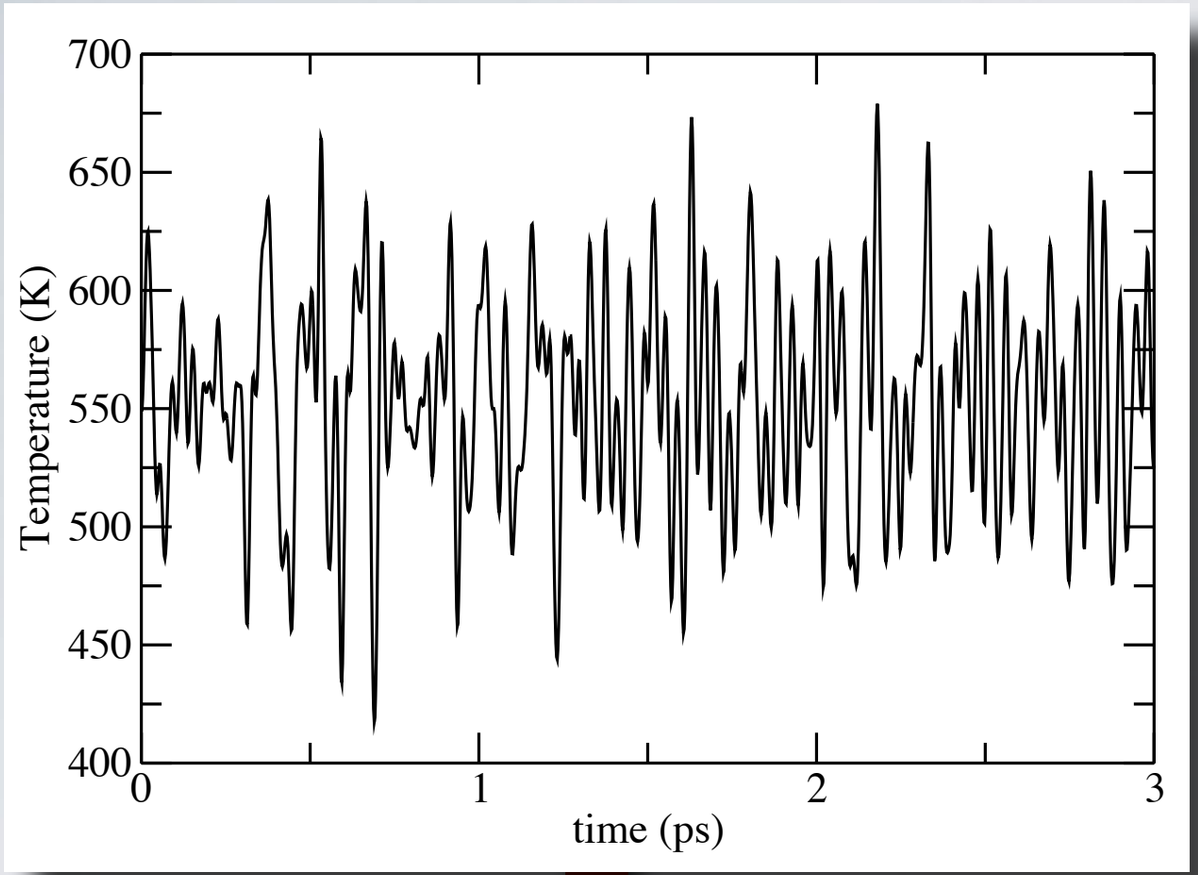
$$\kappa \sim \int_0^\infty d\tau \left\langle \mathbf{J}(0)\, \mathbf{J}(\tau) \right\rangle_{eq}$$

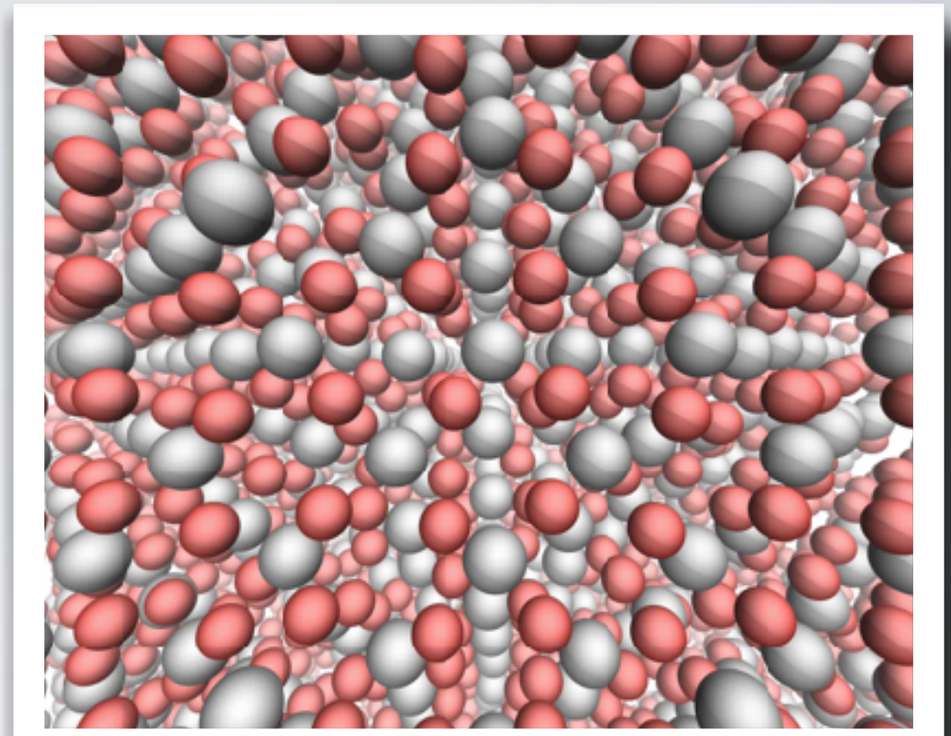
The **thermal conductivity** is related to the **autocorrelation function** of the **heat flux**

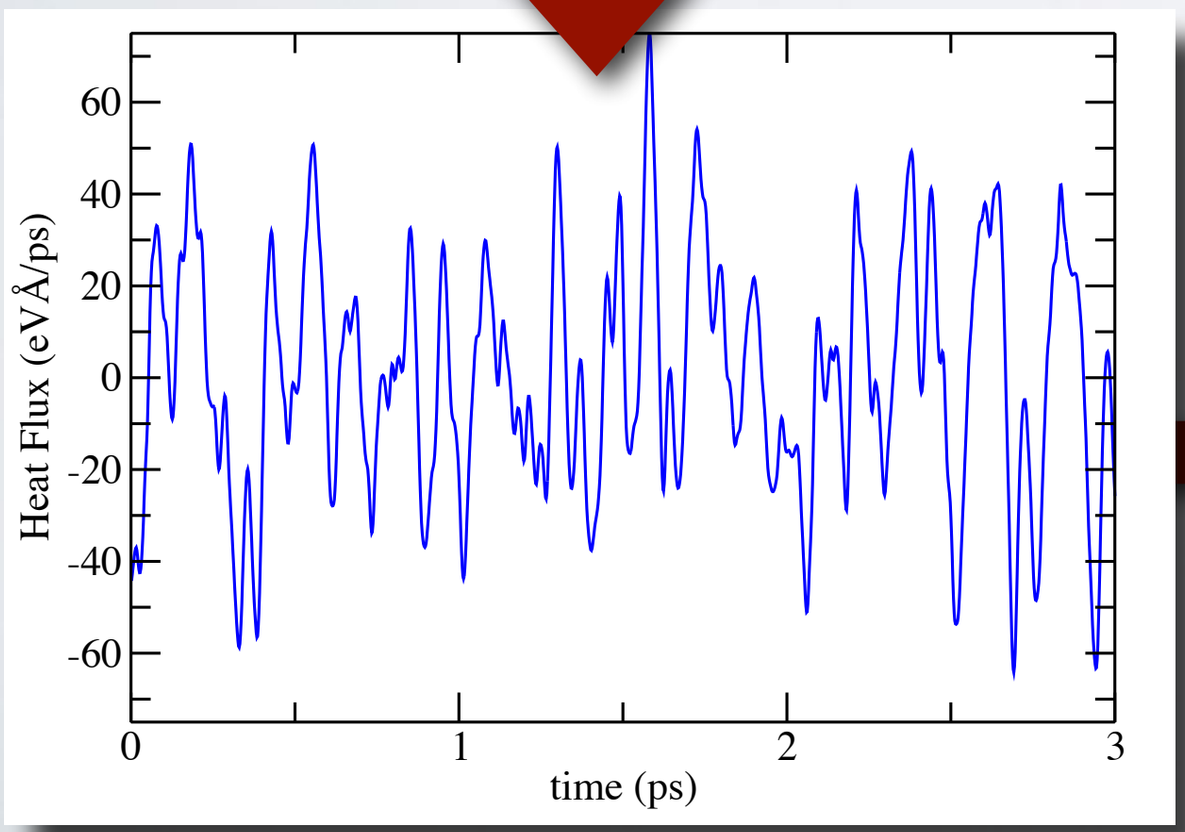


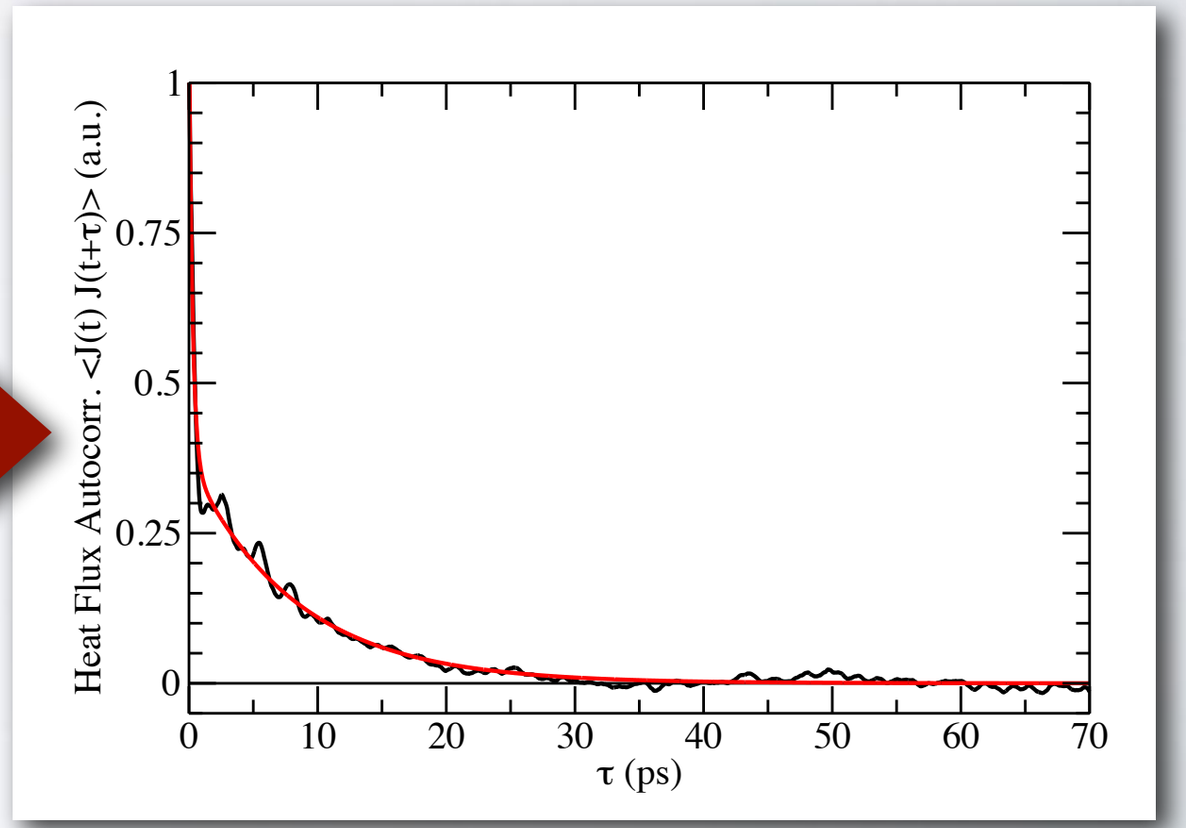


$$T(\mathbf{r},t) = \frac{1}{(4\pi\kappa t)^{3/2}} \exp\left(-\frac{\mathbf{r}^2}{4\kappa t}\right) \quad \Rightarrow \quad \int \langle J(t), J(t+\tau)\rangle \, d\tau \quad \sim \kappa$$


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 ***Heat flux***

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

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:

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

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

$$E_I = T_I + U_I \quad \Rightarrow\!\!\Rightarrow \quad \dot{E}_I = \mathbf{F}_I \cdot \dot{\mathbf{R}}_I + \sum_J (\nabla_{\mathbf{R}_J} U_I) \cdot \dot{\mathbf{R}}_J$$

kinetic energy

potential energy

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

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

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

⇛ Heat flux does **not** depend on **absolute** positions.

DEFINING THE VIRIAL HEAT FLUX

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

Some Simple Examples:

a) Harmonic Approximation

$$U = \frac{1}{2}\sum_{I,J}\Phi_{IJ}\Delta\mathbf{R}_I\Delta\mathbf{R}_J \quad \Rrightarrow \quad \nabla_{\mathbf{R}_J}U = \sum_I \Phi_{IJ}\Delta\mathbf{R}_I$$

$$\nabla_{\mathbf{R}_J}U_I$$

b) Coulomb Potential

$$U = \frac{1}{2}\sum_{I,J}\frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|} \quad \Rrightarrow \quad \nabla_{\mathbf{R}_J}U = \sum_J Z_I Z_J \frac{\mathbf{R}_I - \mathbf{R}_J}{|\mathbf{R}_I - \mathbf{R}_J|^3}$$

$\Rrightarrow$ Required **partitioning** naturally arises since **interactions** (forces) are **pairwise** by **definition**.

WHAT ABOUT FIRST-PRINCIPLES?

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

The potential energy is the **expectation value**

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

of the **many-body** Hamiltonian $\mathbb{H} = \sum_i \left[\hat{T}_i + \frac{1}{2} \sum_{j \neq i} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} - \sum_J \frac{Z_J}{|\mathbf{r}_i - \mathbf{R}_J|} \right]$

***Hellman-Feynman* theorem yields:**

$$\nabla_{\mathbf{R}_J} U = \int n(\mathbf{r}) \frac{Z_J(\mathbf{R}_J - \mathbf{r})}{|\mathbf{r} - \mathbf{R}_J|^3} d\mathbf{r}$$

$$\nabla_{\mathbf{R}_J} U_I \Rightarrow \nabla_{\mathbf{R}_J} U(\mathbf{r})$$

- **Electronic density** *n(**r**)* is the counterpart in the interaction
- *Partitioning* onto electrons **not** discrete, but **continuous** in ***r***
- *Partitioning* onto **well-defined** and **unique**, since it only depends on the **electron density.**

WHAT ABOUT FIRST-PRINCIPLES?

