Hands-On Tutorial Workshop, July 29th 2014

Phonons & Thermal Transport

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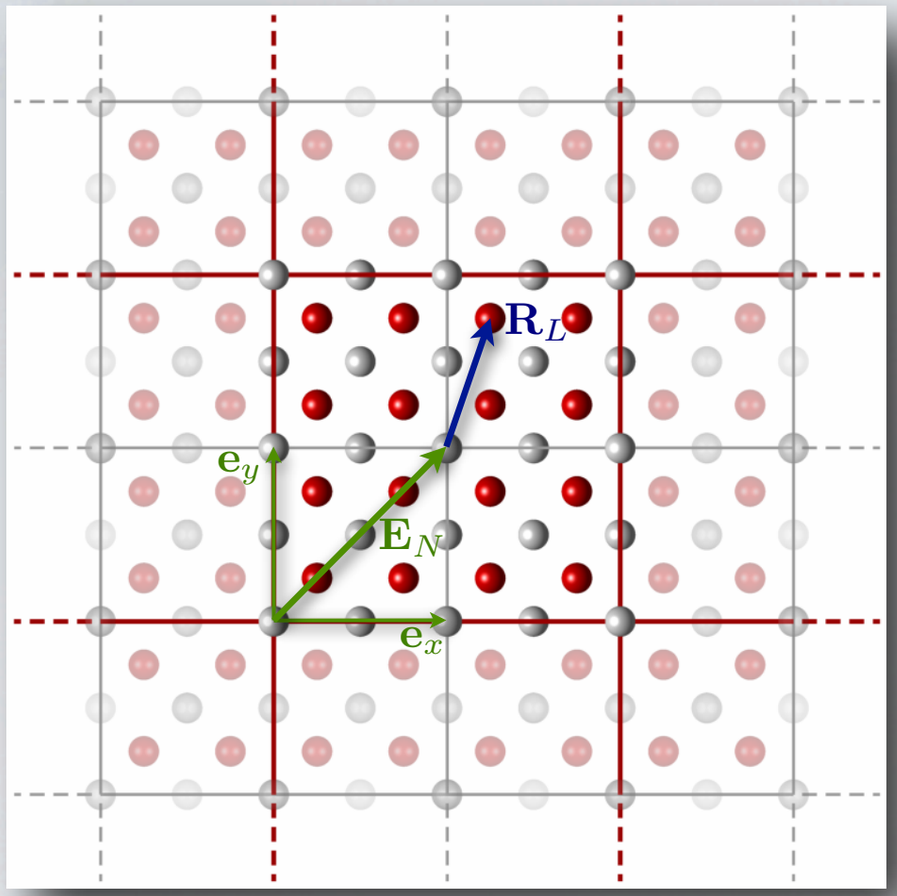
CRYSTALLINE SOLIDS

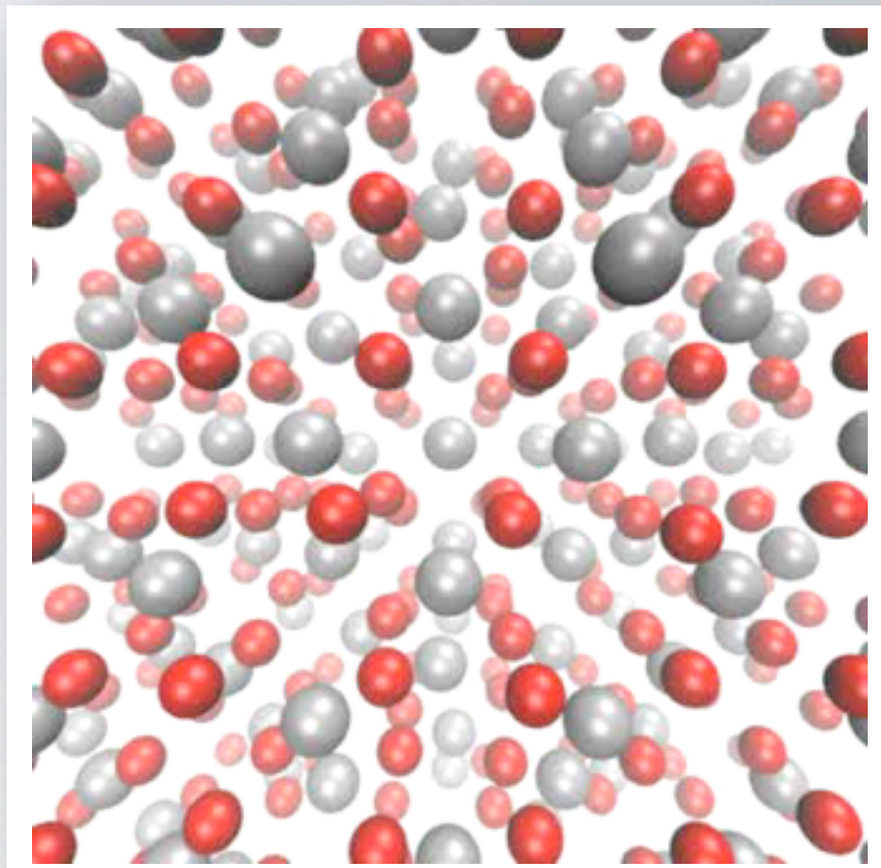
Idealized Crystal Structure



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

cf. Christian Ratsch, Tuesday July 22

Real Materials



Everything moves!

cf. M. Rossi & L. Ghiringhelli, Friday July 25

Perfect periodicity disturbed!

FAILURES OF THE STATIC LATTICE MODEL

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

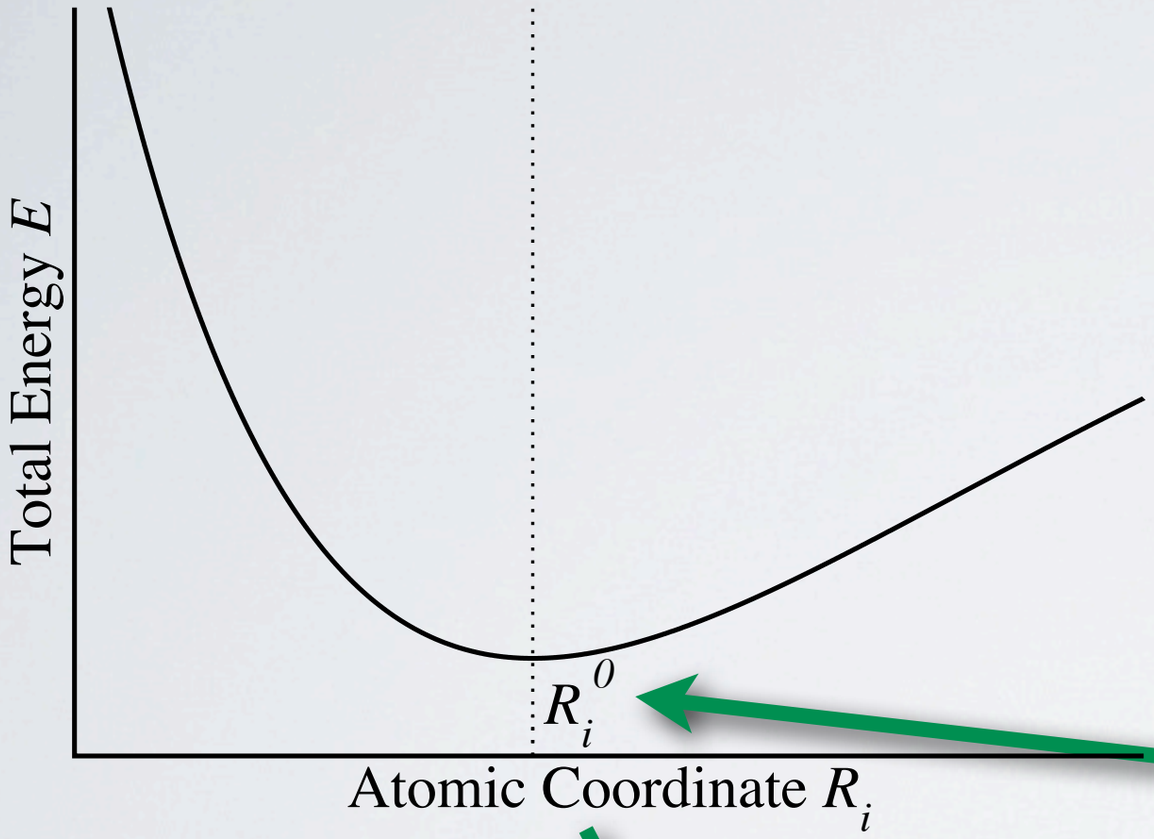
- **Inaccuracies** in the **equilibrium** properties at **0K**:
  Lattice Constants, Cohesive Energies, Elastic Constants,...

- **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 CRYSTAL

THE HARMONIC APPROXIMATION



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

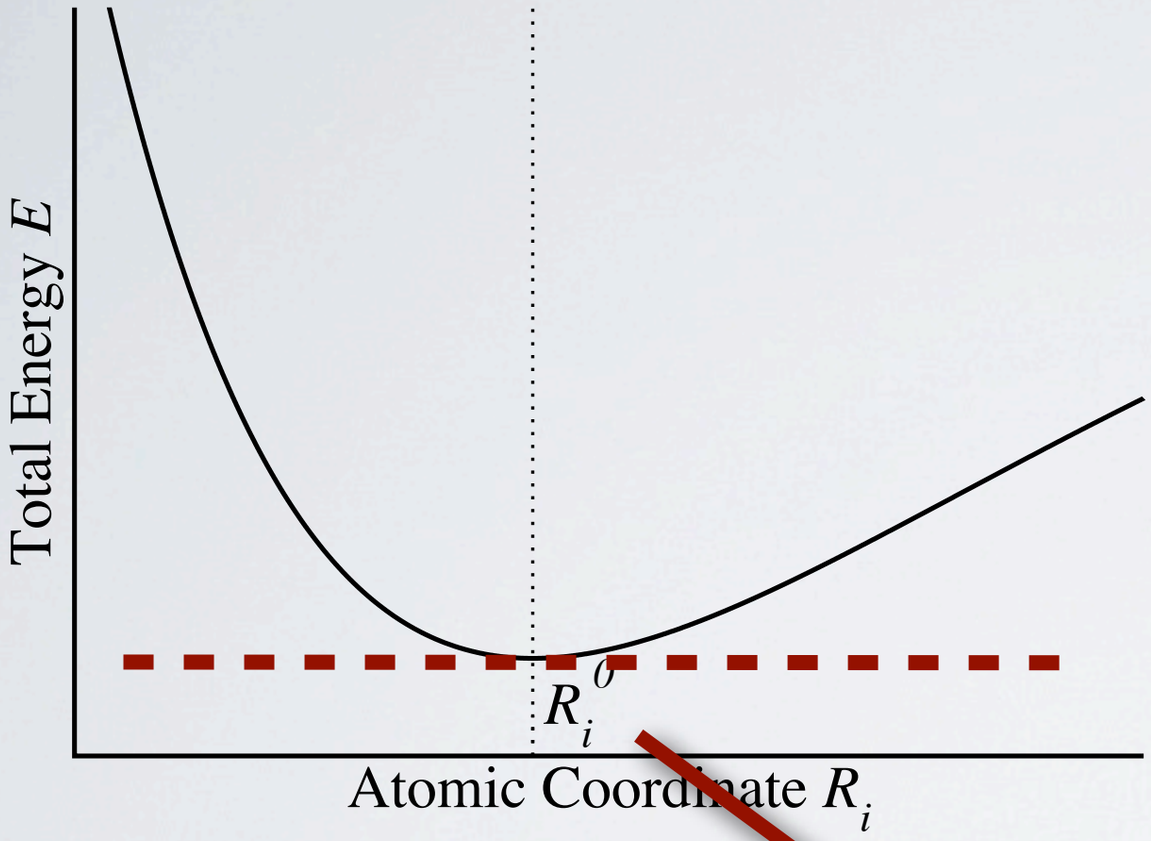
$$E = V\left(\mathbf{R}_1, \mathbf{R}_2, \cdots, \mathbf{R}_N\right)$$

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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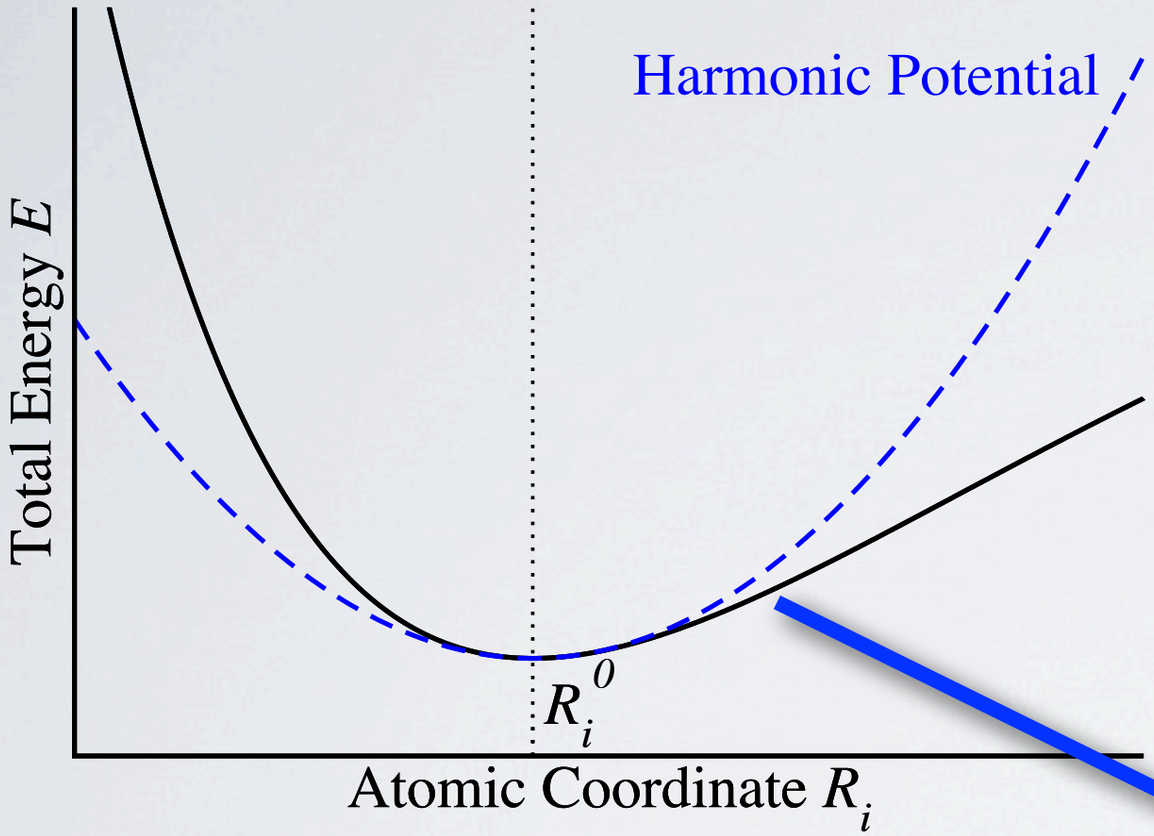
Approximate by Taylor Expansion around the Static Equilibrium R_i^0

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

Forces vanish at $\mathbf{R_0}$

THE HARMONIC APPROXIMATION



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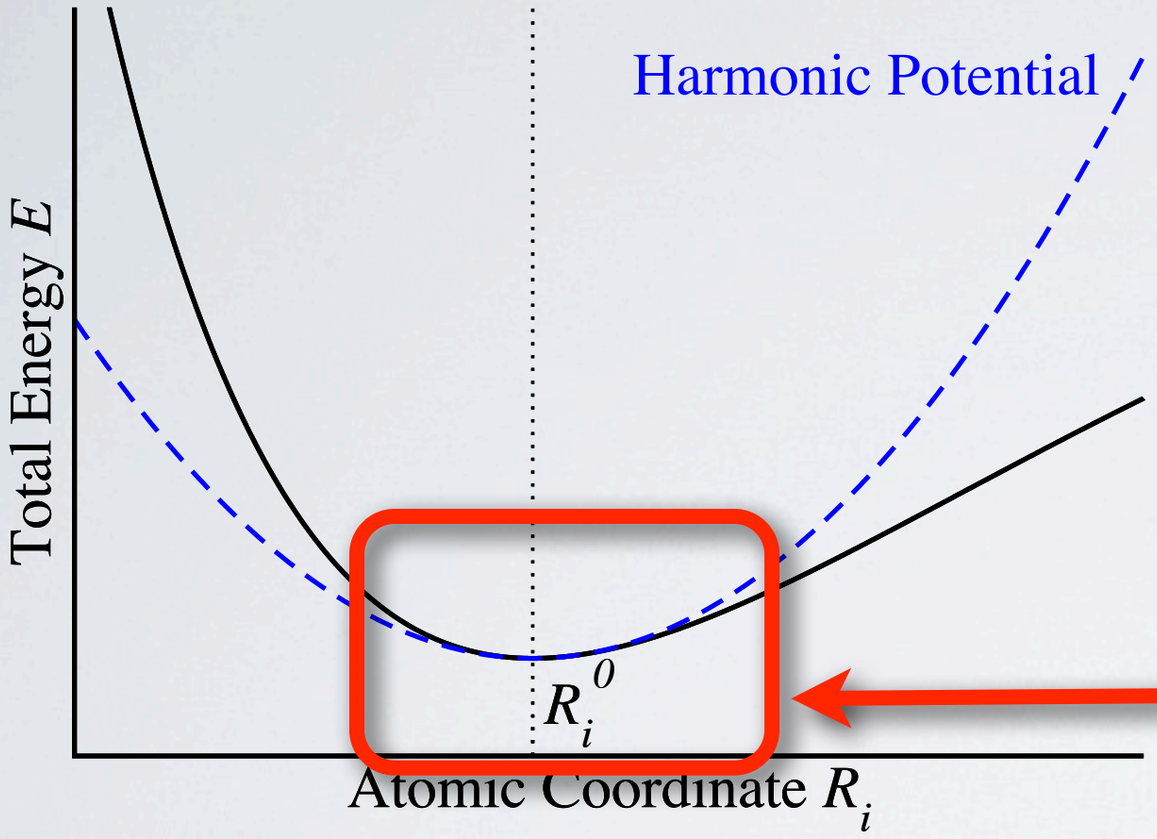
Hessian Φ_{ij}

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 $\boldsymbol{R^0}$!

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

THE HARMONIC APPROXIMATION

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

Static Equilibrium Energy from DFT

Hessian Φ_{ij}

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

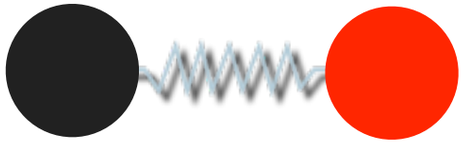
- from **Density-Functional Perturbation Theory**
  S. Baroni, P. Giannozzi, and A. Testa, *Phys. Rev. Lett.* **58**, 1861 (1987) &
  S. Baroni, *et al., Rev. Mod. Phys.* **73**, 515 (2001).

- 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).

⇒ *cf. Christian Carbogno & Manuel Schöttler, Tutorial 6, Tuesday July 29*

THE HARMONIC APPROXIMATION

...in Molecules:



N ... Number of atoms

⇓

Degrees of Freedom: ***3N***
Dimension of Hessian: $9N^2$

Tuesday July 22:

⇒ *Björn Lange, Nuts and Bolts of DFT II*

⇒ *O. Hofmann & L. Nemec, Tutorial 1*

...in Crystalline Solids:

N ... Number of atoms

⇓

Degrees of Freedom: ***3N***
Dimension of Hessian: $9N^2$

BUT:

$N \rightarrow \infty$

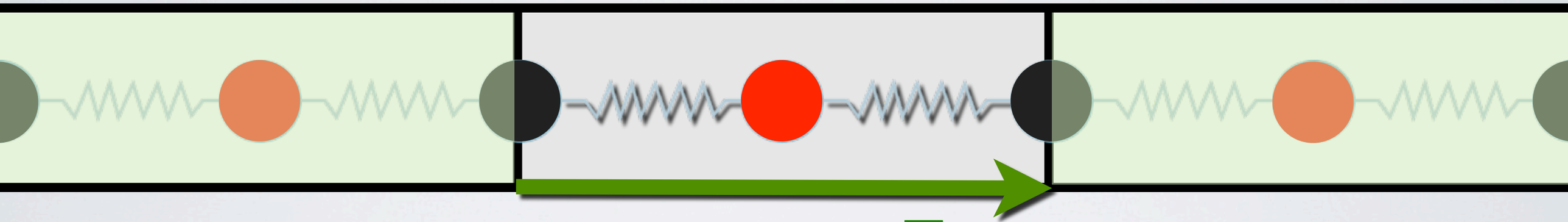
PERIODIC BOUNDARY CONDITIONS

cf. Christian Ratsch, "Electronic Structure Theory for Periodic Systems: The Concepts", Tuesday July 22

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

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

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

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

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)
also see Björn Lange, *Nuts and Bolts of DFT II,* Tuesday July 22

Dynamical matrix:

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

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

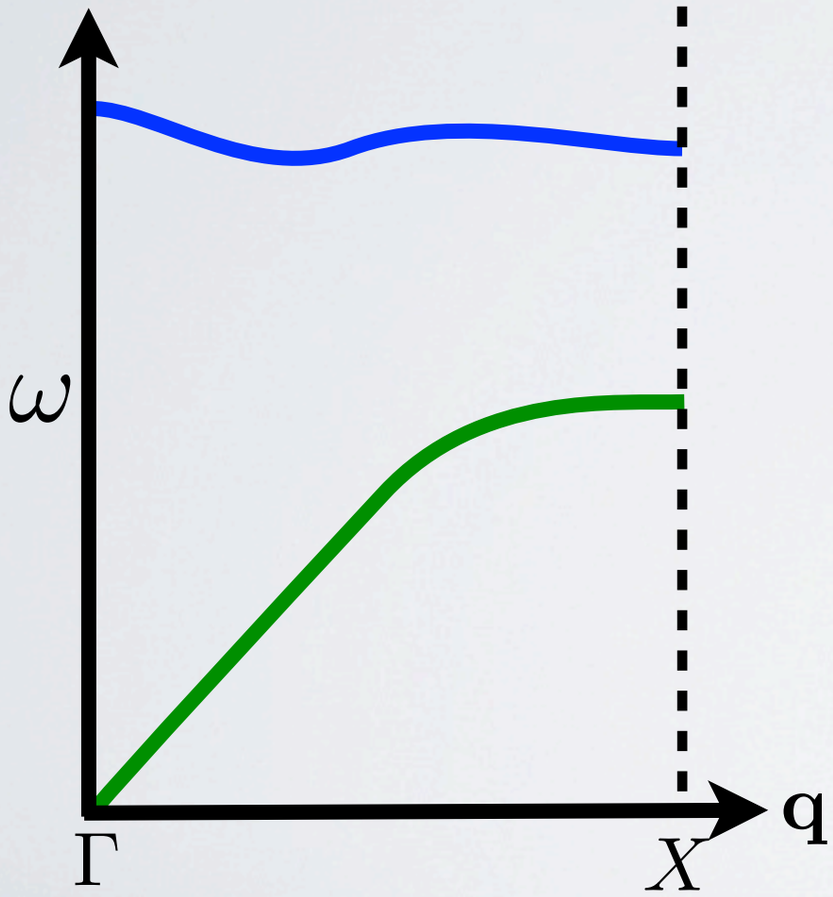
$$\mathbf{R}_j(t) \quad = \quad \mathbf{R}_j^0 + \mathfrak{Re}\left(\sum_s \frac{A_s}{\sqrt{M_i}} e^{i\left(\mathbf{q}\cdot(\mathbf{R}_j^0 - \mathbf{R}_{j'}^0) - \omega_s(\mathbf{q})t\right)} \cdot [\nu_s(\mathbf{q})]_{j'}\right)$$

VIBRATIONS IN A CRYSTAL 101

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

.

For N_p atoms in the unit cell there are:



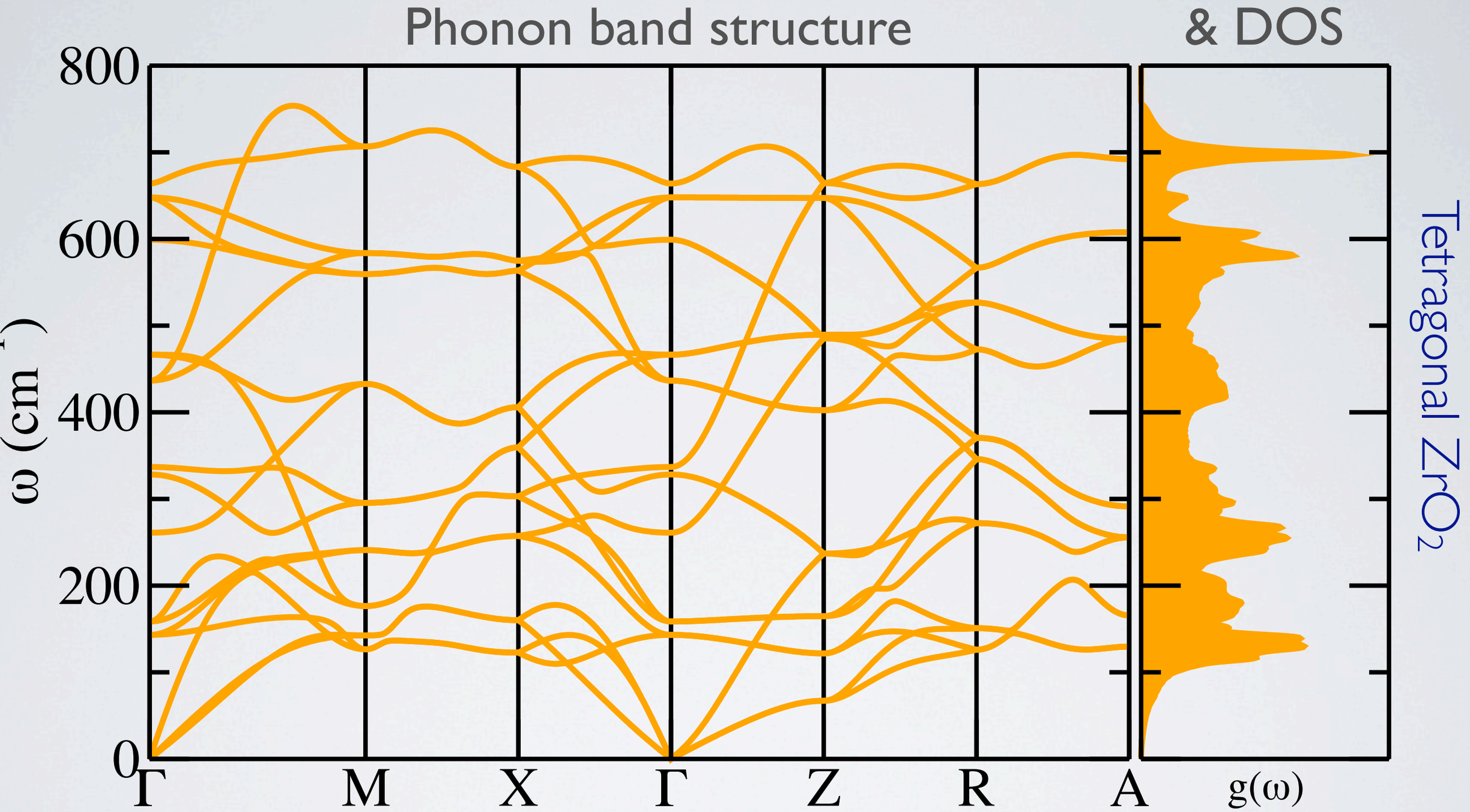
3 Acoustic modes:

- Atoms in unit cell in-phase
- Acoustic modes vanish at **Γ**
- Strong (typically linear) dispersion close to **Γ**

($3N_p$ - 3) Optical modes:

- Atoms in unit cell out-of-phase
- **ω > 0** at **Γ** (and everywhere else)
- Weak dispersion

