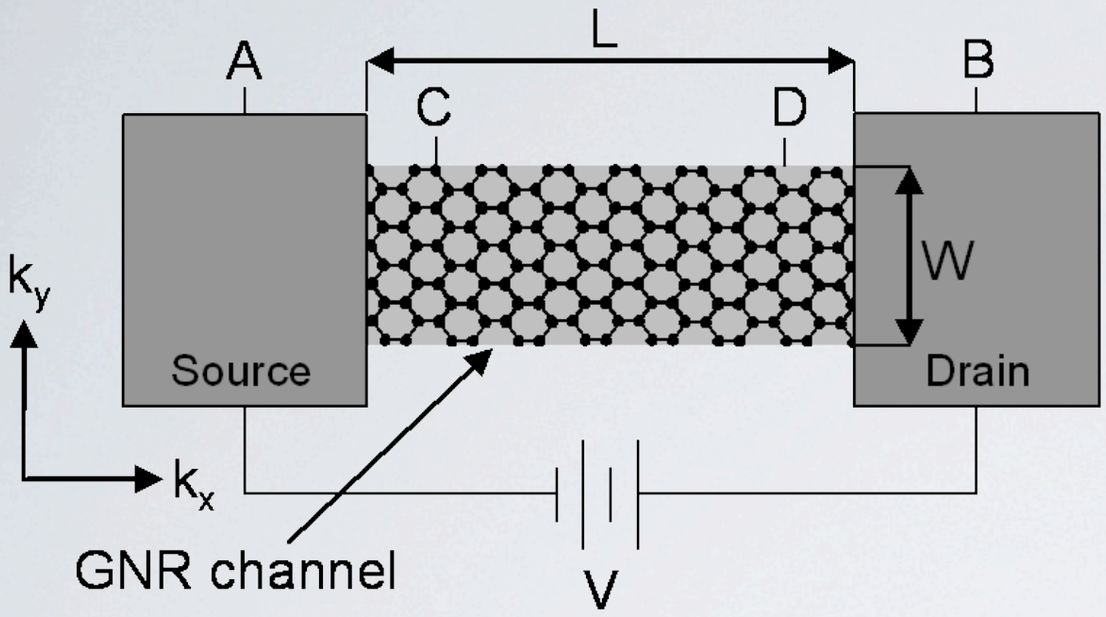
Hands-On Tutorial Workshop, August 12th 2013

Charge and Heat Transport in Solids

Christian Carbogno

Fritz-Haber-Institut
der Max-Planck-Gesellschaft,
Berlin - Germany

Microscopic



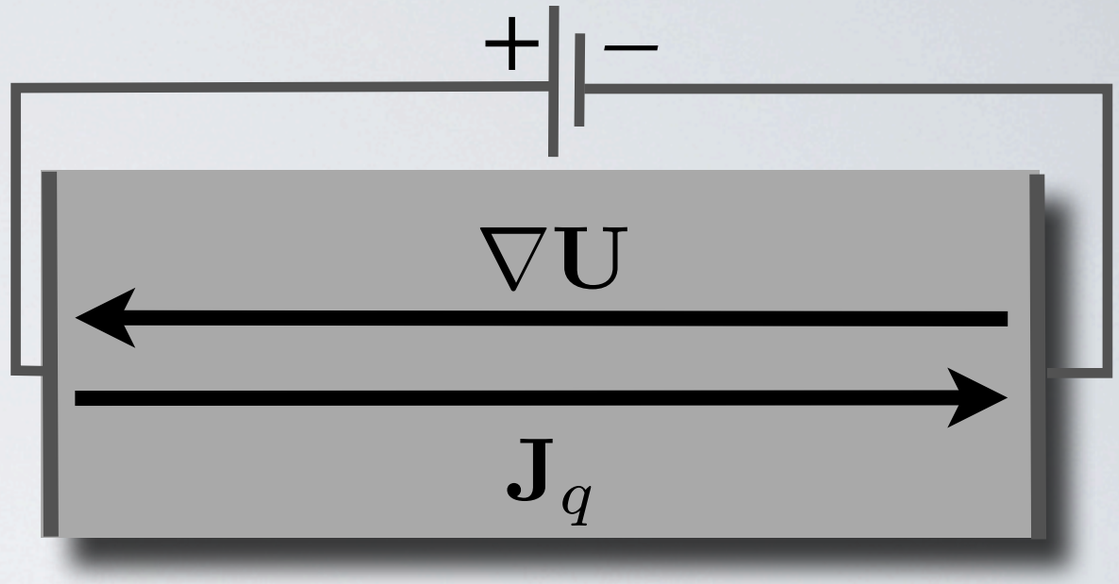
Length-scale: L < 1μm

Potential: $U_1 - U_2 \sim 1\,V$

Field: $\nabla U \gg 10^{-6}\,V/Å$

Flux: $J \sim G(U_1 - U_2)$

Macroscopic



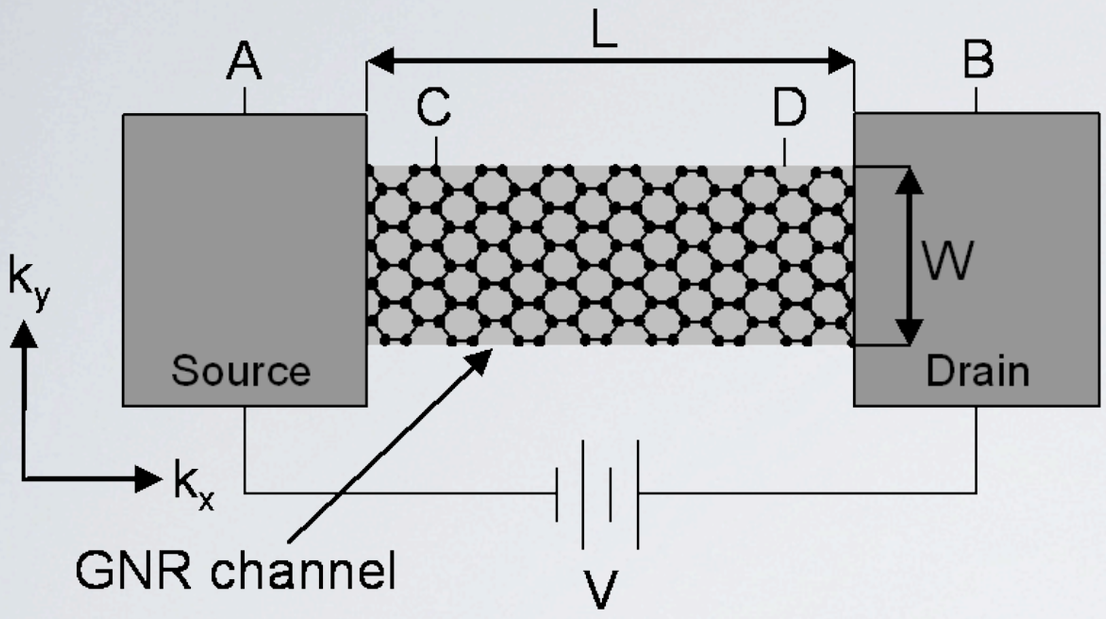
Length-scale: L > 1mm

Potential: $U_1 - U_2 \sim 100V$

Field: $\nabla U \ll 10^{-6}\,V/Å$

local non-equilibrium

Microscopic



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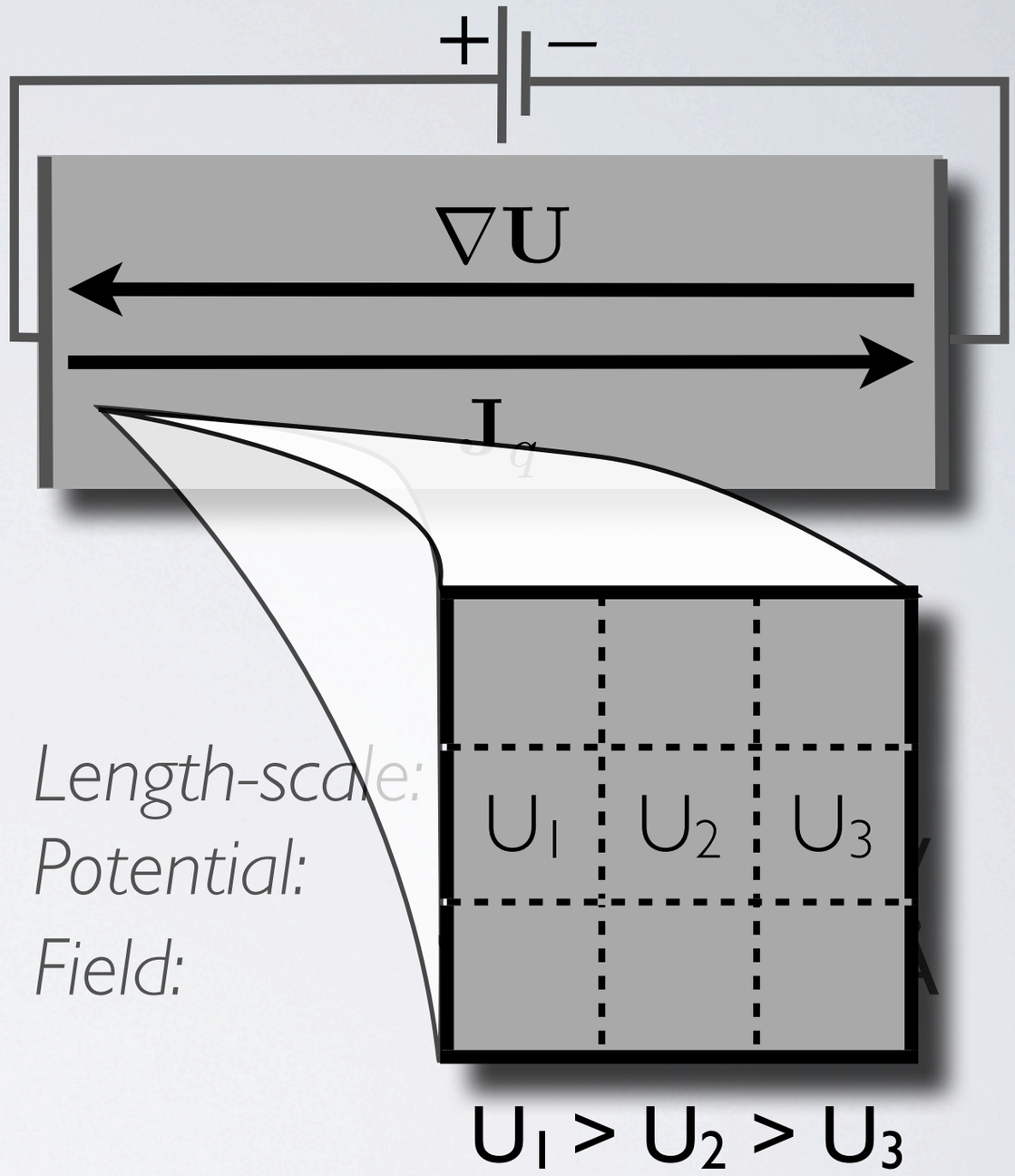
Flux: $J \sim G(U_1 - U_2)$

local non-equilibrium

Macroscopic



Length-scale:

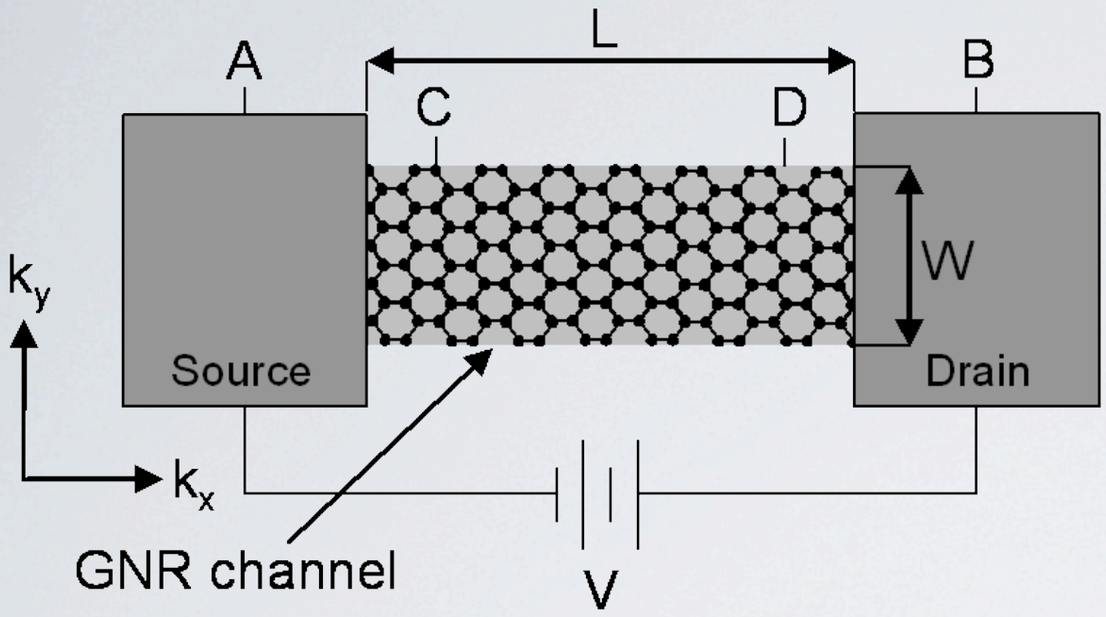
Potential:

Field:

Global non-equilibrium,
but local equilibrium!