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

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

$$\Downarrow$$

$$\mathbf{J}(t) = \sum_I \mathbf{R}_I \left[\dot{T}_I + \sum_J (\nabla_{\mathbf{R}_J} U_I) \cdot \dot{\mathbf{R}}_J \right] + \int \mathbf{r} \left[\sum_J (\nabla_{\mathbf{R}_J} U(\mathbf{r})) \cdot \mathbf{R}_J \right] d\mathbf{r}$$

Kinetic energy of the **nuclei**

Nuclear Coulomb repulsion

Nuclear-Electronic Coulomb attraction

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

⇛ **Unique** and **well-defined!**

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

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

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

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

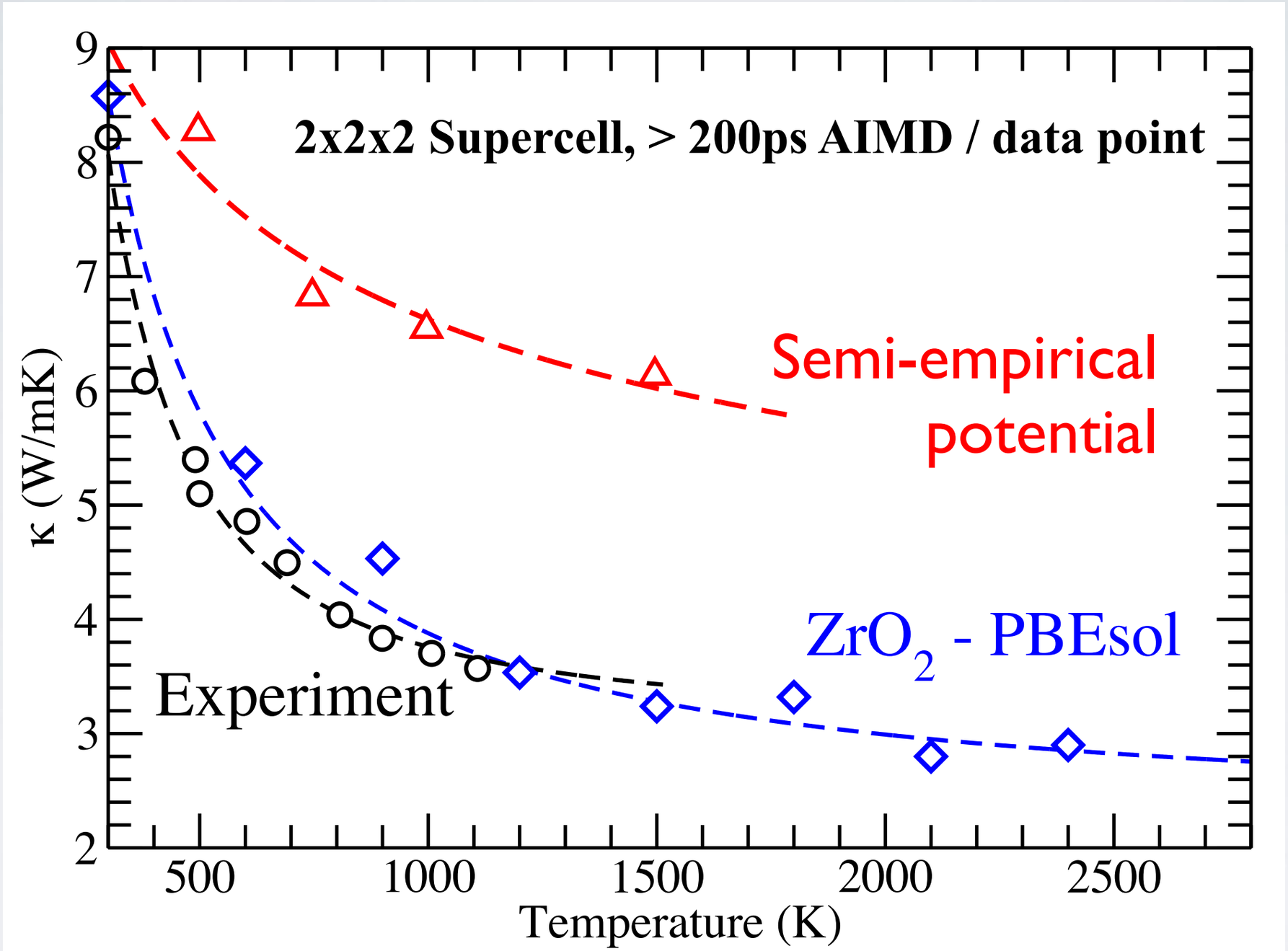
$$- \frac{1}{2V} \sum_{\alpha} \int_{\mathrm{UC}} \mathrm{d}\mathbf{r} \frac{\partial n_{\alpha}^{\mathrm{MP}}(\mathbf{r} - \mathbf{R}_\alpha)}{\partial r_i} (\mathbf{r} - \mathbf{R}_\alpha)_j v_{\mathrm{es,tot}}(\mathbf{r})$$

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

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

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

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).

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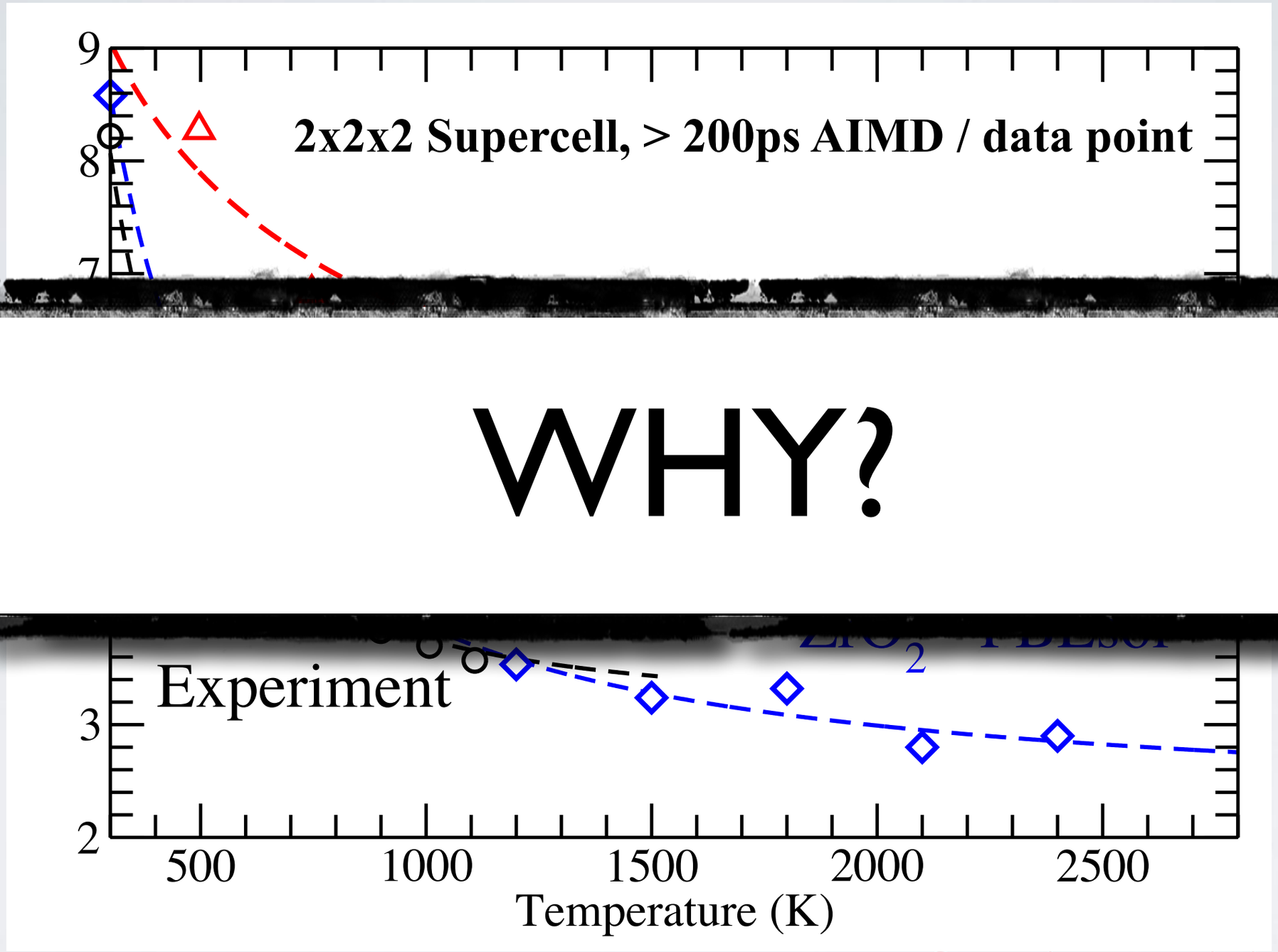

WHY?

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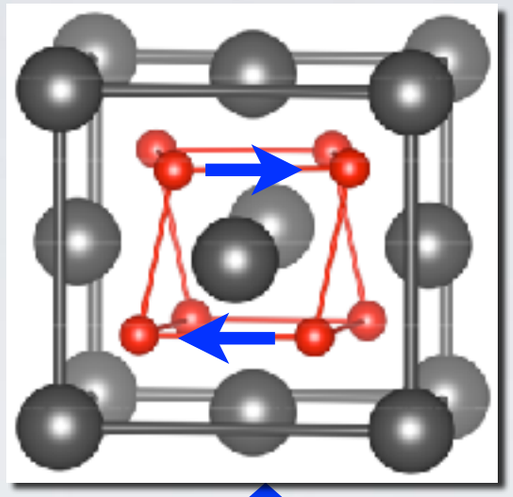
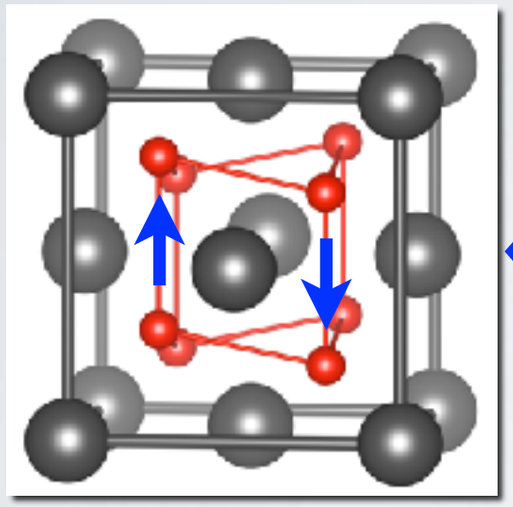