THE HARMONIC APPROXIMATION

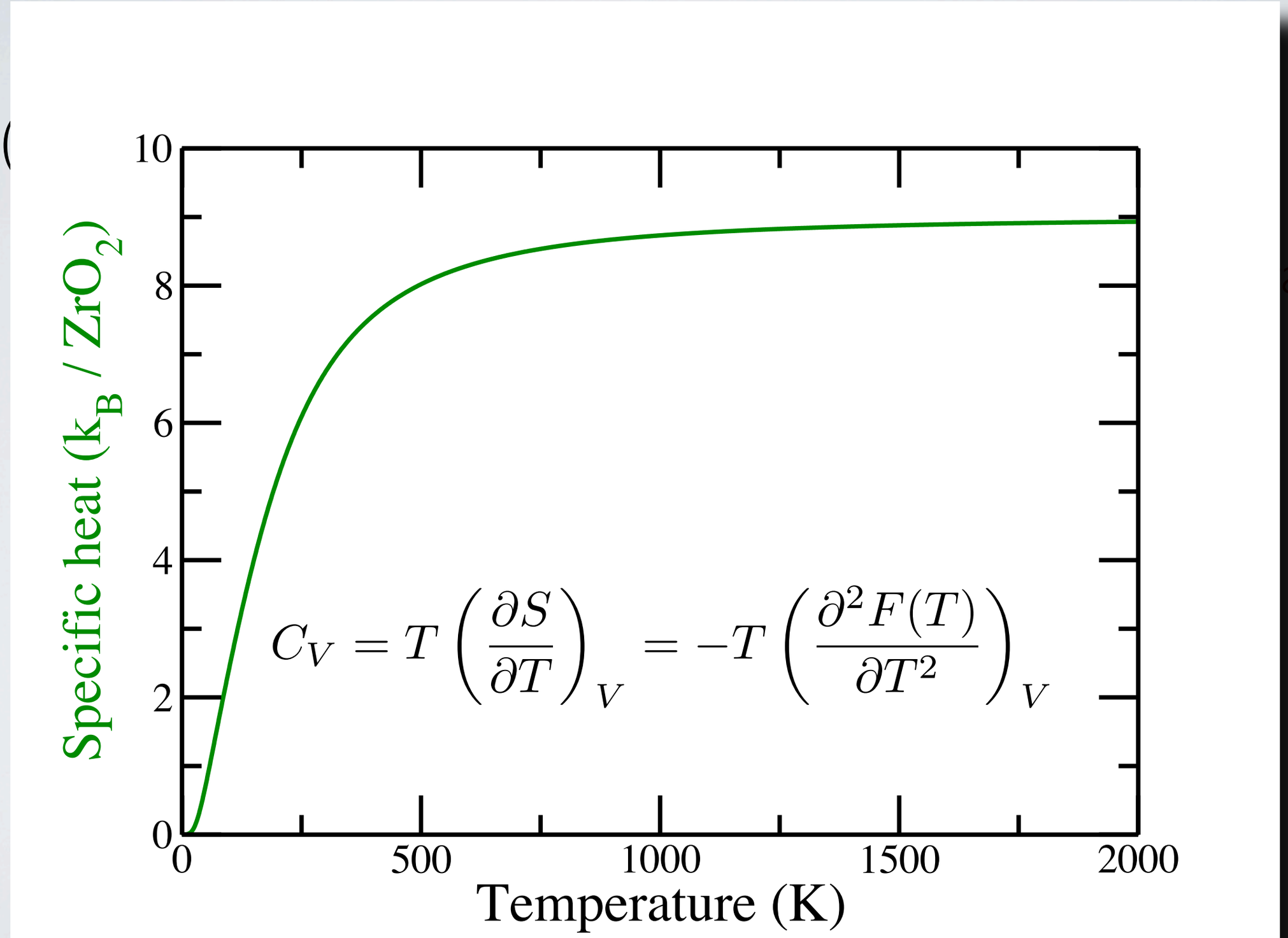


$$g(\omega) = \sum_s \int \frac{d\mathbf{q}}{(2\pi)^3} \delta(\omega - \omega(\mathbf{q})) = \sum_s \int_{\omega(\mathbf{q})=\omega} \frac{dS}{(2\pi)^3} \frac{1}{|\nabla\omega(\mathbf{q})|}$$

THE HARMONIC FREE ENERGY

$F^{ha}($ Energy

ation

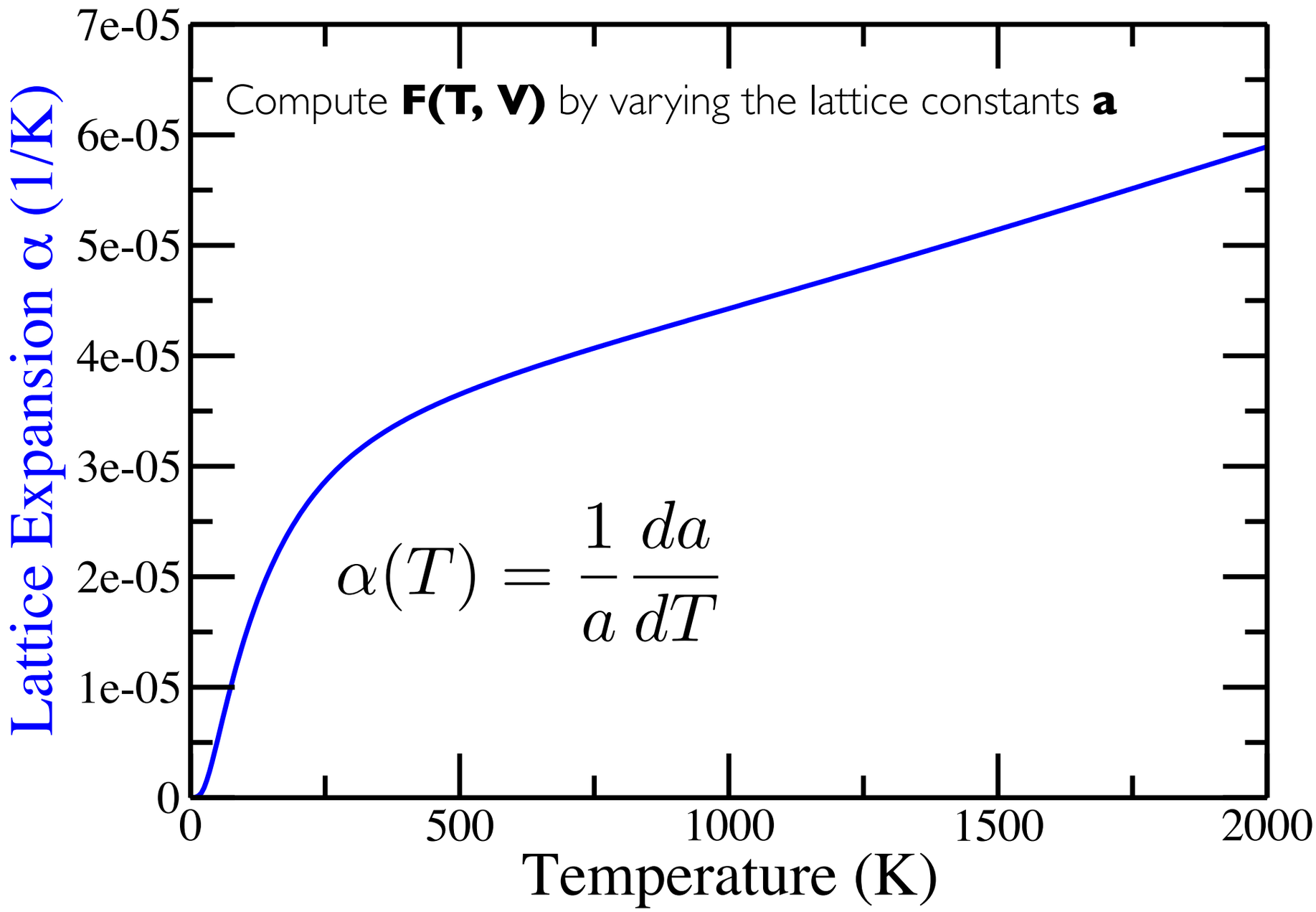


THE HARMONIC FREE ENERGY

$F^{ha}($ Energy

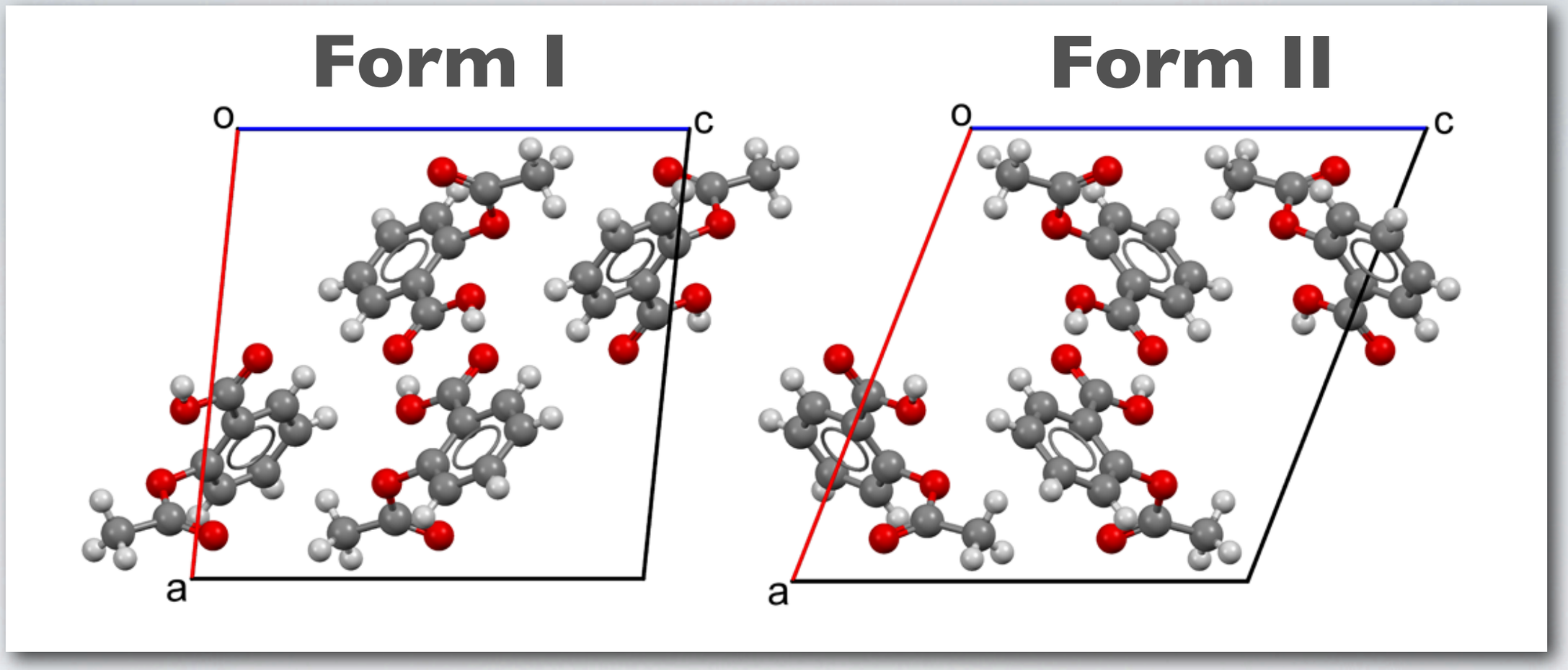
ation

Quasi-harmonic approximation:



THE ASPIRIN "HEADACHE"

Anthony M. Reilly and Alexandre Tkatchenko, *Phys. Rev. Lett.* (in press).



Electronic Structure Theory predicts
the two polymorphs to be **energetically degenerate**.

BUT: FORM I MUCH MORE ABUNDANT!

THE ASPIRIN "HEADACHE"

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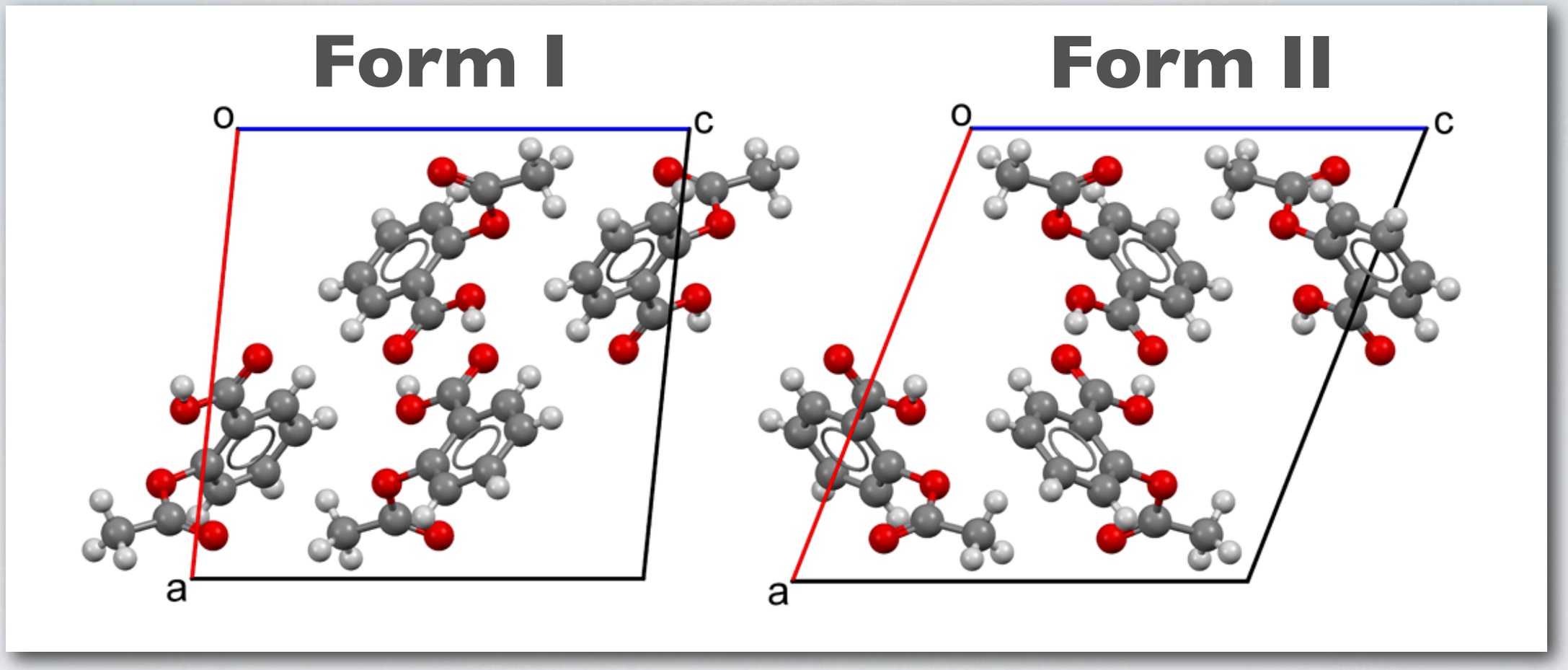

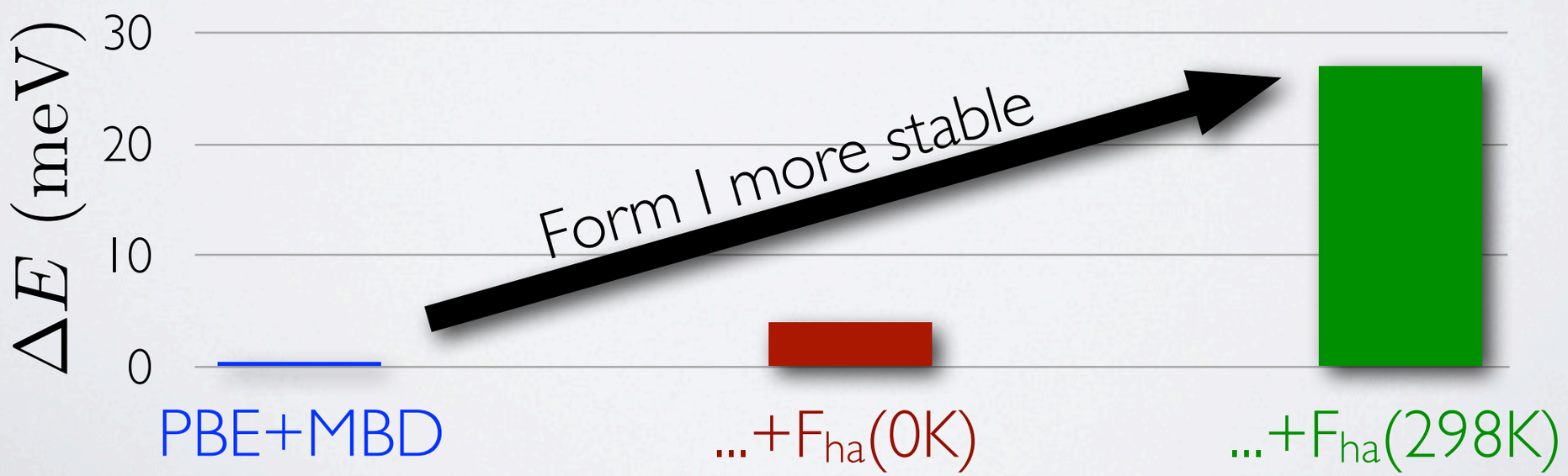

THE ASPIRIN "HEADACHE"

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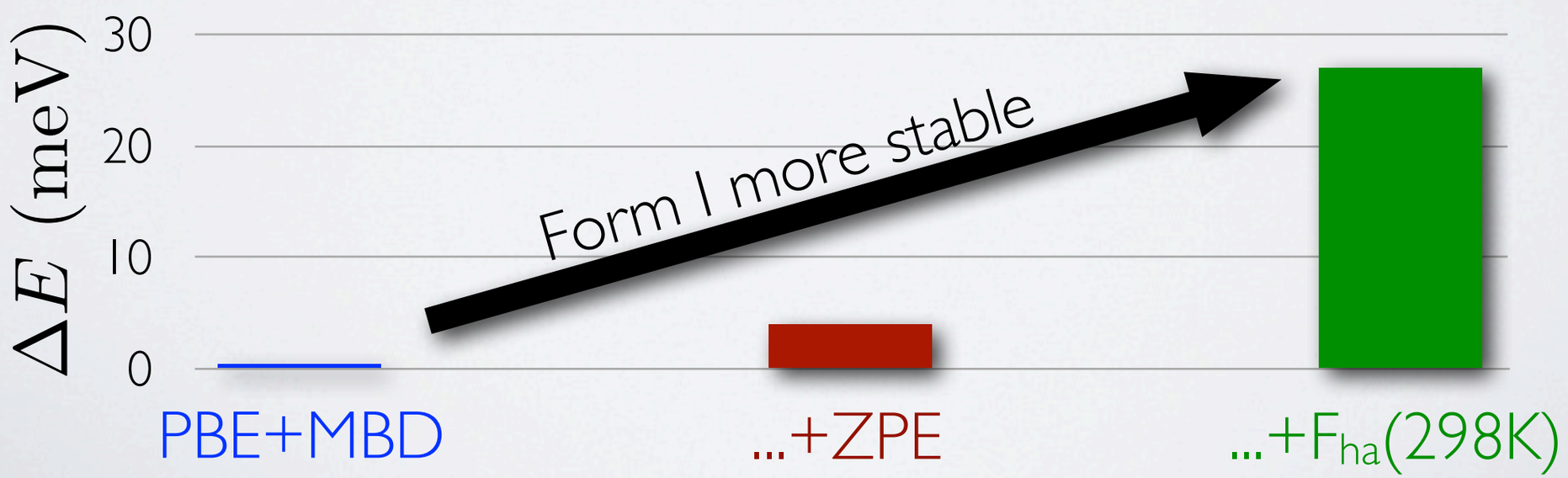
Understanding polymorphism in organic crystals requires...

... **accurate** electronic structure theory

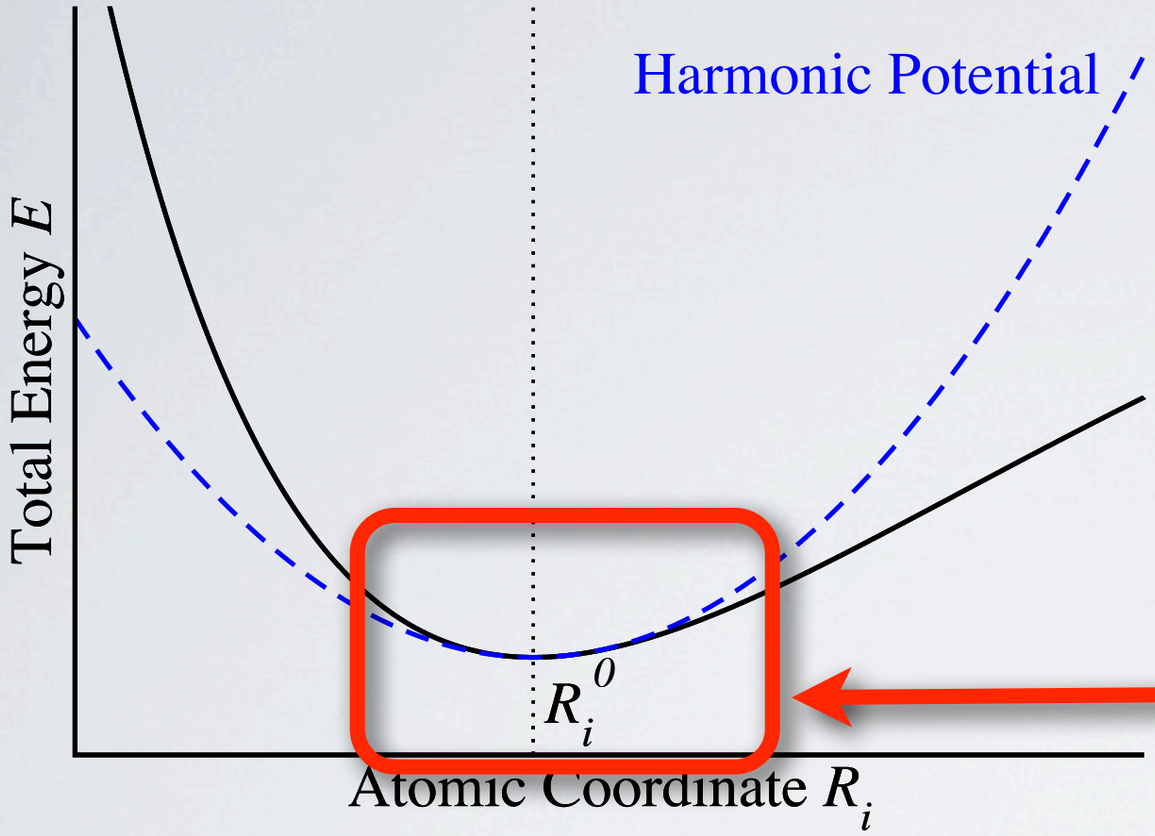
... **correct** description of **many-body dispersion**

... to **account** for **nuclear motion**



II. LIMITS OF THE HARMONIC APPROXIMATION

THE HARMONIC APPROXIMATION



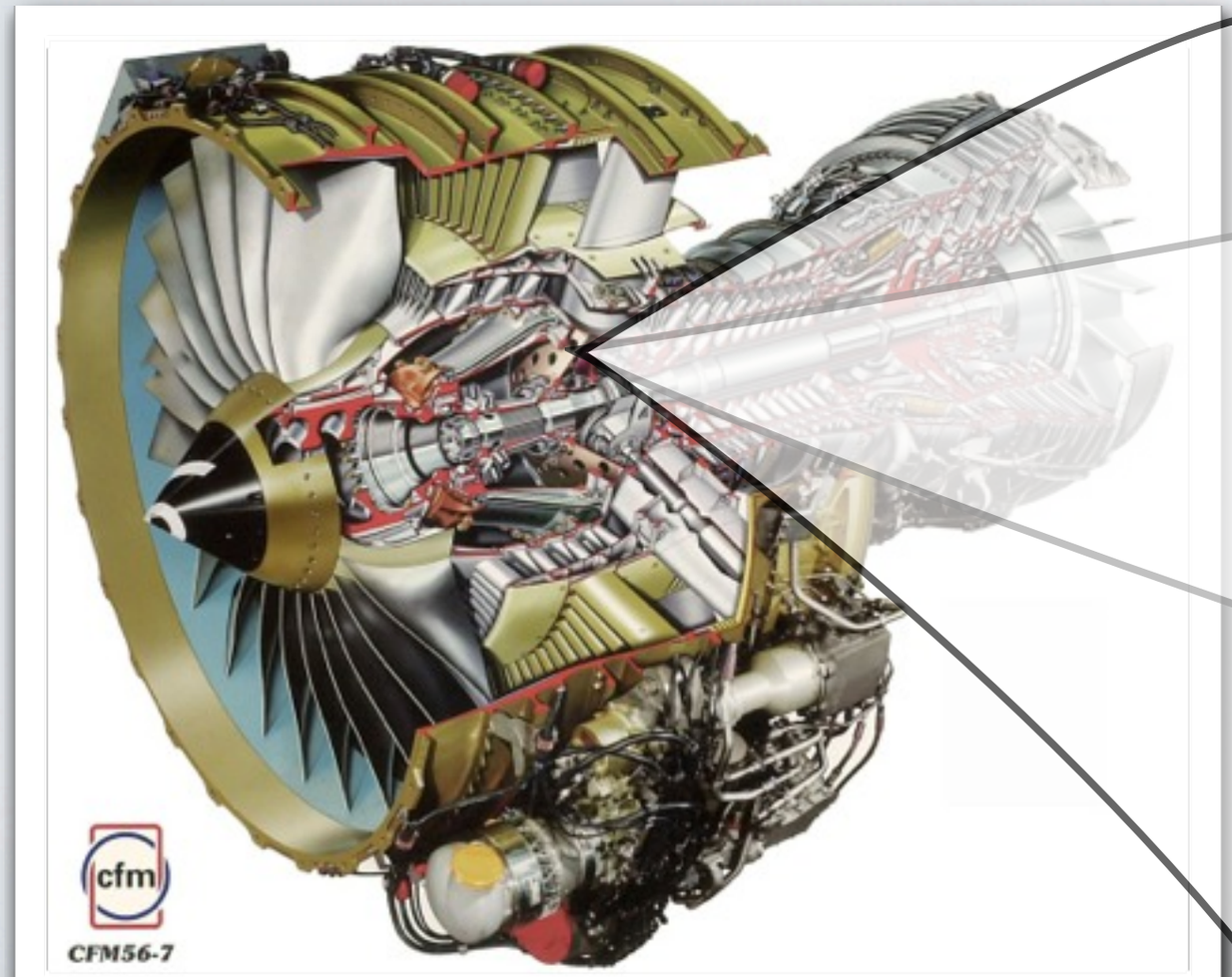
WARNING:

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

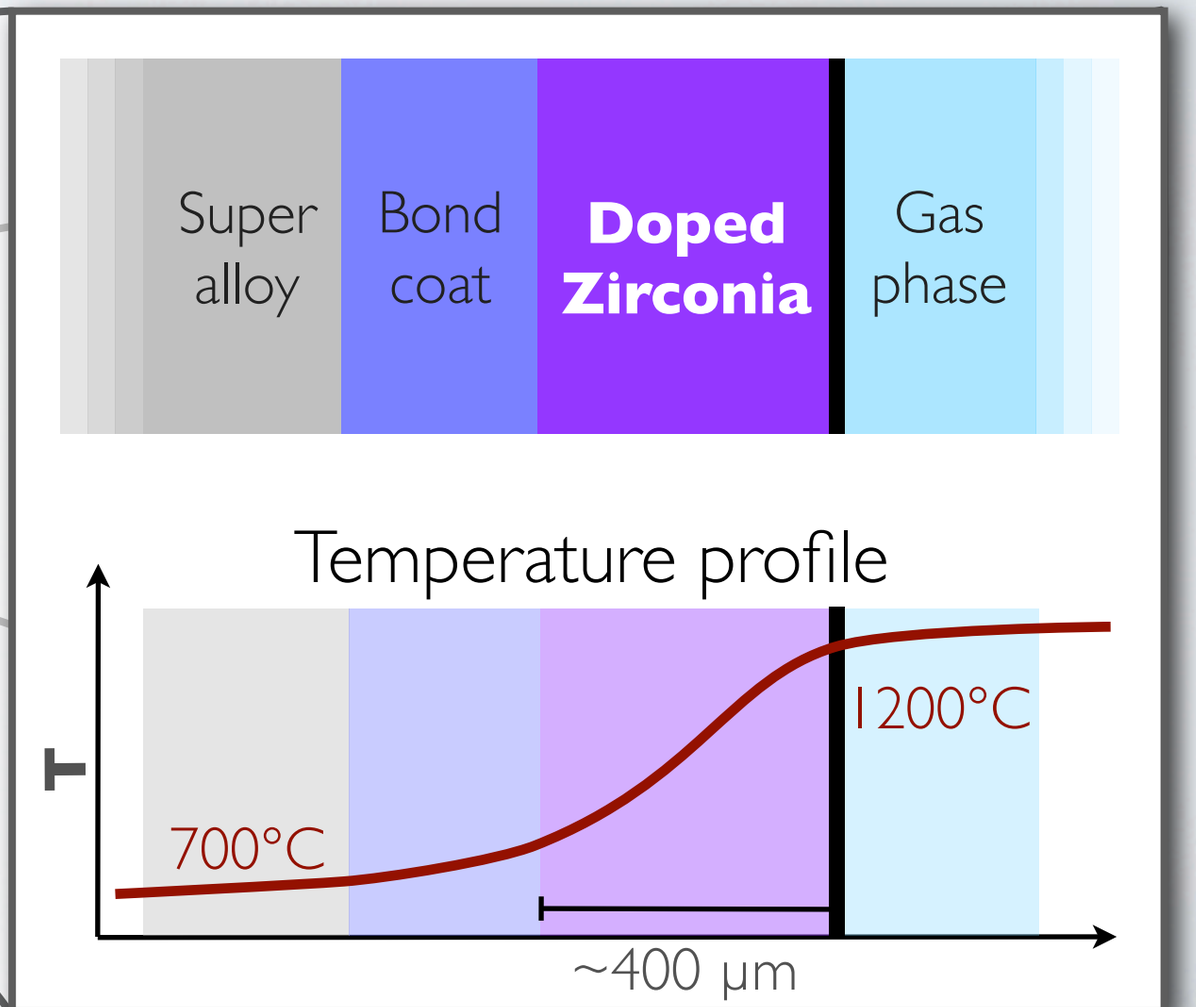
At elevated temperatures the harmonic approximation becomes increasingly **inaccurate** – and often **terribly misleading**!