L. Onsager, *Phys. Rev.* **37**, 405 (1931).

Microscopic



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local non-equilibrium

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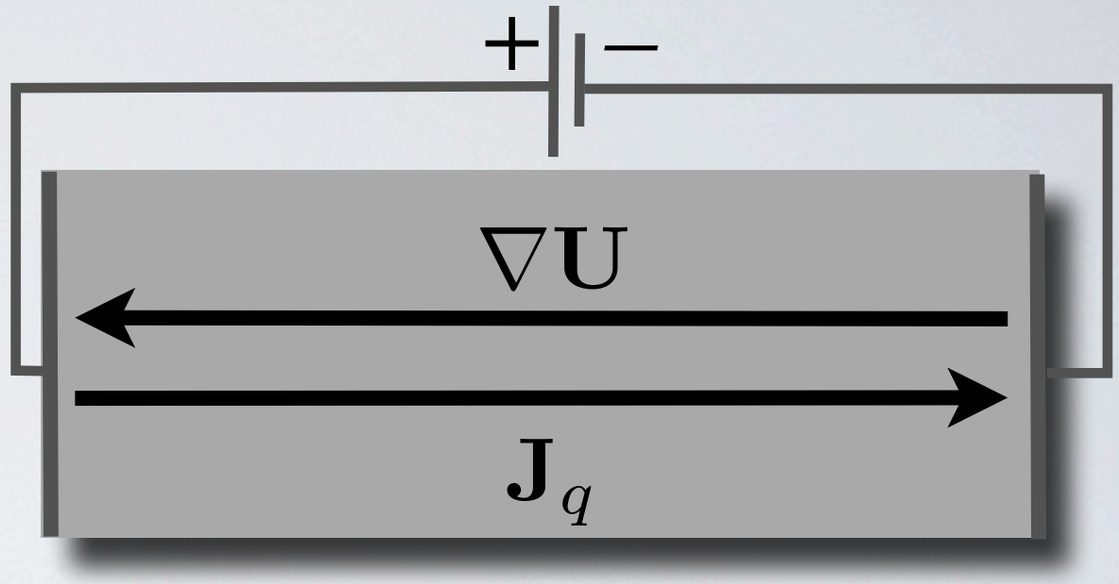


Length-scale: L > 1mm

Potential: $U_1 - U_2 \sim 100V$

Field: $\nabla U \ll 10^{-6}\,V/Å$

Flux: $j(r) \sim \sigma \nabla U(r)$

local equilibrium

L. Onsager, *Phys. Rev.* **37**, 405 (1931).

BASICS OF MACROSCOPIC TRANSPORT

The Continuity Equation:
(valid for any conserved quantity ρ)

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

Proportionality of flux and gradient:

$$\mathbf{j} = -\lambda \nabla \rho$$

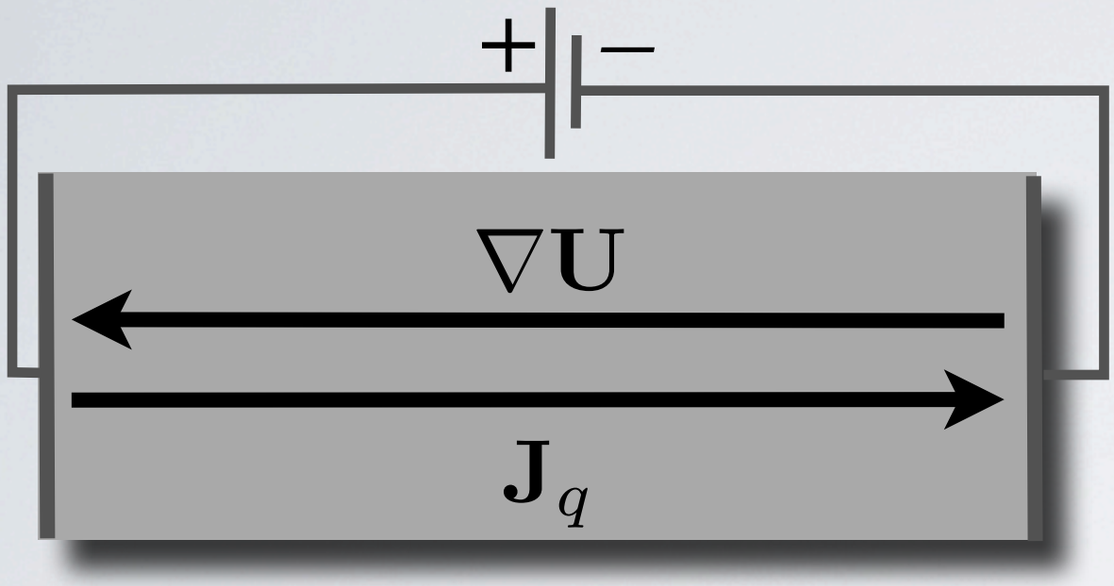
The Diffusion Equation:
(e.g. mass, heat & charge transport)

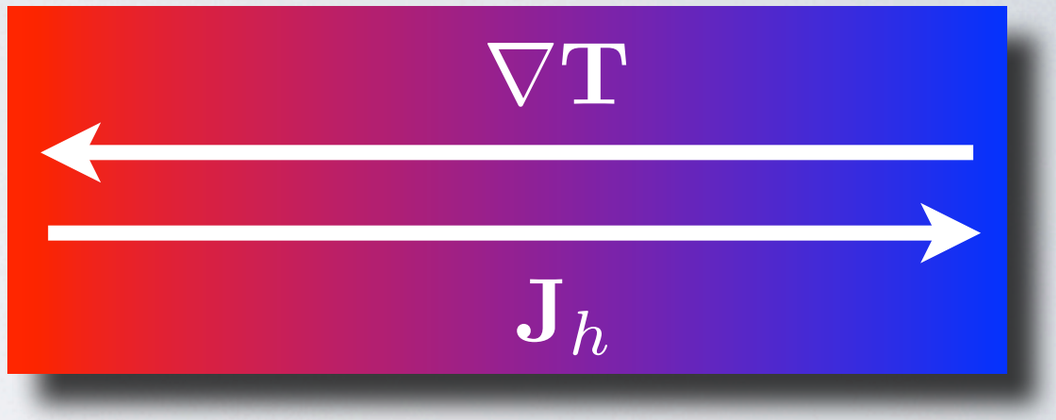
$$\frac{\partial \rho(\mathbf{r}, t)}{\partial t} = \lambda \nabla^2 \rho(\mathbf{r}, t)$$

Analytic Solution:

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

MACROSCOPIC TRANSPORT





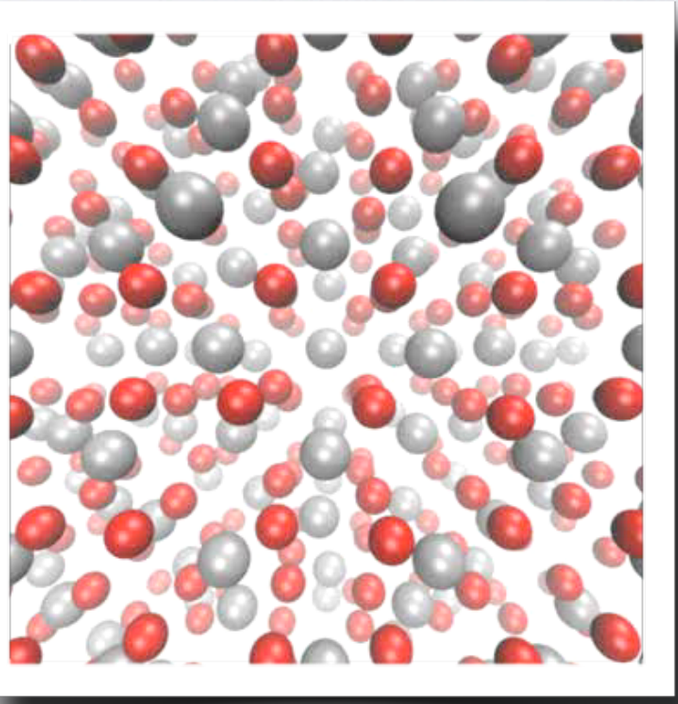
Ohm's Law:

$$\mathbf{J}_q = -\sigma \, \nabla \mathbf{U} = \sigma \, \mathbf{E}$$

Fourier's Law:

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

Can we compute **transport coefficients** from the **electronic & nuclear dynamics**?

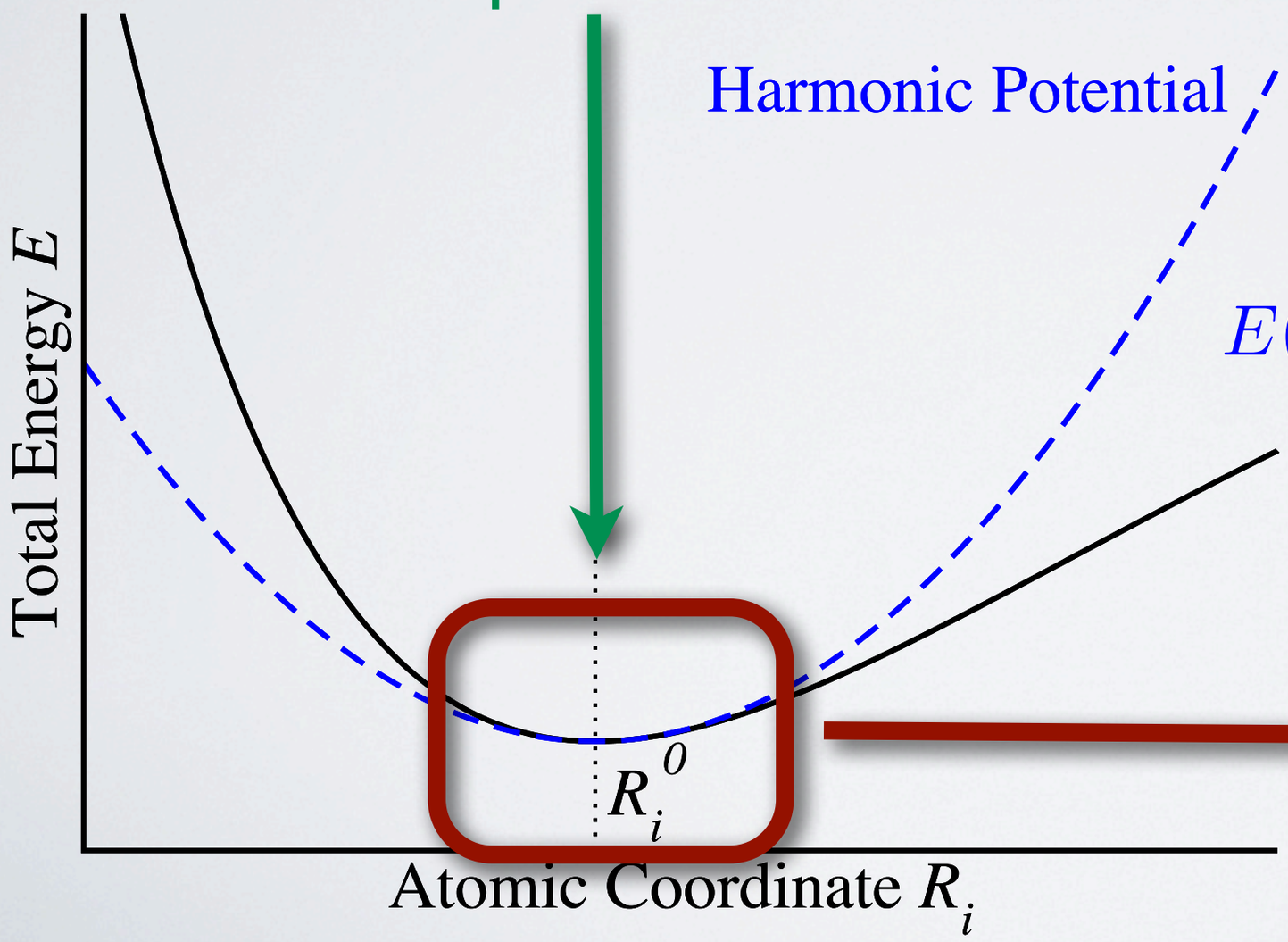


I. THE HARMONIC CRYSTAL

THE INTERATOMIC INTERACTION

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

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



Taylor expansion:

$$E \approx$$

$$E(\mathbf{R}_0) + \frac{1}{2}\sum_{i,j} \Phi^{i,j}\left(\Delta\mathbf{R}_i\right)\left(\Delta\mathbf{R}_j\right)$$

Only valid for small elongations!