dy > 0

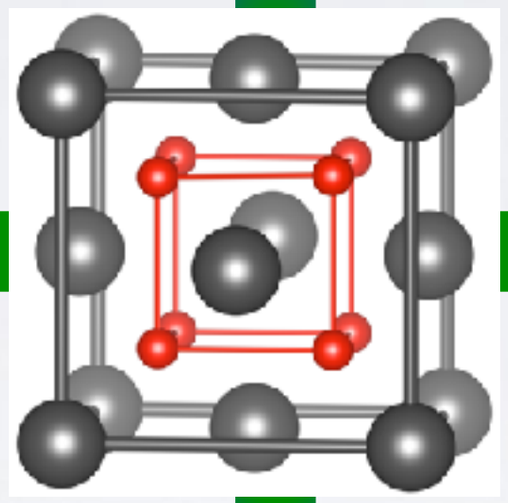
dz,dx = 0

Tetragonal

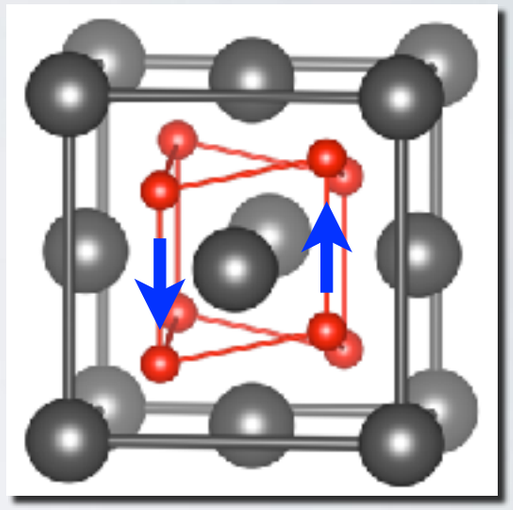


dz < 0

dx,dy = 0

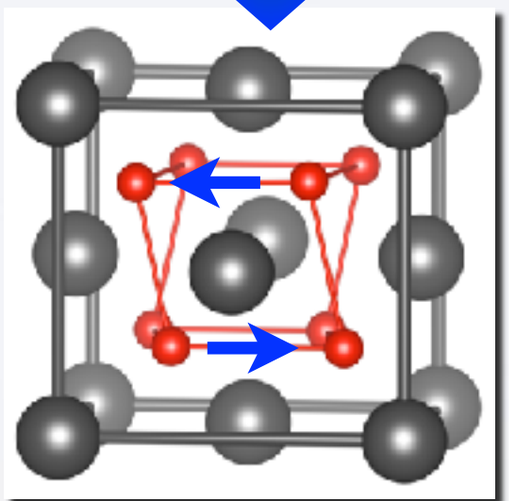


Tetragonal



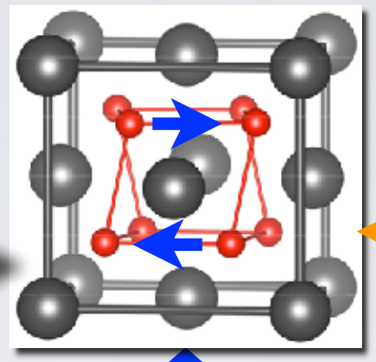
dz > 0

dx,dy = 0



dy < 0

dz,dx = 0



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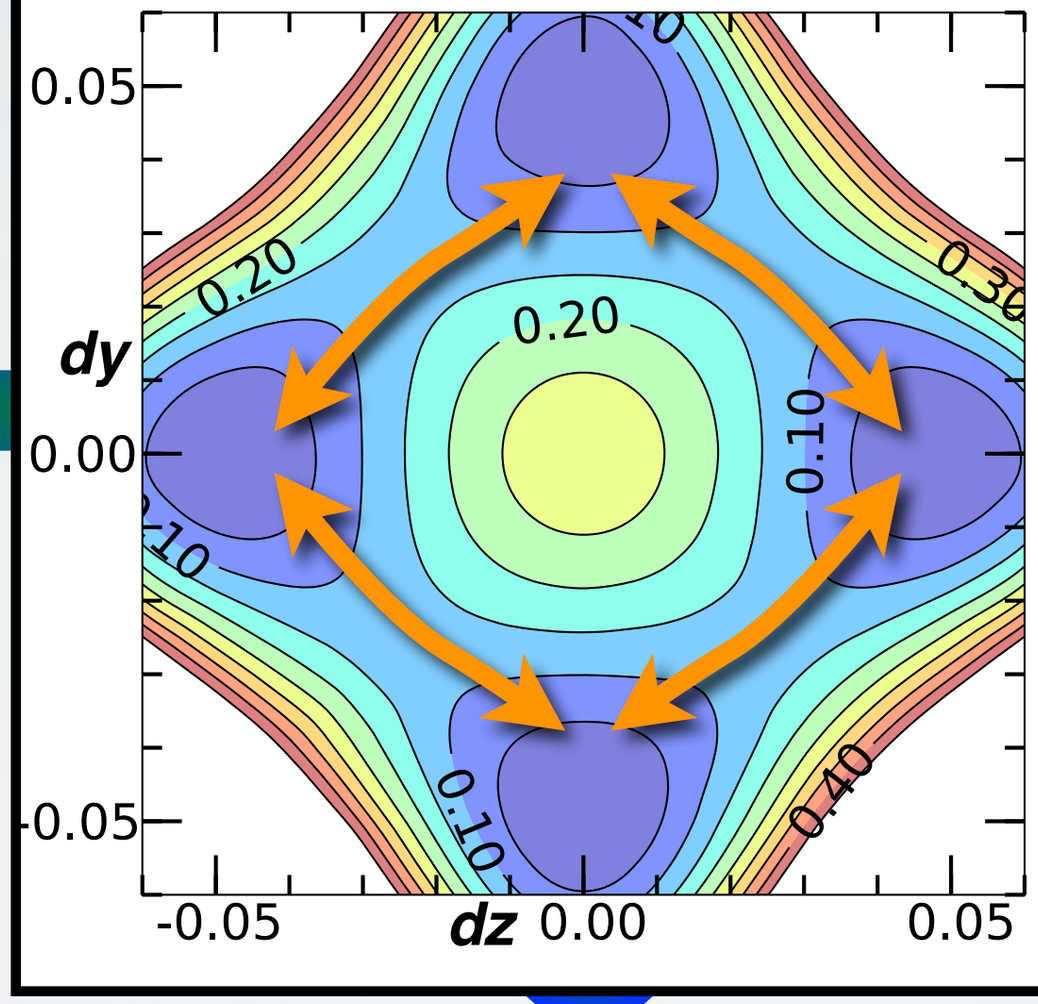
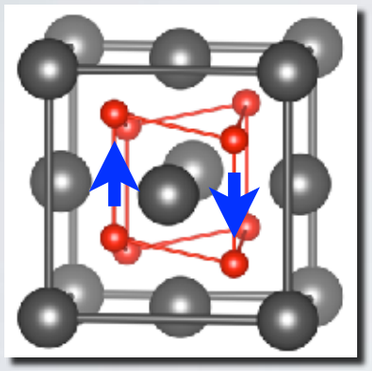
dz,dx = 0

Switches

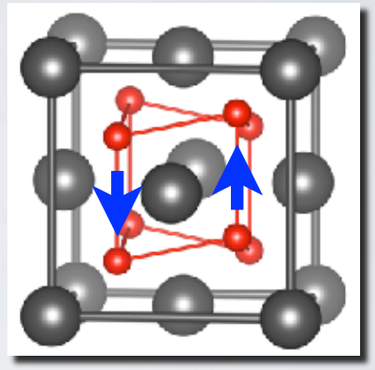


Tetragonal

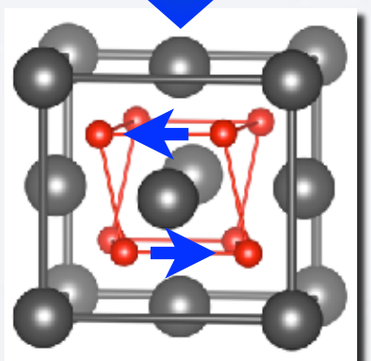


dz < 0
dx,dy = 0

Tetragonal

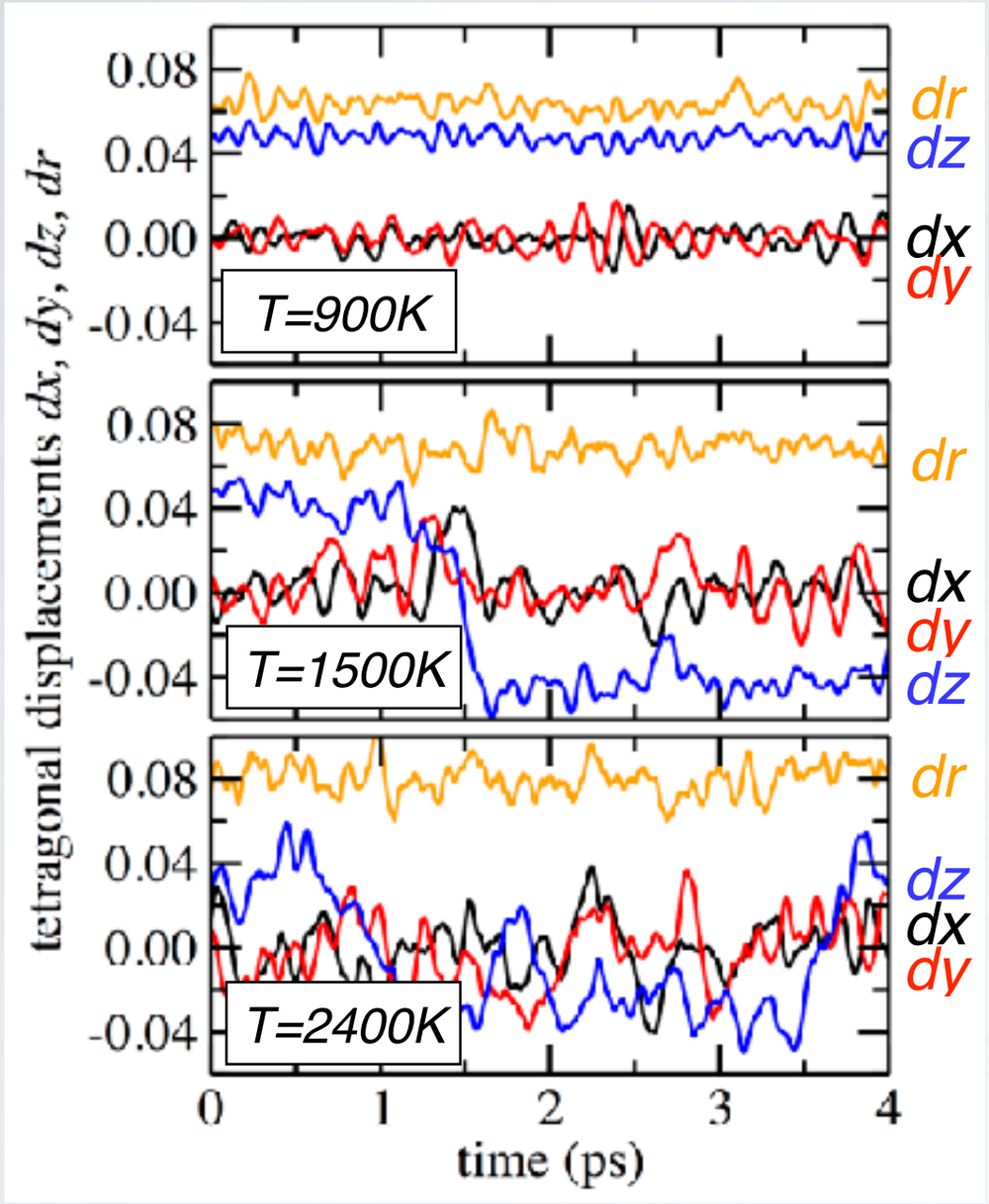


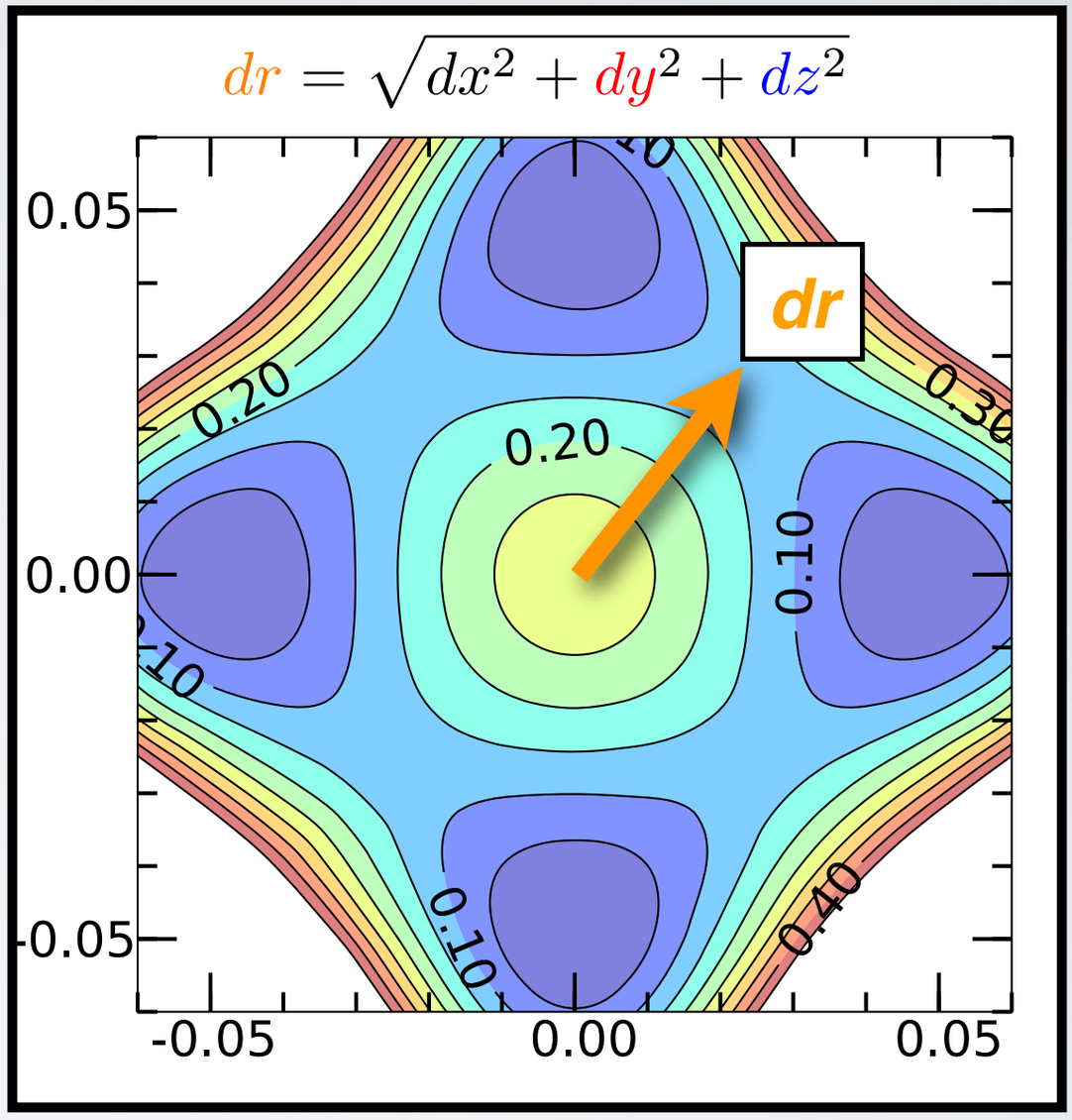
dz > 0
dx,dy = 0



dy < 0
dz,dx = 0

Ab initio MD Evidence

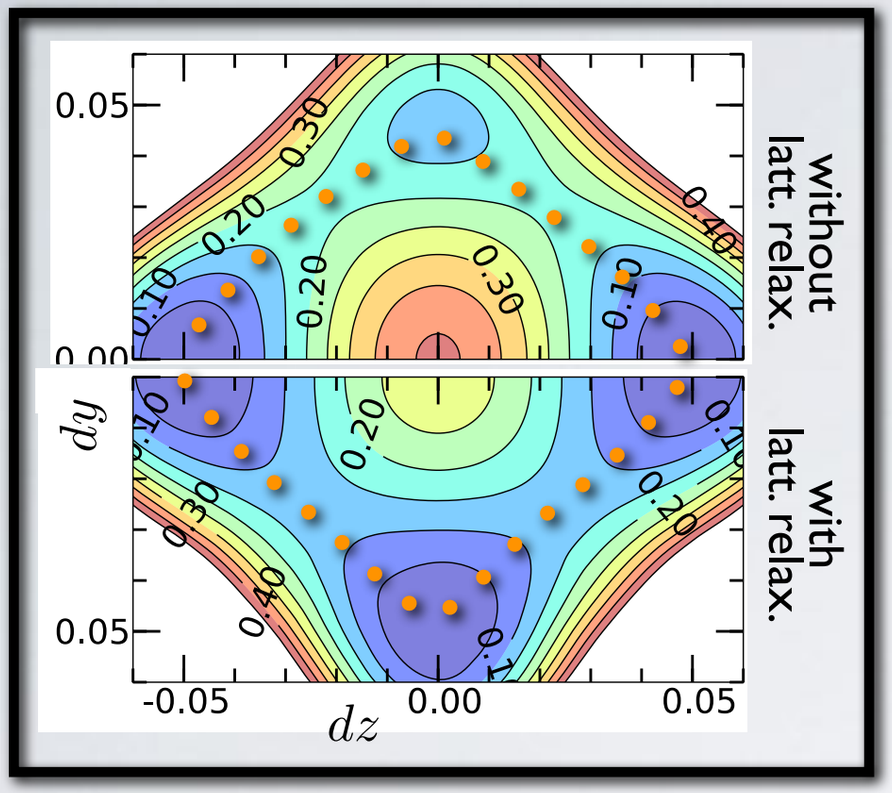




Distance ***dr*** finite at **all** temperatures!