THERMAL BARRIER COATINGS

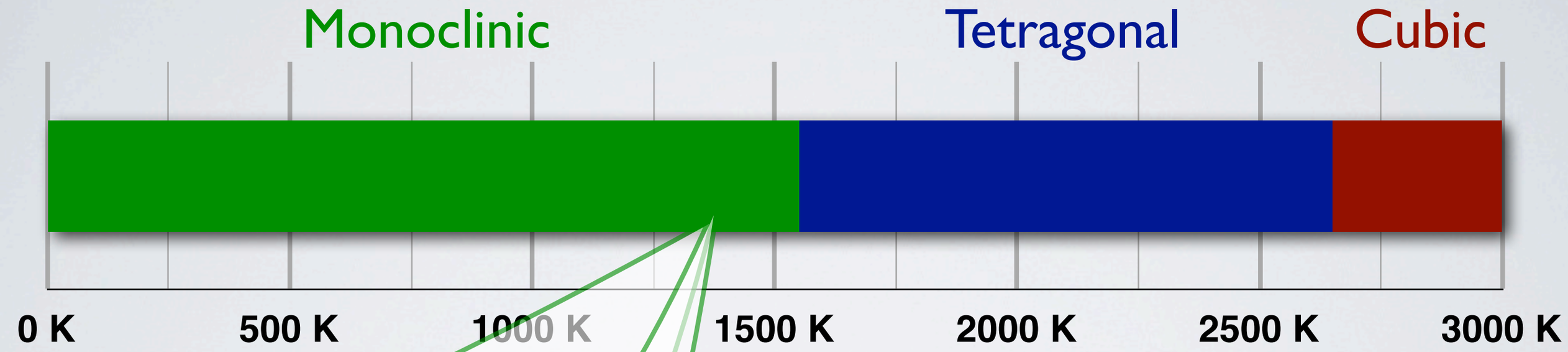
Zirconia-based coatings play a crucial role in **thermal barrier coatings**.

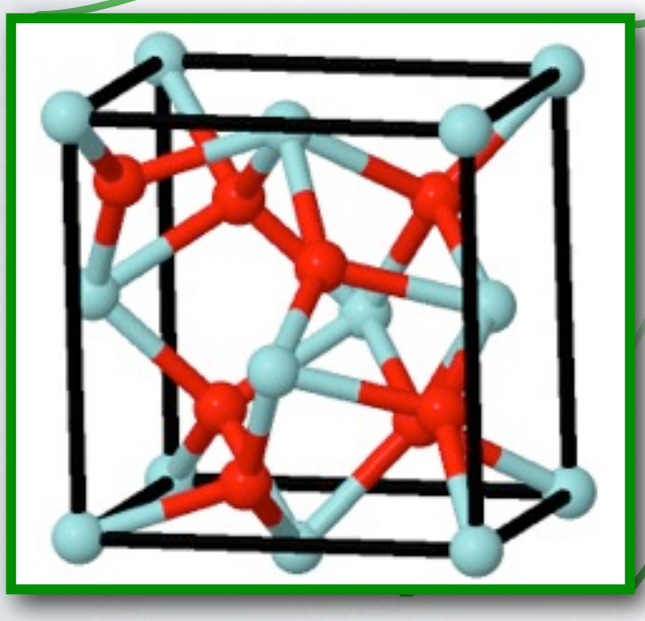


CFM 56-7 airplane engine



PHASE DIAGRAM OF ZrO_2



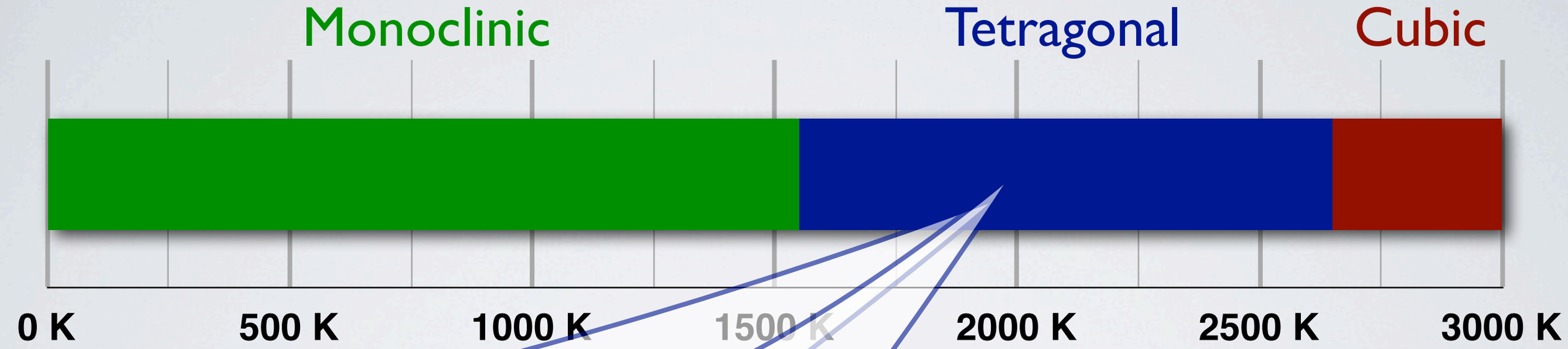


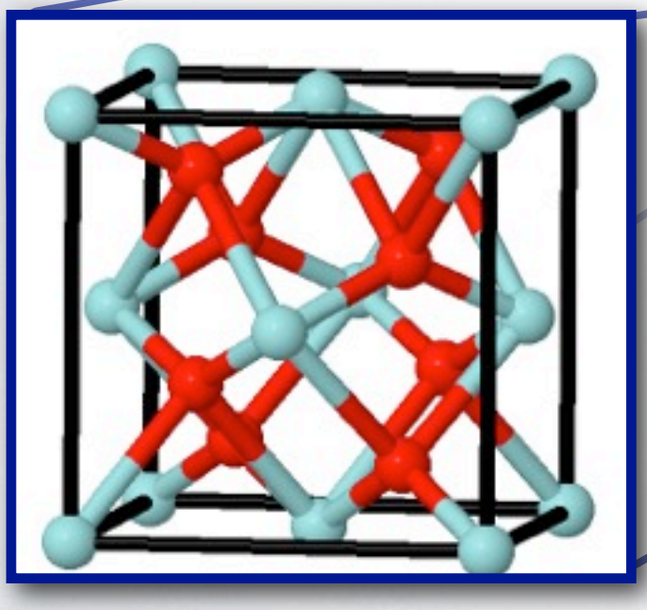
T < 1200°C

„Monoclinic“

Baddeleyite Structure

PHASE DIAGRAM OF ZrO_2



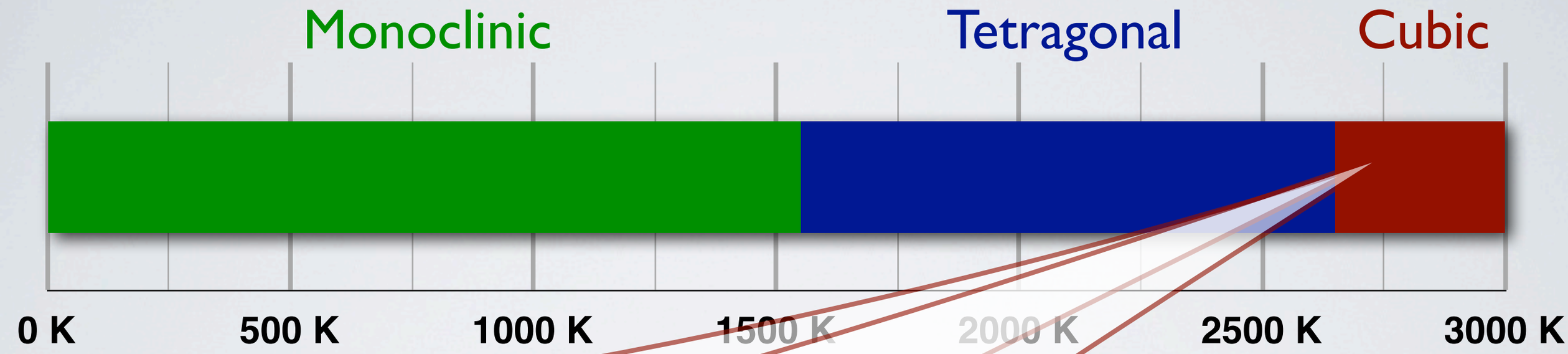


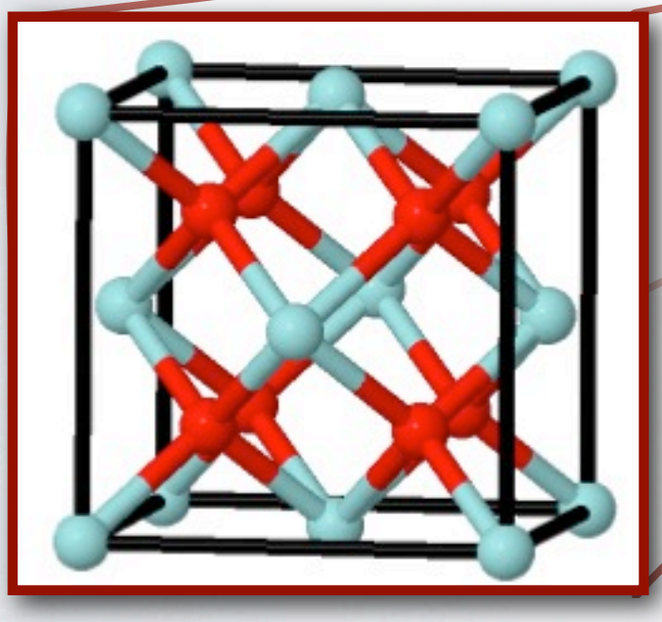
1200°C < T < 2400°C

„Tetragonal“

$P4_2/nmc$ Structure

PHASE DIAGRAM OF ZrO_2



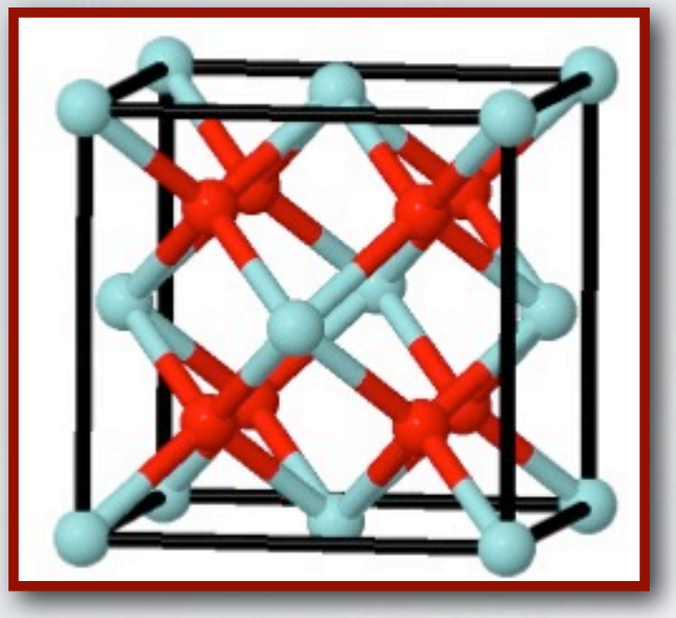


T > 2400°C

„Cubic“

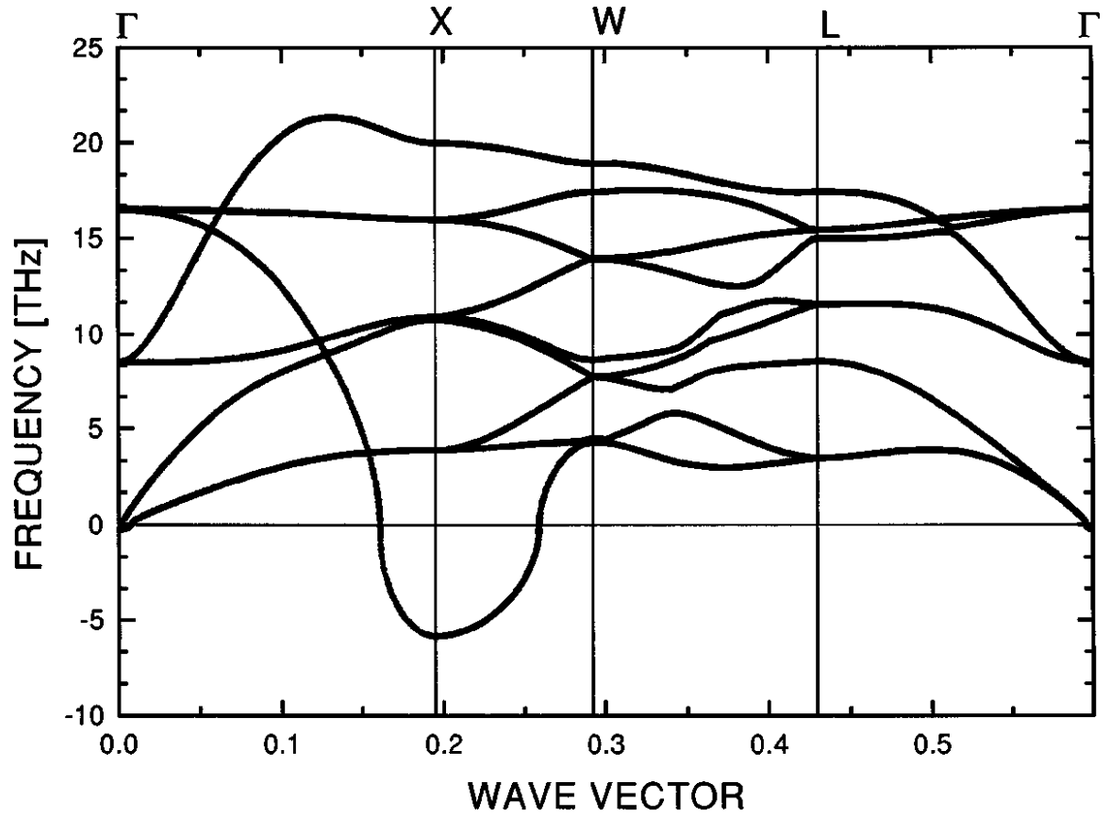
Fluorite Structure

THE SOFT MODE OF CUBIC ZrO_2



„Cubic“

Fluorite Structure



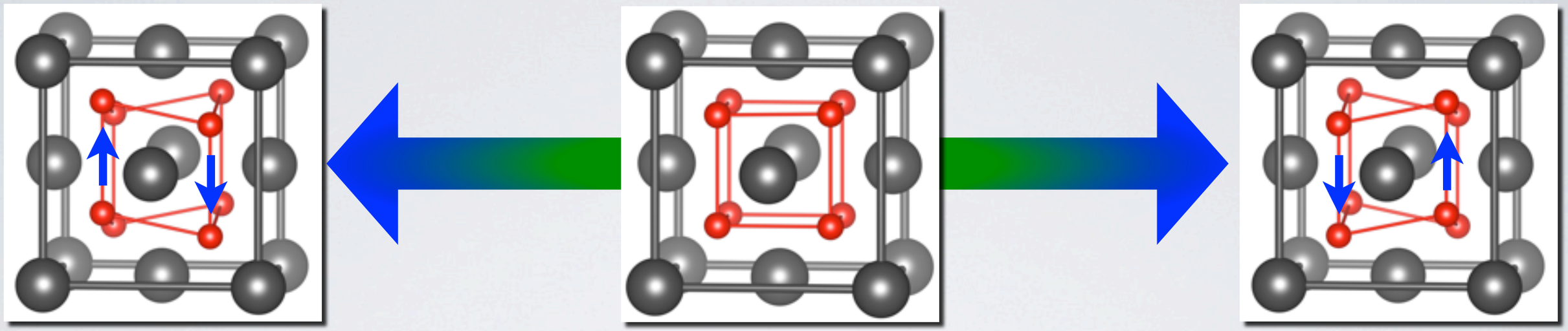
K. Parlinski, Z. Q. Li, and Y. Kawazoe,
Phys. Rev. Lett. **78**, 4063 (1997).

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

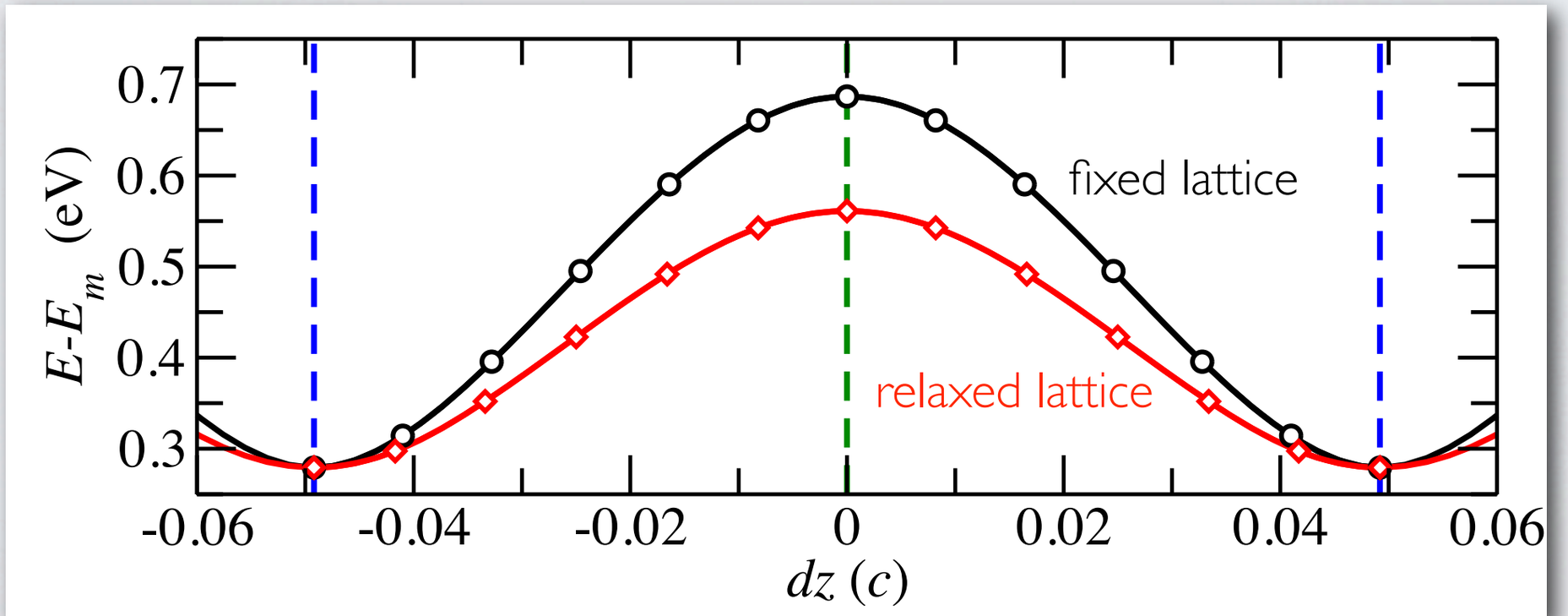
$$\mathbf{D}(\mathbf{X})\ [\nu(\mathbf{X})] = \omega^2(\mathbf{X})\ [\nu(\mathbf{X})] \quad \Rightarrow \quad \omega_1^2(\mathbf{X}) < 0$$

The Tetragonal-Cubic Phase Transition

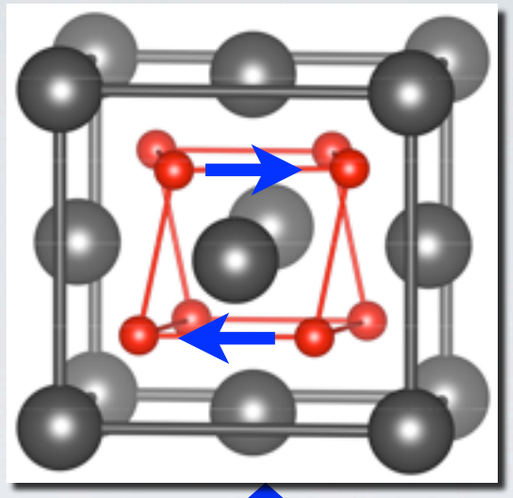
Tetragonal | Cubic | Tetragonal



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



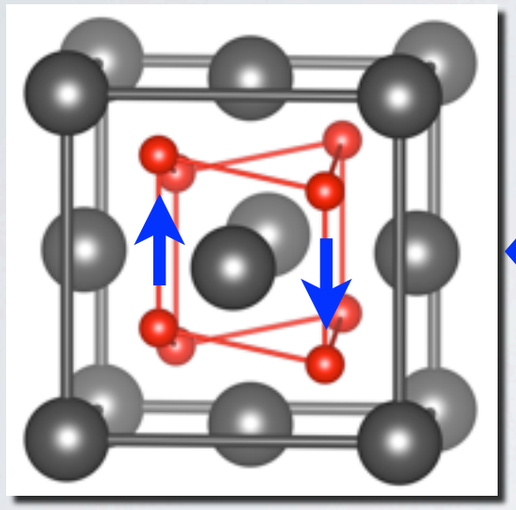
S. Fabris, A.T. Paxton, and M.W. Finnis, *Phys. Rev. B* **63**, 094101 (2001).
M. Sternik and K. Parlinski, *J. Chem. Phys.* **123**, 204708 (2005).



dy > 0

dz,dx = 0

Tetragonal



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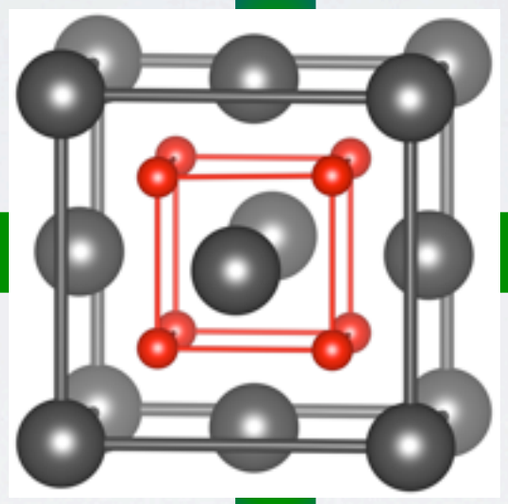
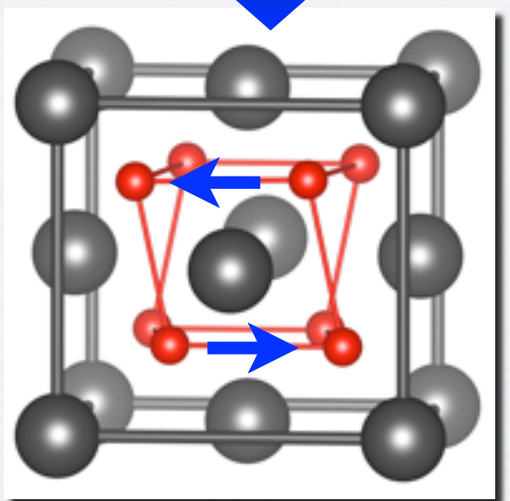
dx,dy = 0





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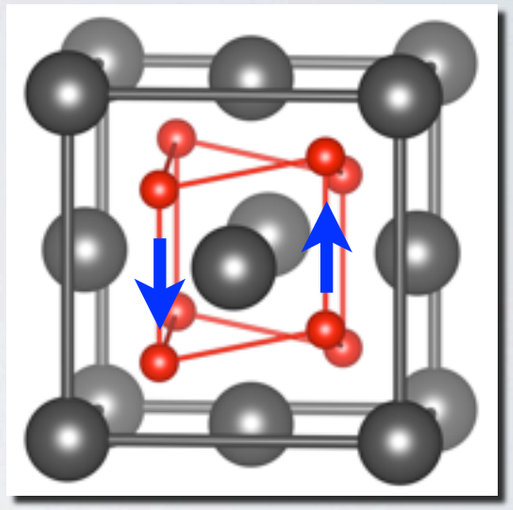
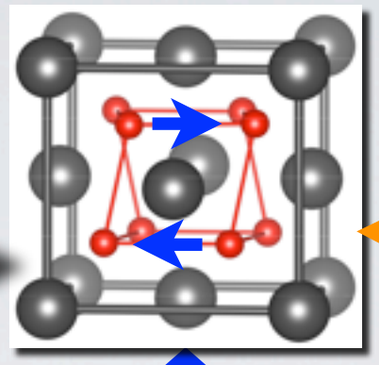
Tetragonal