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

Forces vanish at $\mathbf{R_0}$

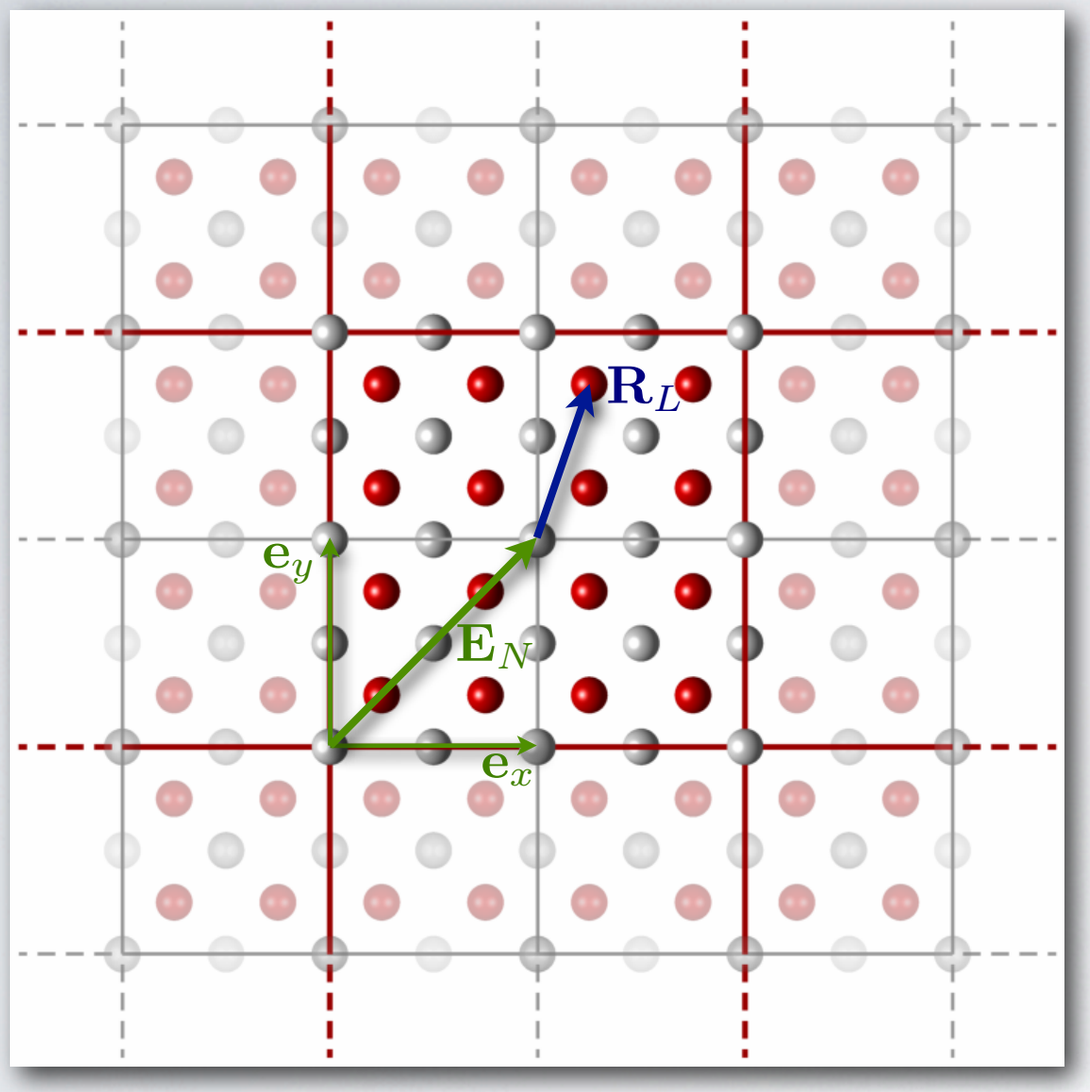
Hessian Φ_{ij}

Determine ***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).

THE HARMONIC SOLID



Periodic Boundary Conditions
⇒ Reciprocal Space **q**

$$D_{ij}(\mathbf{q}) = \sum_{\mathbf{E}_N} \frac{e^{i(\mathbf{q}\cdot\mathbf{E}_N)}}{\sqrt{M_i M_j}} \Phi_{ij}$$

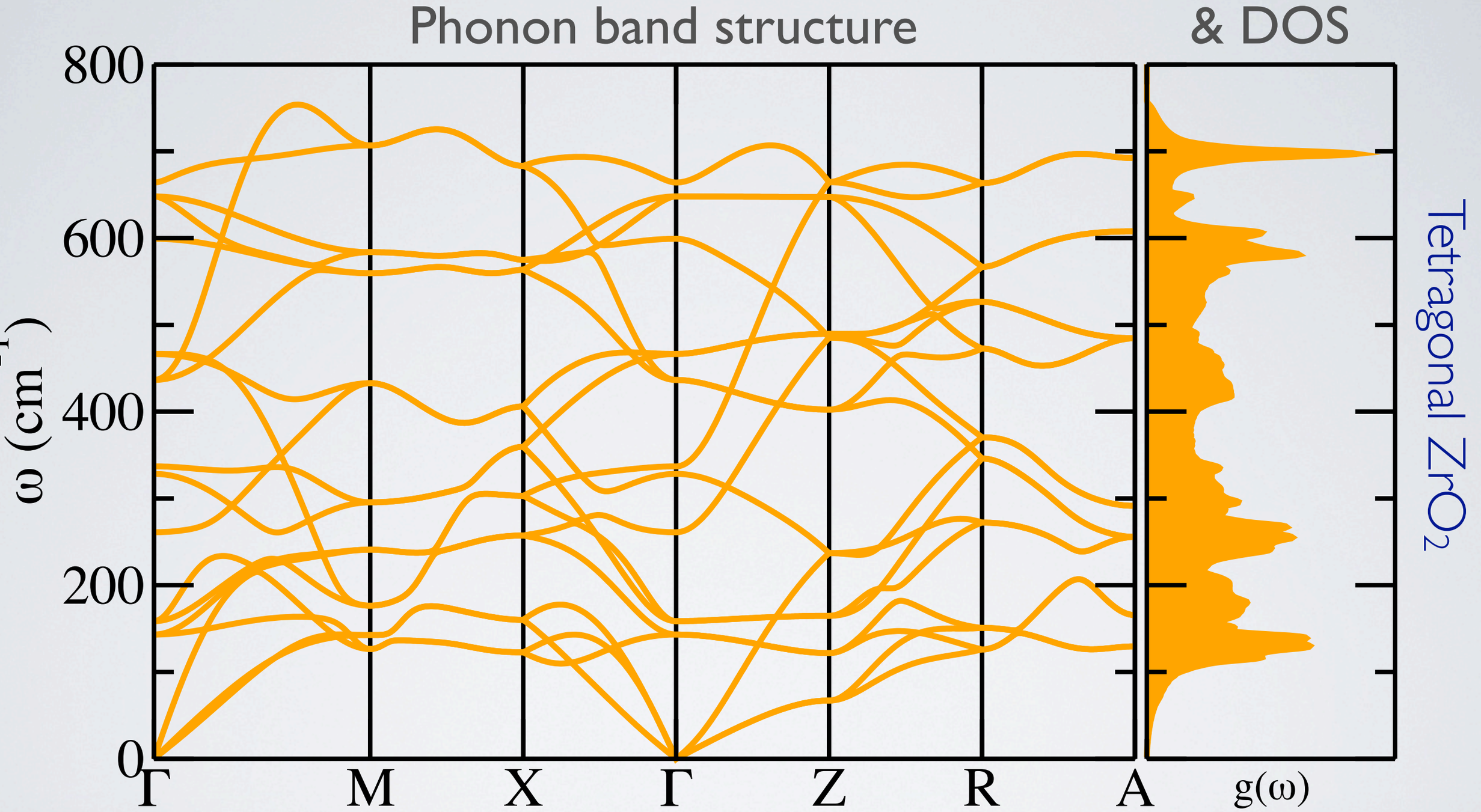
Eigenvalue problem:

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

Real space: Superposition of *harmonic oscillations*

$$\mathbf{R} \quad = \quad R_0 + \sum_s A_s \ \frac{\cos\left(\phi_s + \omega_s t\right)}{\sqrt{M_i}} \cdot \nu_s$$

THE HARMONIC APPROXIMATION



Group velocity (speed of sound):