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

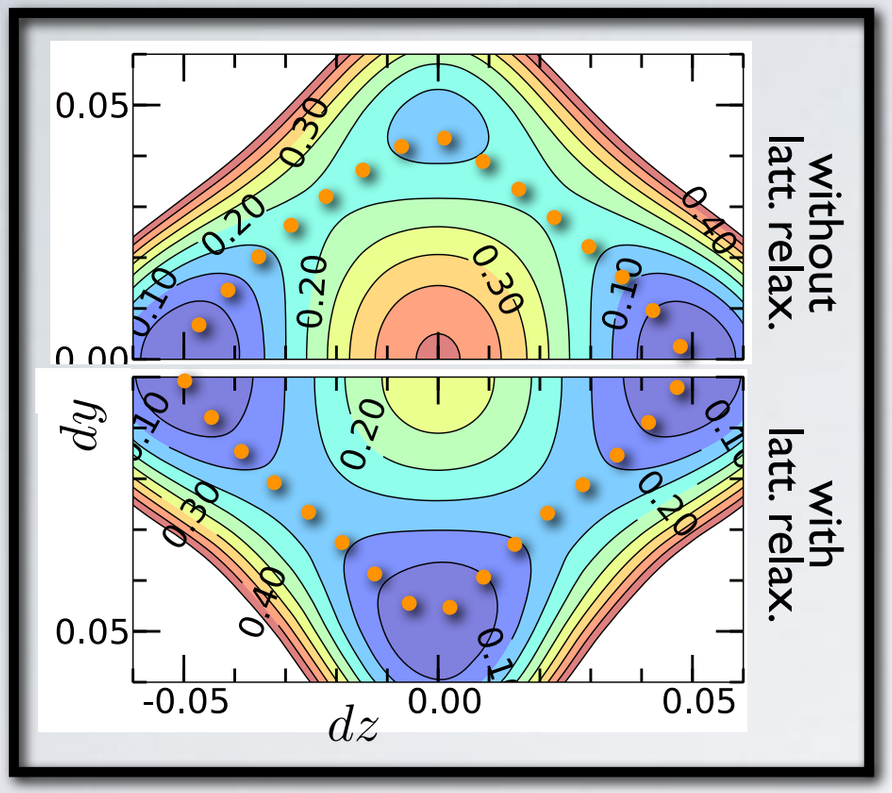
pristine ZrO_2



$E_{barrier}$

140 / 70 meV

pristine ZrO_2

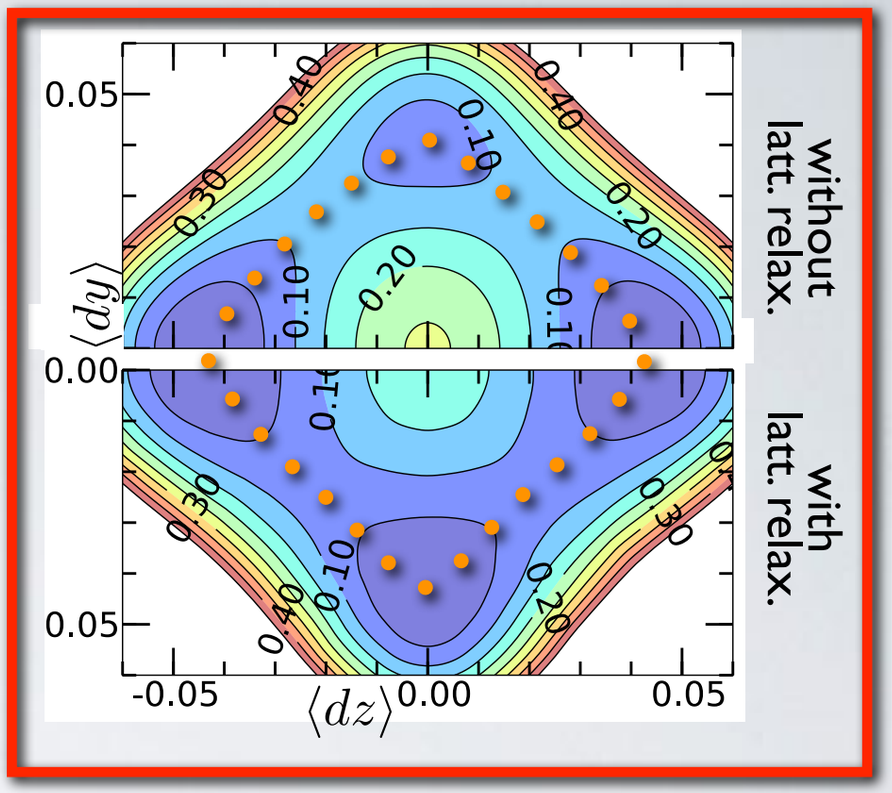


$E_{barrier}$

140 / 70 meV

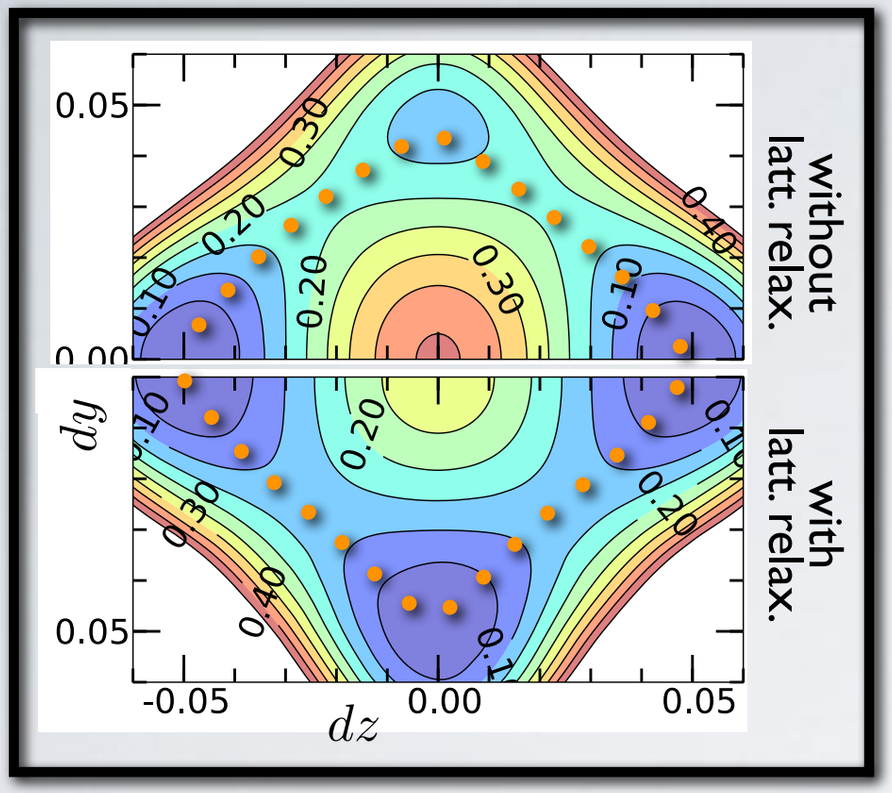
80 / 40 meV

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



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

pristine ZrO_2



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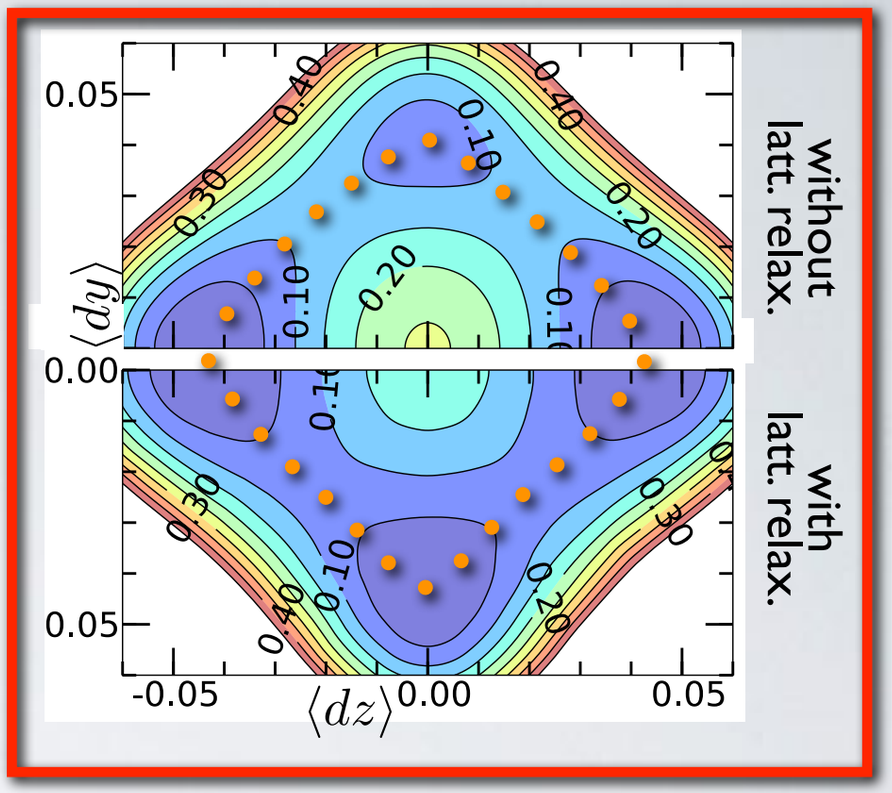
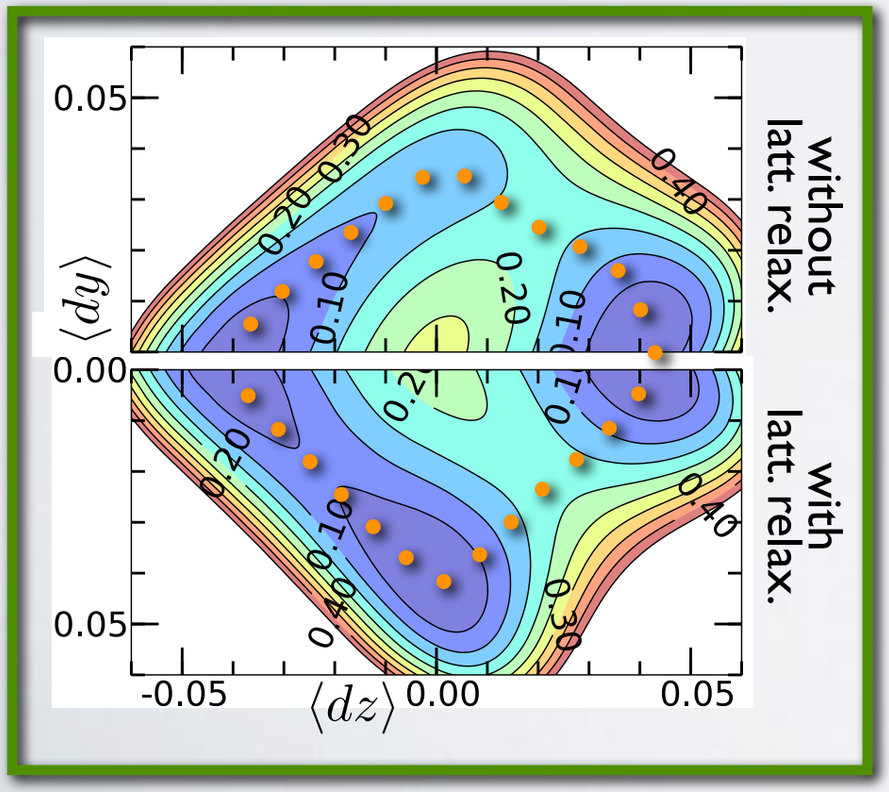