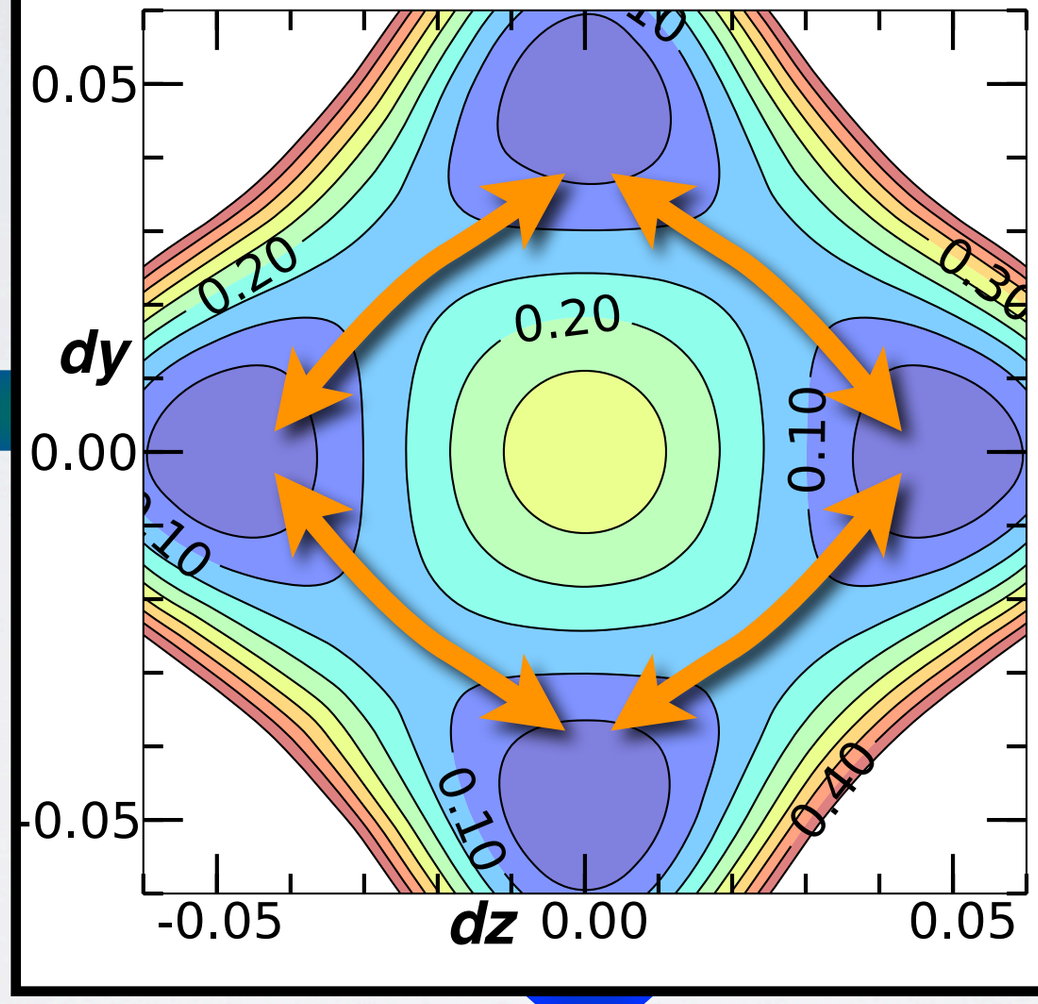
dz > 0

dx,dy = 0

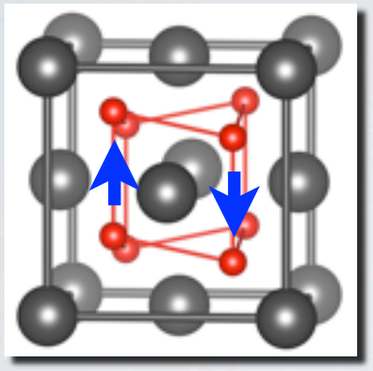


dy > 0
dz,dx = 0

Ferroelastic Switches

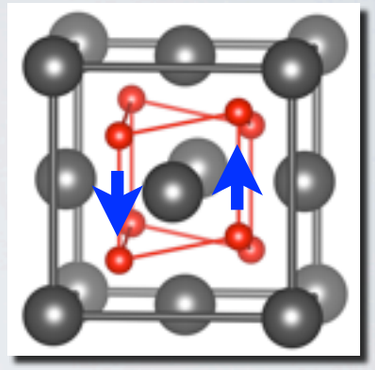


Tetragonal

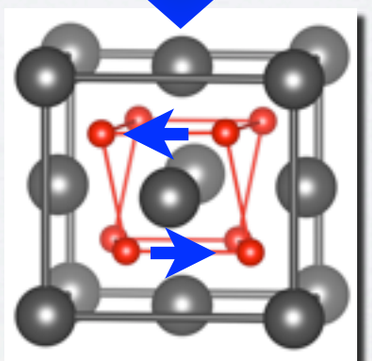


dz < 0
dx,dy = 0

Tetragonal

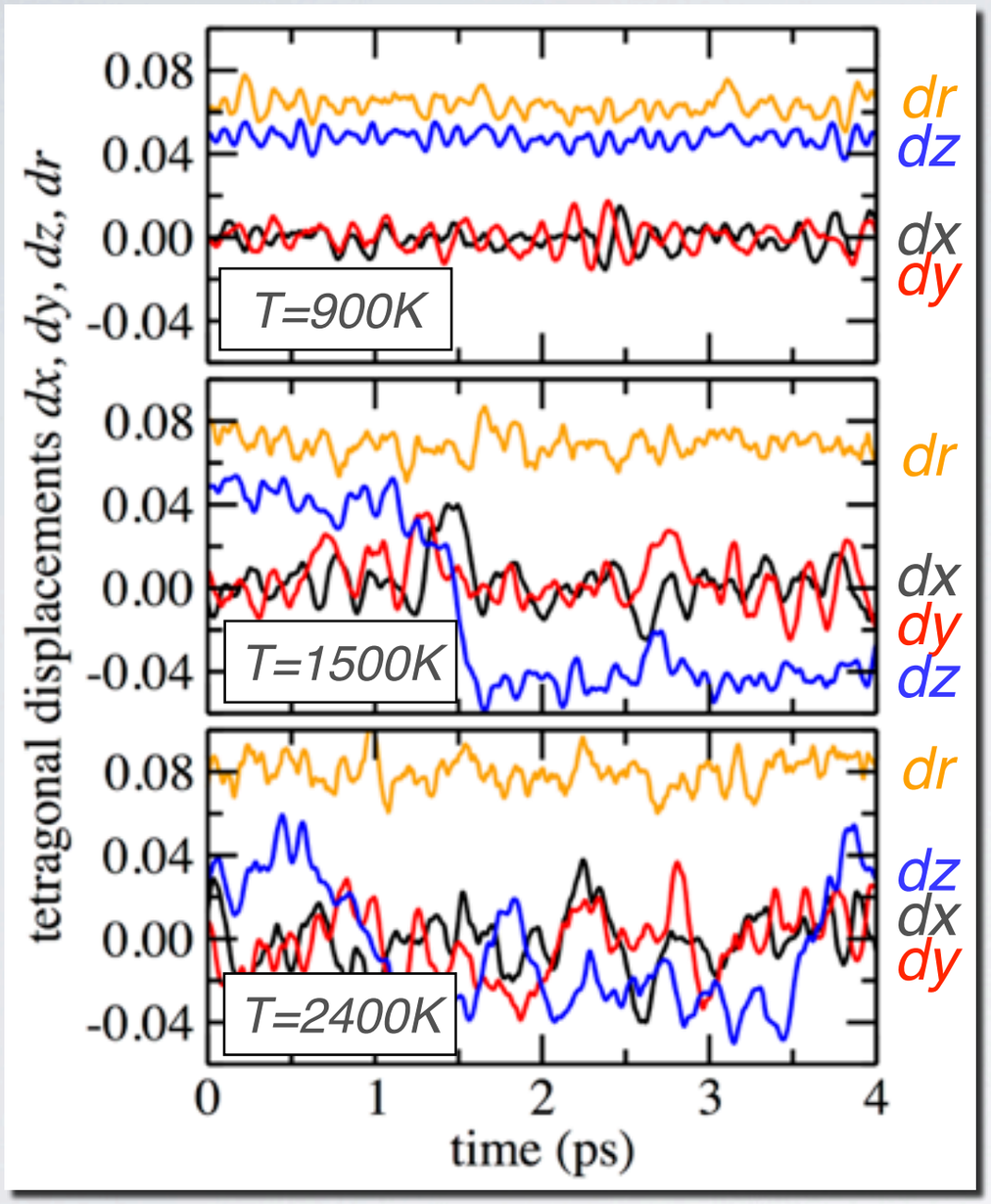


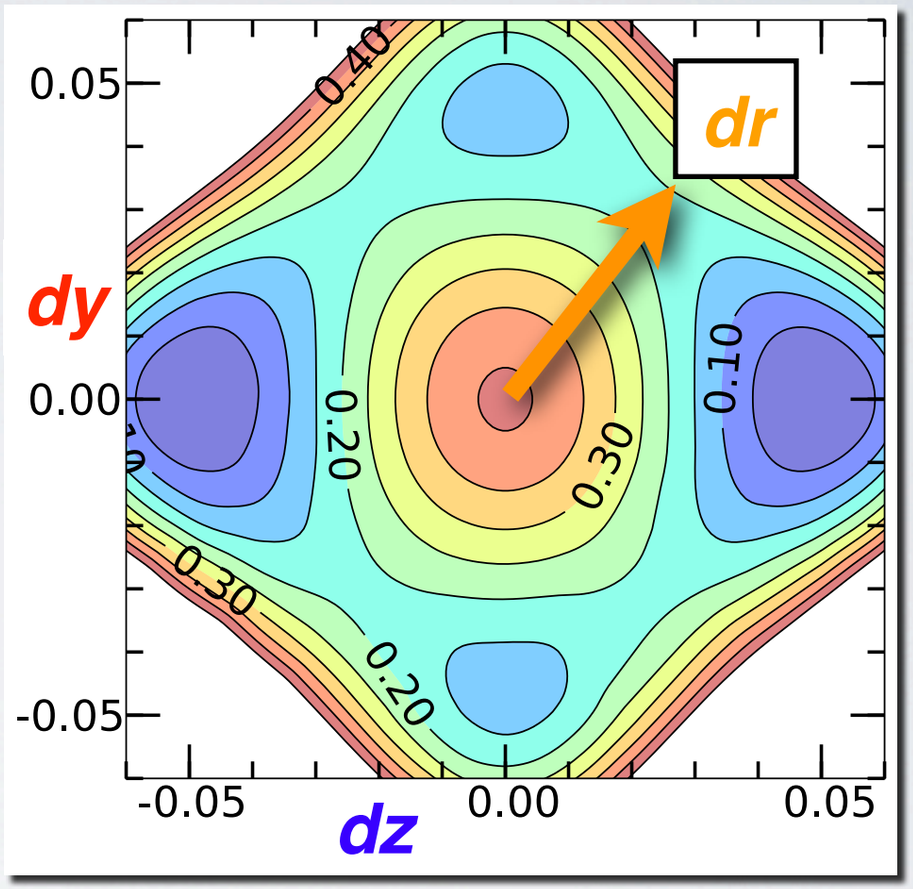
dz > 0
dx,dy = 0



dy < 0
dz,dx = 0

Ab initio MD Evidence for Ferroelastic Switching



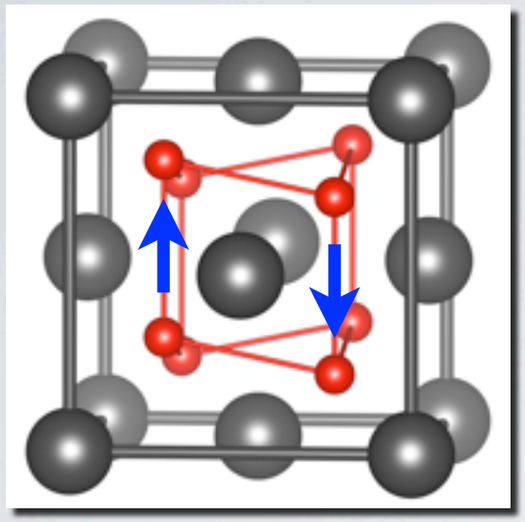


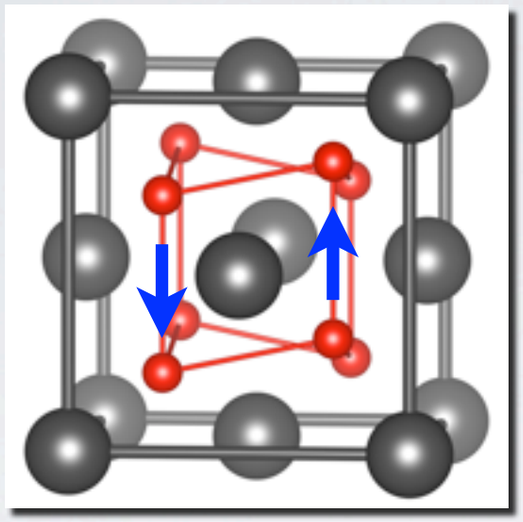
Distance from cubic geometry $dr = \sqrt{dx^2 + dy^2 + dz^2}$ always conserved!

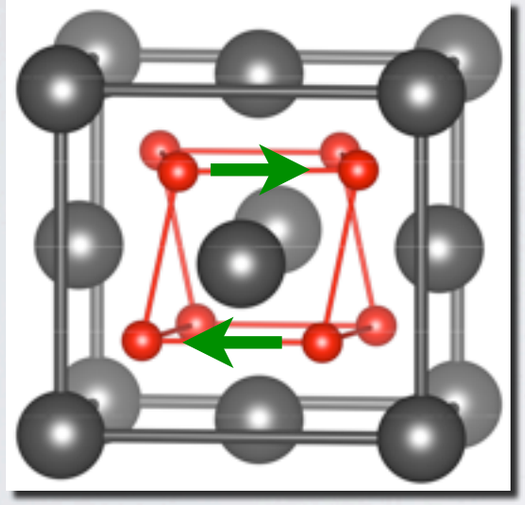
$\Rightarrow$ *Ferroelastic switches* are an intrinsic feature of the dynamics in ZrO_2.

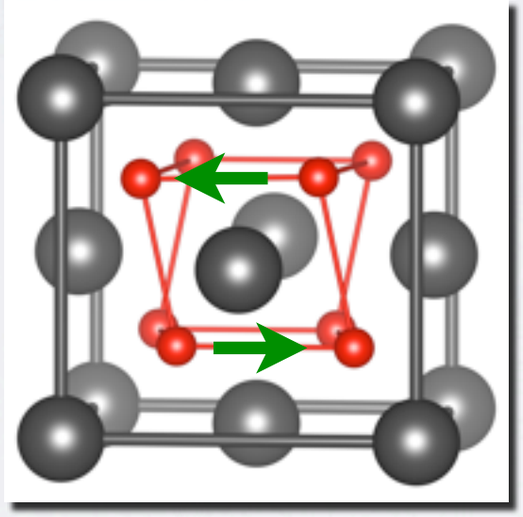
The Dynamics of Zirconia

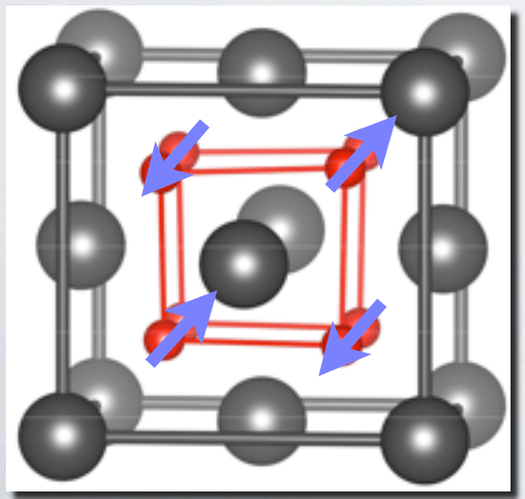
C. Carbogno, C. G. Levi, C. G. Van de Walle, and M. Scheffler *(submitted)*.

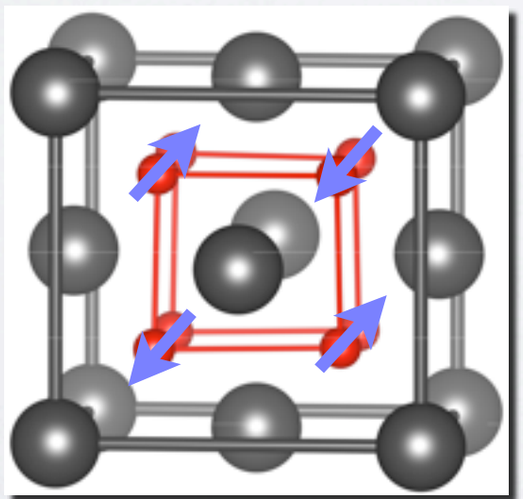












ZrO_2 exhibits **not one**, **but six degenerate** equilibrium configurations.

⇓

Ferroelastic 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.

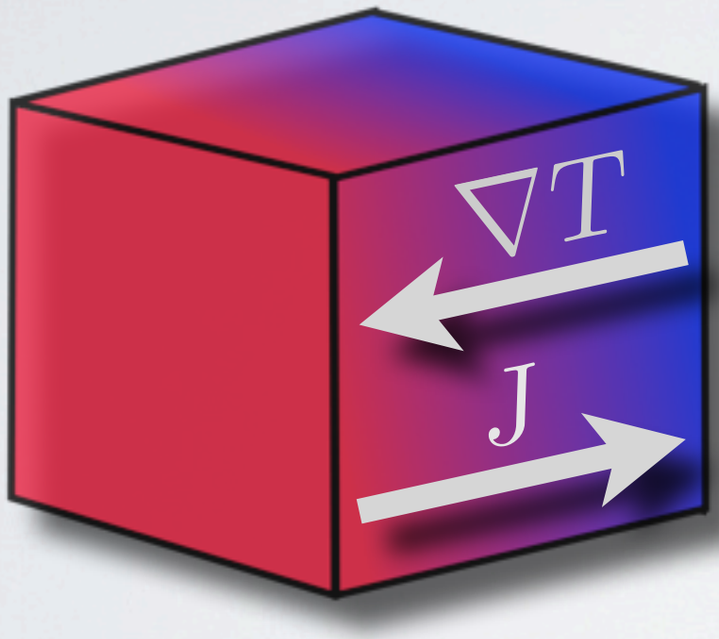
The harmonic approximation can be very useful to approximatively asses dynamic and thermodynamic effects at low temperatures.

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

III. HEAT TRANSPORT

HEAT TRANSPORT

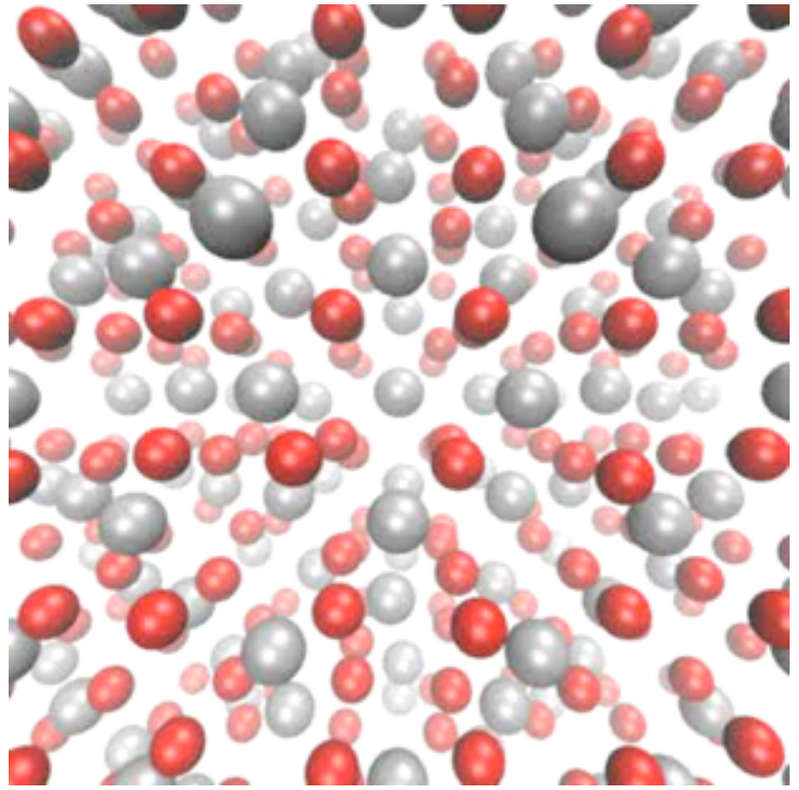
Macroscopic Effect:



Fourier's Law:

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

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



Microscopic Mechanisms

BASICS OF MACROSCOPIC TRANSPORT

The Continuity Equation:
(valid for any conserved quantity)

$$\frac{\partial T}{\partial t} + \nabla \cdot \mathbf{j} = 0$$

Proportionality of flux and gradient:

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

The Diffusion Equation:
(also applies to mass & charge transport)

$$\frac{\partial T(\mathbf{r},t)}{\partial t} = \kappa \nabla^2 T(\mathbf{r},t)$$

Analytic Solution:

$$T(\mathbf{r},t) = \frac{1}{(4\pi\kappa t)^{3/2}} \exp\left(-\frac{\mathbf{r}^2}{4\kappa t}\right)$$

HARMONIC APPROXIMATION

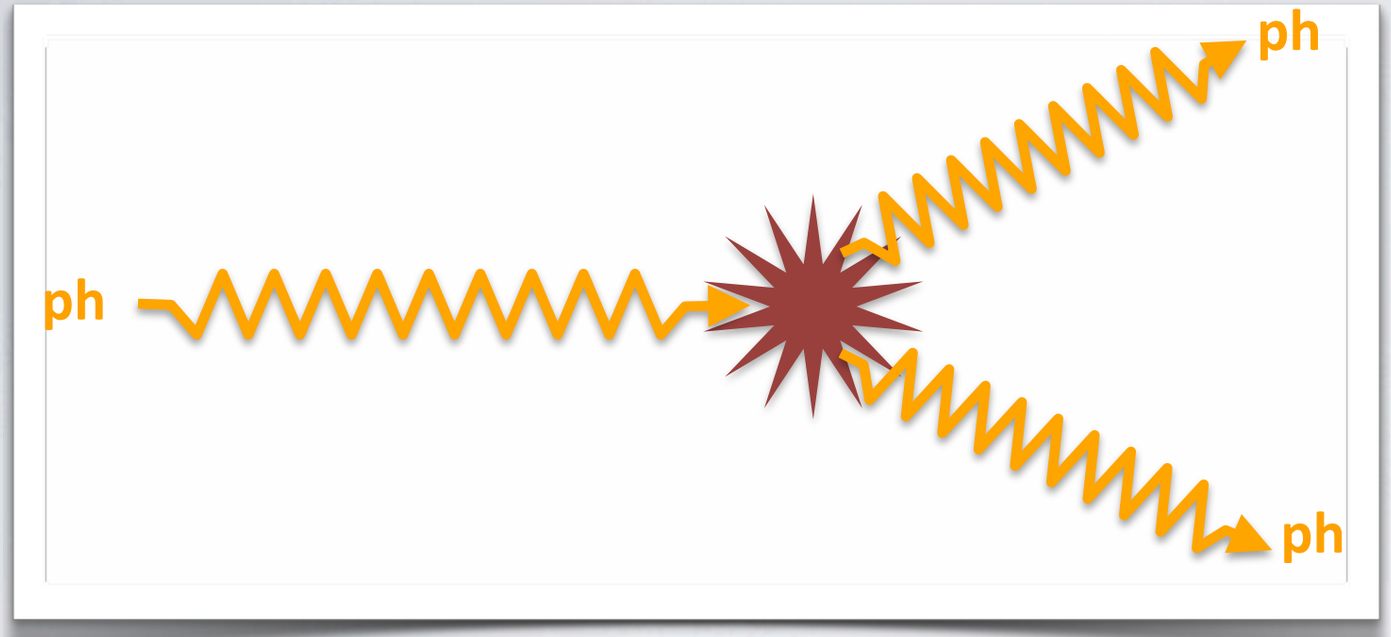
$$\mathbf{R}_j(t) \quad = \quad \mathbf{R}_j^0 + \mathfrak{Re}\left(\sum_s \frac{A_s}{\sqrt{M_i}} e^{i\left(\mathbf{q}\cdot(\mathbf{R}_j^0 - \mathbf{R}_{j'}^0) - \omega_s(\mathbf{q})t\right)} \cdot \left[\nu_s(\mathbf{q})\right]_{j'} \right)$$

$$E = \frac{1}{2}\sum E_s = \frac{1}{2}\sum_s \sum_{\mathbf{q}} \overbrace{|A_s|^2}^{n} \omega_s^2(\mathbf{q})$$

$$\mathbf{J} = \frac{1}{2}\sum_s \sum_{\mathbf{q}} |A_s|^2 \omega_s^2(\mathbf{q}) \cdot \underbrace{\frac{\partial \omega_s(\mathbf{q})}{\partial \mathbf{q}}}_{v_s^g(\mathbf{q})} \not\propto \nabla T$$

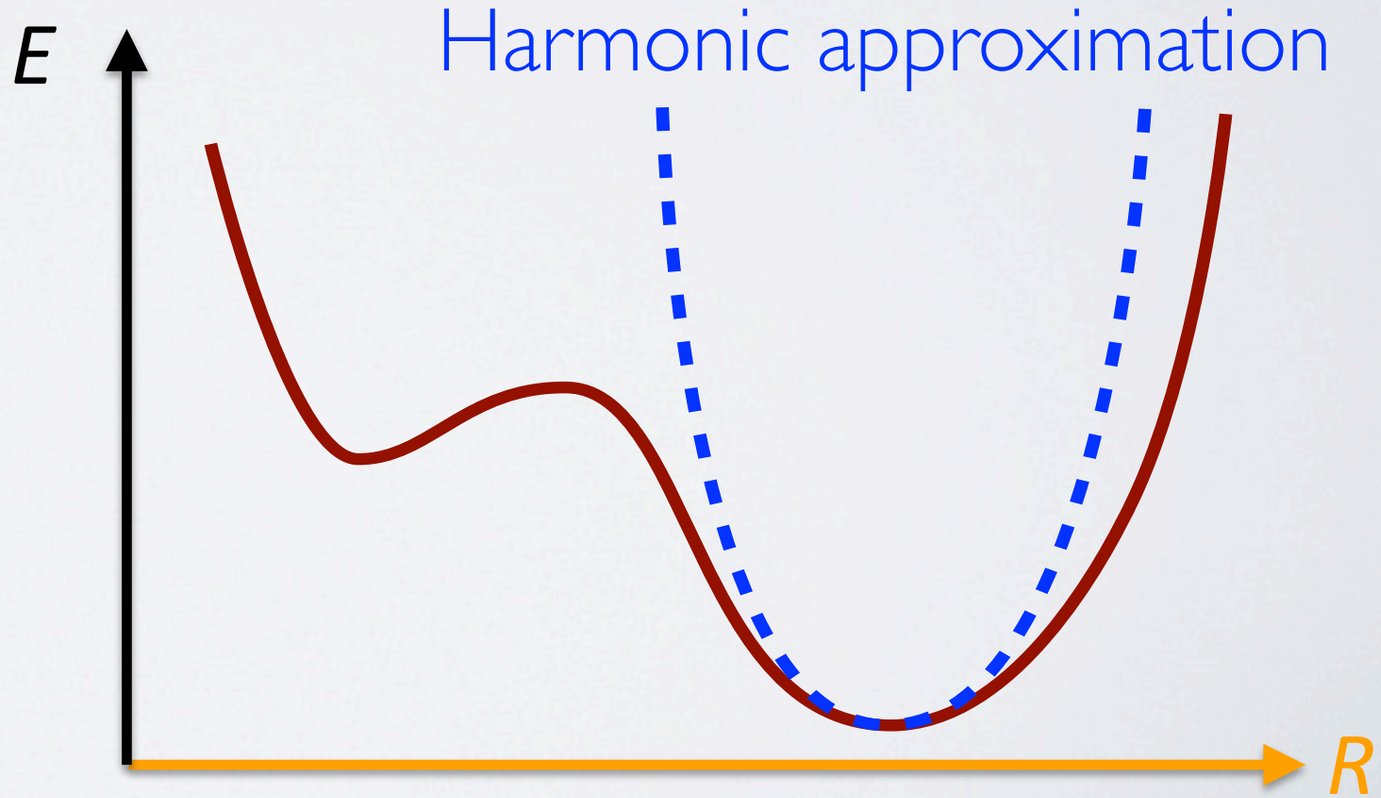
Thermal Conductivity diverges: $\kappa \longrightarrow \infty$