$$c_s = \frac{\partial \omega(\mathbf{q})}{\partial \mathbf{q}}$$

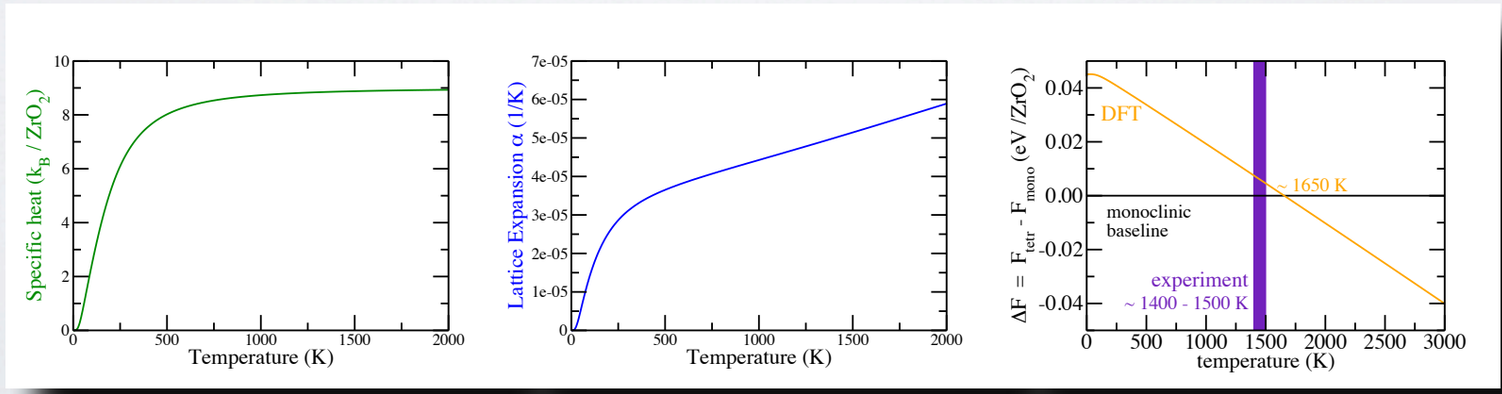
THE HARMONIC FREE ENERGY

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

Static Equilibrium Energy

Zero-point vibration

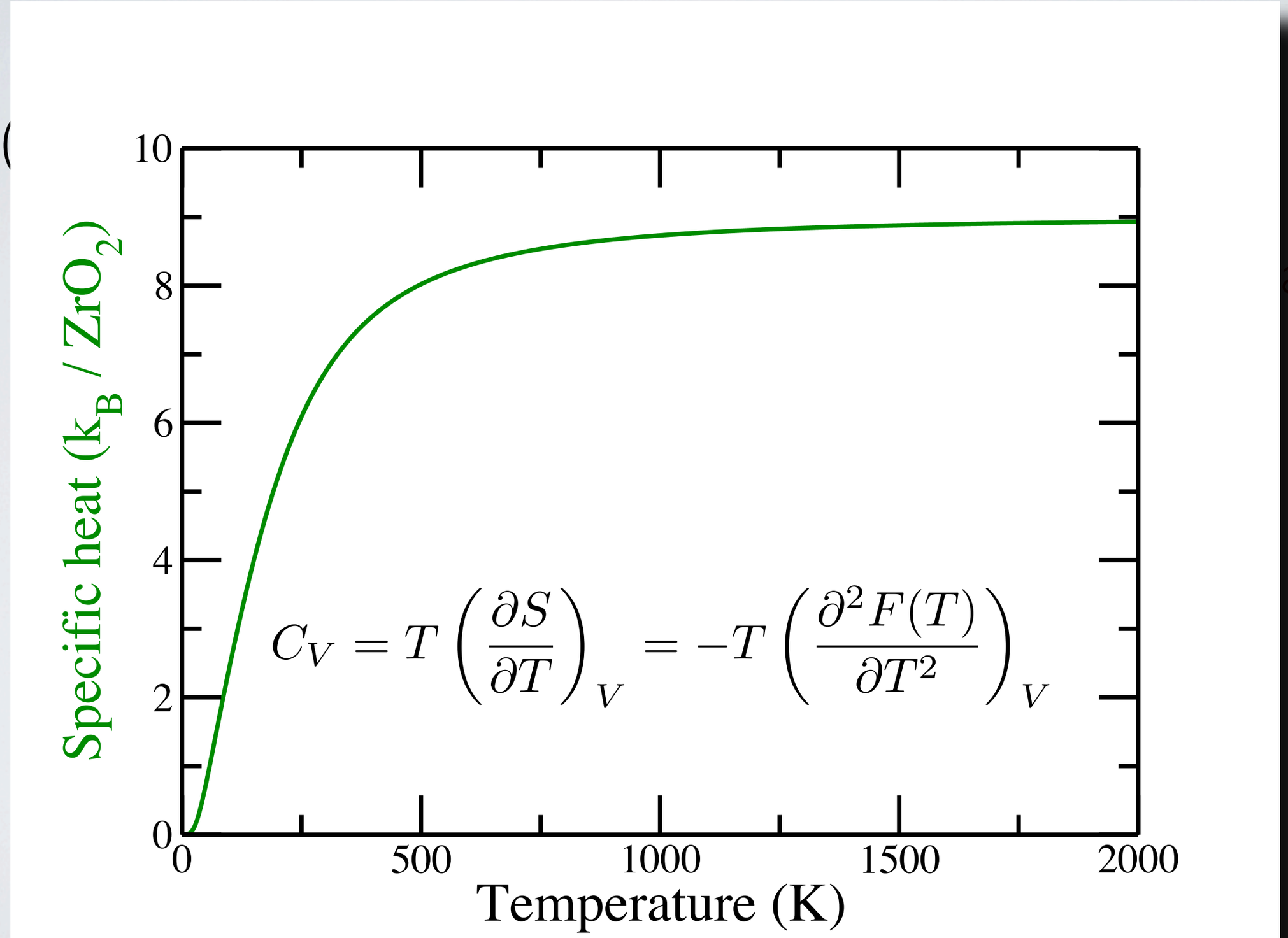
Thermally induced vibrations



THE HARMONIC FREE ENERGY

$F^{ha}($ Energy

ation

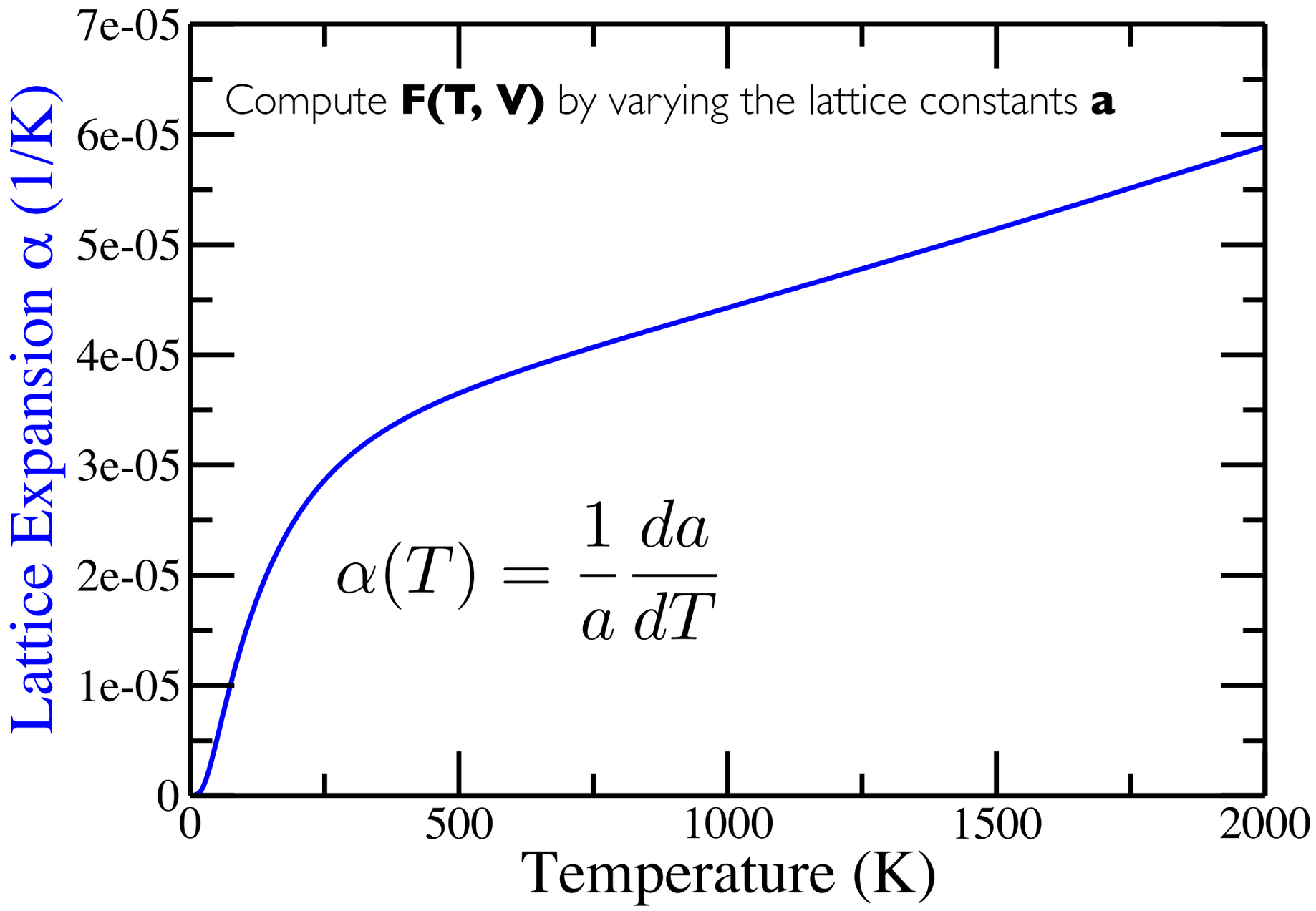


THE HARMONIC FREE ENERGY

$F^{ha}($ Energy

ation

Quasi-harmonic approximation:

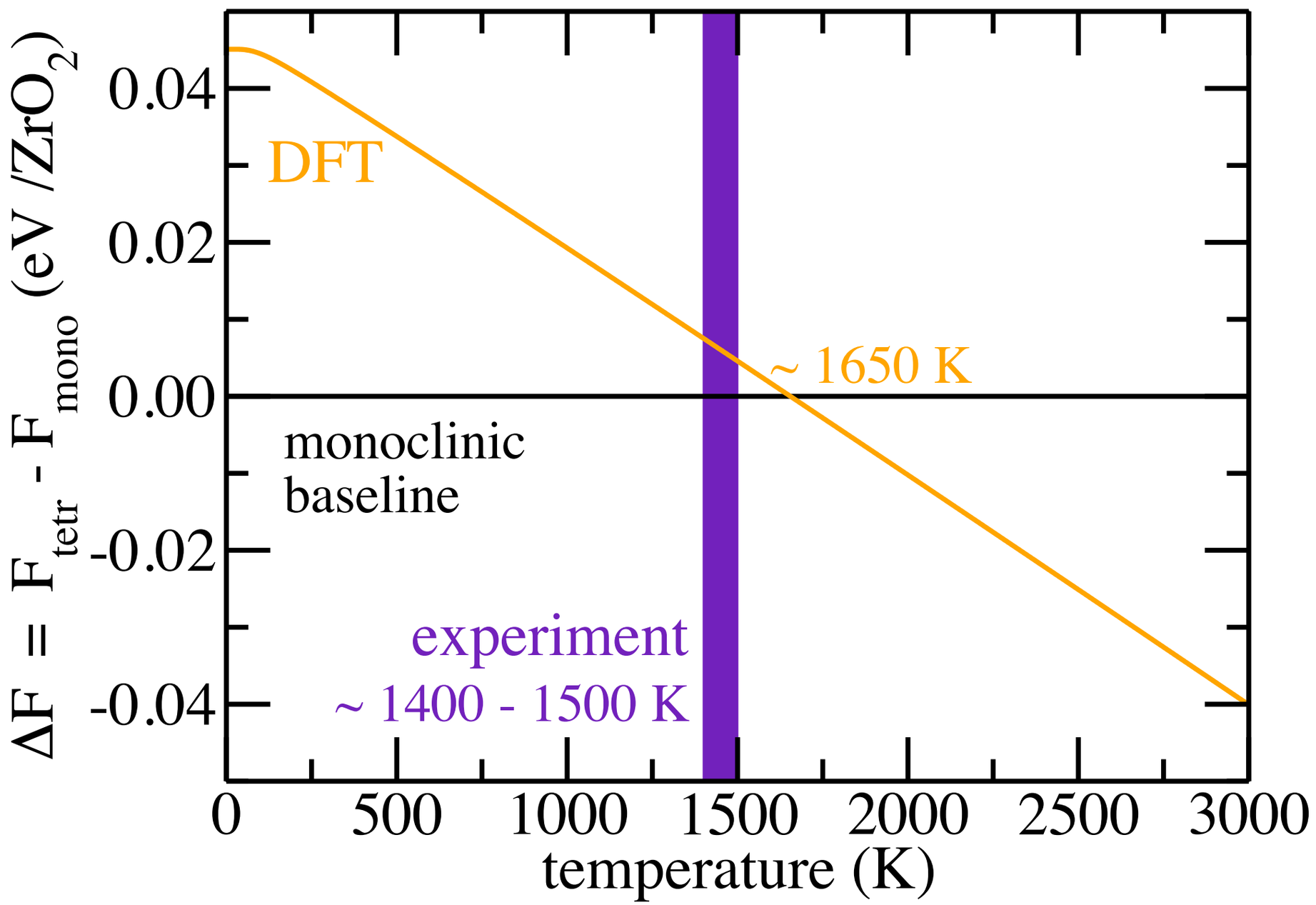


THE HARMONIC FREE ENERGY

$F^{ha}($ Energy

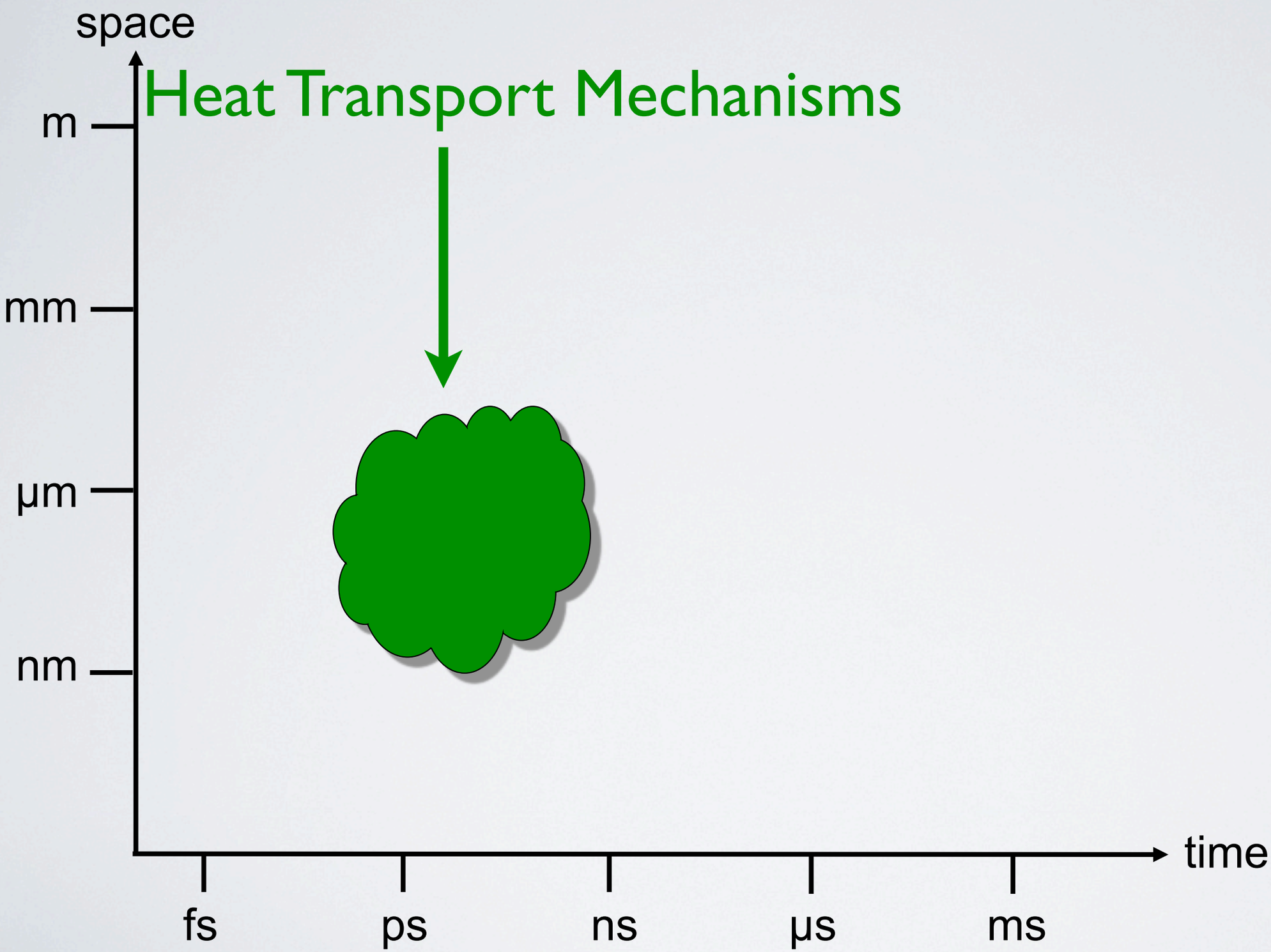
ation

Harmonic free energy difference:

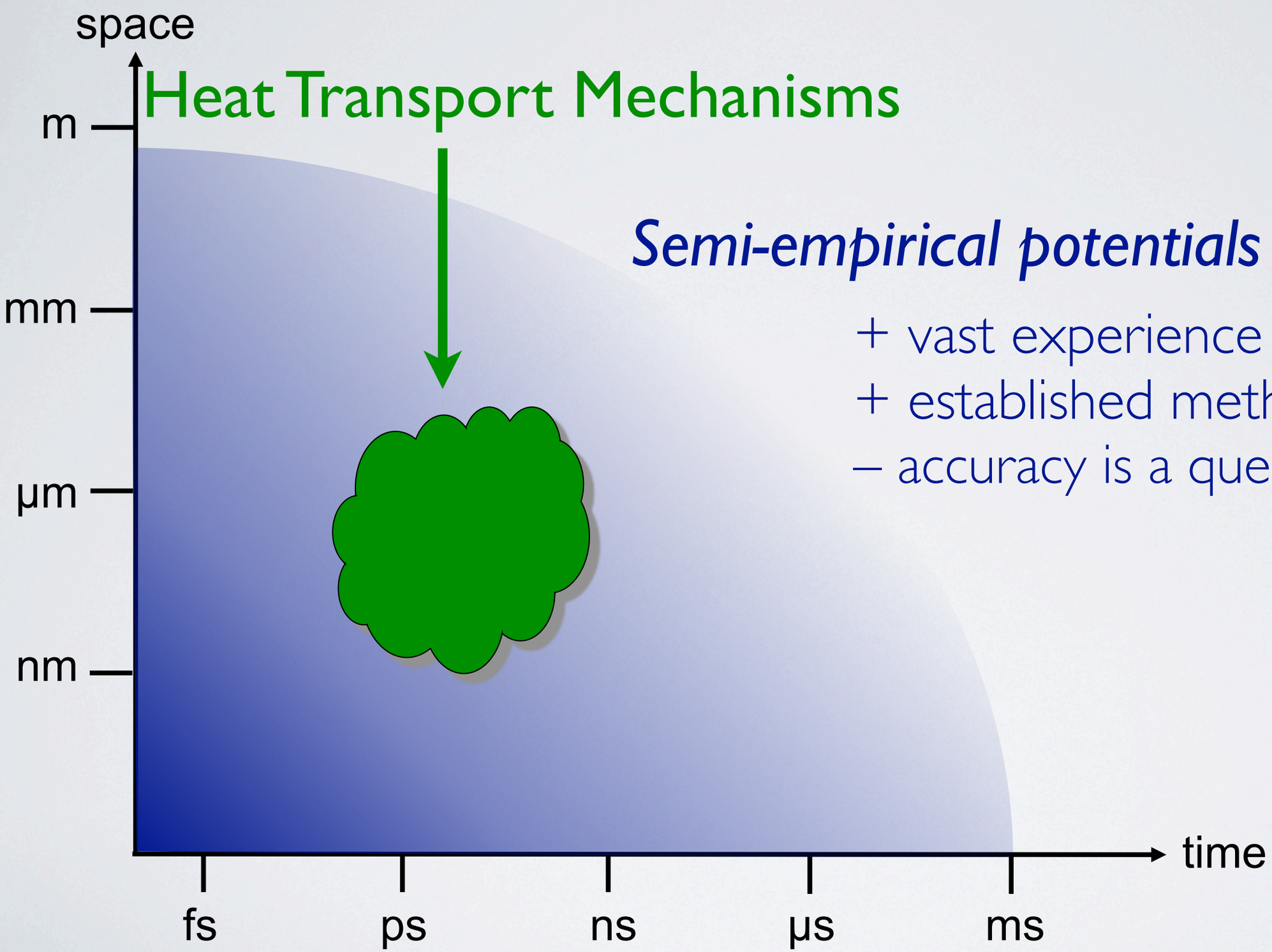


II. HEAT TRANSPORT

TIME AND LENGTH SCALES



TIME AND LENGTH SCALES



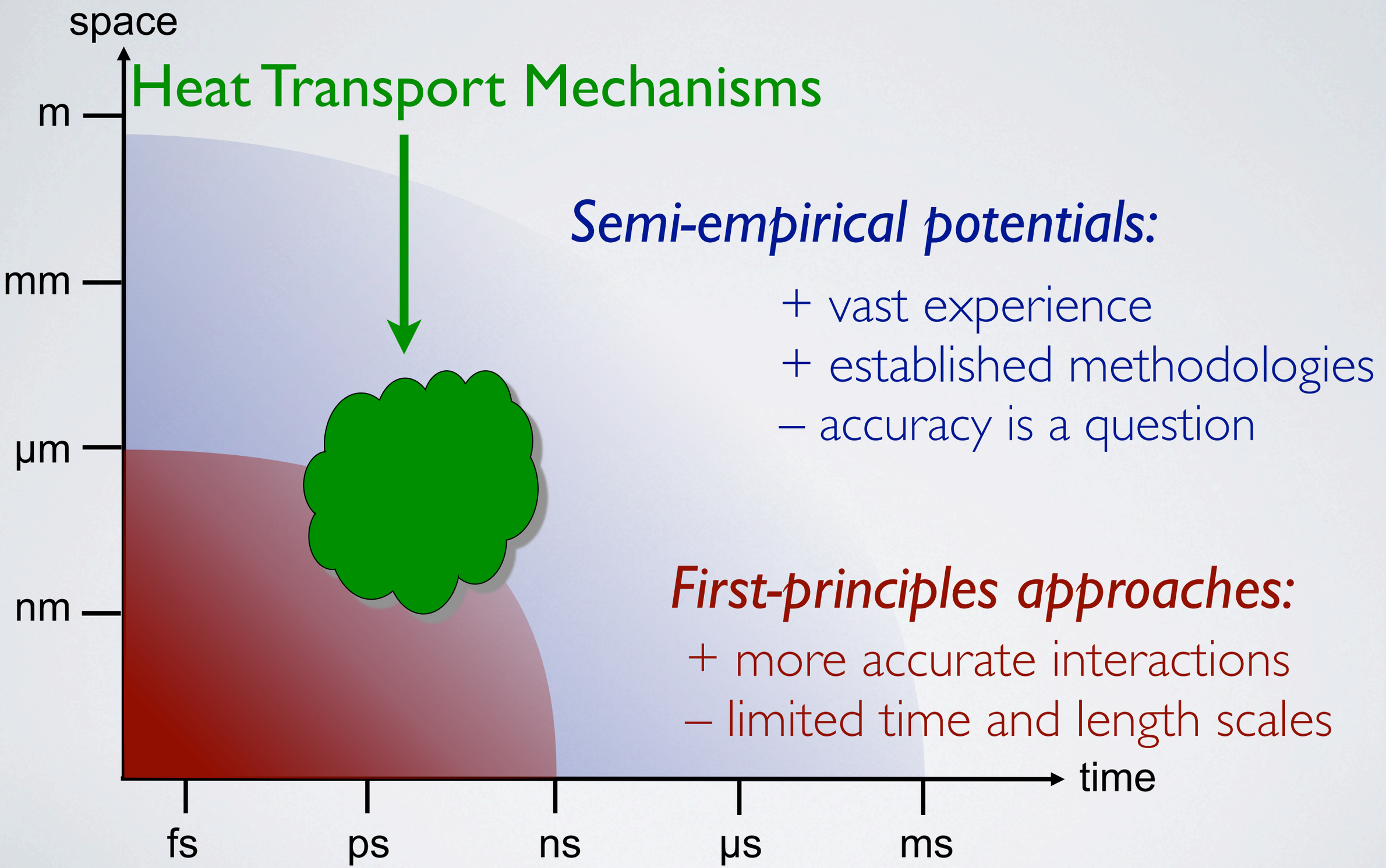
Semi-empirical potentials

\+ 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:

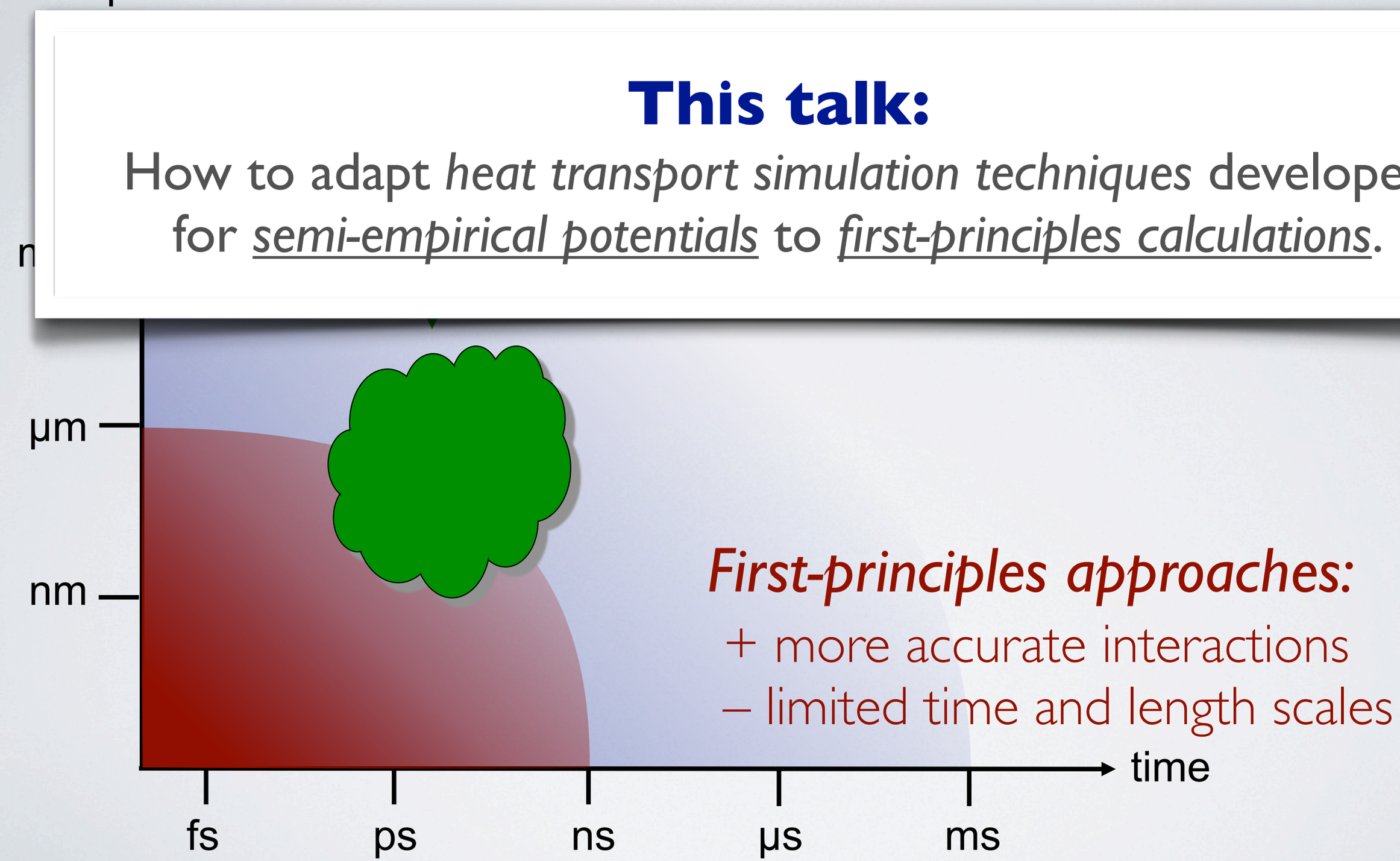
\+ more accurate interactions

– limited time and length scales

TIME AND LENGTH SCALES

This talk:

How to adapt *heat transport simulation techniques* developed for *semi-empirical potentials* to *first-principles calculations*.