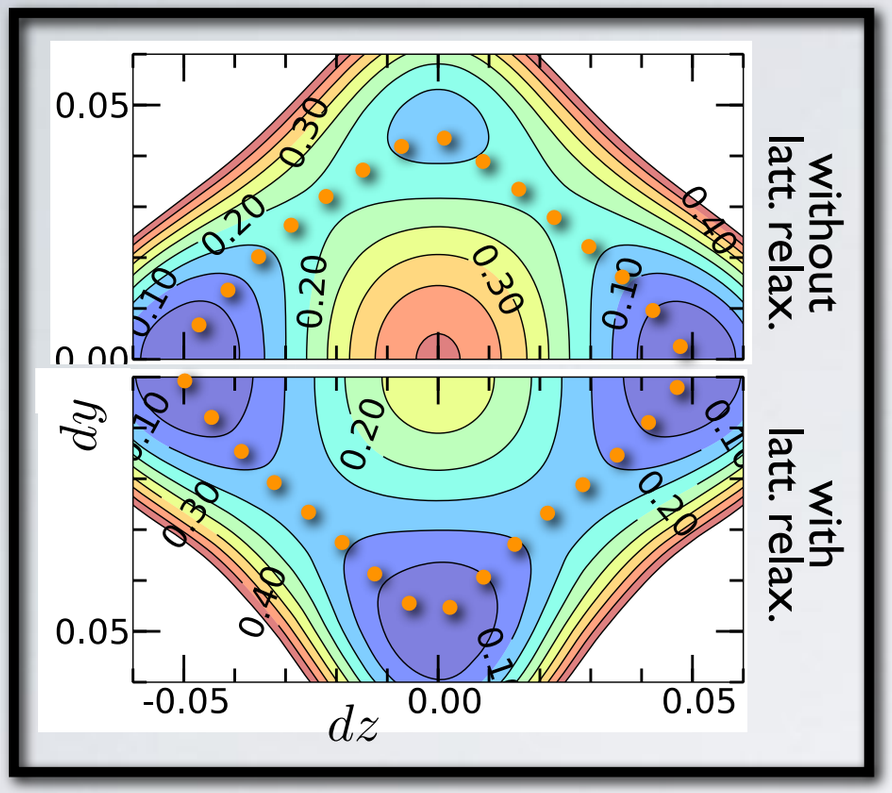


6.25 mol-% $YO_{1.5}$ doped ZrO_2

80 / 30 meV

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

pristine ZrO_2

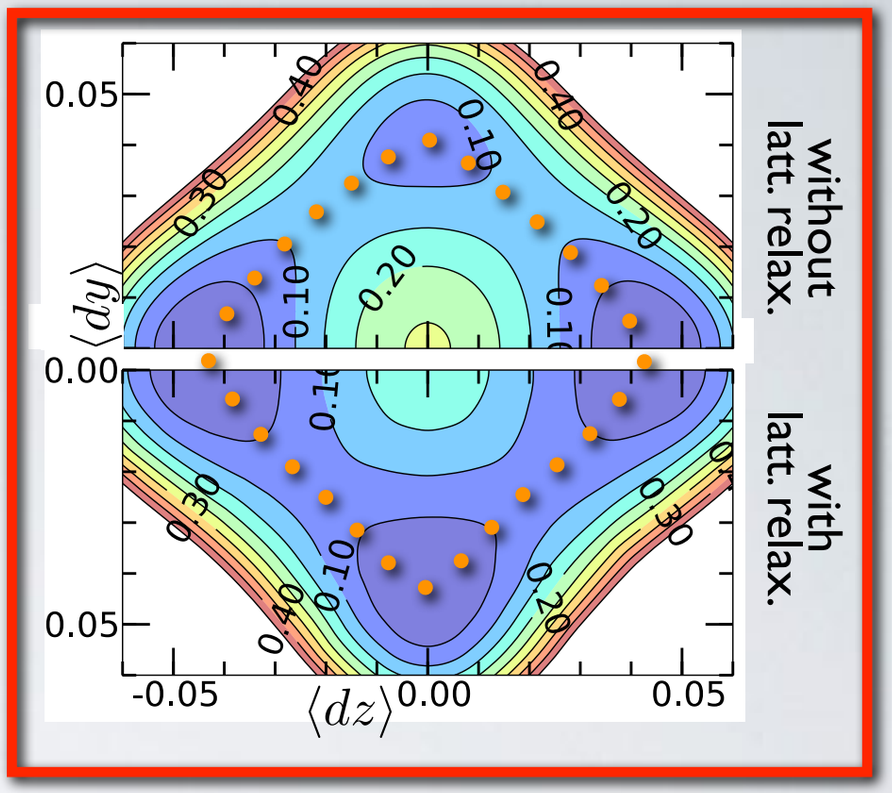


$E_{barrier}$

140 / 70 meV

80 / 40 meV

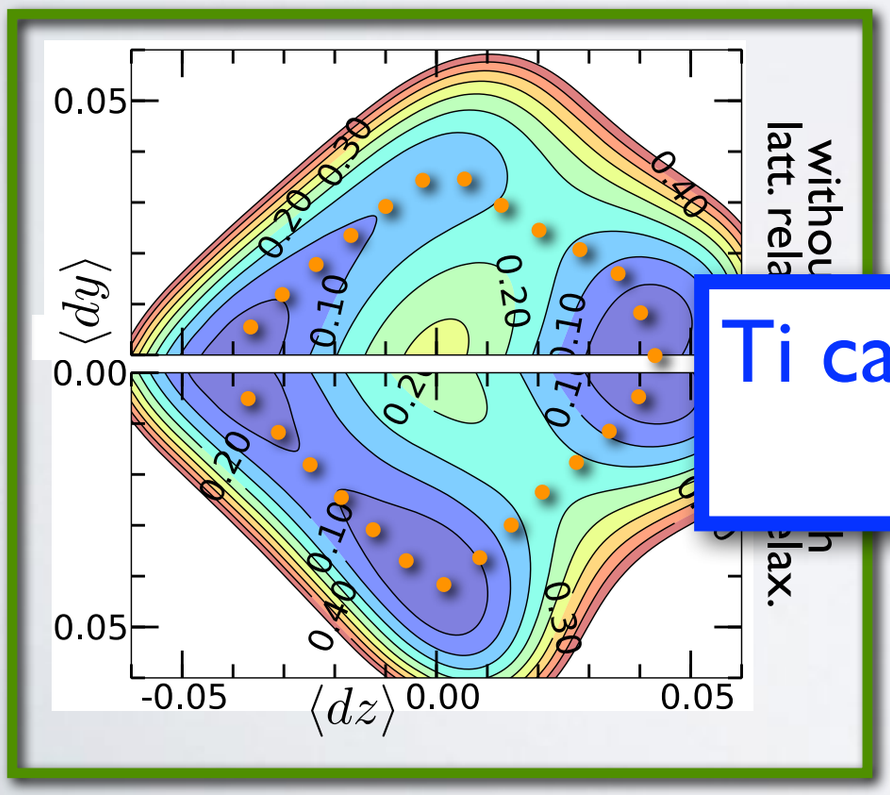
6.25 mol-% $ZrO_{1.5}$ doped ZrO_2



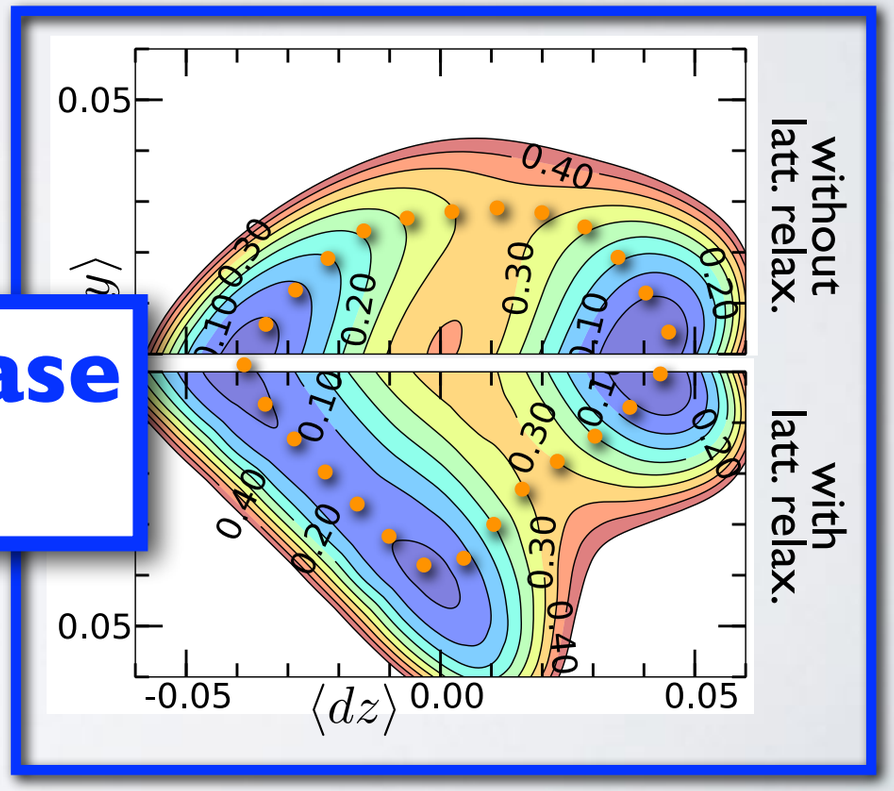
80 / 30 meV

Ti cations even **increase** the barriers!

160 / 100 meV



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



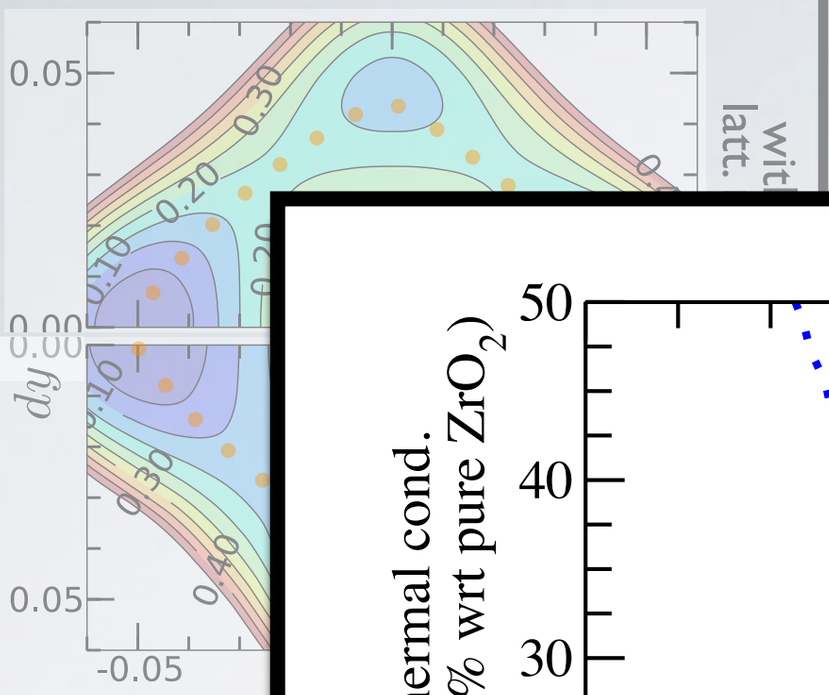
6.25 mol-% $YO_{1.5}$ + 3.125 mol-% TiO_2 doped ZrO_2