HEAT CONDUCTIVITY 101

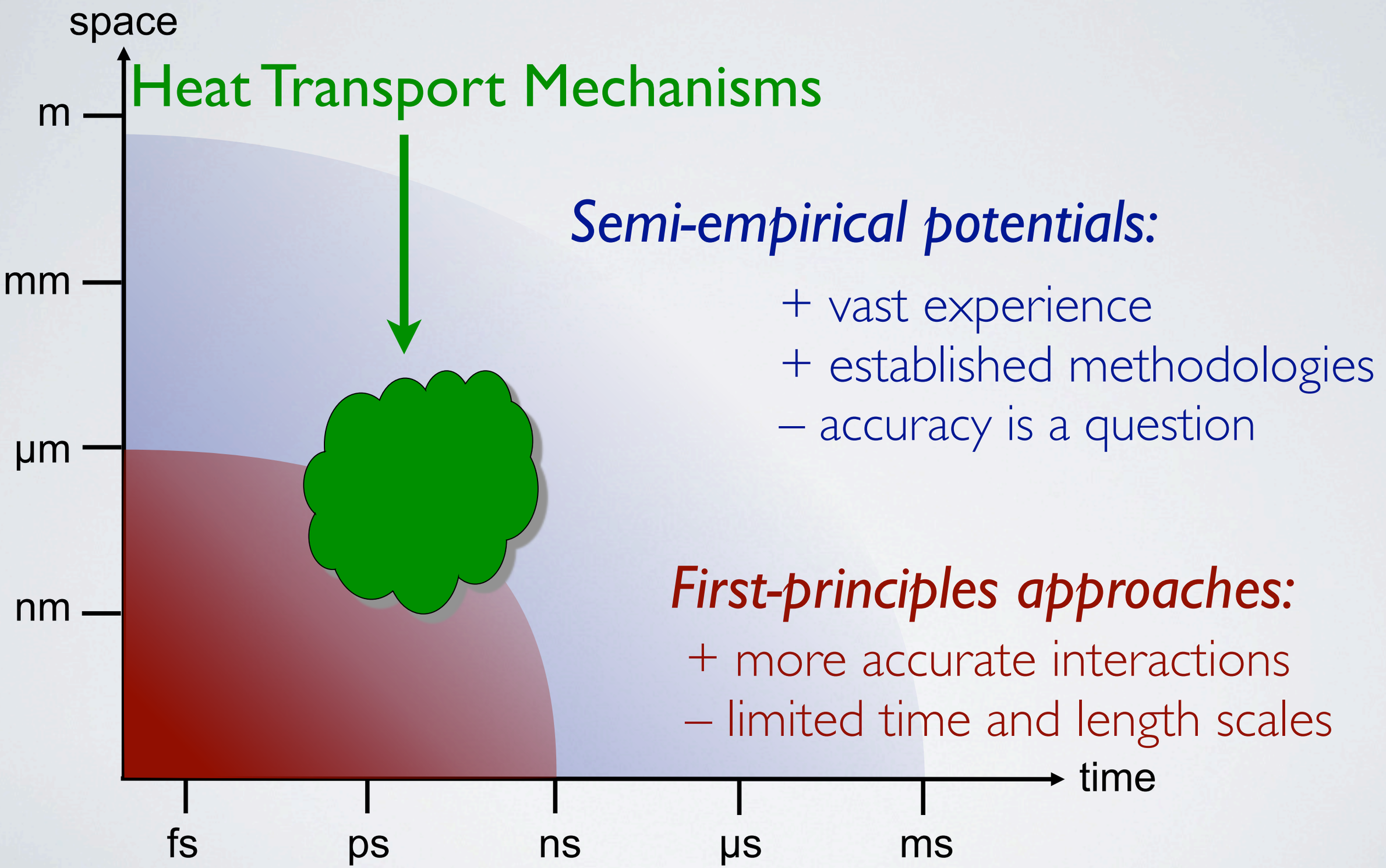


The **phonon-phonon interaction** limits the **vibrational thermal conductivity.**

Deviations from the harmonic approximation limit the **vibrational thermal conductivity.**



TIME AND LENGTH SCALES



Semi-empirical potentials:

\+ vast experience

\+ established methodologies

– accuracy is a question

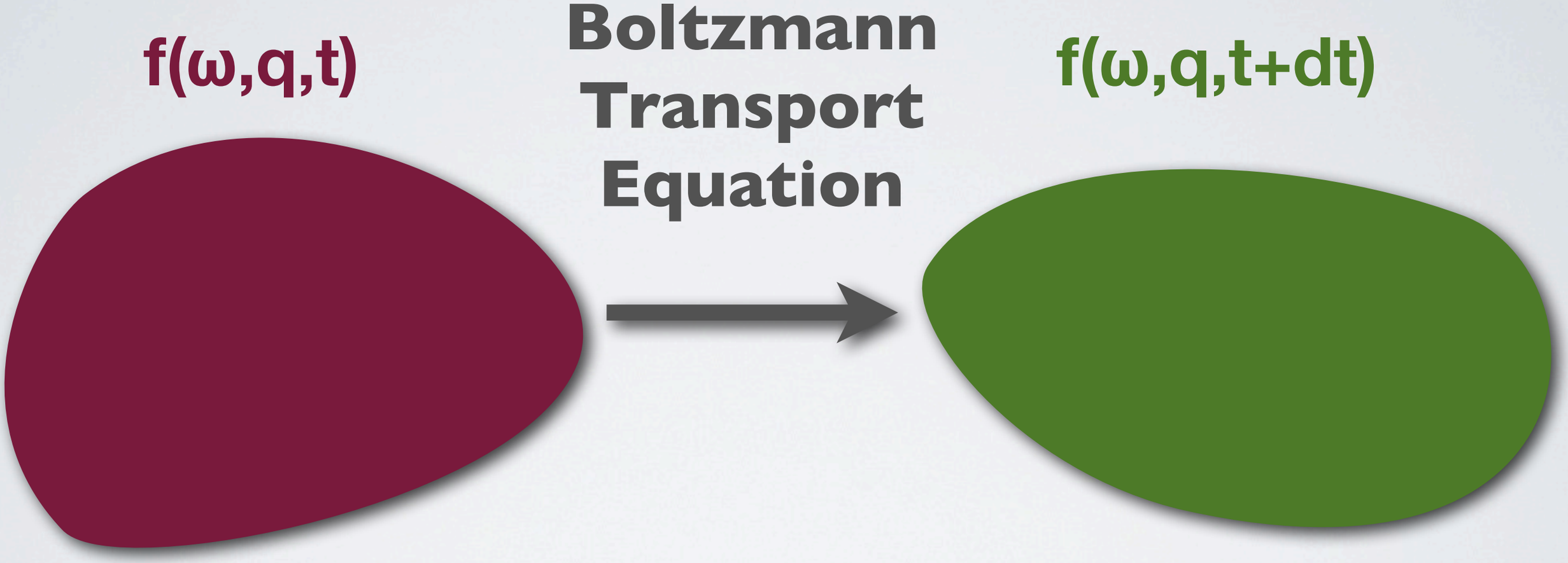
First-principles approaches:

\+ 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**!

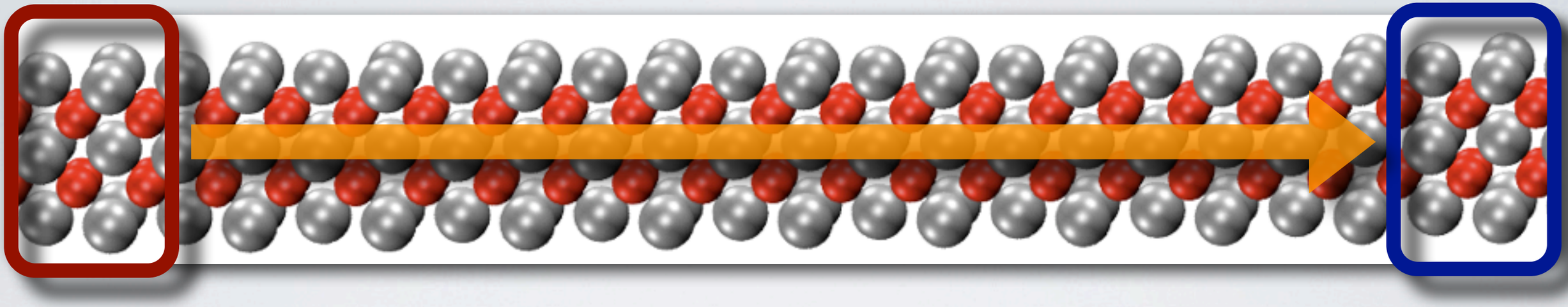
FIRST-PRINCIPLES APPROACHES

	Order of interaction	Validity & Applicability	Finite Size Effects	Disorder
Boltzmann-Transport Eq.	~□(r^3)	low T	Minute	Parameter
Non-Equilib. MD				
Laser-flash 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).



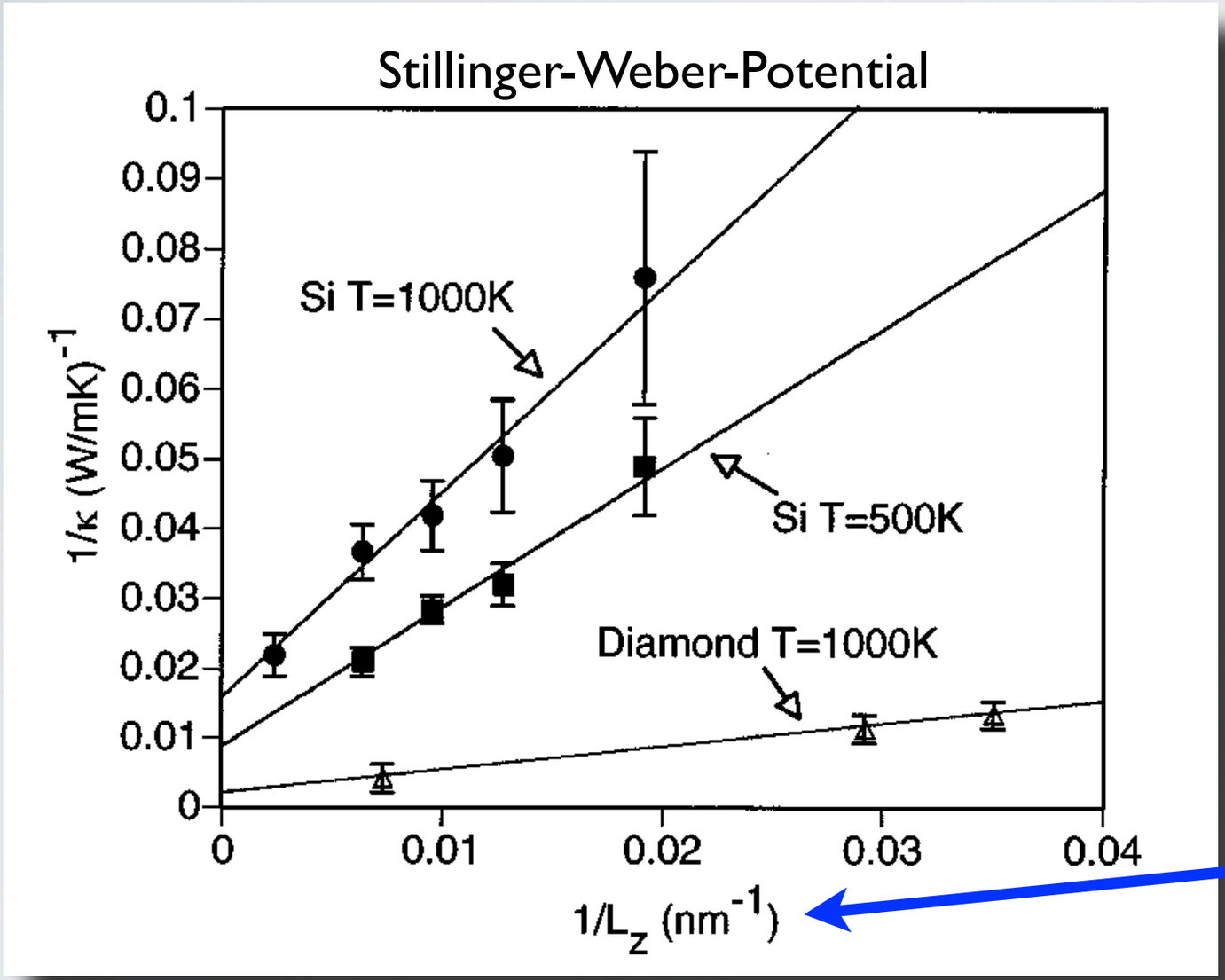
heat source → • Temperature gradient ∇T • Stationary heat flux **J** → **heat sink**

⇓

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

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

FINITE SIZE EFFECTS



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

Finite Size Corrections

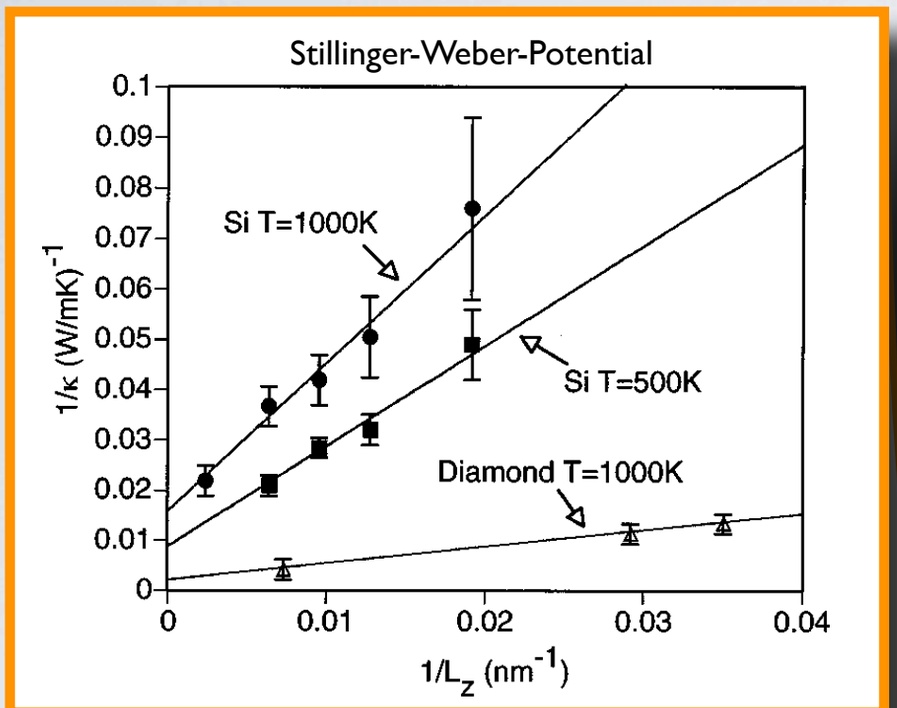
$$\frac{1}{\kappa} \sim \left(\frac{1}{l_\infty} + \frac{4}{L_z} \right)$$

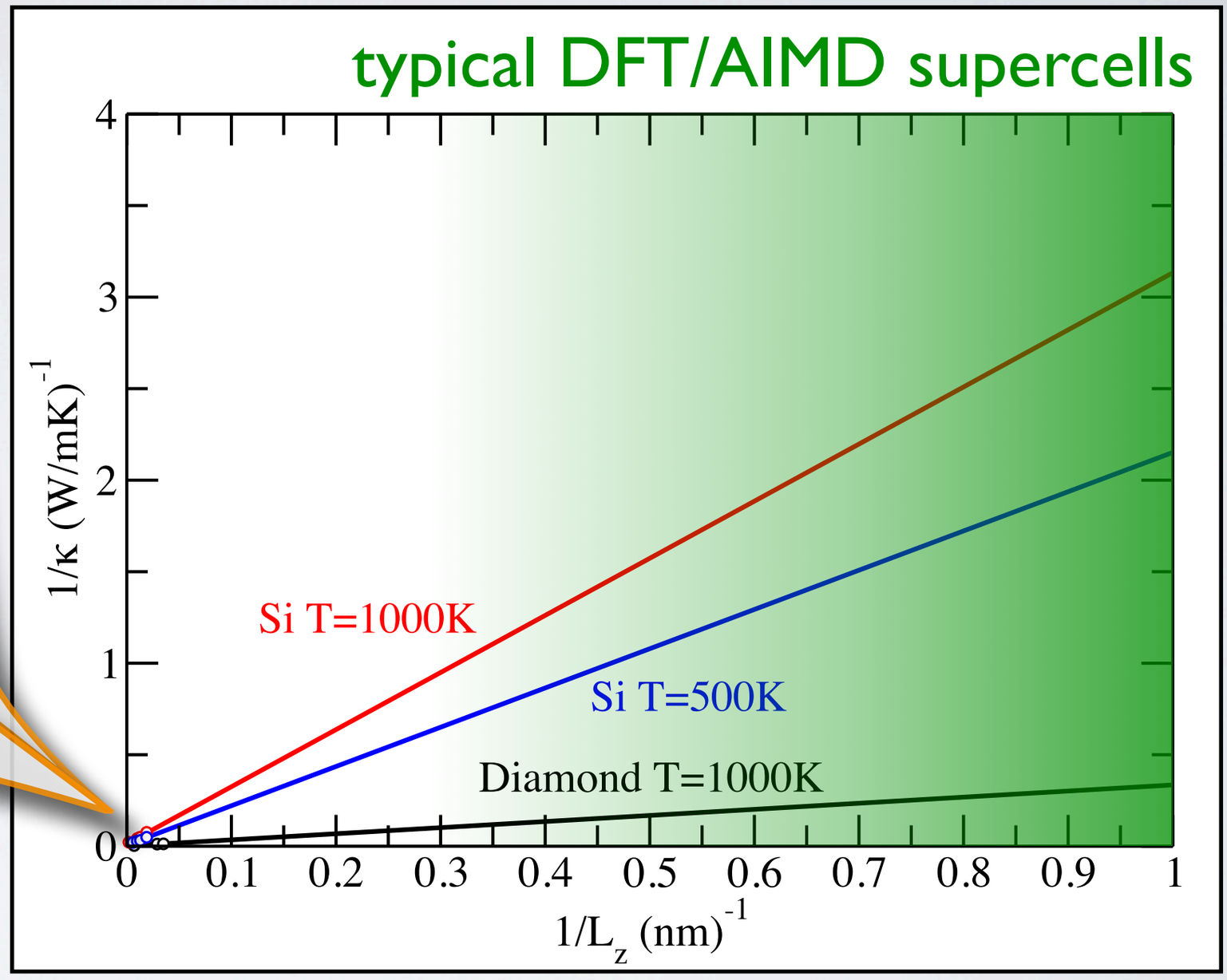
mean free path

supercell length

FINITE SIZE EFFECTS

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

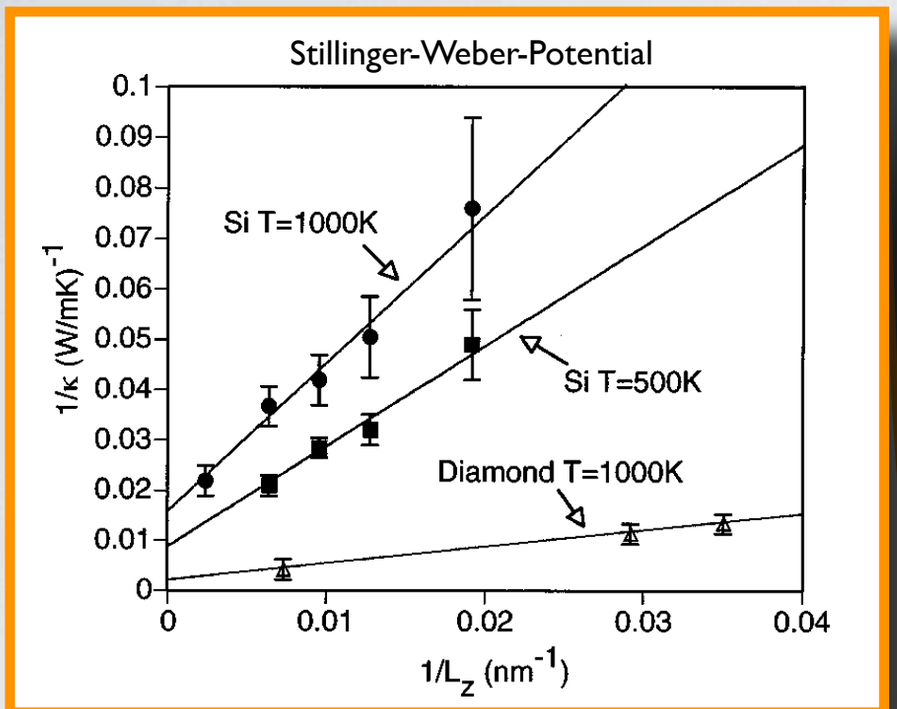


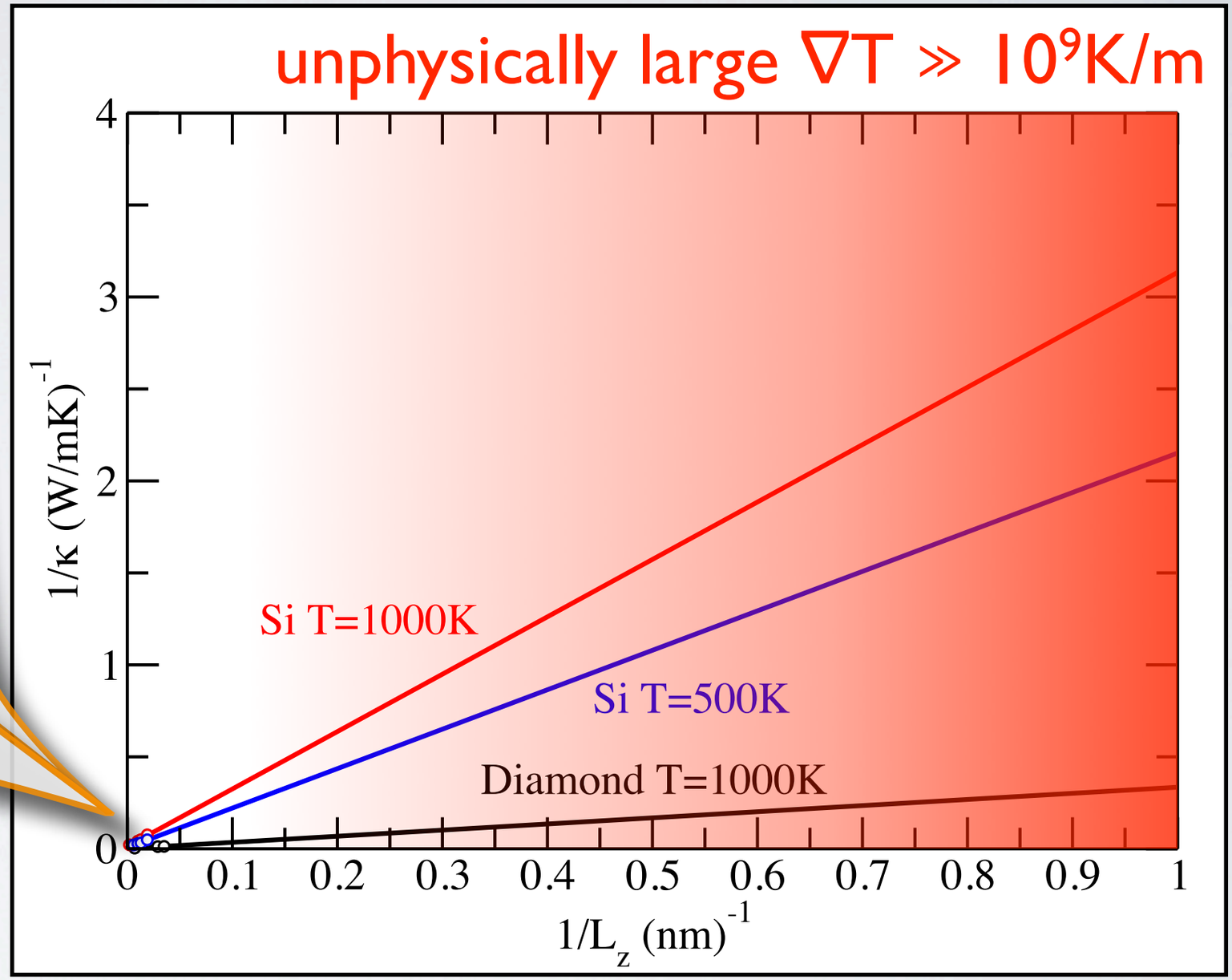


Non-equilibrium MD exhibits strong finite-size artifacts
in supercells typically accessible within DFT/AIMD.

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.	~□(r^3)	low T	Minute	Parameter
Non-Equilib. MD	Full	all T	Huge	as in supercell
Laser-flash MD				
Green-Kubo MD				

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

„LASER FLASH“ MEASUREMENTS

W. J. Parker *et al., J. Appl. Phys.* **32**,1679 (1961).

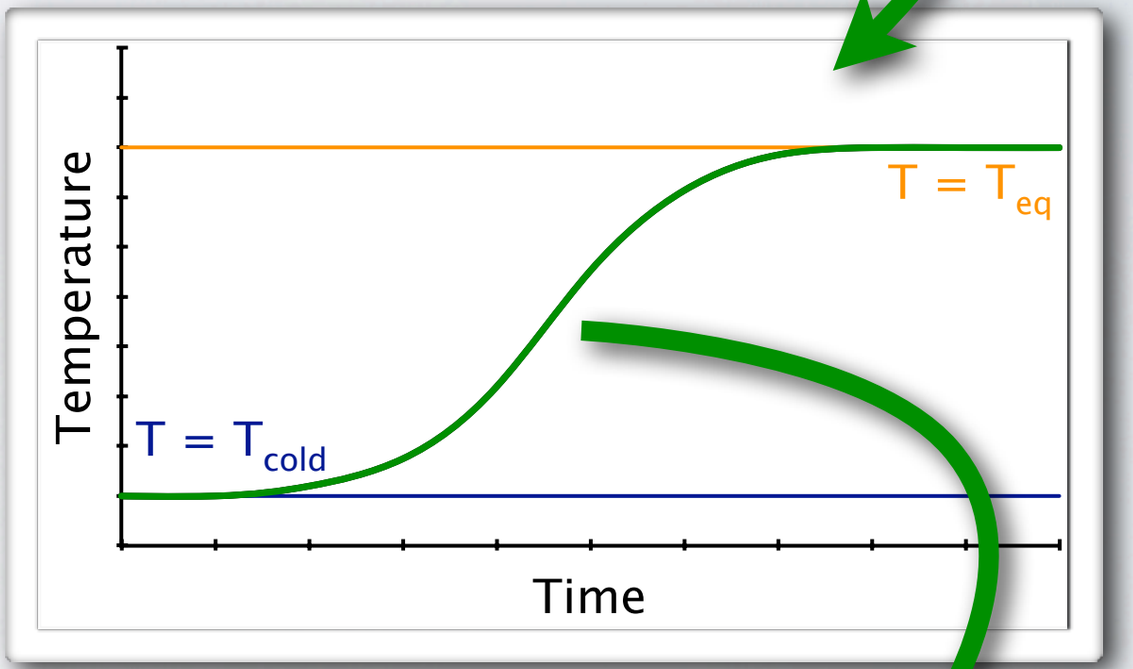
„LASER FLASH“ MEASUREMENTS

W. J. Parker *et al., J. Appl. Phys.* **32**,1679 (1961).

heat diffusion

$T = T_{hot}$

$T = T_{cold}$



Heat Diffusion Equation:

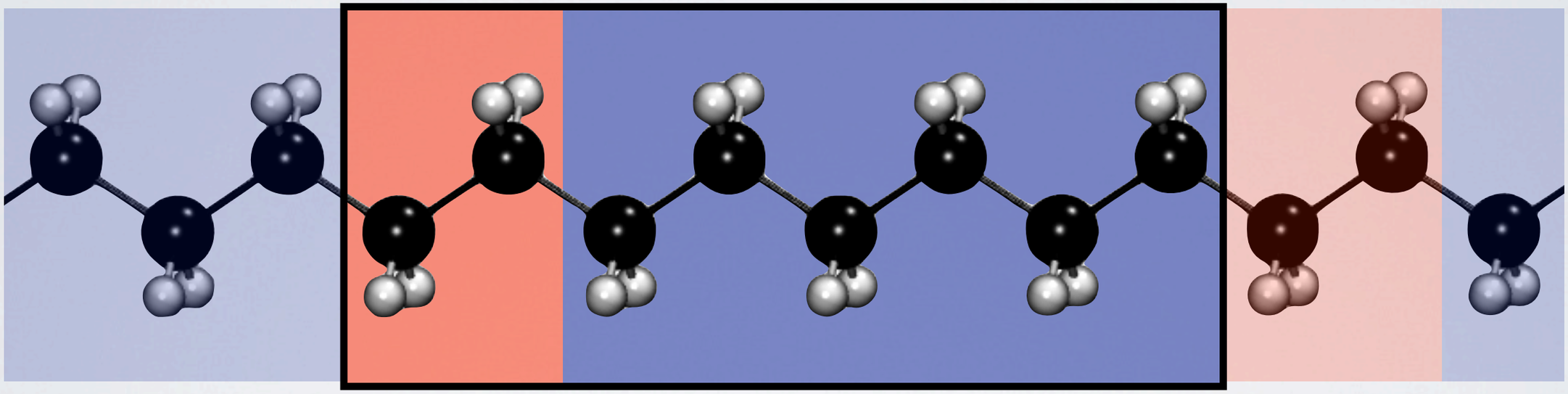
$$\frac{\partial T(x,t)}{\partial t} + \alpha \frac{\partial^2 T(x,t)}{\partial x^2} = 0$$

Extract the ***heat diffusivity α*** by fitting **T(x,t)**

„LASER FLASH“ SIMULATIONS

T. M. Gibbons and S. K. Estreicher, *Phys. Rev. Lett.* **102**, 255502 (2009).

Mimic the ***„Laser-Flash Measurements“***
in ***ab initio MD simulations***:



(A) **Prepare two supercells:** a **small hot** one and a **large cold** one.