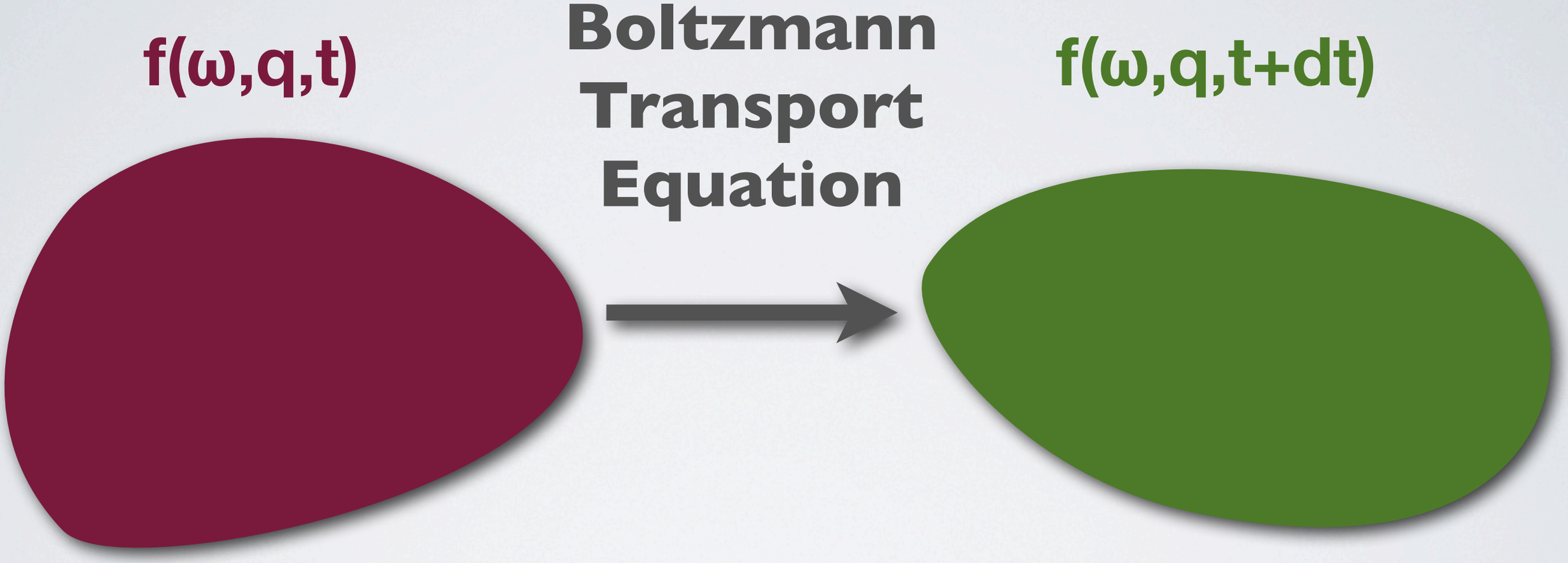
First-principles approaches:

\+ 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

$$\kappa \sim \sum_s c_s^2 \; \omega_s^2 \; n_s(n_s+1) \; \tau_s$$

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

Harmonic phonon theory

?

Phonon Lifetimes from First Principles

- from **Density Functional Perturbation Theory**
  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**, 1441112 (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**!

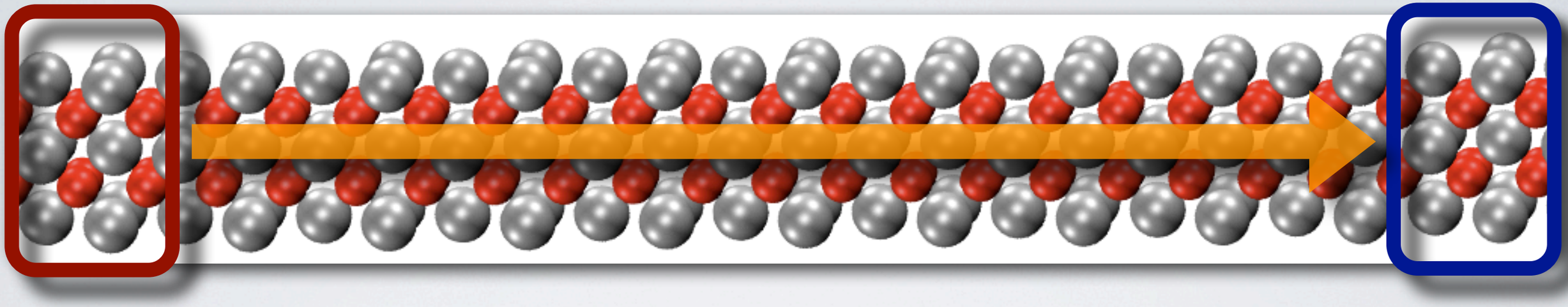
FIRST-PRINCIPLES APPROACHES

	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).



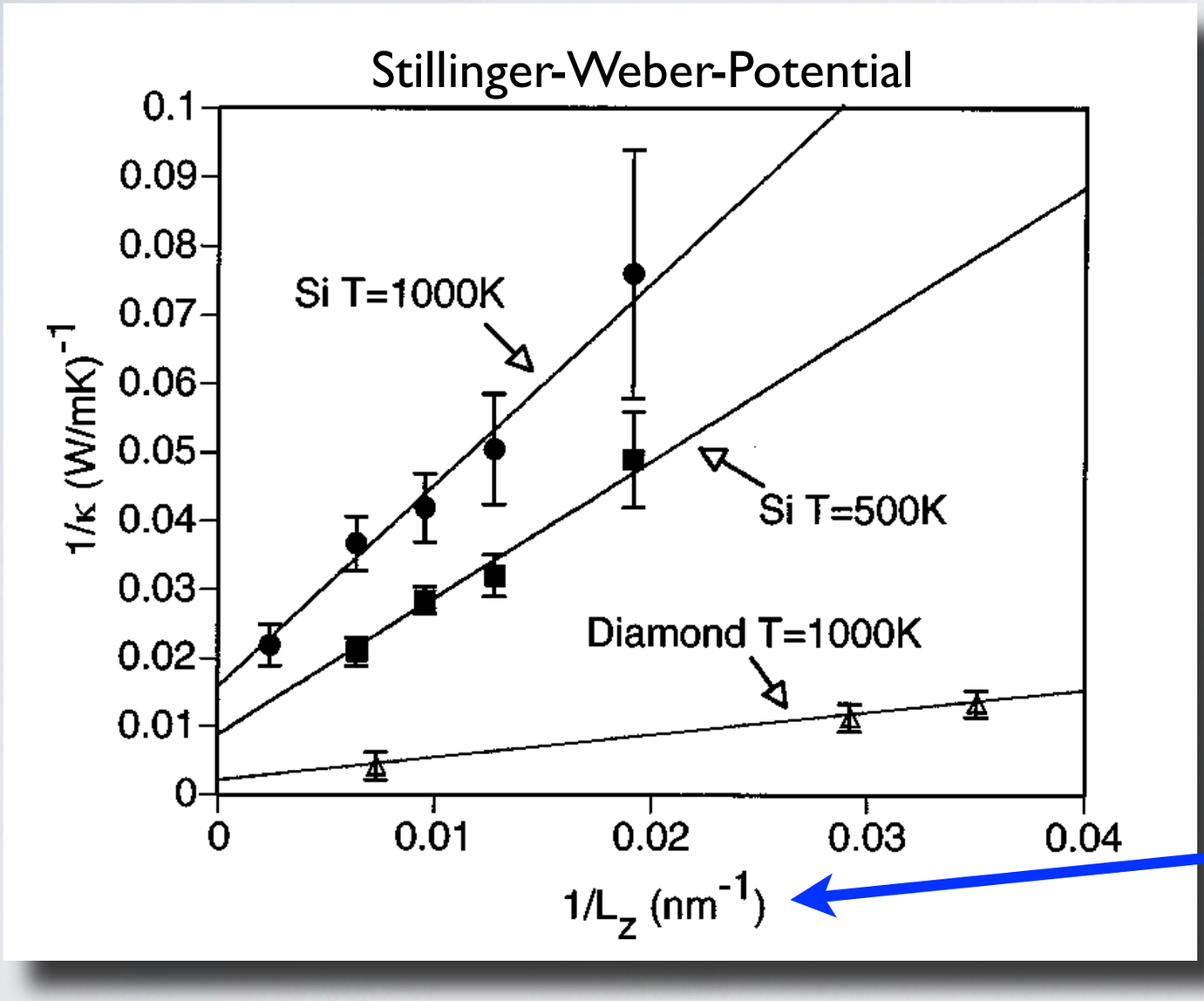
heat source → • Temperature gradient ∇T • Stationary heat flux **J** → **heat sink**

⇓

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

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

FINITE SIZE EFFECTS



Finite Size Corrections

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

mean free path

supercell length

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

FINITE SIZE EFFECTS

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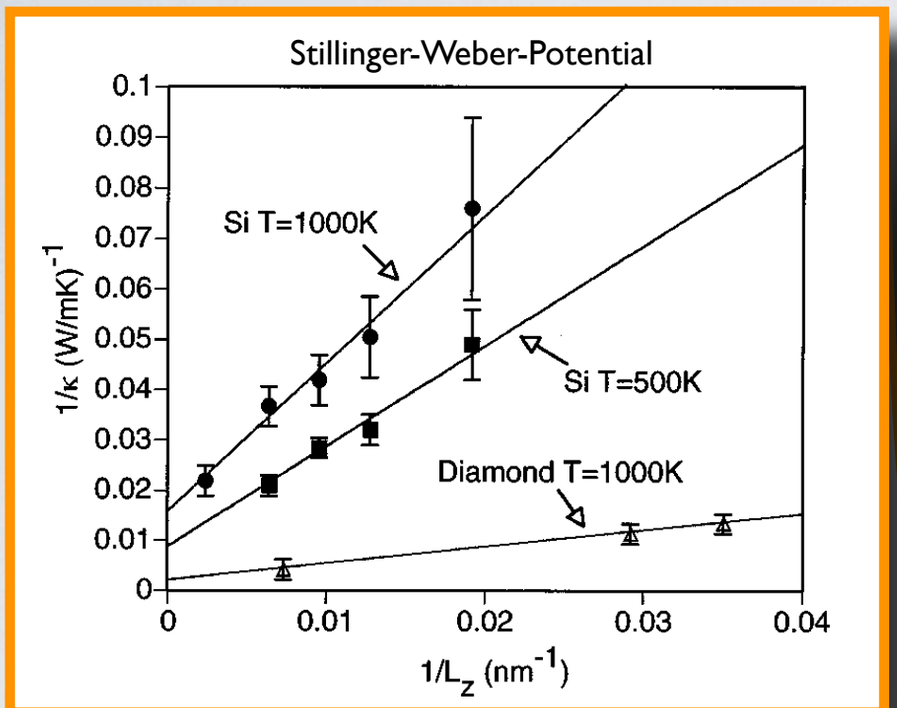

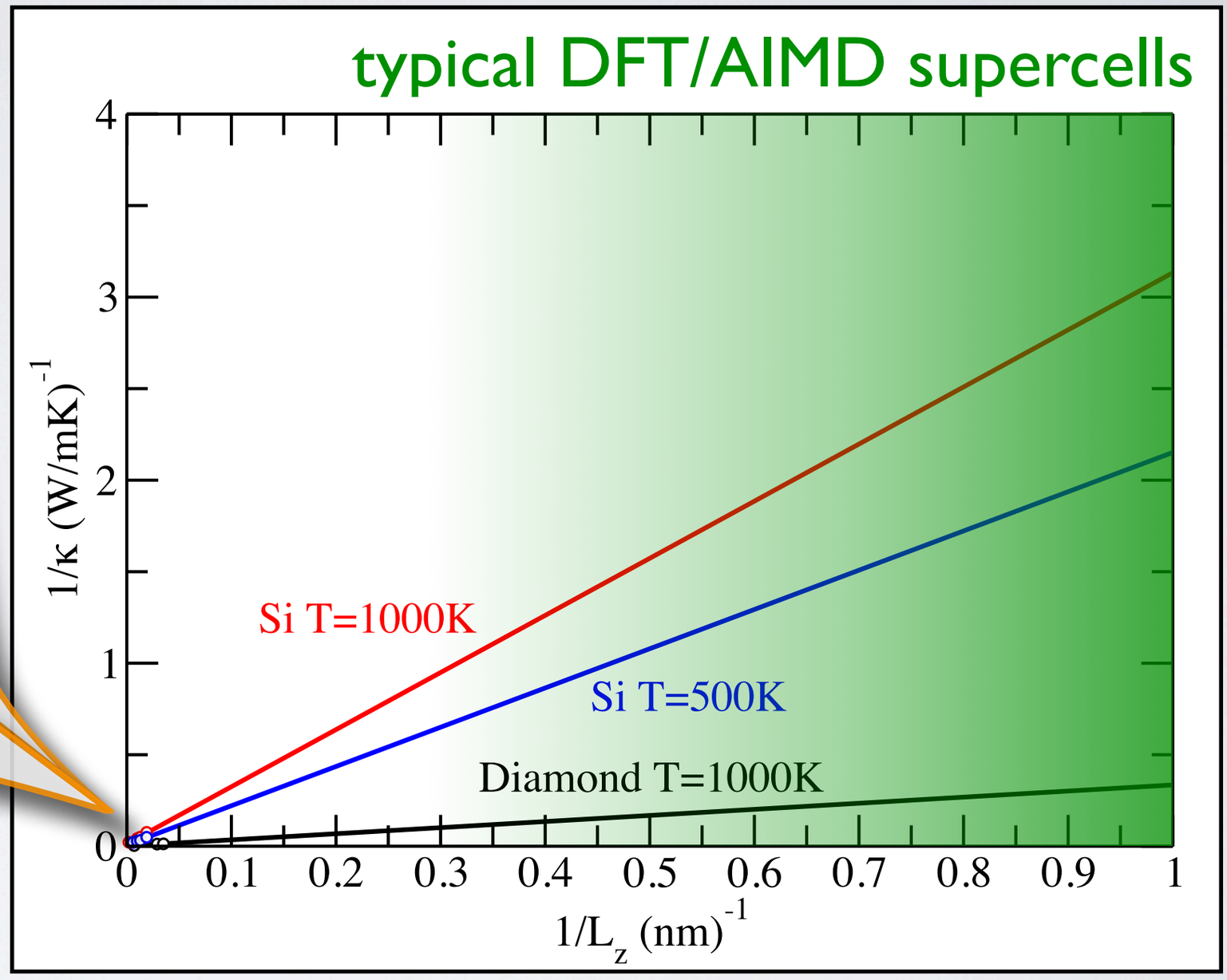

Non-equilibrium MD exhibits strong finite-size artifacts
in supercells typically accessible within DFT/AIMD.