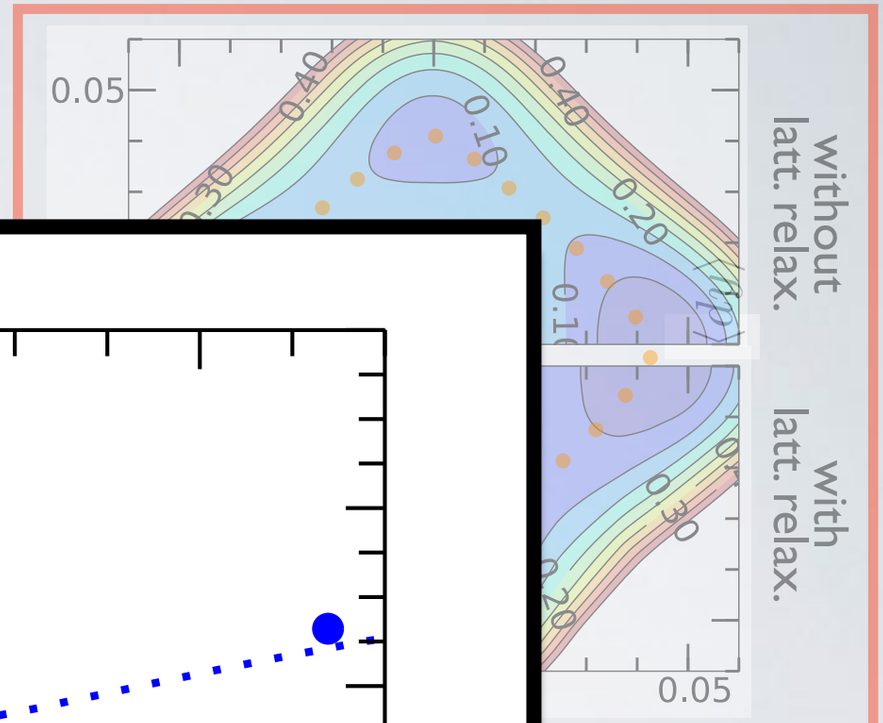
pristine ZrO_2

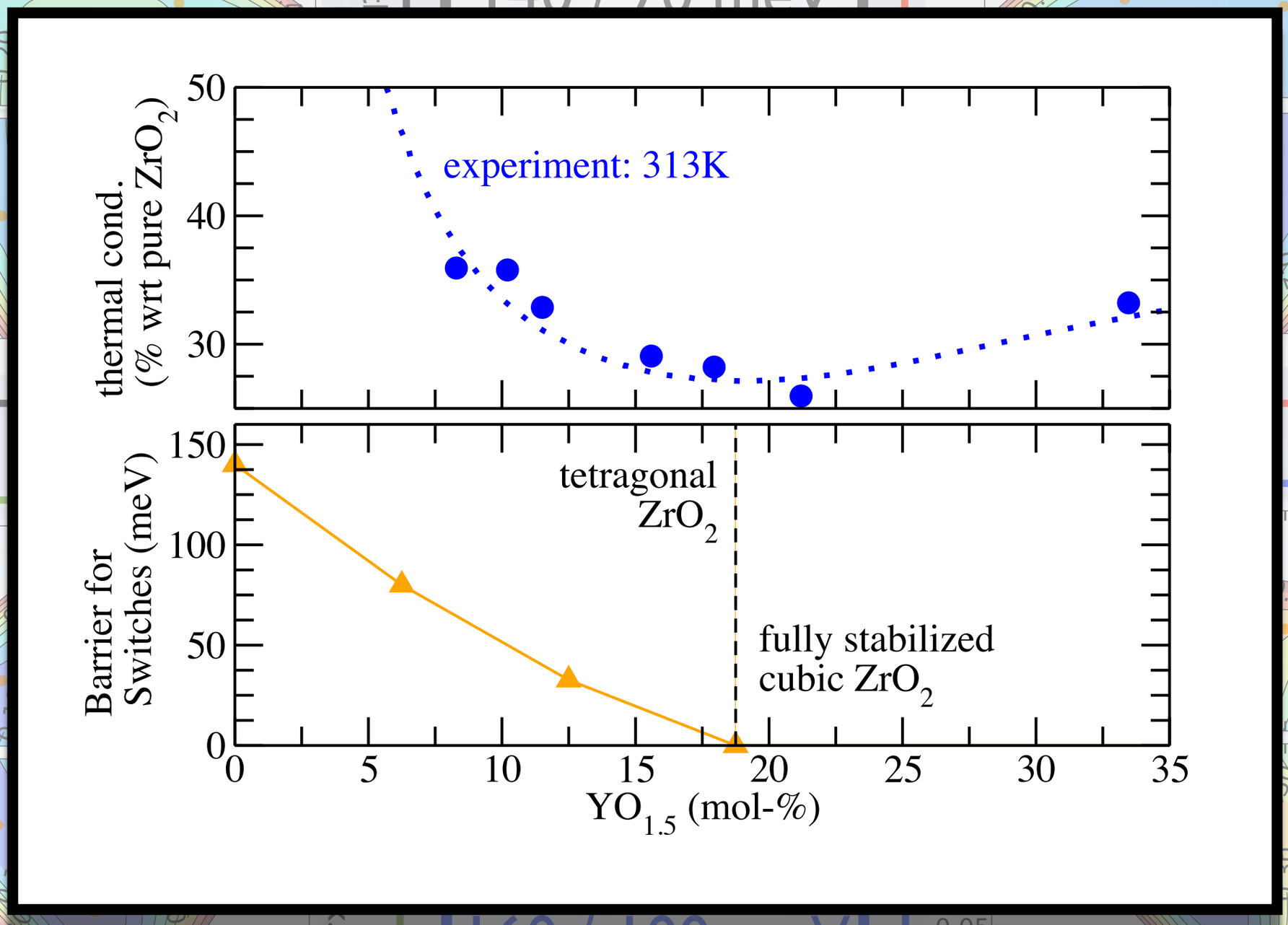
$E_{barrier}$

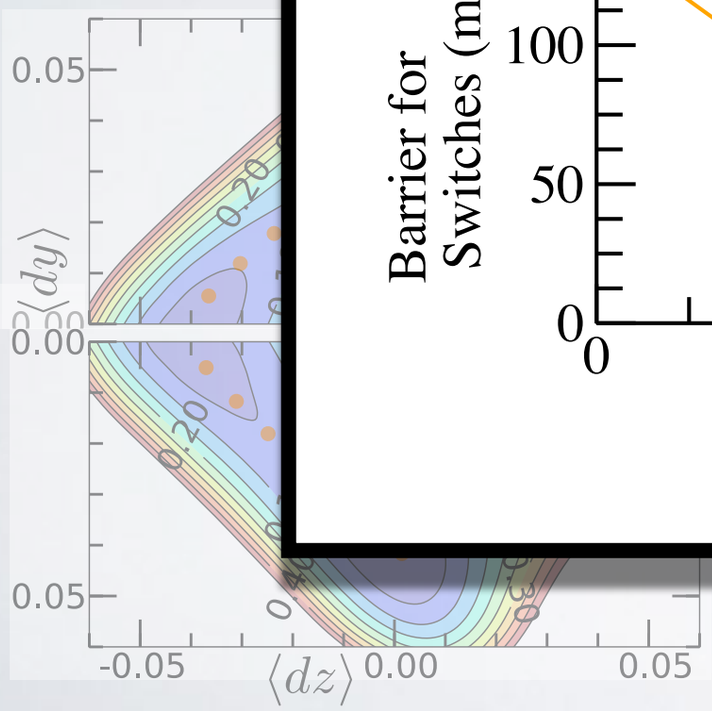
140 / 70 meV

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

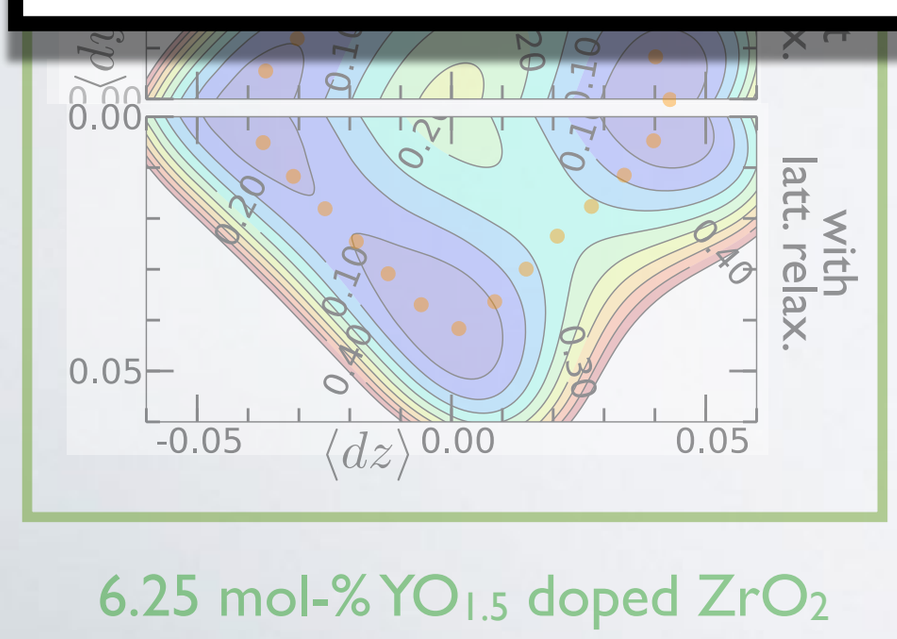
pristine ZrO_2

$E_{barrier}$

140 / 70 meV

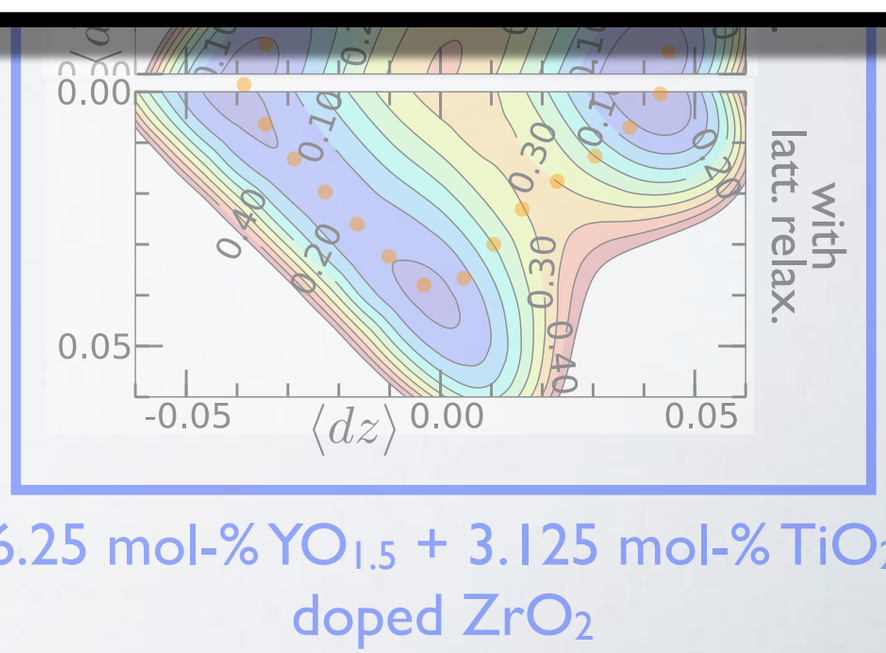
6.25 mol-% $ZrO_{1.5}$ doped ZrO_2

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



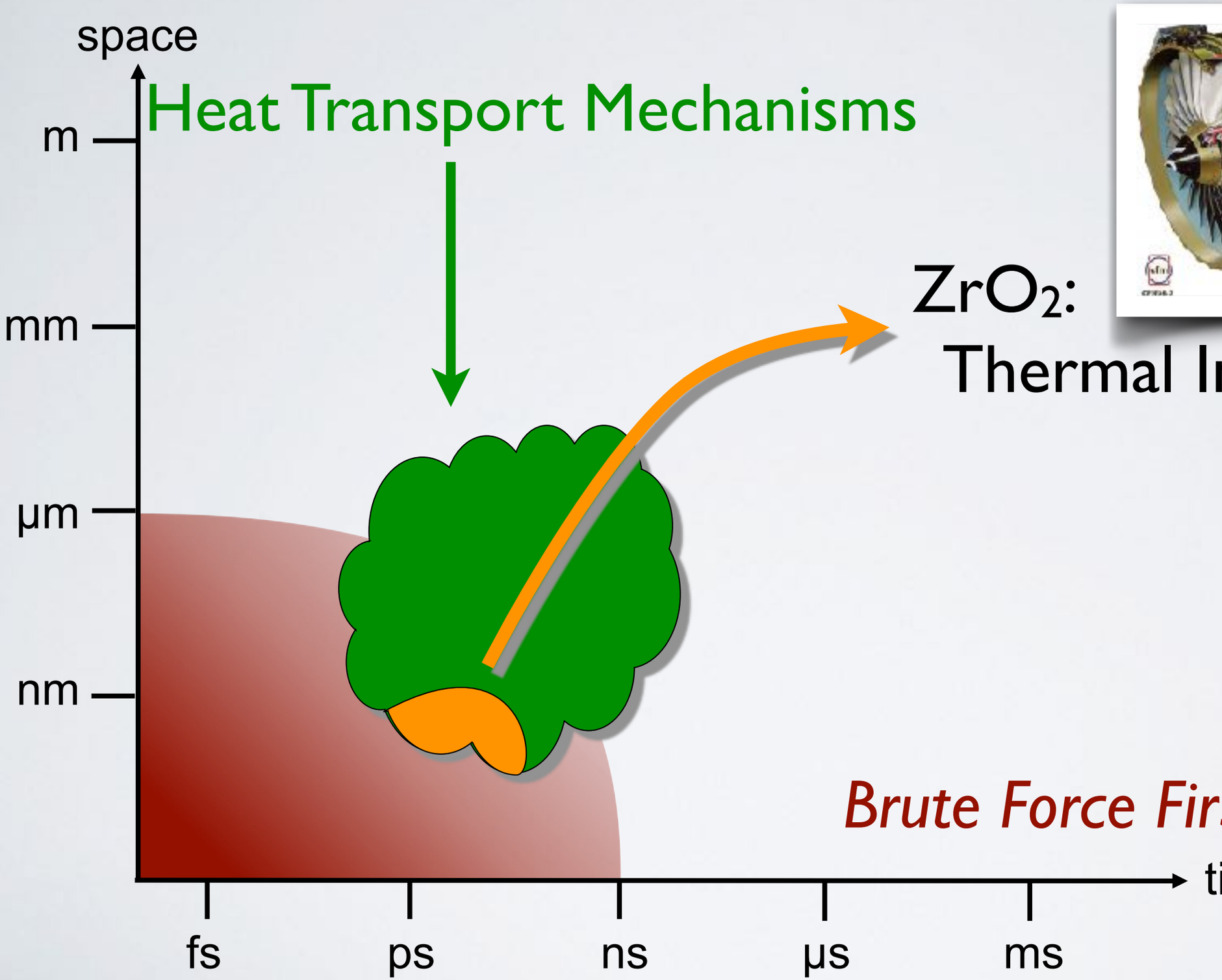
6.25 mol-% $YO_{1.5}$ doped ZrO_2

160 / 100 meV

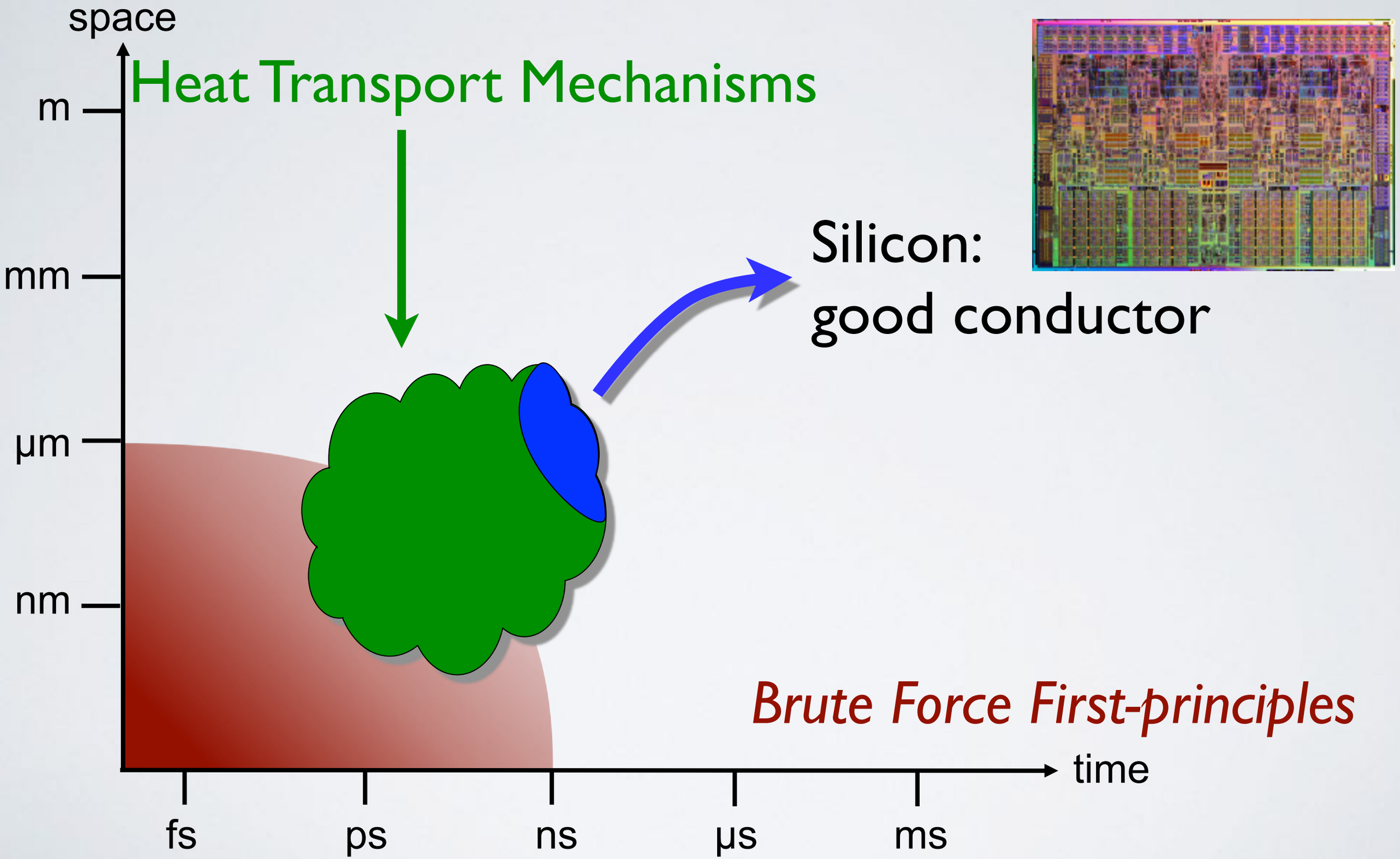


6.25 mol-% $YO_{1.5}$ + 3.125 mol-% TiO_2 doped ZrO_2

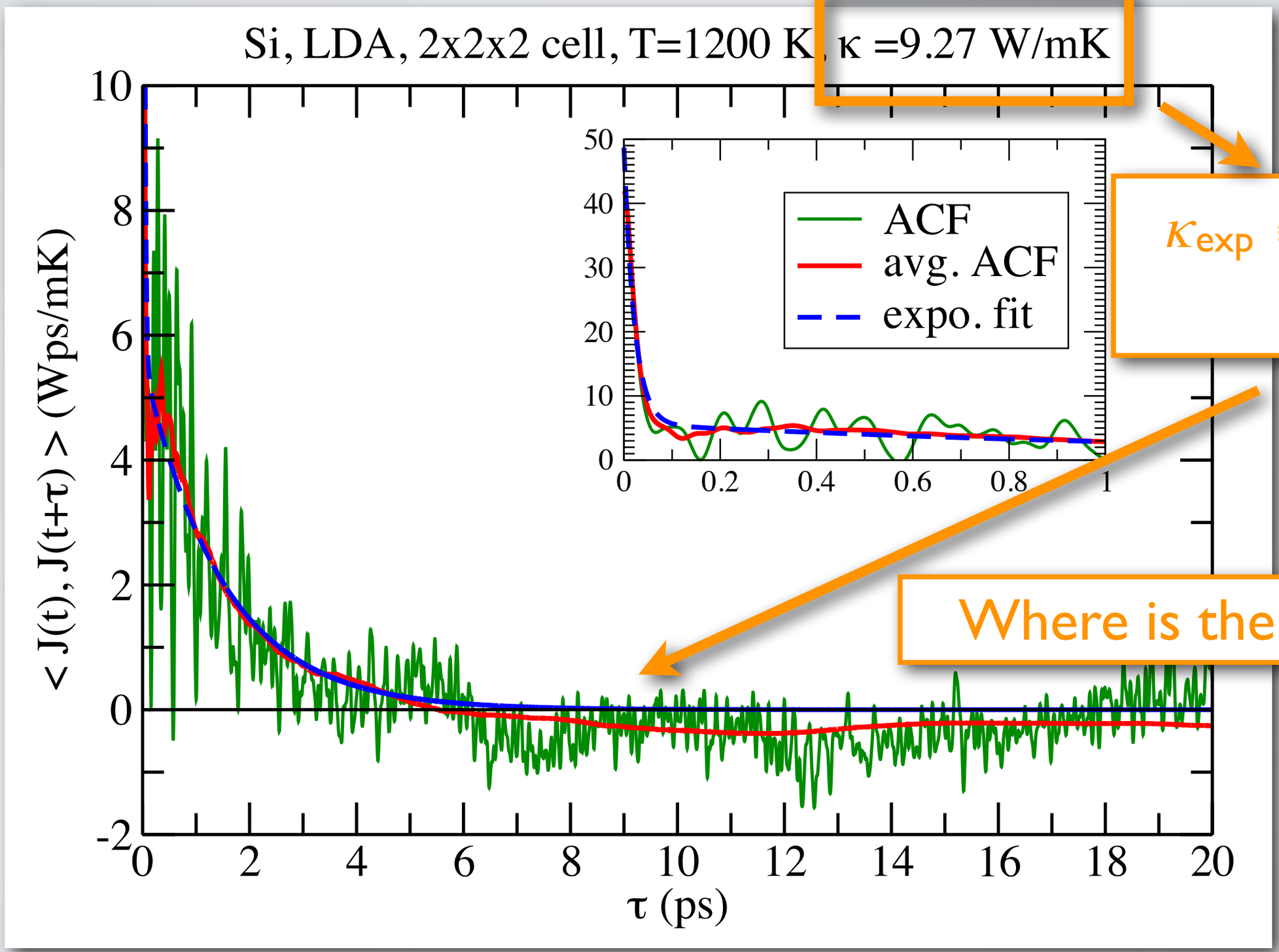
TIME AND LENGTH SCALES



TIME AND LENGTH SCALES



SILICON AT HIGH TEMPERATURES

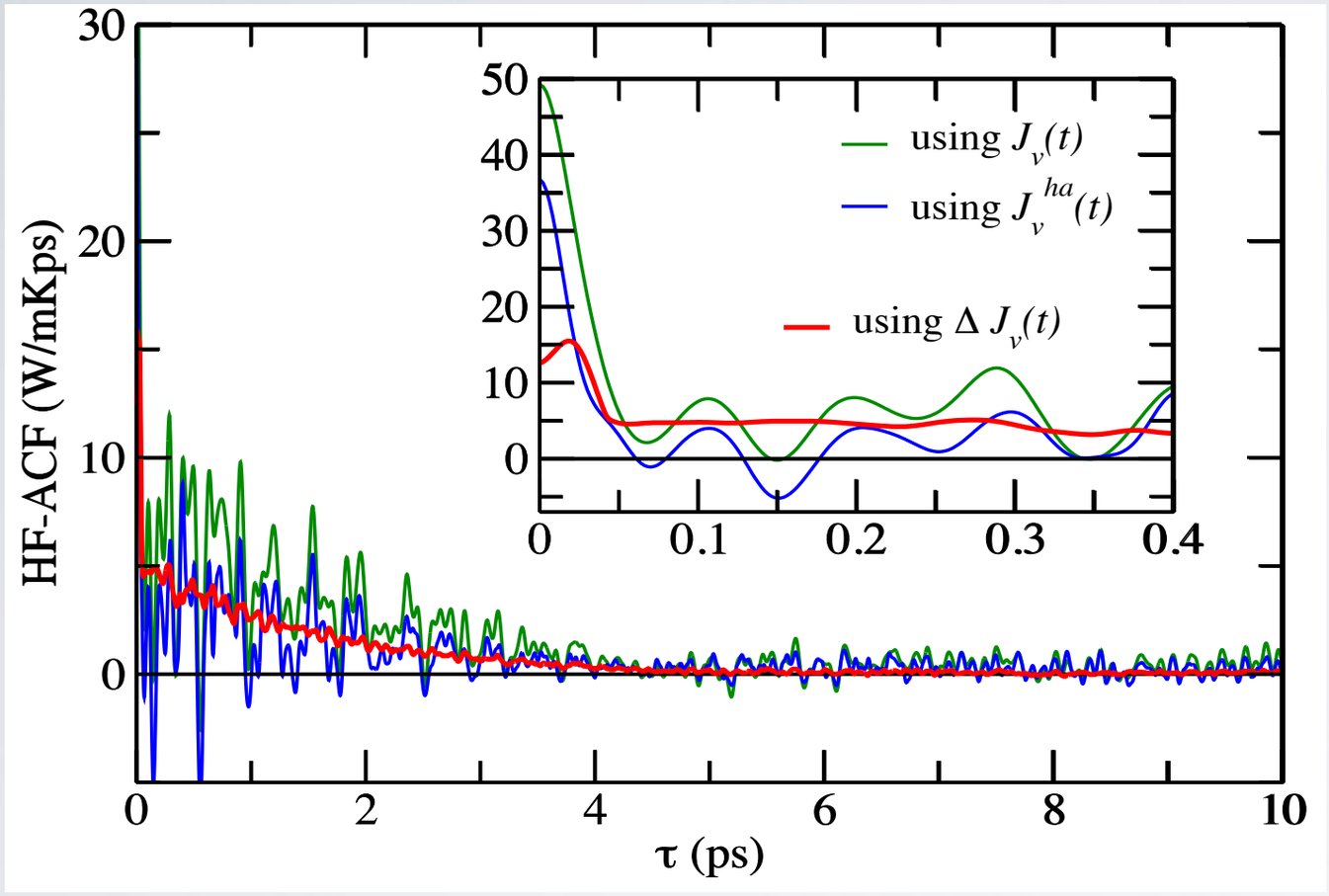


Experiment Si: C. Glassbrenner and G. Slack, *Phys Rev* **134**, A1058 (1964).

Numerical Challenge:

Time and Size Convergence

HOW TO BOOST CONVERGENCE?



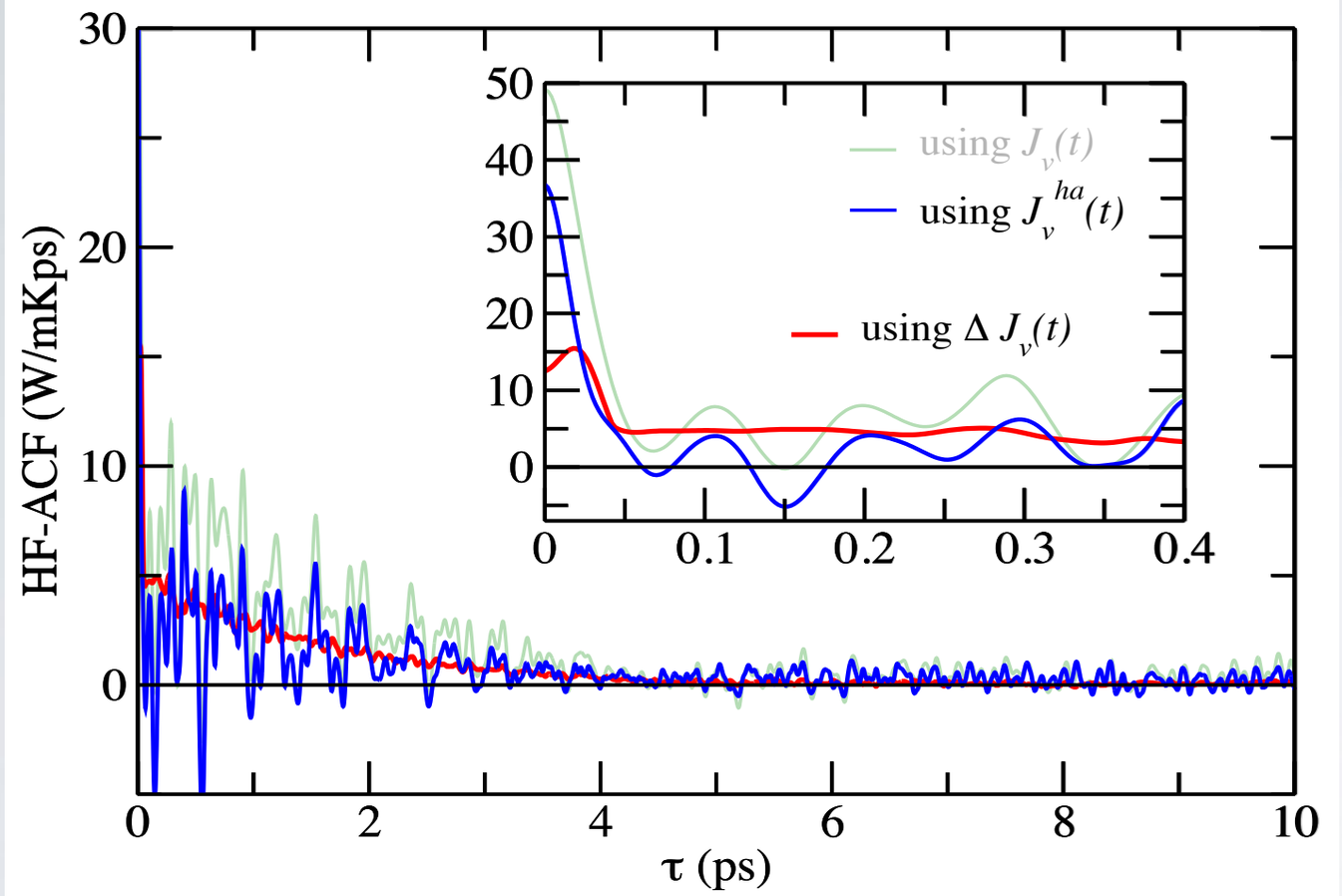
Decompose heat flux into contributions from higher/lower orders of the Taylor expansion