Setup of the Cell in Non-Equilibrium

In the **harmonic approximation**, the **positions $\mathbf{r}_i$** and the **velocities $\mathbf{v}_i$** are related to the **vibrational eigenfrequencies ω_s** and -vectors **$\mathbf{e}_s$**.

$$r_{0i} + \Delta\mathbf{r}_i = + \sum_s A_s(T) \frac{\cos(\Phi_s + \omega_s t)}{\sqrt{M_i}} \cdot \mathbf{e}_s$$

$$\mathbf{v}_i = - \sum_s A_s(T) \frac{\sin(\Phi_s + \omega_s t)}{\sqrt{M_i}} \cdot \omega_s \cdot \mathbf{e}_s$$

Maxwell-Boltzmann distributed amplitudes

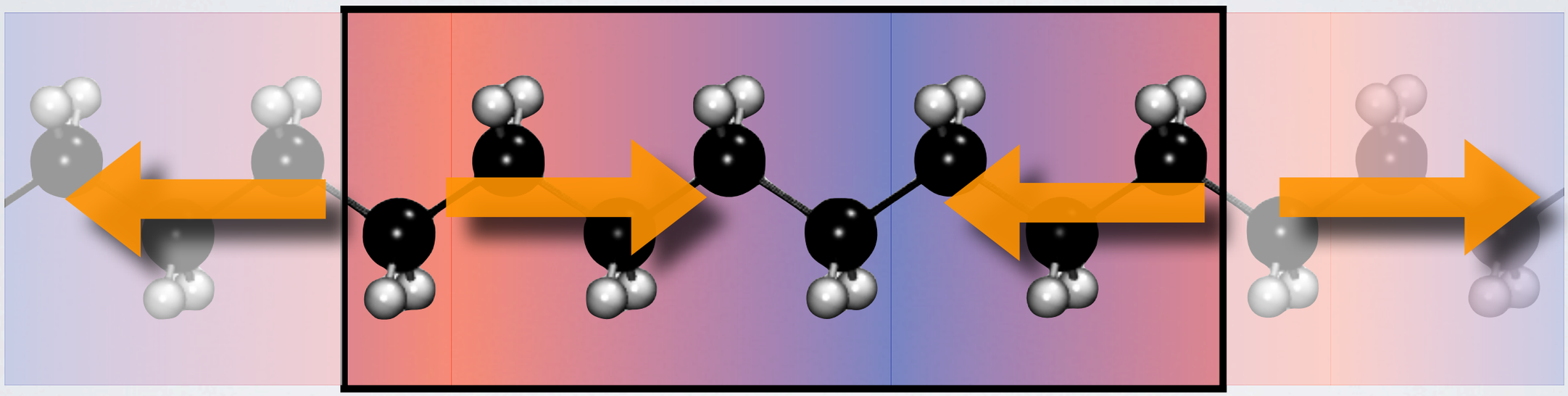
random phase

harmonic approximation

„LASER FLASH“ SIMULATIONS

T. M. Gibbons and S. K. Estreicher, *Phys. Rev. Lett.* **102**, 255502 (2009).

Mimic the ***„Laser-Flash Measurements“***
in ***ab initio MD simulations***:

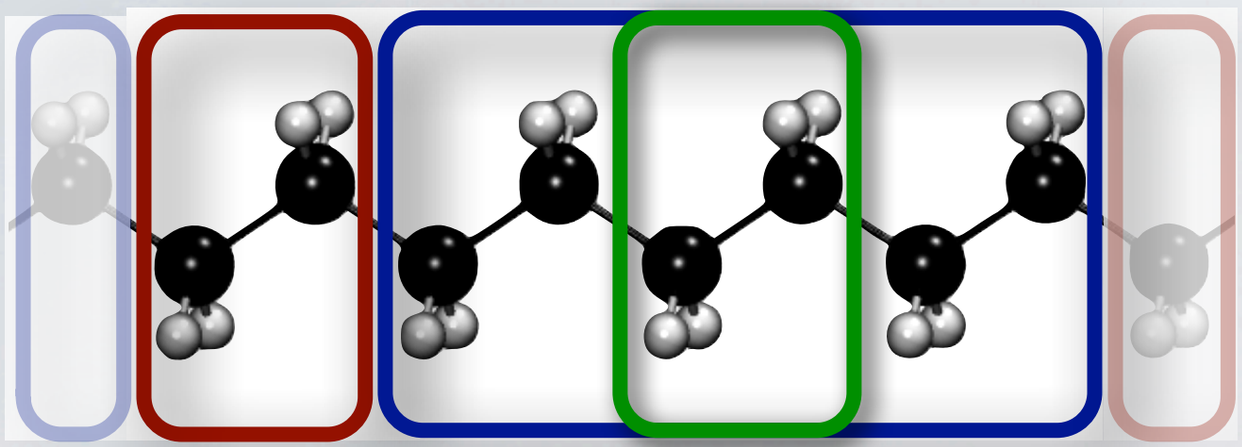


(A) **Prepare two supercells:** a **small hot** one and a **large cold** one.

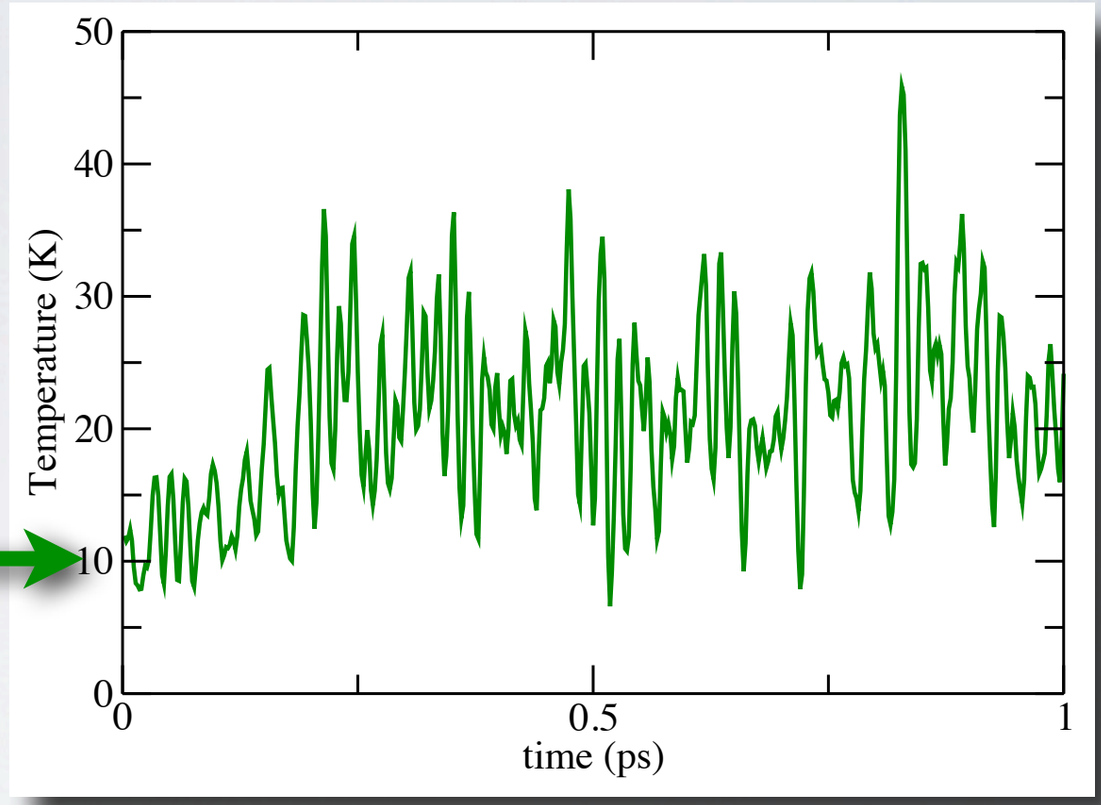
(B) Let the **heat diffuse** via *ab initio* MD
and **monitor** the temperature profile **T(x,t)**.

„LASER FLASH“ SIMULATIONS

T. M. Gibbons and S. K. Estreicher, *Phys. Rev. Lett.* **102**, 255502 (2009).



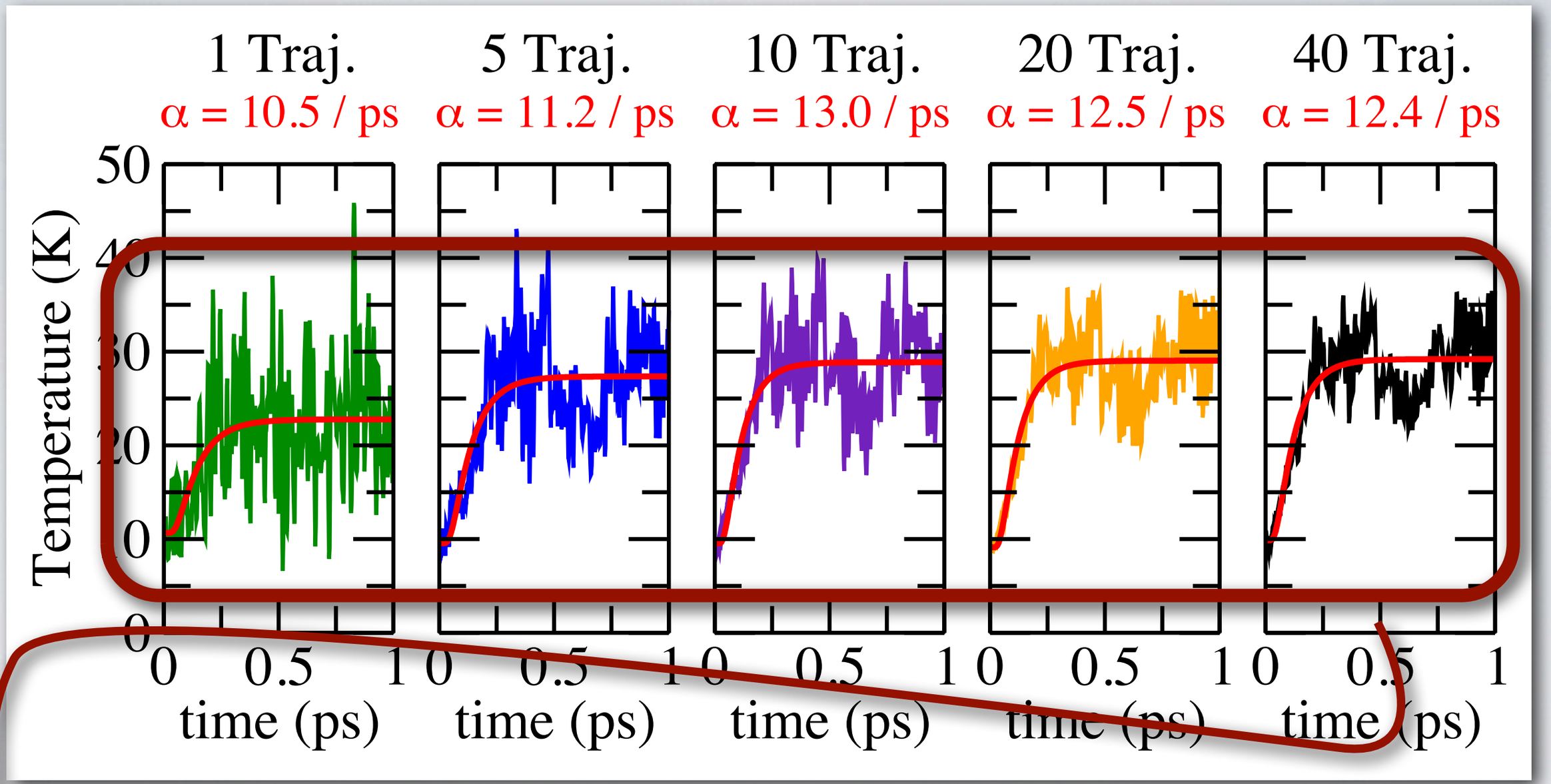
Monitor temperature of the central cell



The finite number of atoms leads to large temperature fluctuations.

„LASER FLASH“ SIMULATIONS

T. M. Gibbons and S. K. Estreicher, *Phys. Rev. Lett.* **102**, 255502 (2009).

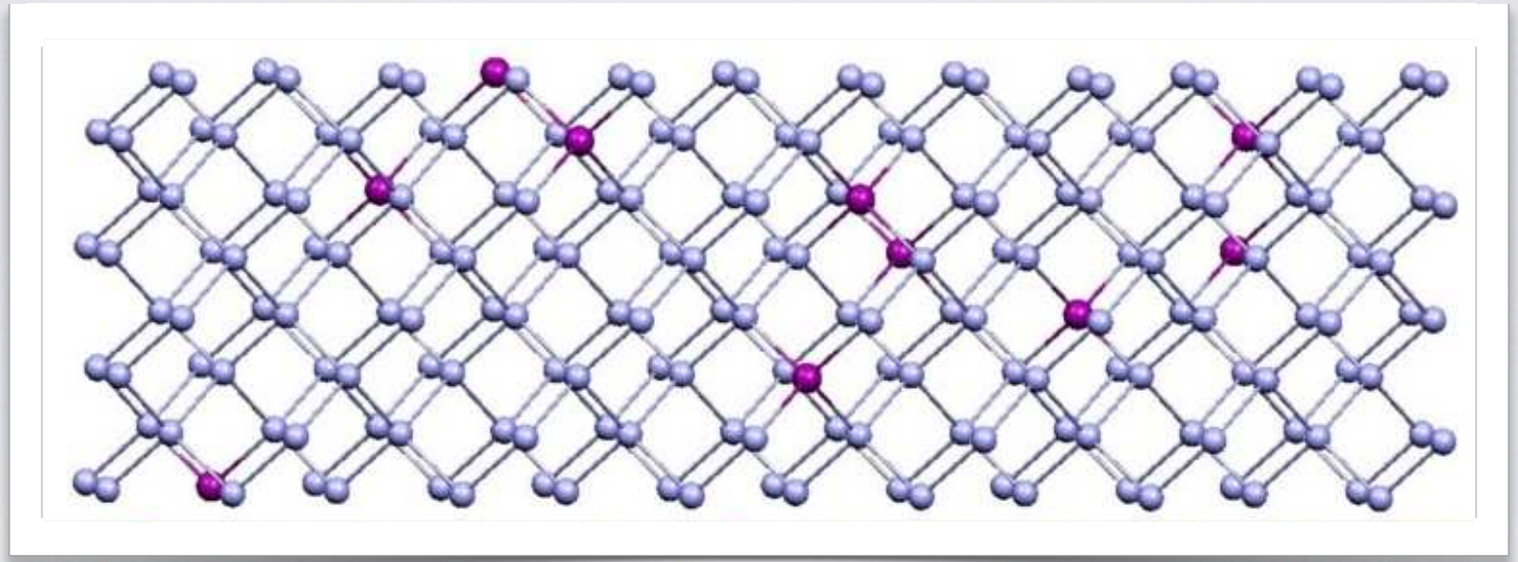


Fit to

$$T(x,t) = T_{cold} + (T_{final} - T_{cold}) \sum_{n} (-1)^n \exp\left(-n^2 \pi^2 \alpha\, t\right)$$

APPLICATION TO IMPURITIES IN SI

T. M. Gibbons, By. Kang, S. K. Estreicher, and C. Carbogno, *Phys. Rev. B* **84**, 035317 (2011).

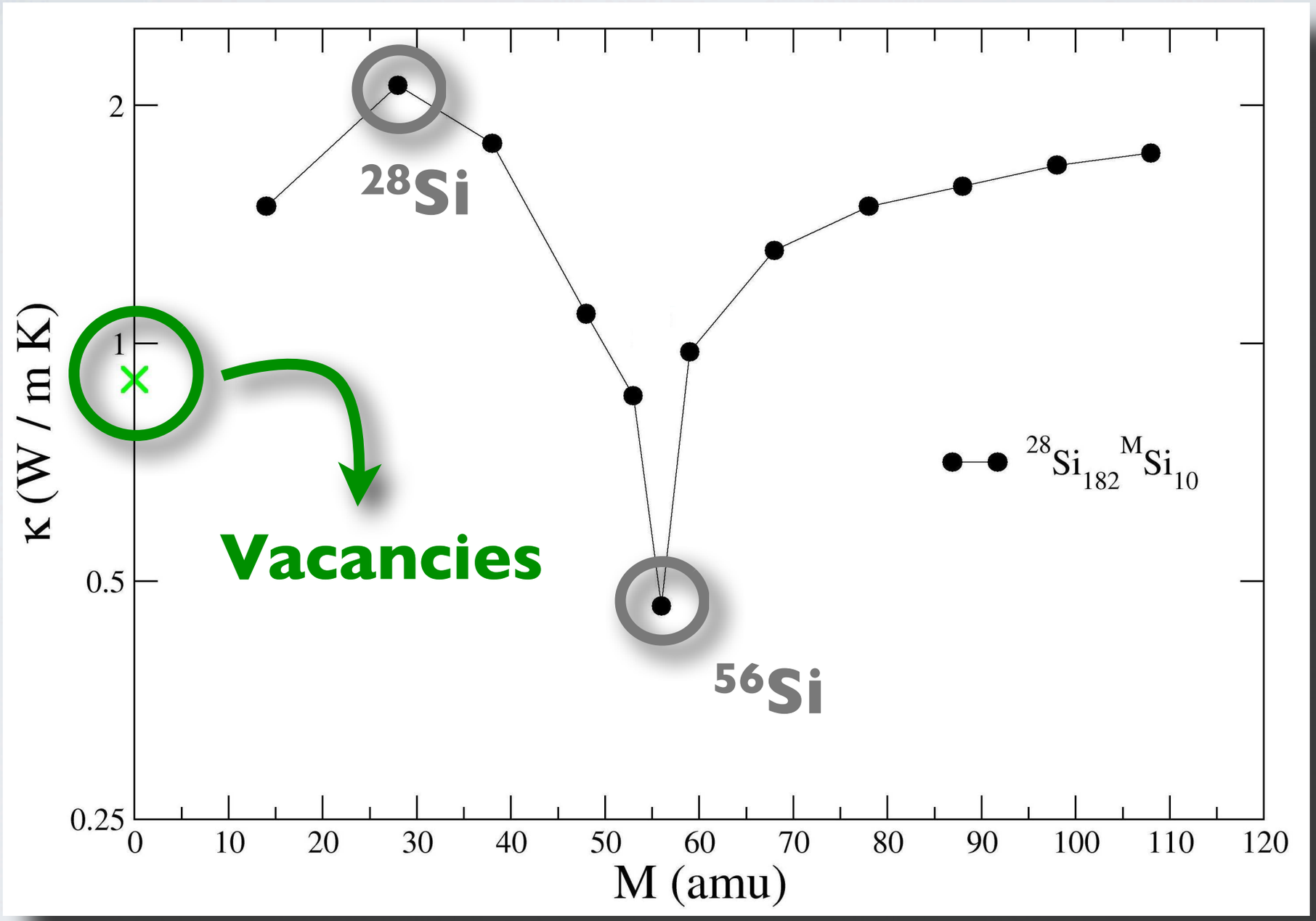


Si_{192} supercell containing **~5.2% impurities**

How do the
properties of the impurities
affect the
thermal conductivity of the system?

APPLICATION TO IMPURITIES IN SI

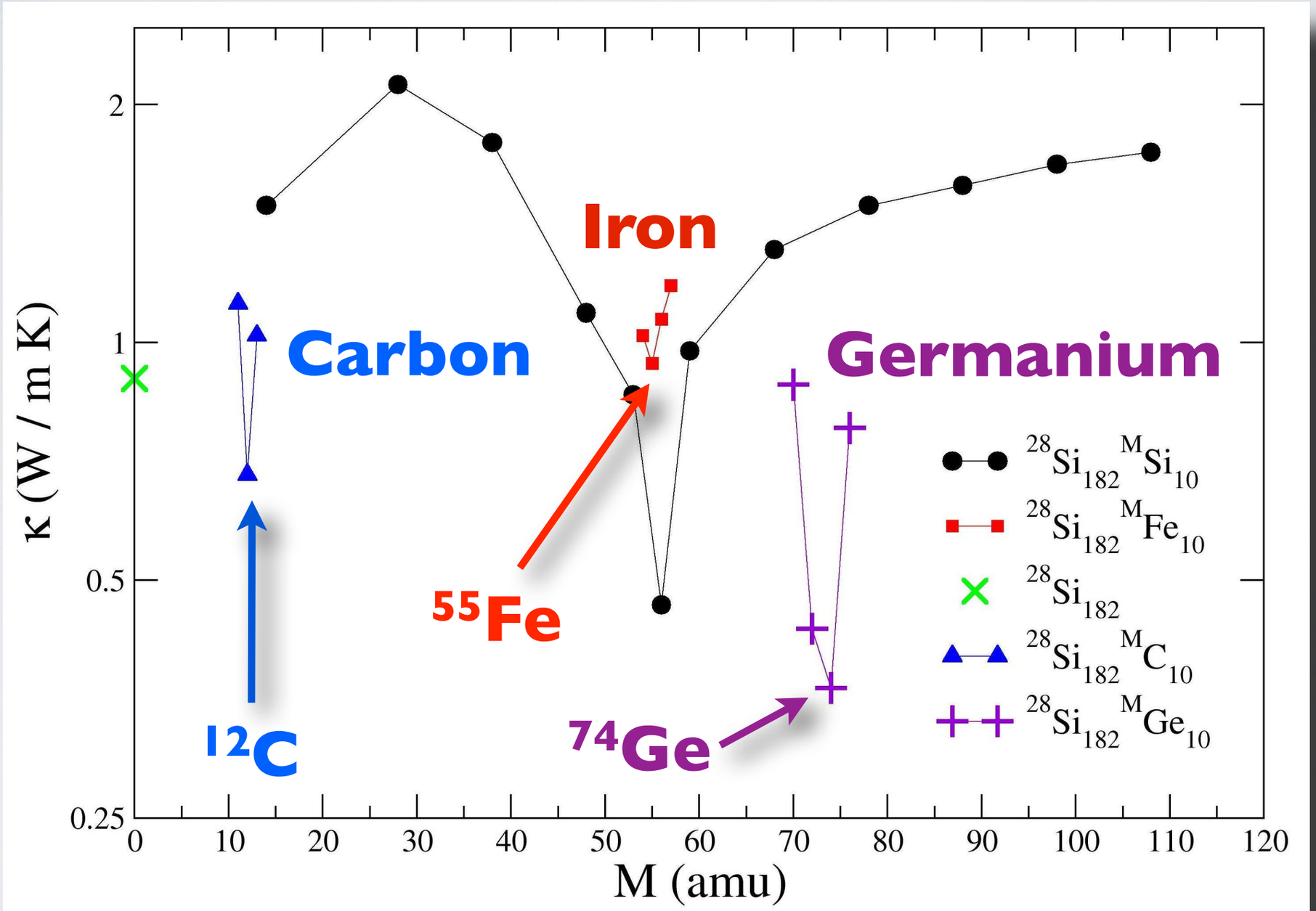
T. M. Gibbons and S. K. Estreicher, *Phys. Rev. Lett.* **102**, 255502 (2009).



Thermal conductivity can be controlled via the impurities‘ mass!

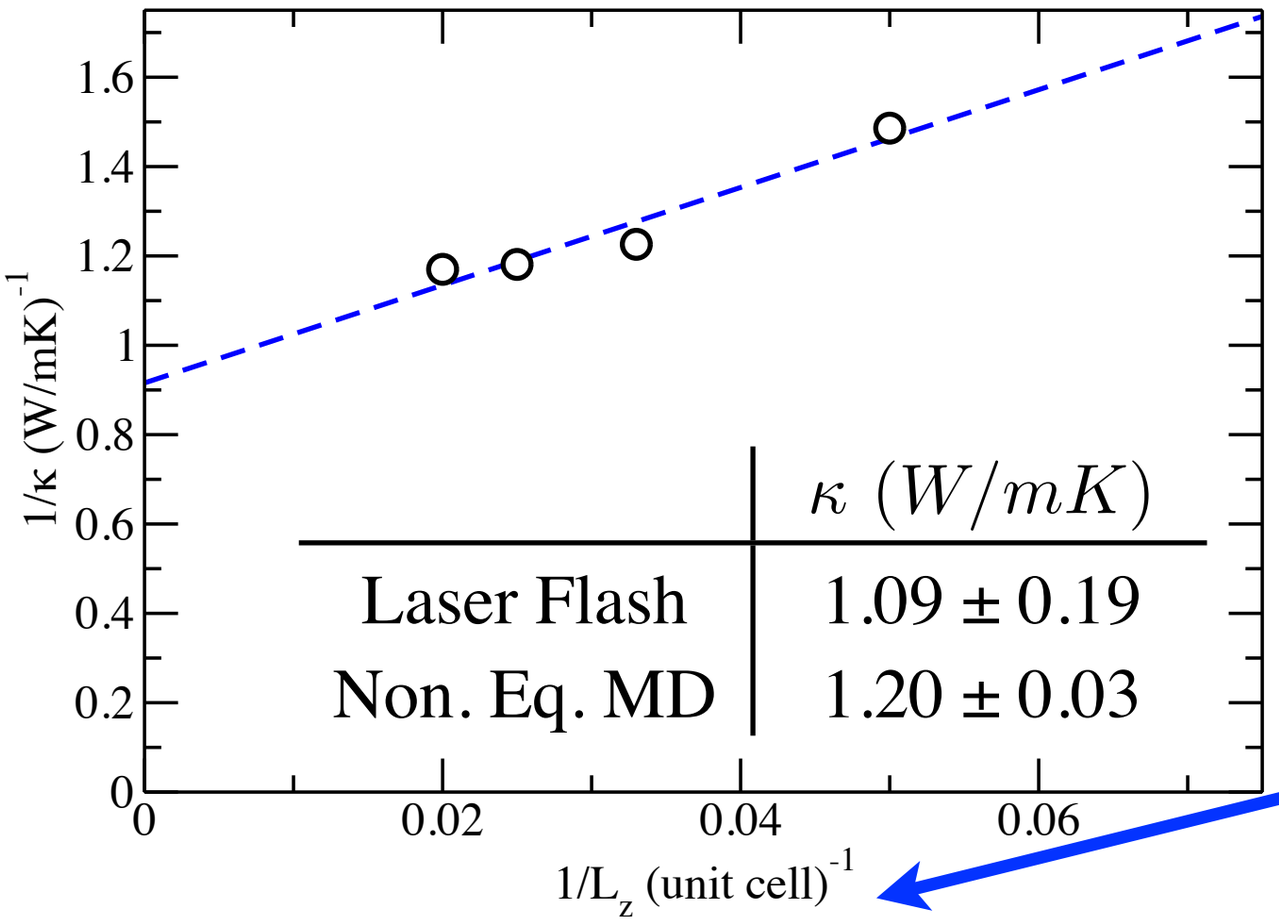
APPLICATION TO IMPURITIES IN SI

T. M. Gibbons, By. Kang, S. K. Estreicher, and C. Carbogno, *Phys. Rev. B* **84**, 035317 (2011).



Not all impurities are created equal!