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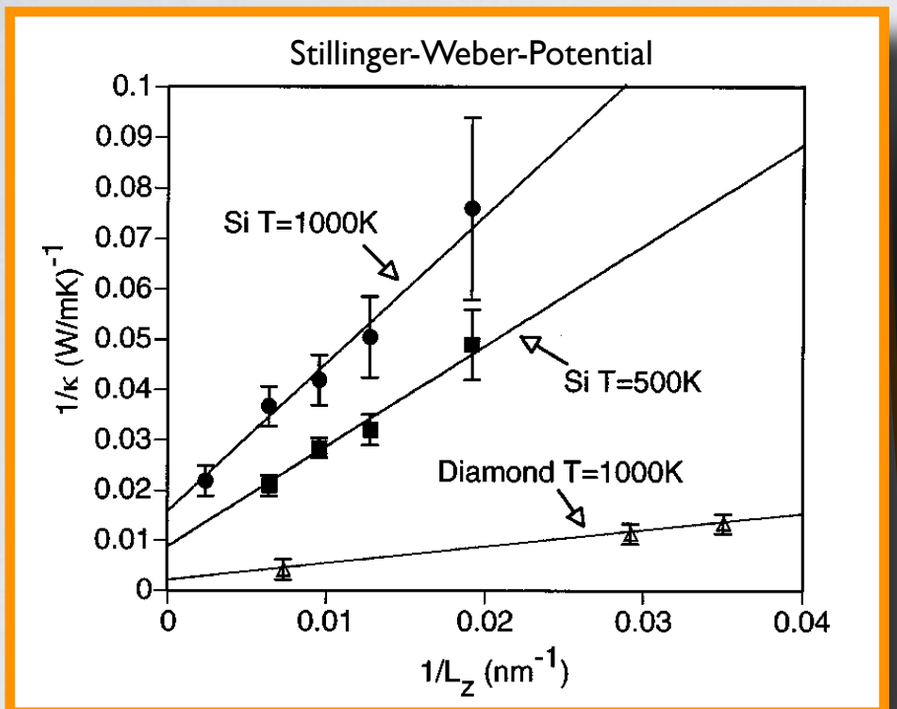

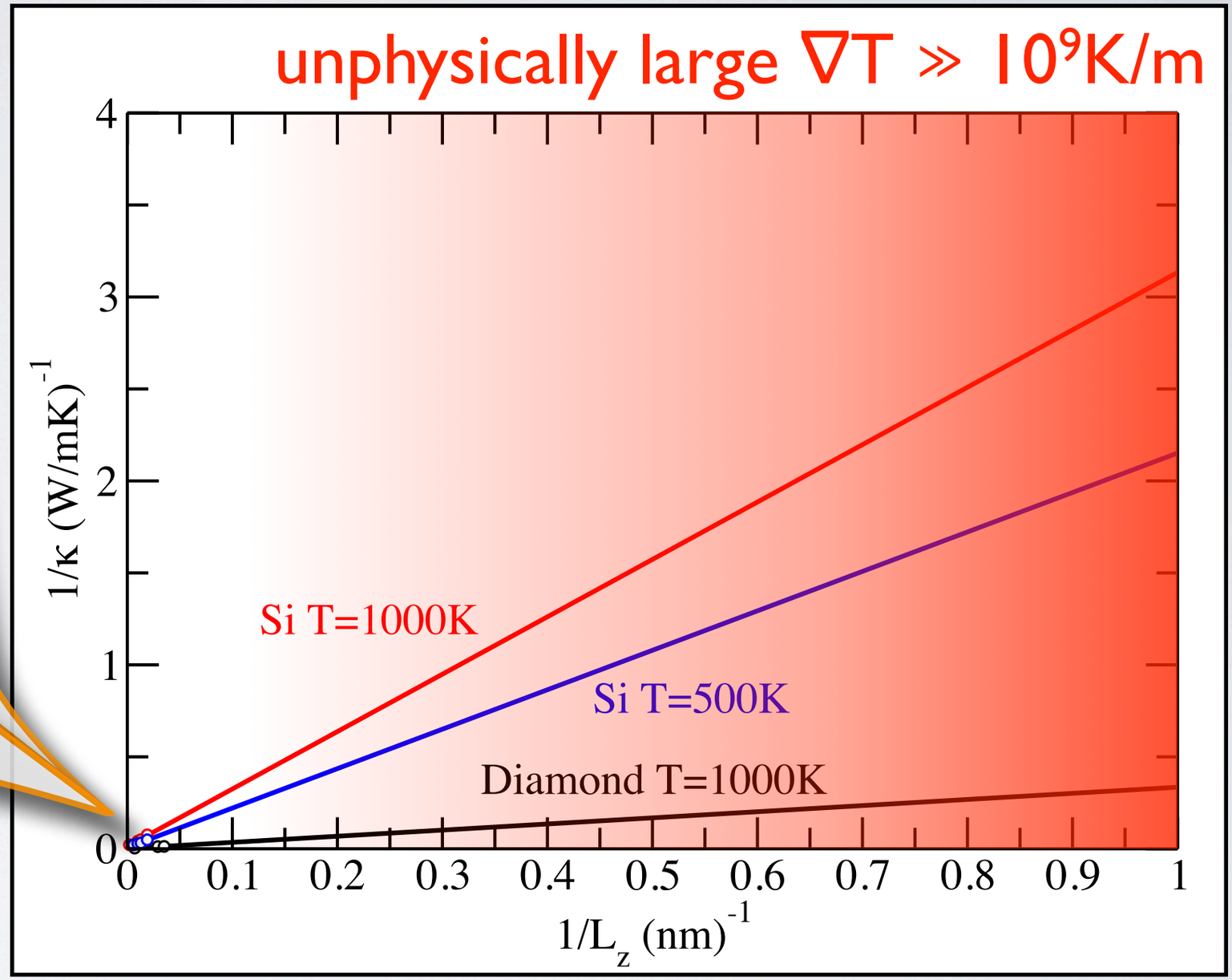

Non-equilibrium MD can suffer from non-linear artifacts
in supercells typically accessible within DFT/AIMD.

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).

$T = T_{cold}$

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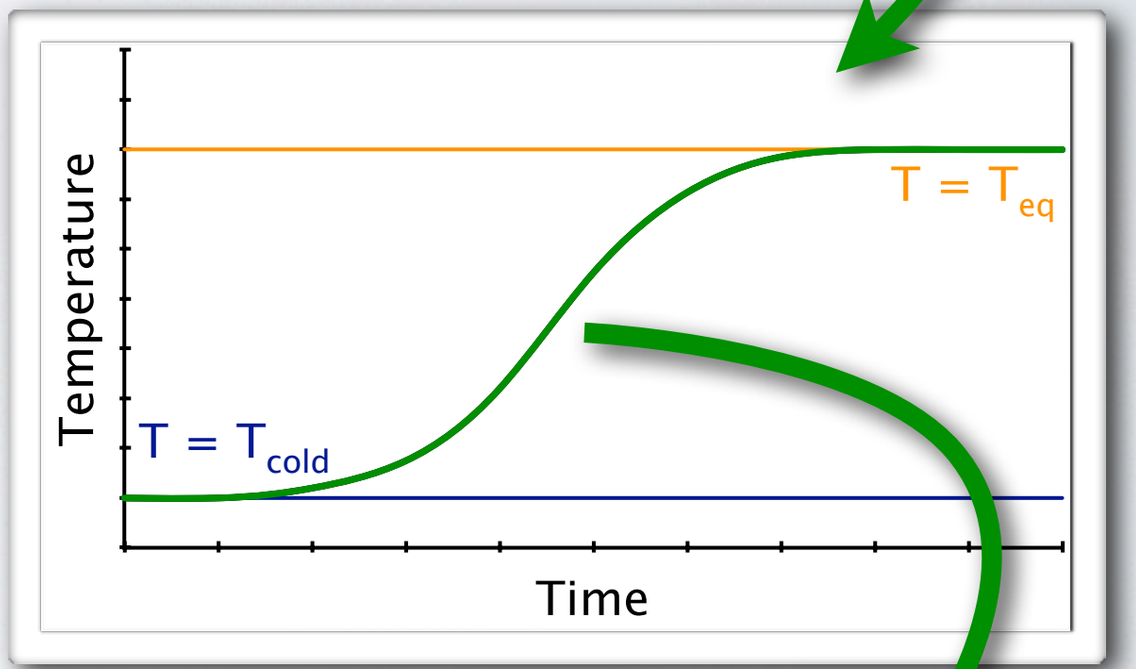
heat diffusion

$T = T_{hot}$

$T = T_{cold}$



Heat Diffusion Equation:

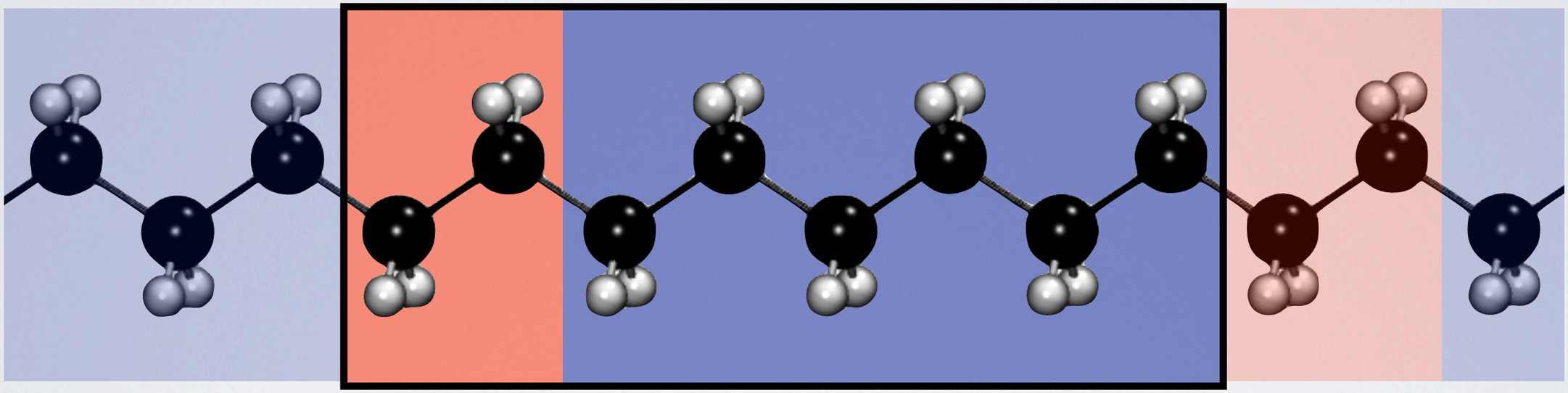
$$\frac{\partial T(x,t)}{\partial t} + \alpha \frac{\partial^2 T(x,t)}{\partial x^2} = 0$$

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

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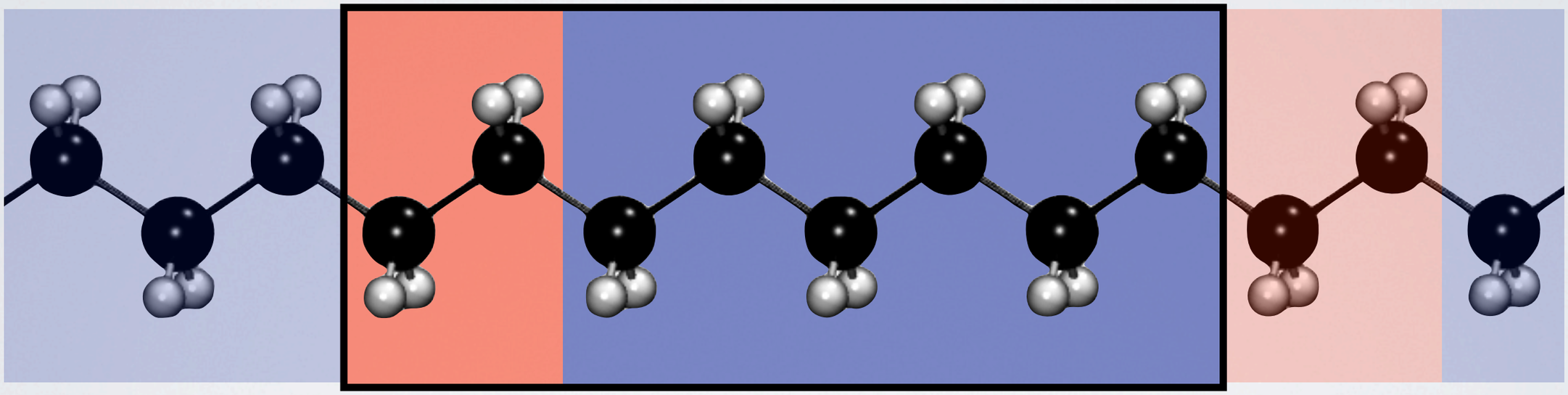