$$J_v(t) = \Delta J_v(t) + J_v^{ha}(t)$$

$$\langle J_v, J_v \rangle = \langle \Delta J_v, \Delta J_v \rangle + \langle J_v^{ha}, \Delta J_v \rangle + \langle \Delta J_v, J_v^{ha} \rangle + \langle J_v^{ha}, J_v^{ha} \rangle$$

Rapid Decay!

HOW TO BOOST CONVERGENCE?



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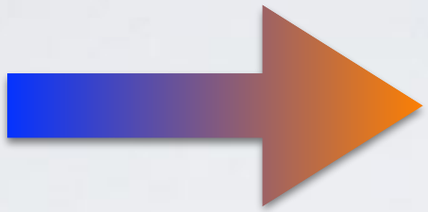
Slow Decay!

Can be (time and size) converged independently!

THE QUASI-PARTICLE PICTURE

Real Space

$$\mathbf{J}^{ha}(t) = \sum_{ij} \sigma_i^{ha} \mathbf{V_i}$$



Reciprocal Space

$$\mathbf{J}^{ha}(t) = \sum_{s\mathbf{q}} n_s(\mathbf{q},t)\ \omega_s^2(\mathbf{q})\ \mathbf{v}_s(\mathbf{q})$$

occupation	phonon	group
number	frequency	velocity

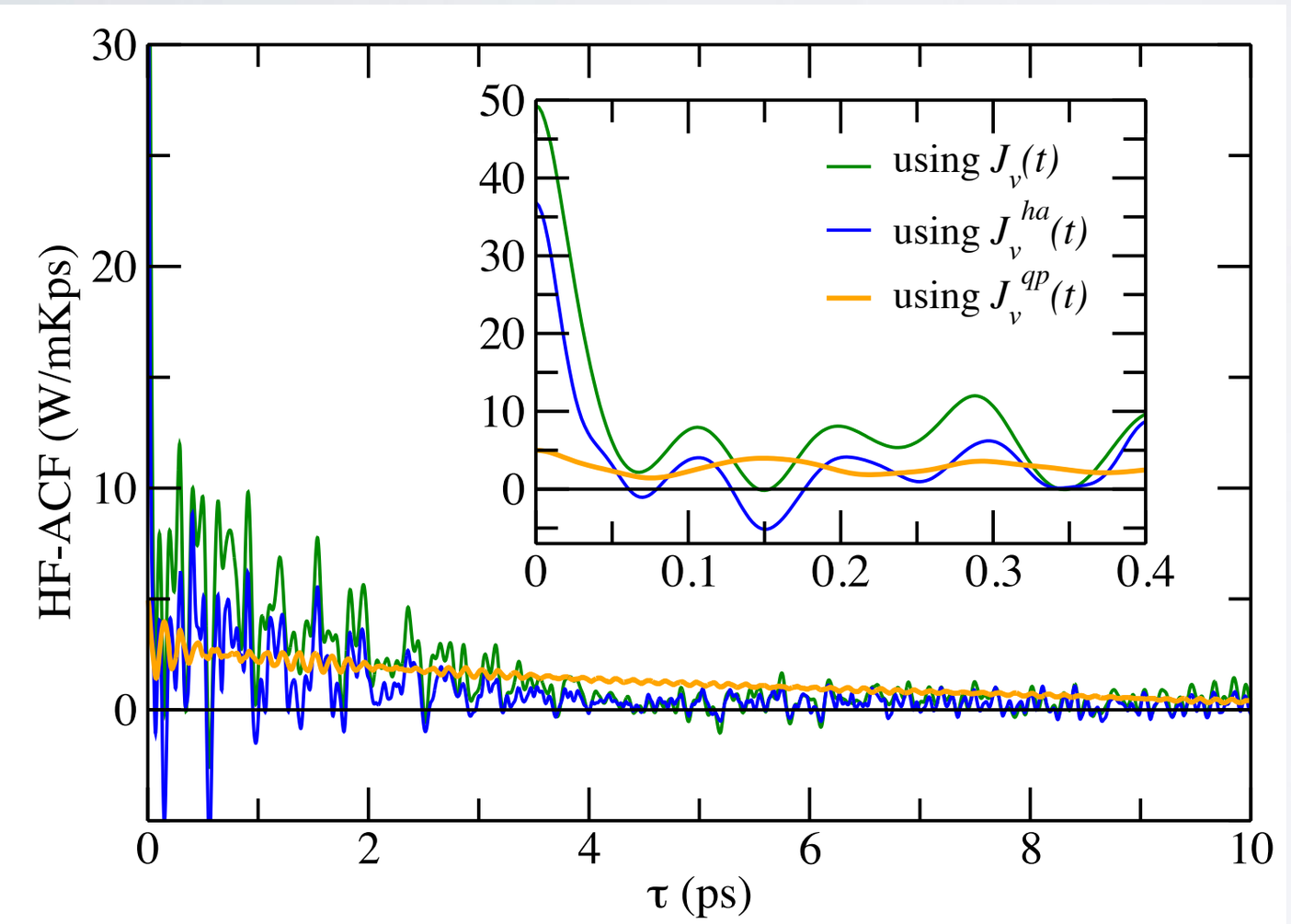
THE QUASI-PARTICLE PICTURE

Real Space

$$\mathbf{J}^{ha}(t) = \sum_{ij} \sigma_i^{ha} \mathbf{V_i}$$

Reciprocal Space

$$\mathbf{J}^{ha}(t) = \sum_{s\mathbf{q}} n_s(\mathbf{q},t)\, \omega_s^2(\mathbf{q})\, \mathbf{v}_s(\mathbf{q})$$

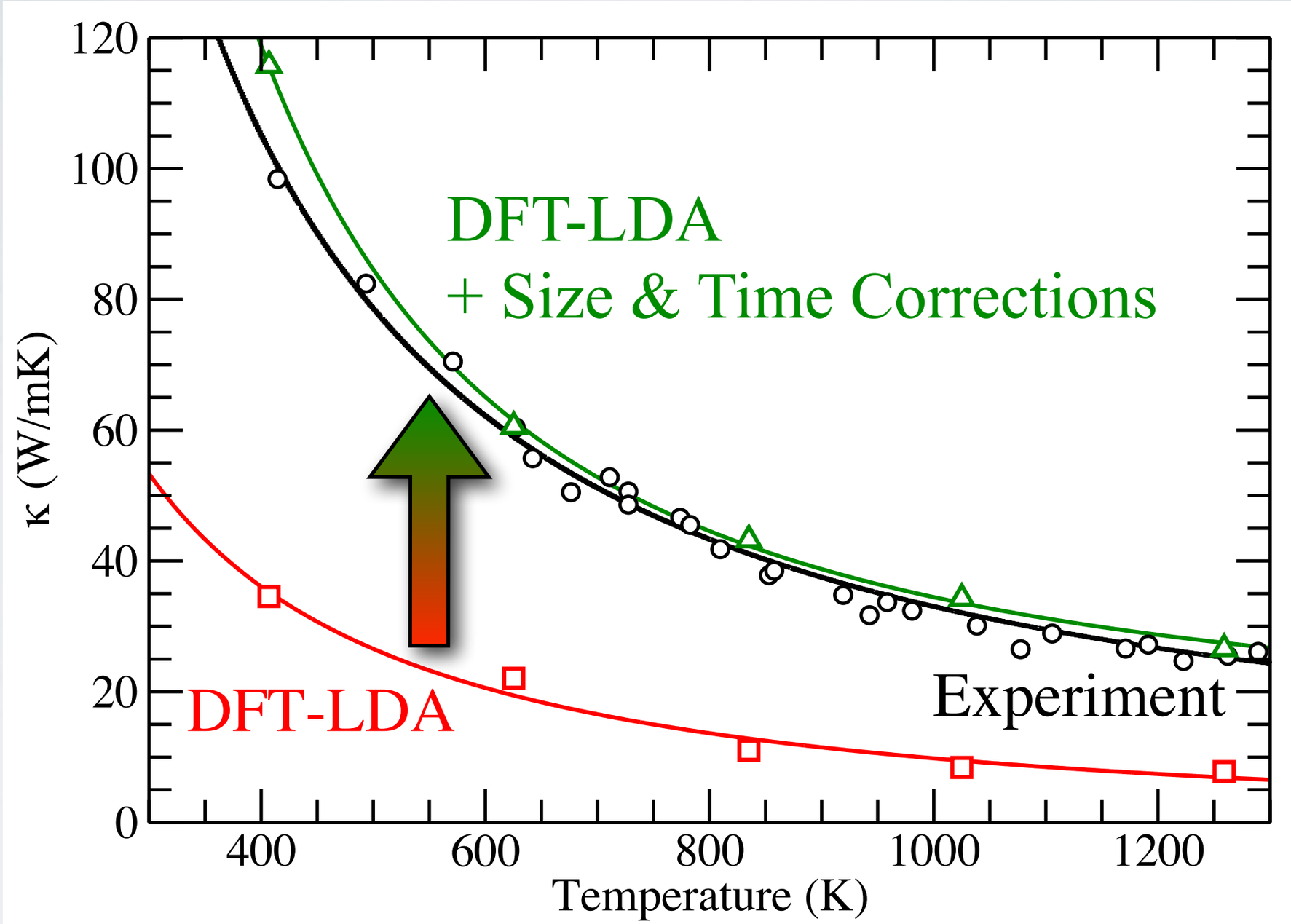


Real & Reciprocal space picture give exact same thermal conductivity!