FINITE SIZE EFFECTS



	$\kappa\ (W/mK)$
Laser Flash	1.09 ± 0.19
Non. Eq. MD	1.20 ± 0.03

Finite Size Corrections

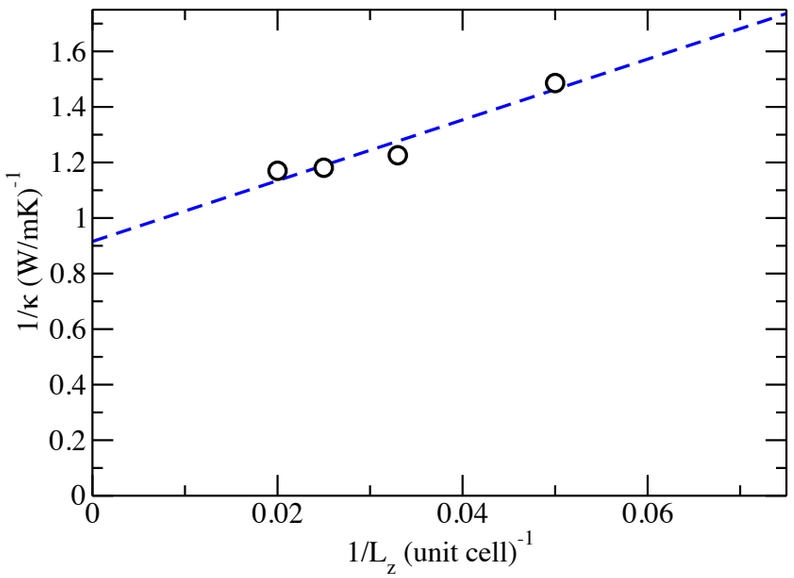
$$\frac{1}{\kappa} \sim \left(\frac{1}{l_\infty} + \frac{4}{L_z} \right)$$

mean free path

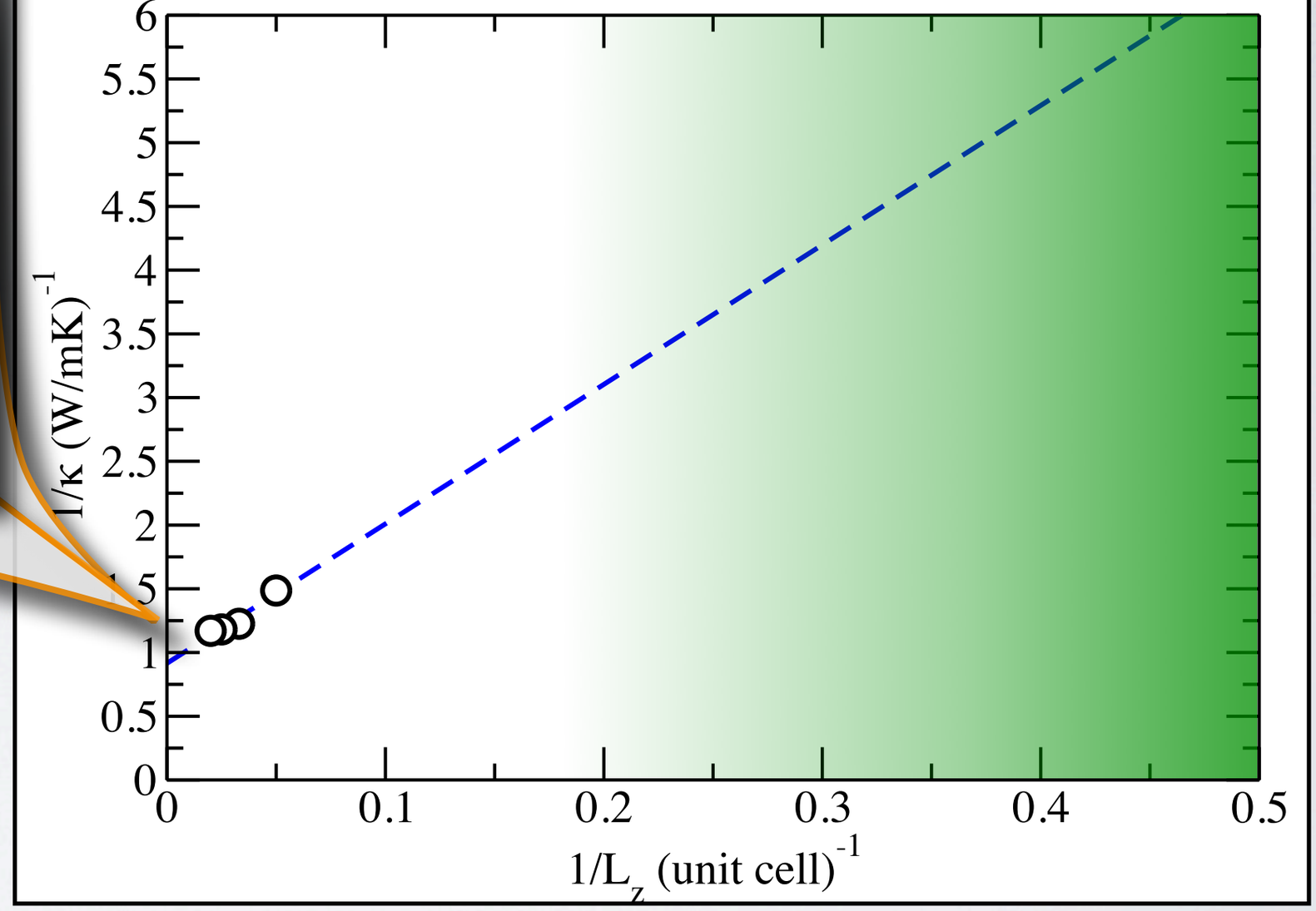
supercell length

SiGe, Stillinger-Weber Potential,
Courtesy of Philip Howell, Siemens AG

FINITE SIZE EFFECTS

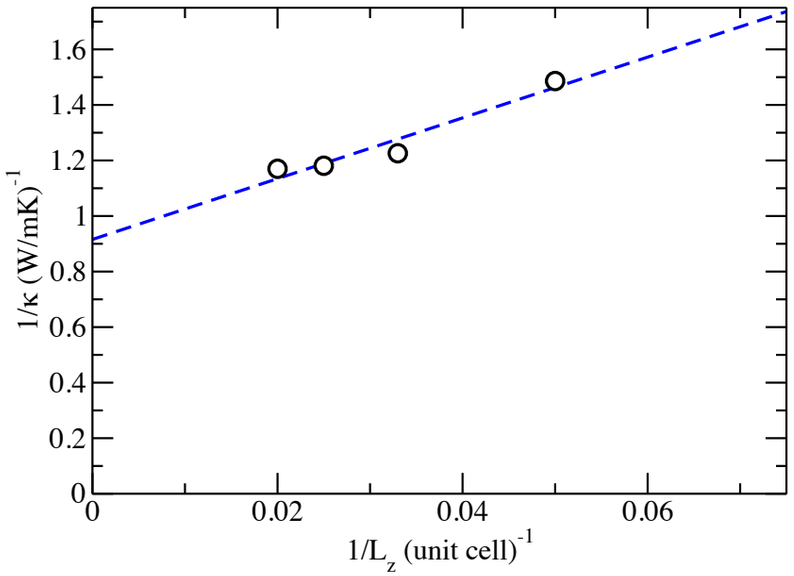


typical DFT/AIMD supercells

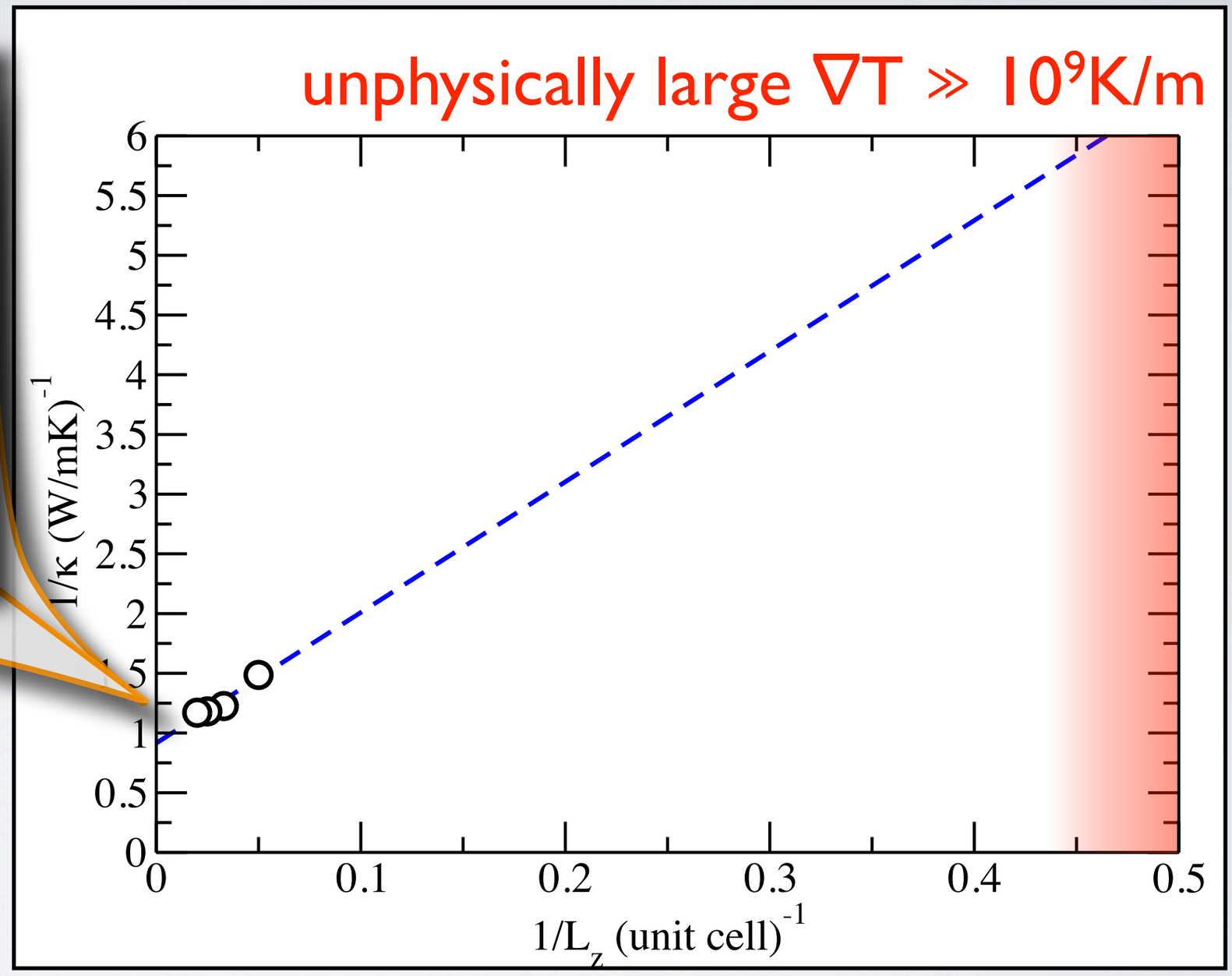


Laser-flash approach exhibits strong finite-size artifacts in supercells typically accessible within DFT/AIMD.

FINITE SIZE EFFECTS



unphysically large $\nabla T \gg 10^9$K/m



Preparation of the supercell in **non-equilibrium** via the **harmonic approximation** allows to use rather small thermal gradients.

FIRST-PRINCIPLES APPROACHES

	Order of interaction	Validity & Applicability	Finite Size Effects	Disorder
Boltzmann-Transport Eq.	~□(r^3)	low T	Minute	Parameter
Non-Equilib. MD	Full	all T	Huge	as in supercell
Laser-flash MD	Full	low T	Medium-Large	as in supercell
Green-Kubo MD				

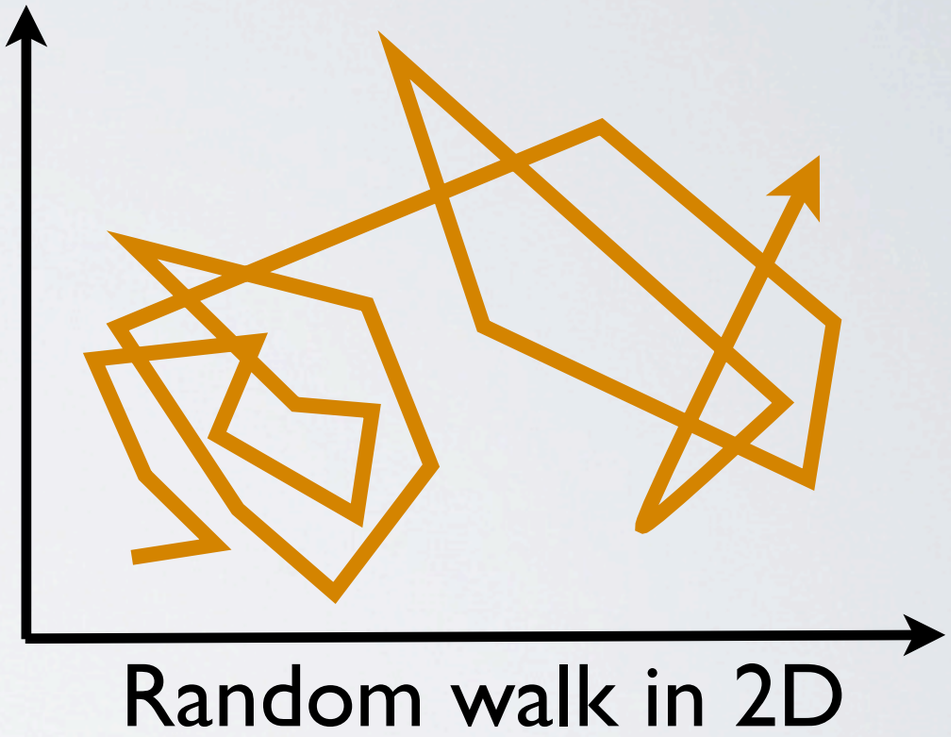
Laser-flash MD yields **accurate qualitative results** at **low temperatures** within **moderate computational costs**. **Quantitative** predictions require **finite size corrections**, though.

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

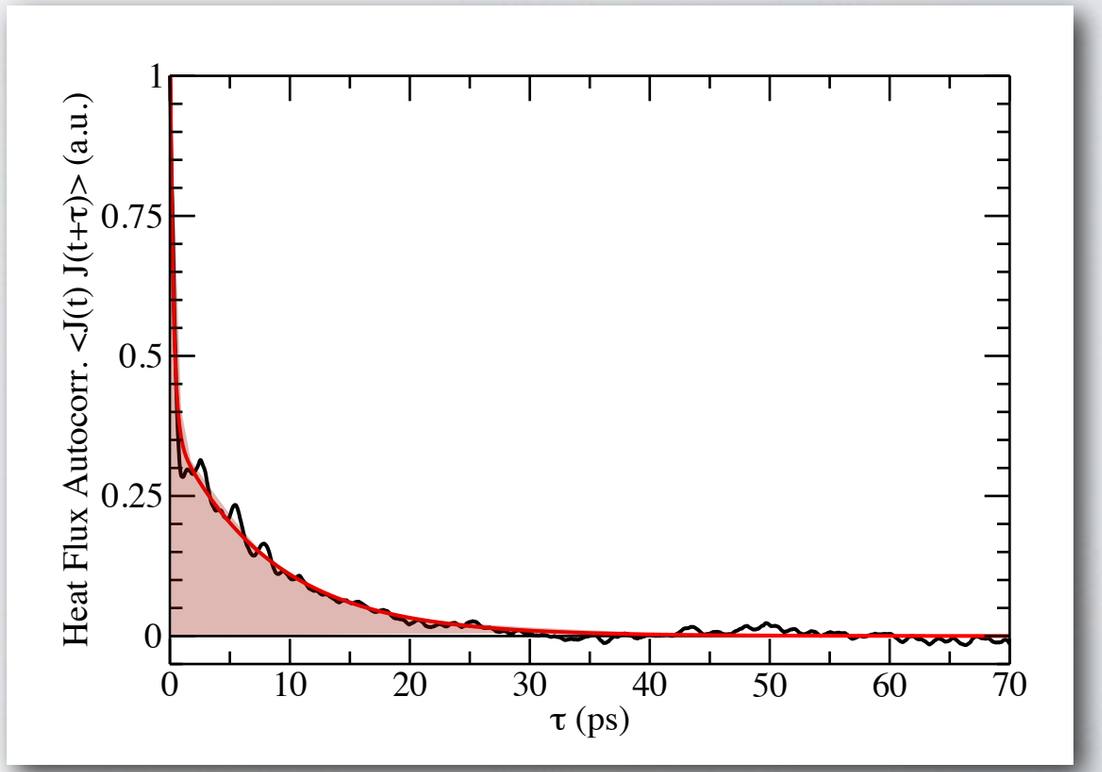
Simulations of the **thermodynamic equilibrium**

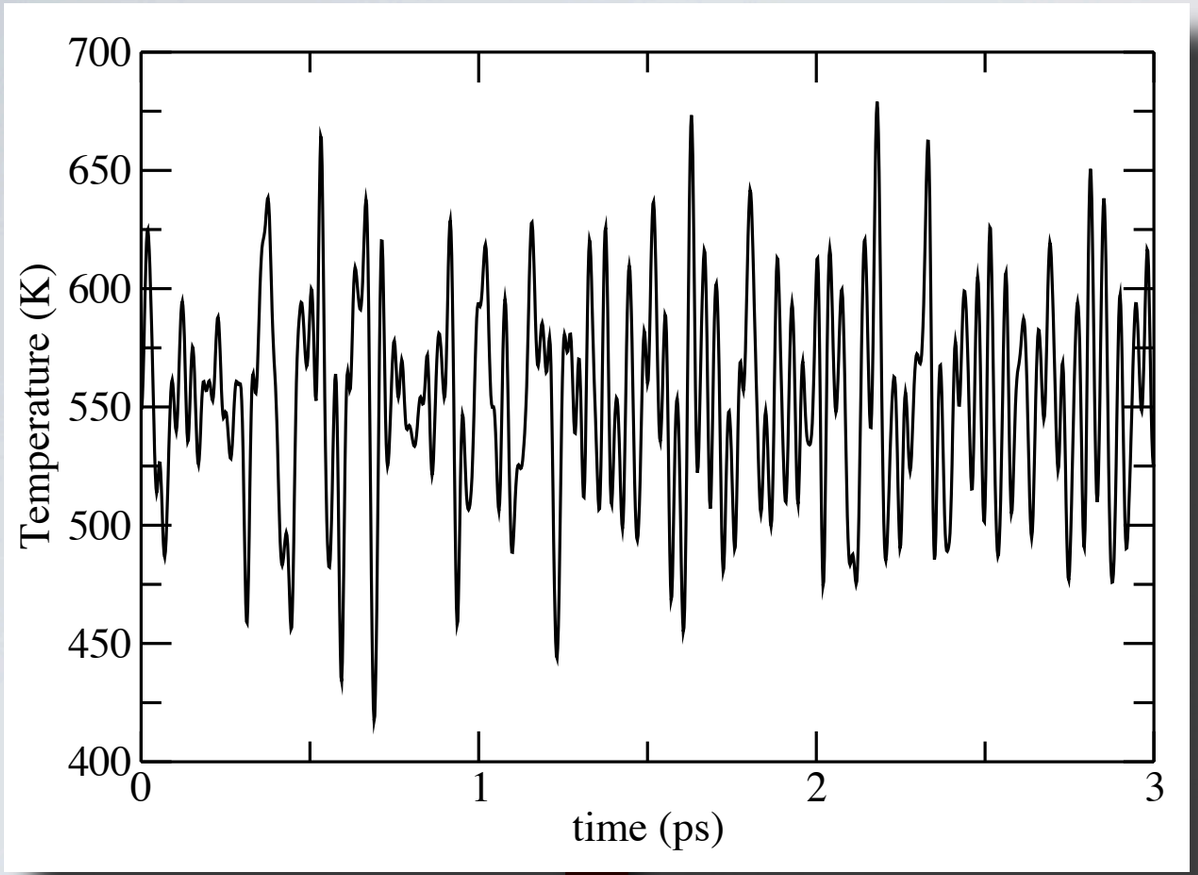
⇓ ⇓ ⇓

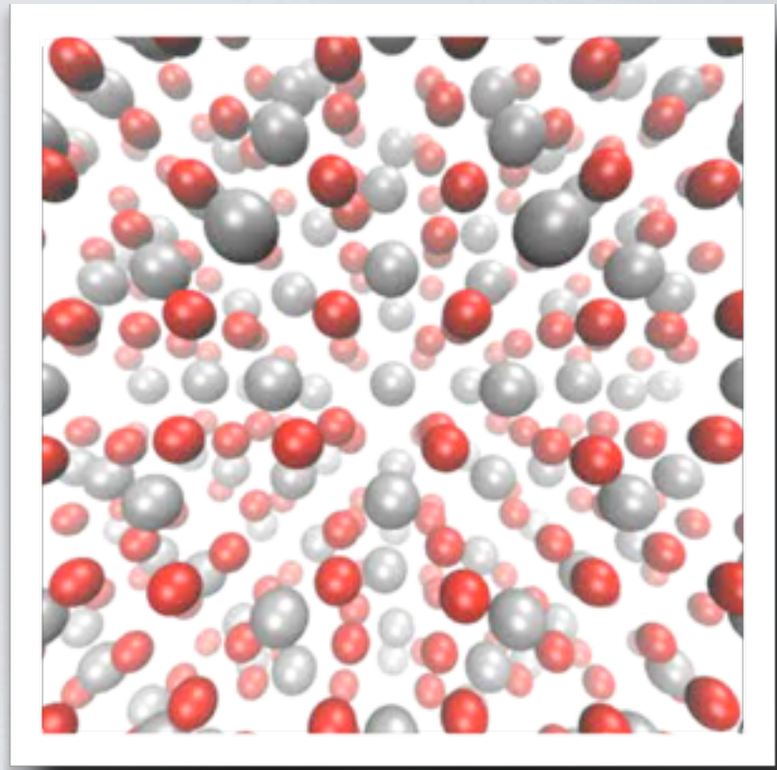
Information about **non-equilibrium processes**

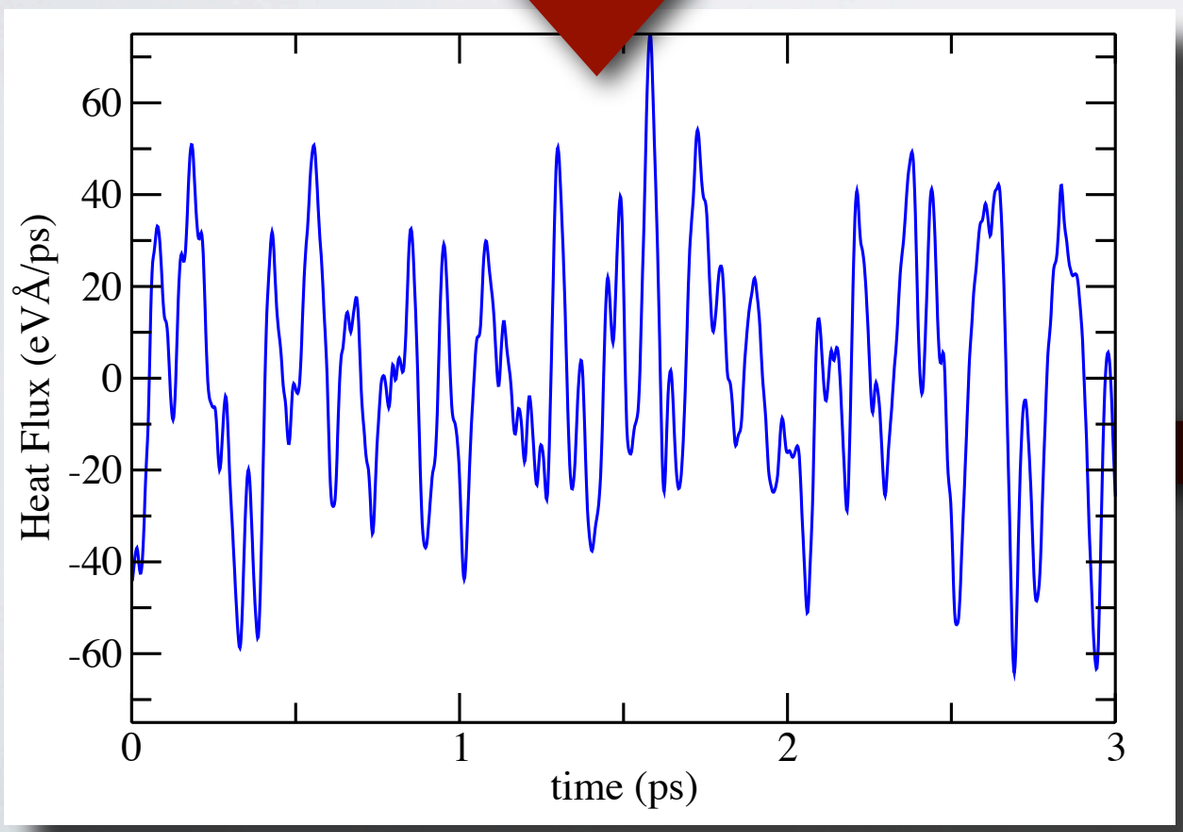
$$\kappa \sim \int_0^\infty d\tau \left\langle \mathbf{J}(0)\ \mathbf{J}(\tau) \right\rangle_{eq}$$

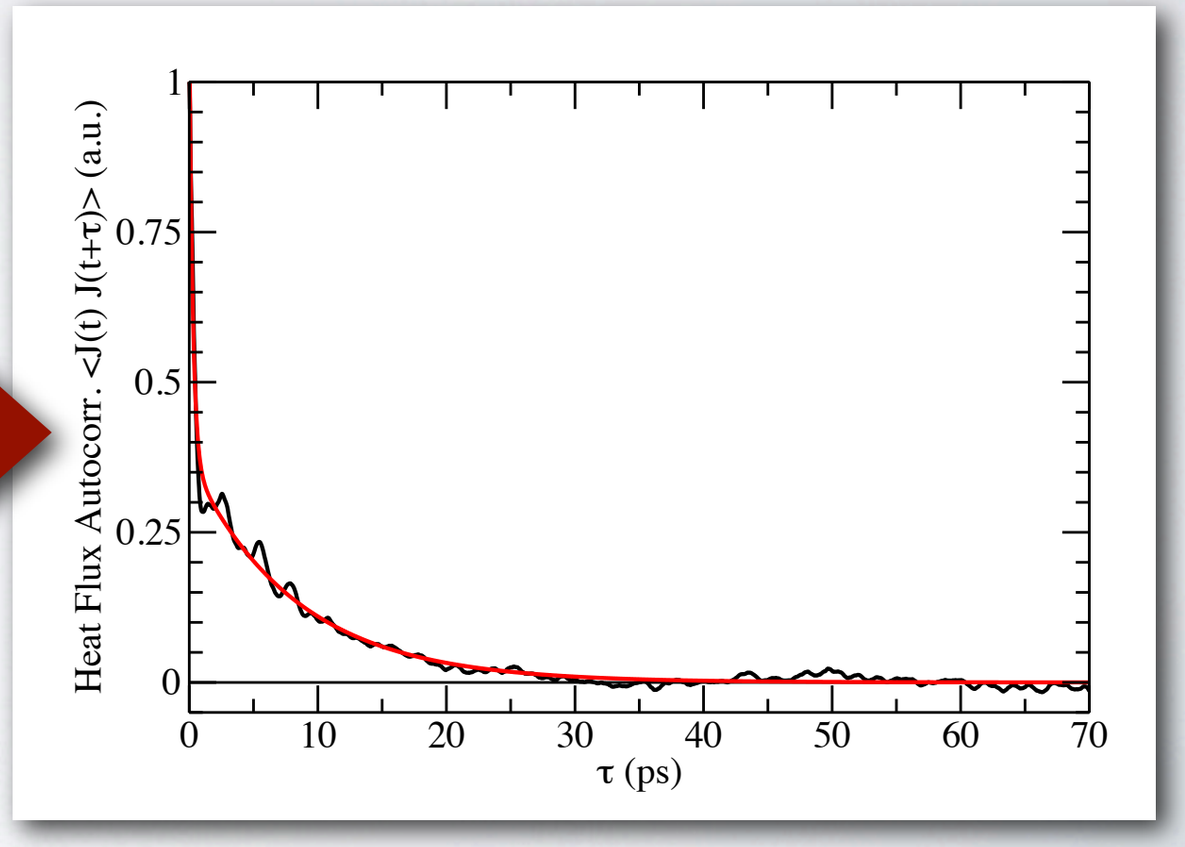
The **thermal conductivity** is related to the **autocorrelation function** of the **heat flux**




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




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


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

THE ATOMISTIC HEAT FLUX

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

$$\mathbf{J}(t) = \frac{d}{dt}\left(\sum_i \mathbf{r}_i(t)\,\varepsilon_i(t)\right)$$

$\mathbf{r}_i$ ⋯ Position of atom i

ε_i ⋯ Energy of atom i

Energy contribution ε_i of the **individual atoms** required!

⇒ Green-Kubo Method hitherto only used with classical potentials!

THE *AB INITIO* HEAT FLUX

$$\mathbf{J}(t) = \frac{d}{dt}\int \mathbf{r}\cdot\varepsilon(\mathbf{r},t)\,d\mathbf{r} \qquad \varepsilon(\mathbf{r},t) \quad \cdots \quad \text{Energy density}$$

Energy Density in Density Functional Theory:

B. Delley *et al.*, *Phys. Rev. B* **27**, 2132 (1983).
N. Chetty, and R. M. Martin, *Phys. Rev. B* **45**, 6074 (1992).

$$\int \varepsilon(\mathbf{r},\{\mathbf{R}\})\,d\mathbf{r} \quad \Leftrightarrow \quad \text{Harris-Foulkes Total Energy Functional}$$

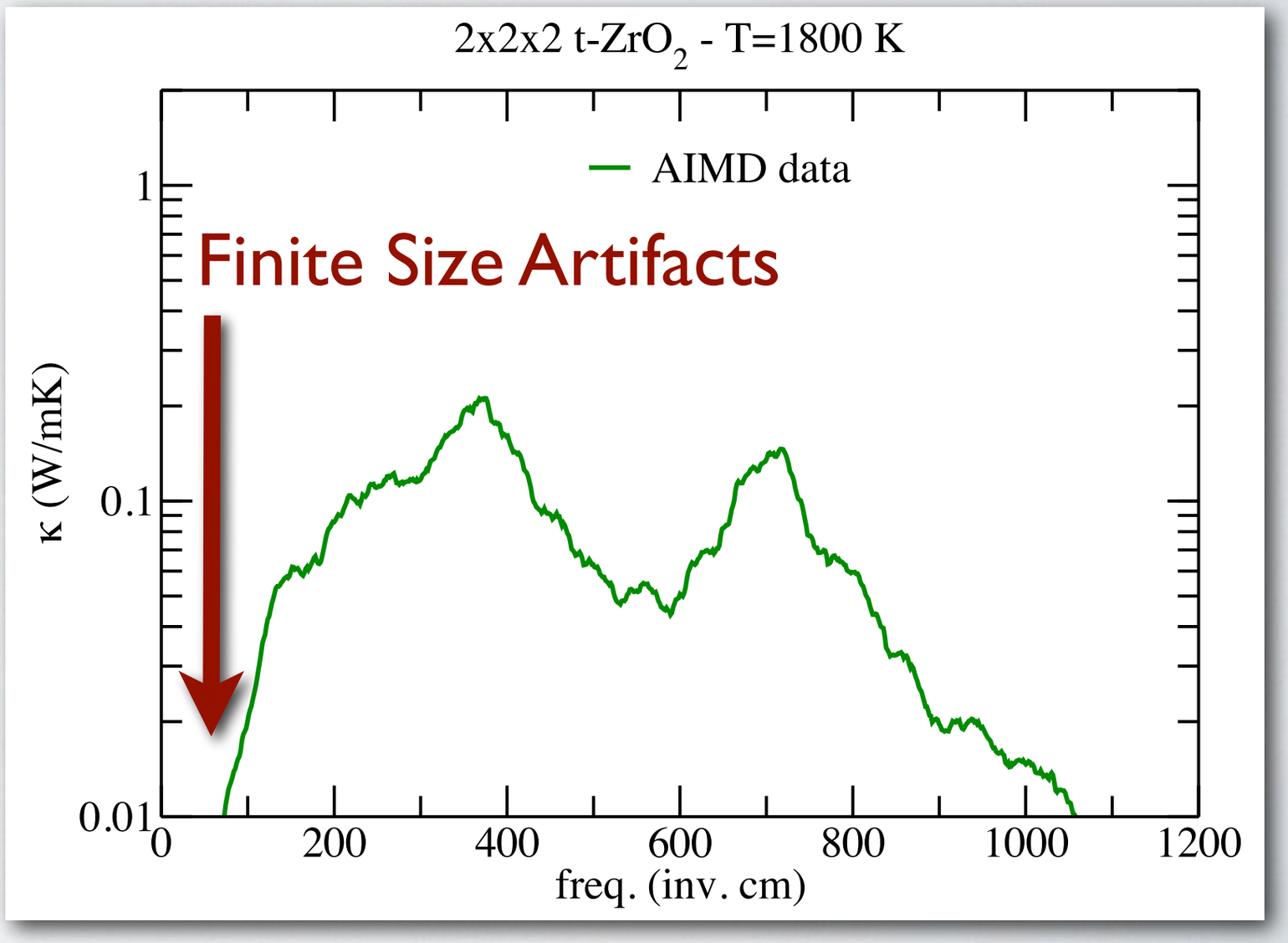
$$\begin{aligned}\varepsilon(\mathbf{r},\{\mathbf{R}\}) \quad = \quad & \sum_i T_i + \sum_l \varepsilon_l f_l^{occ} |\Psi_l(\mathbf{r})|^2 - n(\mathbf{r}) v_{xc}\left[n(\mathbf{r})\right] \\ & + E_{xc}\left[n(\mathbf{r})\right] - \frac{1}{2} n(\mathbf{r}) v_{es}(\mathbf{r}) + \frac{1}{2}\sum_{ij} \frac{Z_i Z_j}{|\mathbf{R}_i - \mathbf{R}_j|}\delta\left(\mathbf{r}-\mathbf{R}_i\right)\end{aligned}$$

ASSESSING THE THERMAL CONDUCTIVITY

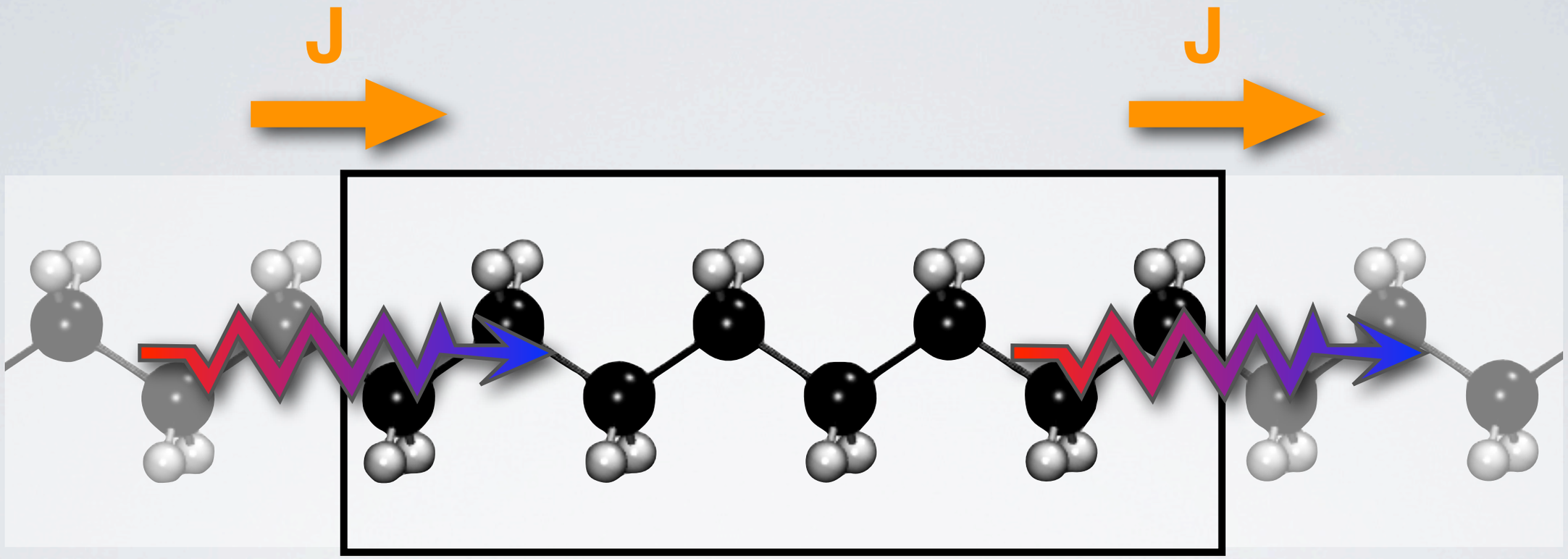
$$\kappa = \frac{V}{3k_B T^2} \int_0^\infty d\tau \, \langle \, \mathbf{J}(0) \, \mathbf{J}(\tau) \rangle_{eq} \quad \xrightarrow{\text{Fourier Trans.}} \quad \kappa = \frac{V}{3k_B T^2} \lim_{\omega \to 0} |\mathbf{J}(\omega)|^2$$

Finite Size Artifacts
artificially reduce the
thermal conductivity
at **low frequencies!**

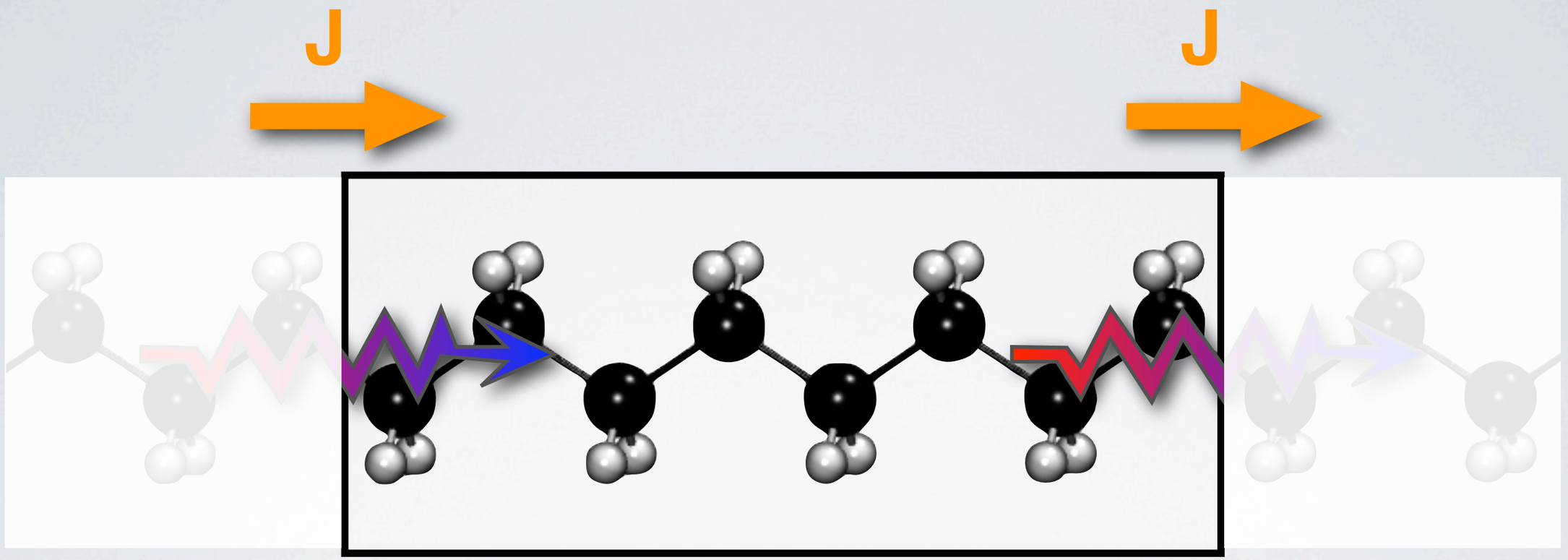
J. L. Feldman *et al.*,
Phys. Rev. B **48**, 12589 (1993).



PERIODIC BOUNDARY CONDITIONS



PERIODIC BOUNDARY CONDITIONS



$$\mathbf{J}(t) = \frac{d}{dt}\int \mathbf{r}\cdot\varepsilon(\mathbf{r},t)\,d\mathbf{r}$$

Small heat flux through boundaries
leads to **huge change in energy barycenter.**

ELIMINATING THE FINITE SIZE ARTIFACTS

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

Helfands' Heat Flux

Hardys' Heat Flux

$$\mathbf{J}(t) = \frac{d}{dt}\int \mathbf{r}\cdot\varepsilon(\mathbf{r},t)\,d\mathbf{r} = \int \mathbf{v}\cdot\varepsilon(\mathbf{r},t)\,d\mathbf{r} + \int \mathbf{r}\cdot\frac{d\varepsilon(\mathbf{r},t)}{dt}\,d\mathbf{r}$$

Convective Heat Flux

Virial Heat Flux

$$\mathbf{J}_v = \int \mathbf{r}\cdot\frac{d\varepsilon(\mathbf{r},t)}{dt}\,d\mathbf{r} = \int \mathbf{v}\cdot\sigma(\mathbf{r})\,d\mathbf{r}$$

σ(r) ... Stress density

ELIMINATING THE FINITE SIZE ARTIFACTS

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

$\mathbf{J}(t)$ ... $\frac{t)}{} d\mathbf{r}$

Formulas for analytical stress

F. Knuth, FHI

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

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

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

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

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

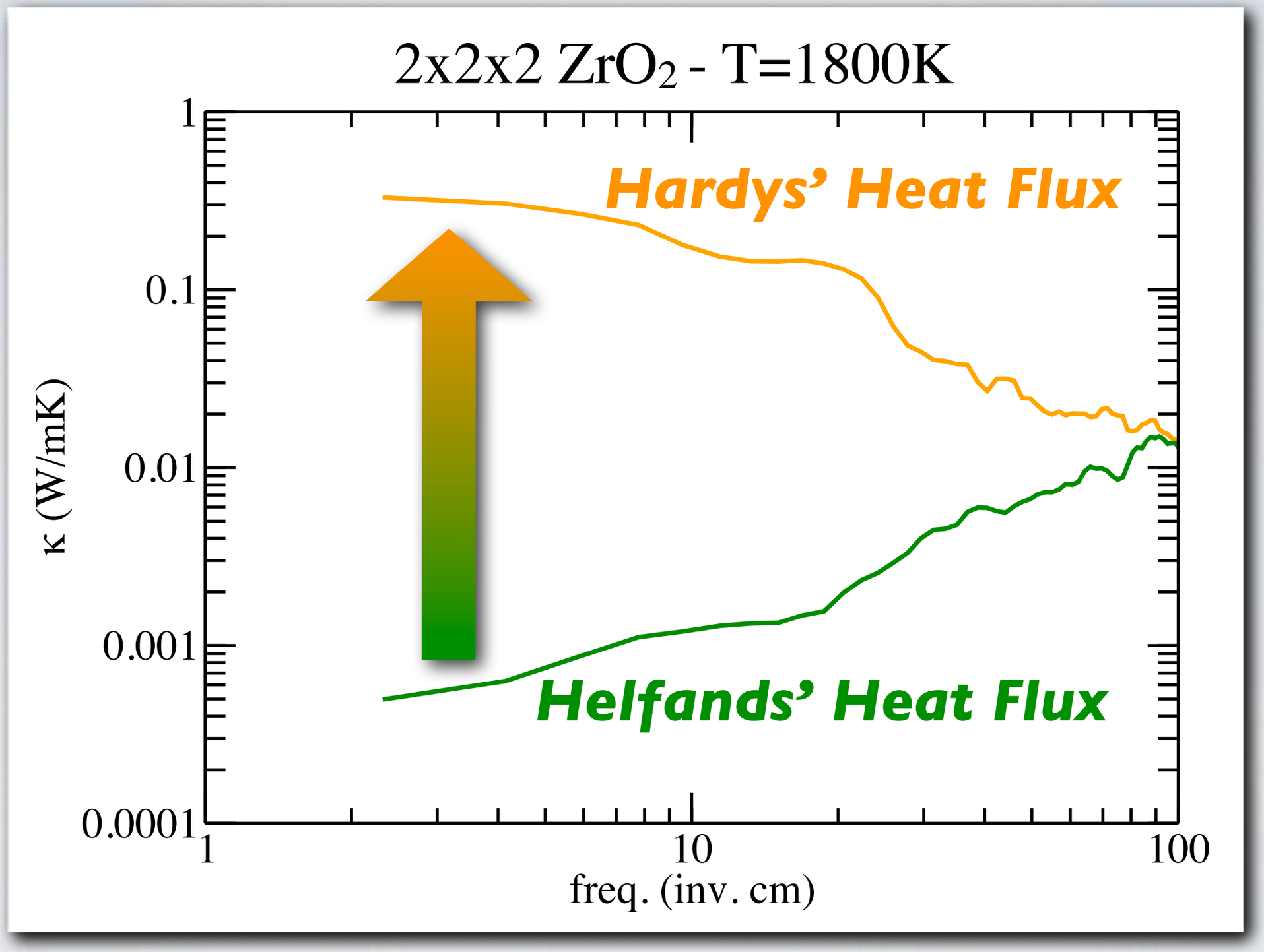
$$\sigma_{ij}^{\mathrm{kin}} = \frac{1}{V} \sum_{k} \sum_{\alpha, l(\alpha)} \sum_{\beta, m(\beta)} f_k c_{kl} c_{km} \int_{\mathrm{UC}} \mathrm{d}\mathbf{r}\, \varphi_l(\mathbf{r} - \mathbf{R}_\alpha)(\mathbf{r} - \mathbf{R}_\alpha)_j \left[\frac{\partial}{\partial r_i} \frac{\partial}{\partial r_j}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

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

$\mathbf{J}$ ... $(\quad)$ ...sity

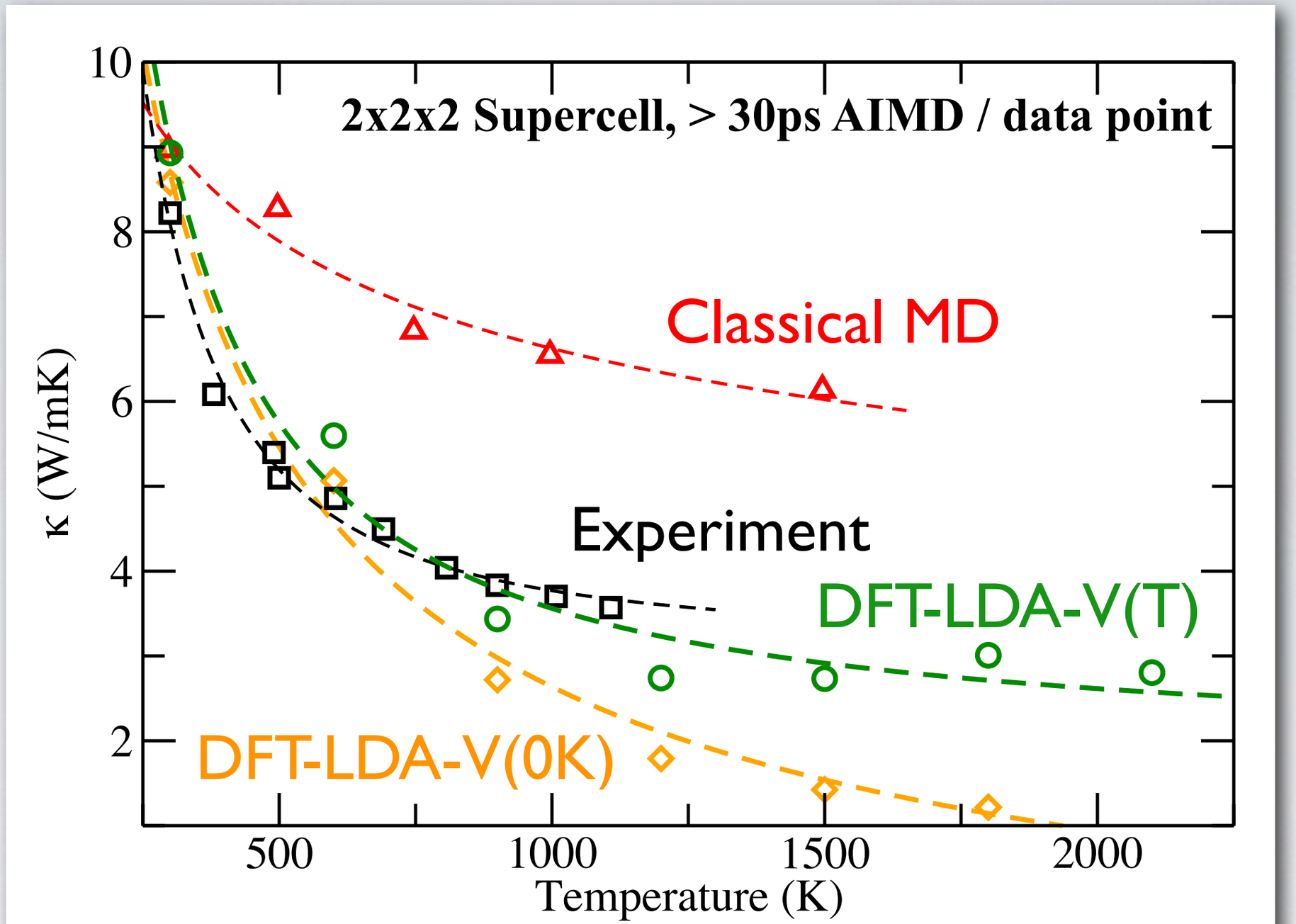
ELIMINATING THE FINITE SIZE ARTIFACTS

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



FINITE SIZE ARTIFACTS ELIMINATED!

APPLICATION TO ZIRCONIA



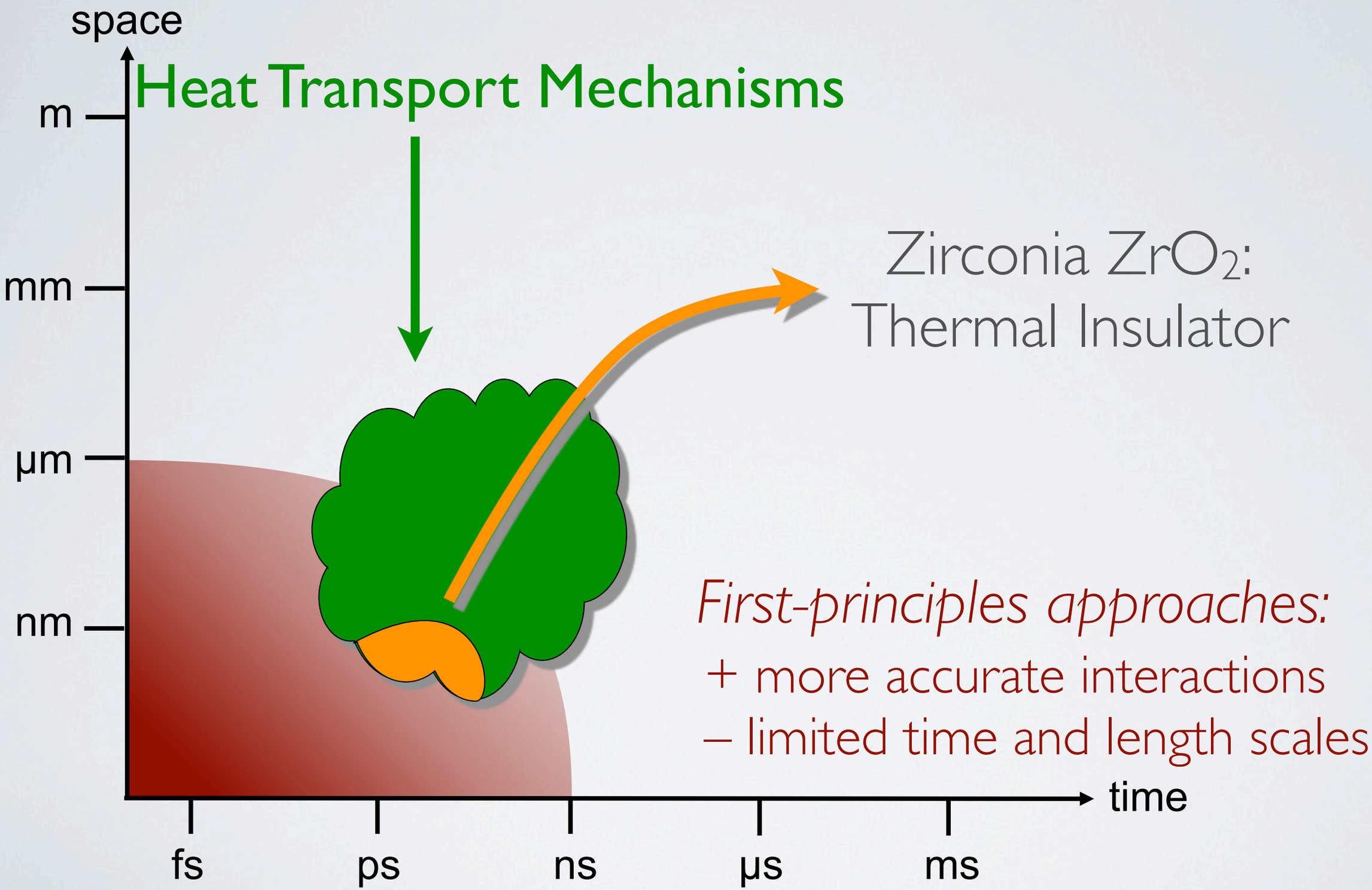
Experiment:

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).

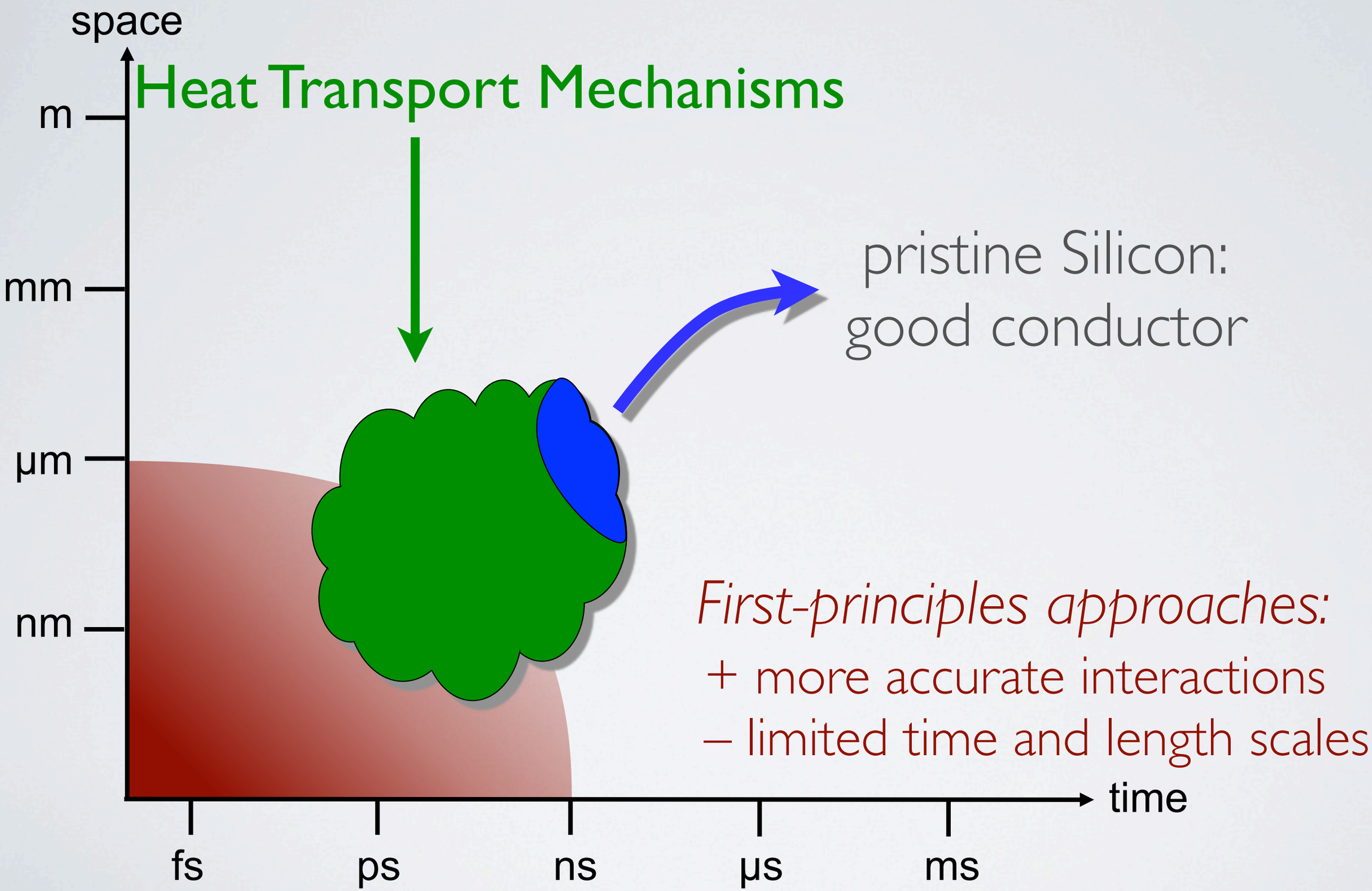
Classical MD:

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

TIME AND LENGTH SCALES



TIME AND LENGTH SCALES



FIRST-PRINCIPLES APPROACHES

	Order of interaction	Validity & Applicability	Finite Size Effects	Disorder
Boltzmann-Transport Eq.	~□(r^3)	low T	Minute	Parameter
Non-Equilib. MD	Full	all T	Huge	as in supercell
Laser-flash MD	Full	low T	Medium-Large	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**!