Reciprocal space heat flux better suited for extrapolation!

J. Chen, G. Zhang, and B. Li, Physics Letters A **374**, 2392 (2010).

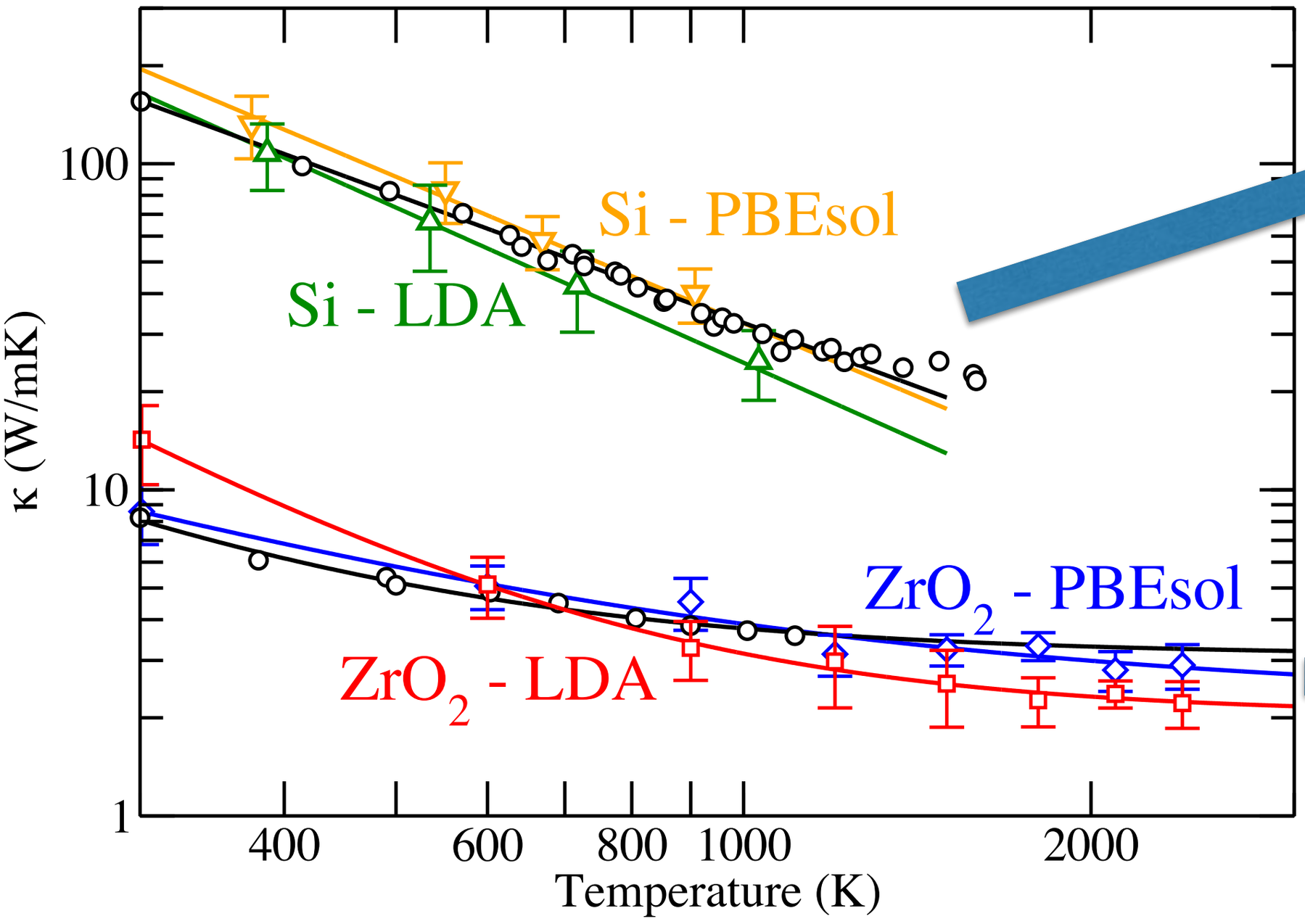
EXTRAPOLATED CONDUCTIVITY

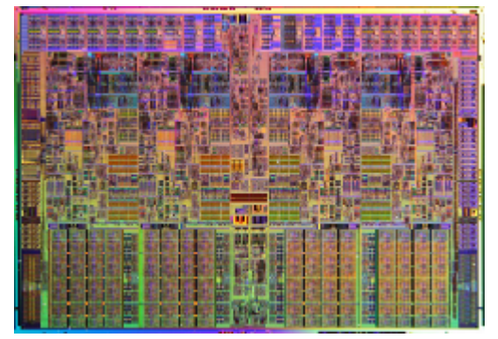


Extrapolation procedure yields satisfactory results!

APPLICATION TO SILICON AND ZIRCONIA

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

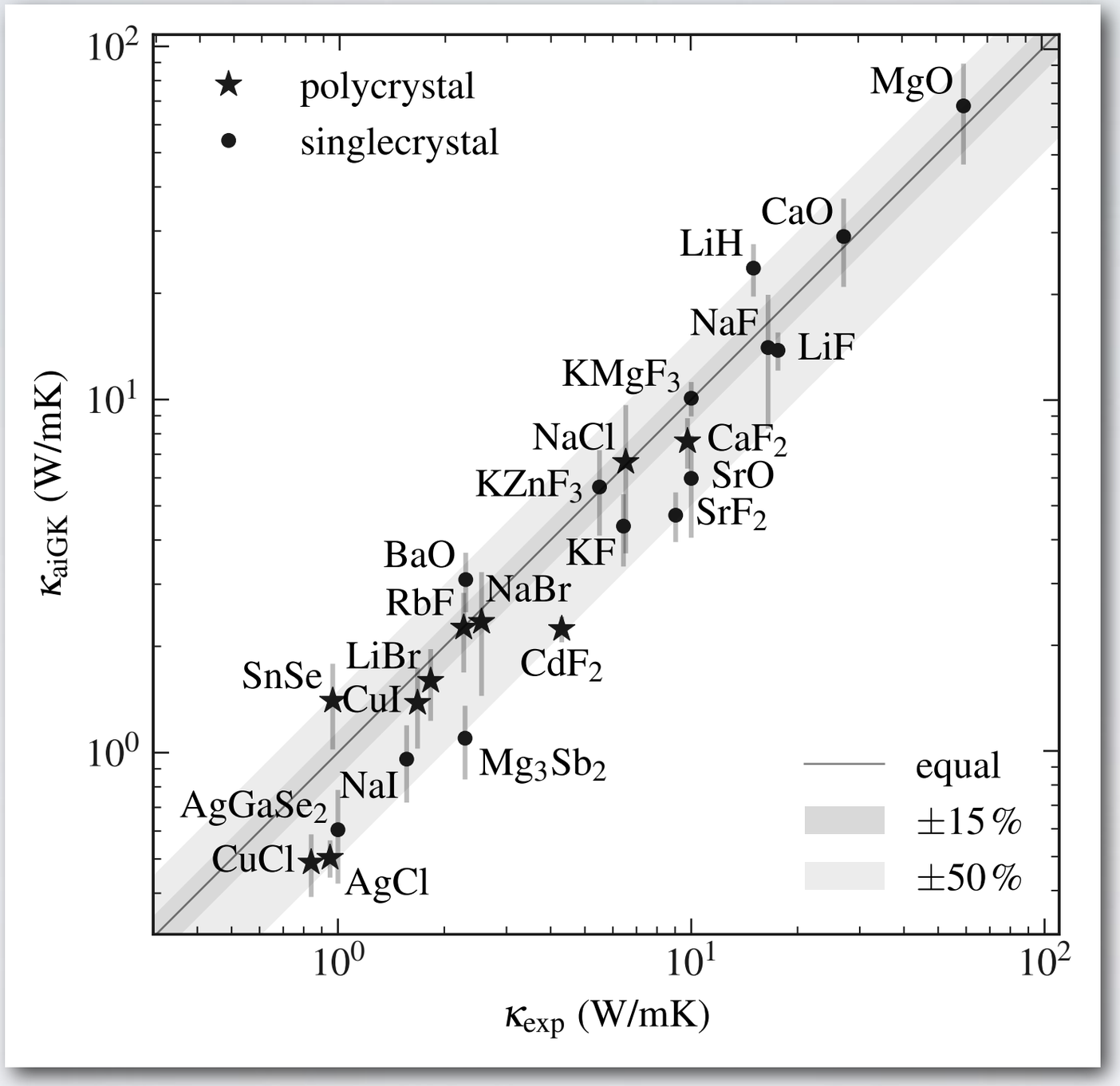




Accurate computation of the thermal conductivities in solids achievable from first principles.

SOME MORE EXAMPLES..

Knoop *et al.*, *to be submitted.*



FIRST-PRINCIPLES APPROACHES

	Order of interaction	Validity & Applicability	Finite Size Effects	Disorder
Boltzmann-Transport Eq.	$\sim\mathcal{O}(r^{3\text{-}4})$	weak anharmonic effects	Minute	Parameter
Green-Kubo MD	Full	all anharmonic effects	Small	as in supercell

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

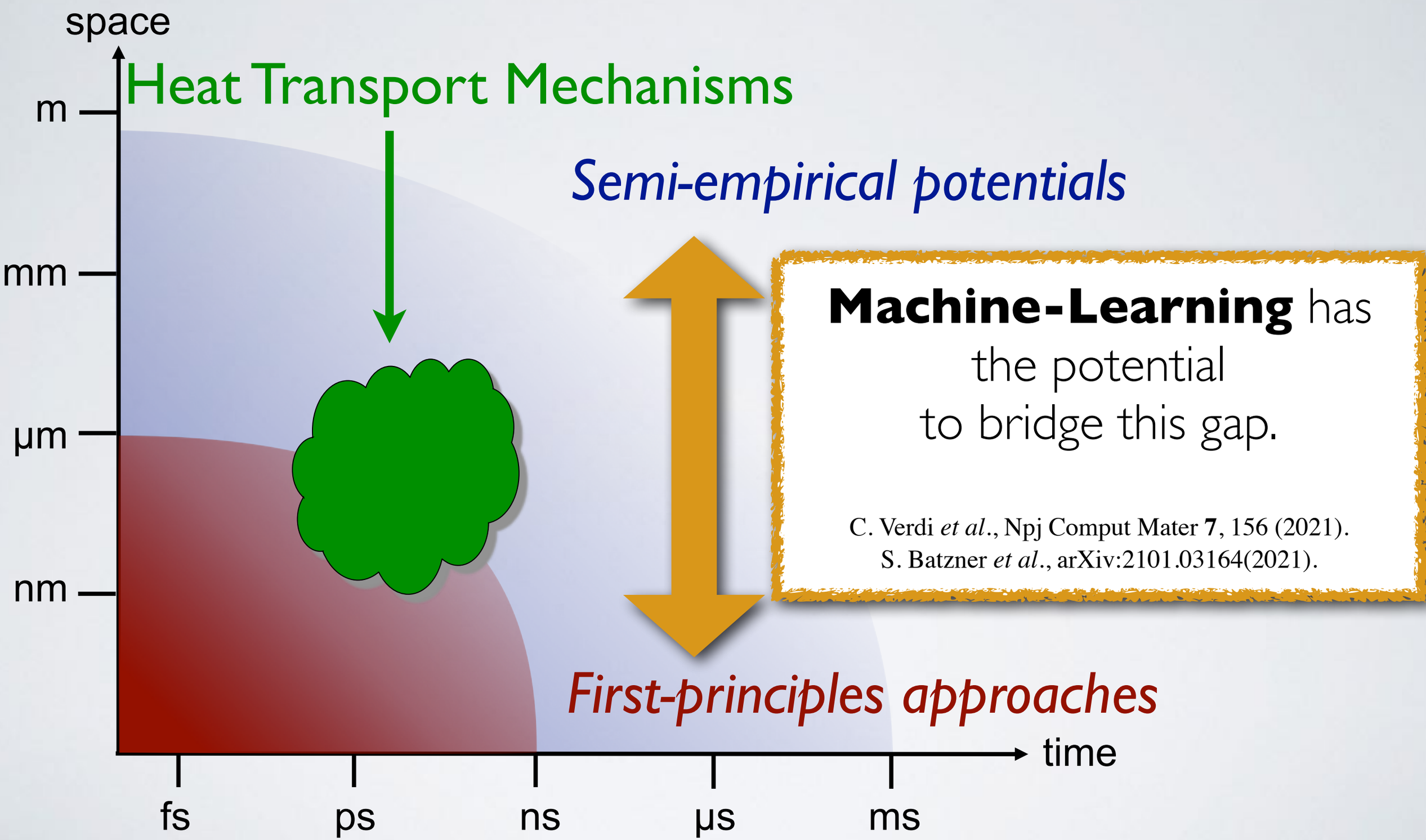
SUMMARY

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.

TIME AND LENGTH SCALES



Machine-Learning has the potential to bridge this gap.

C. Verdi *et al*., Npj Comput Mater **7**, 156 (2021).
S. Batzner *et al*., arXiv:2101.03164(2021).

SUMMARY

We have introduced the harmonic approximation under periodic boundary conditions.

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