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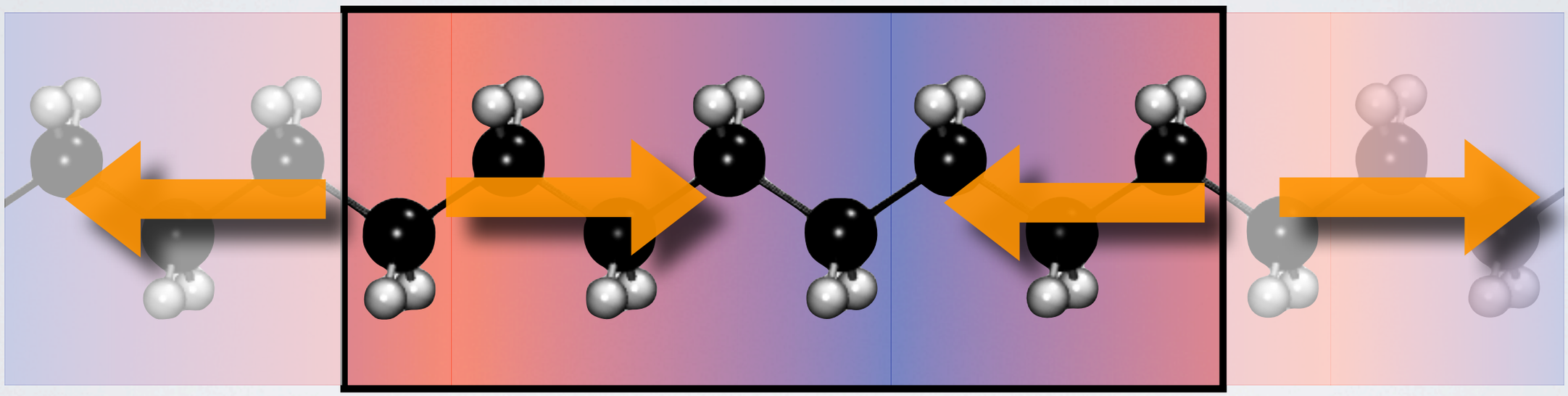
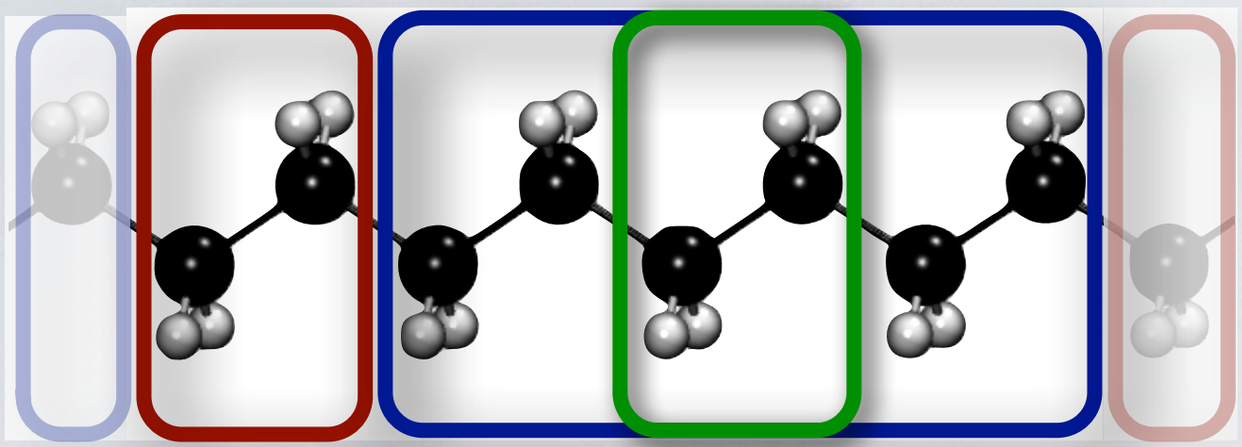


(A) **Prepare two supercells:** a **small hot** one and a **large cold** one.

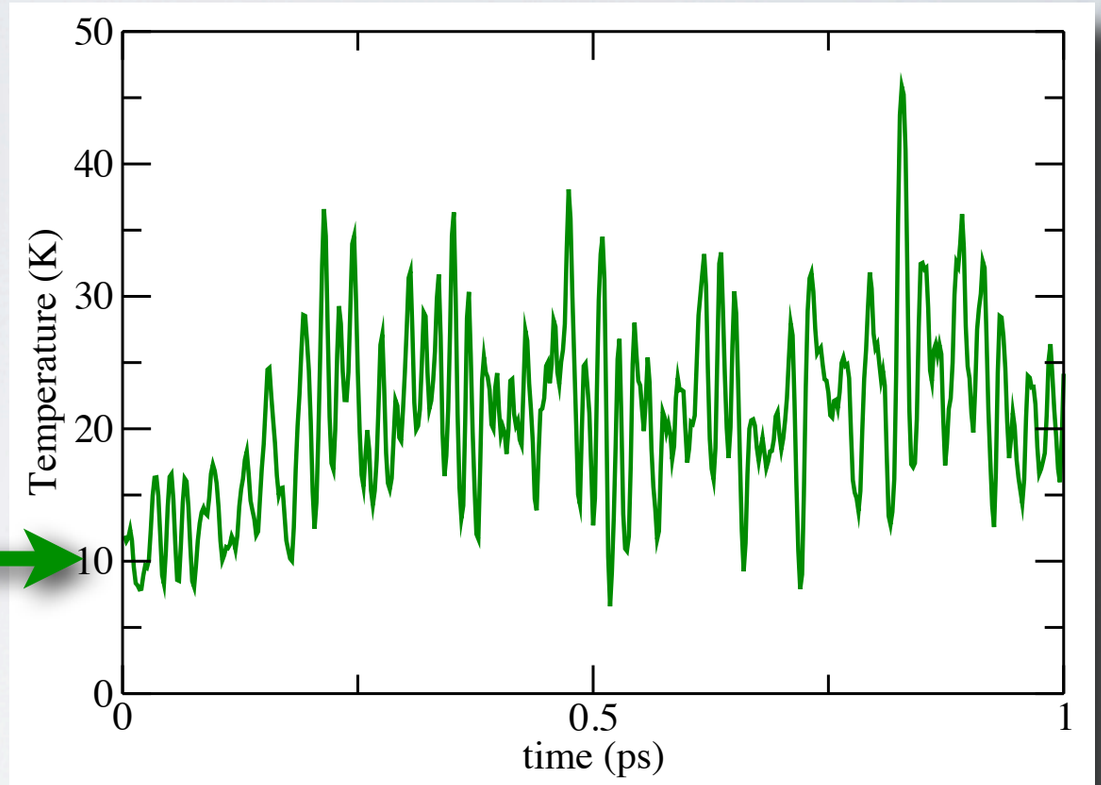
(B) Let the **heat diffuse** via *ab initio* MD
and **monitor** the temperature profile **T(x,t)**.

„LASER FLASH“ SIMULATIONS

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



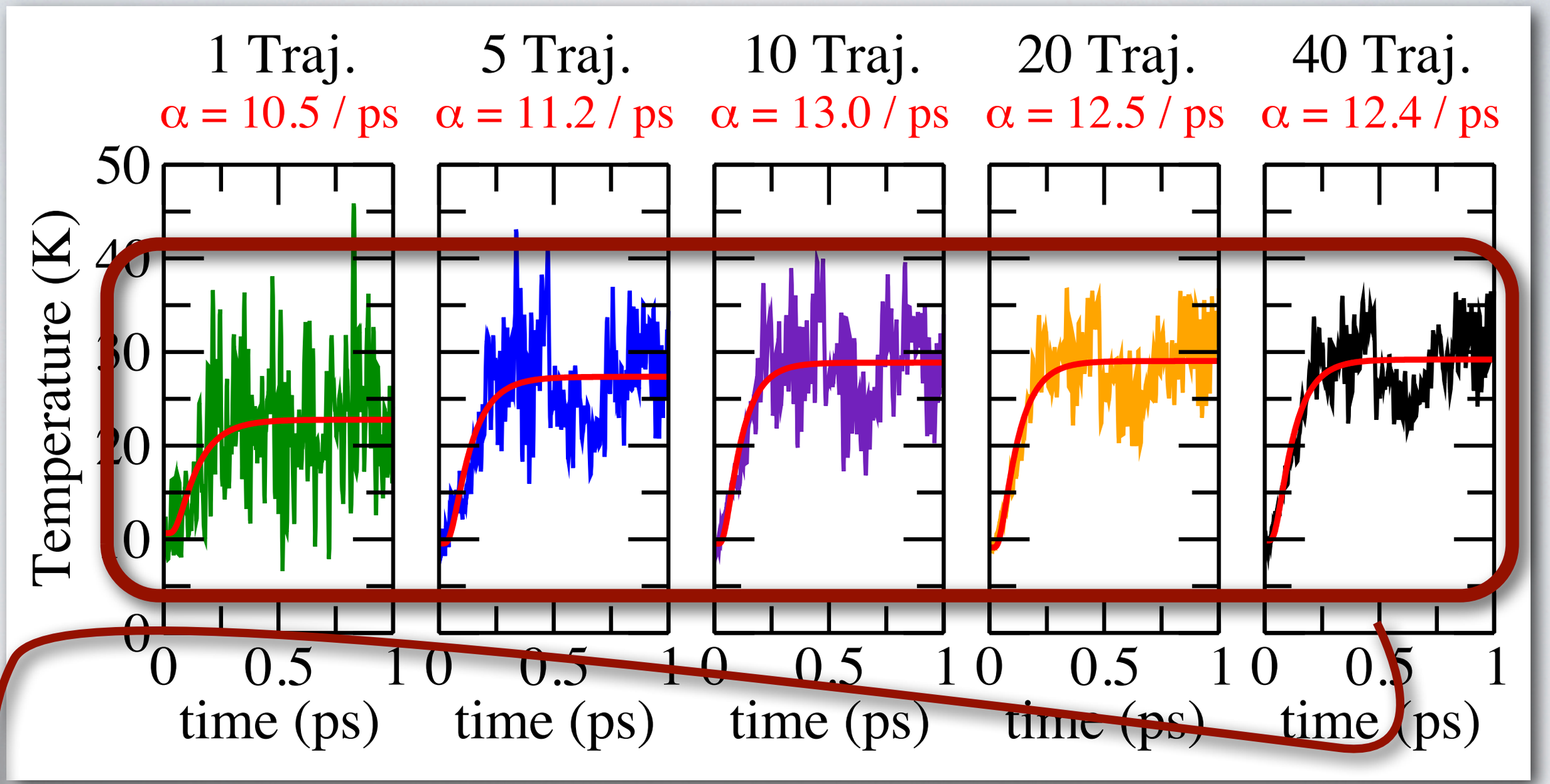
Monitor temperature of the central cell



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).

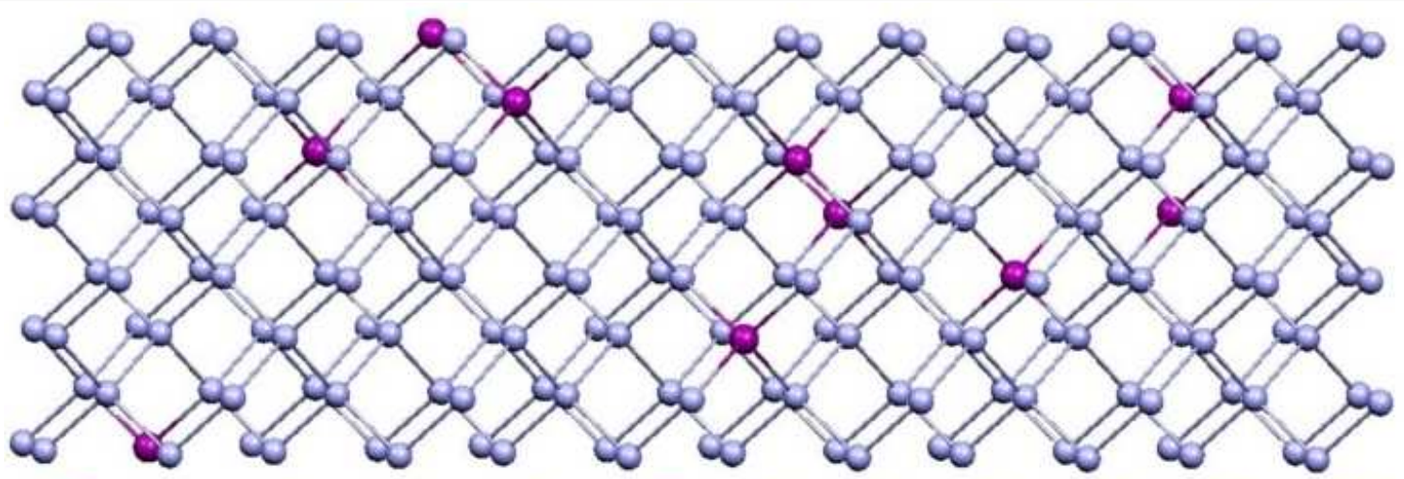


Fit to

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

APPLICATION TO IMPURITIES IN SI

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

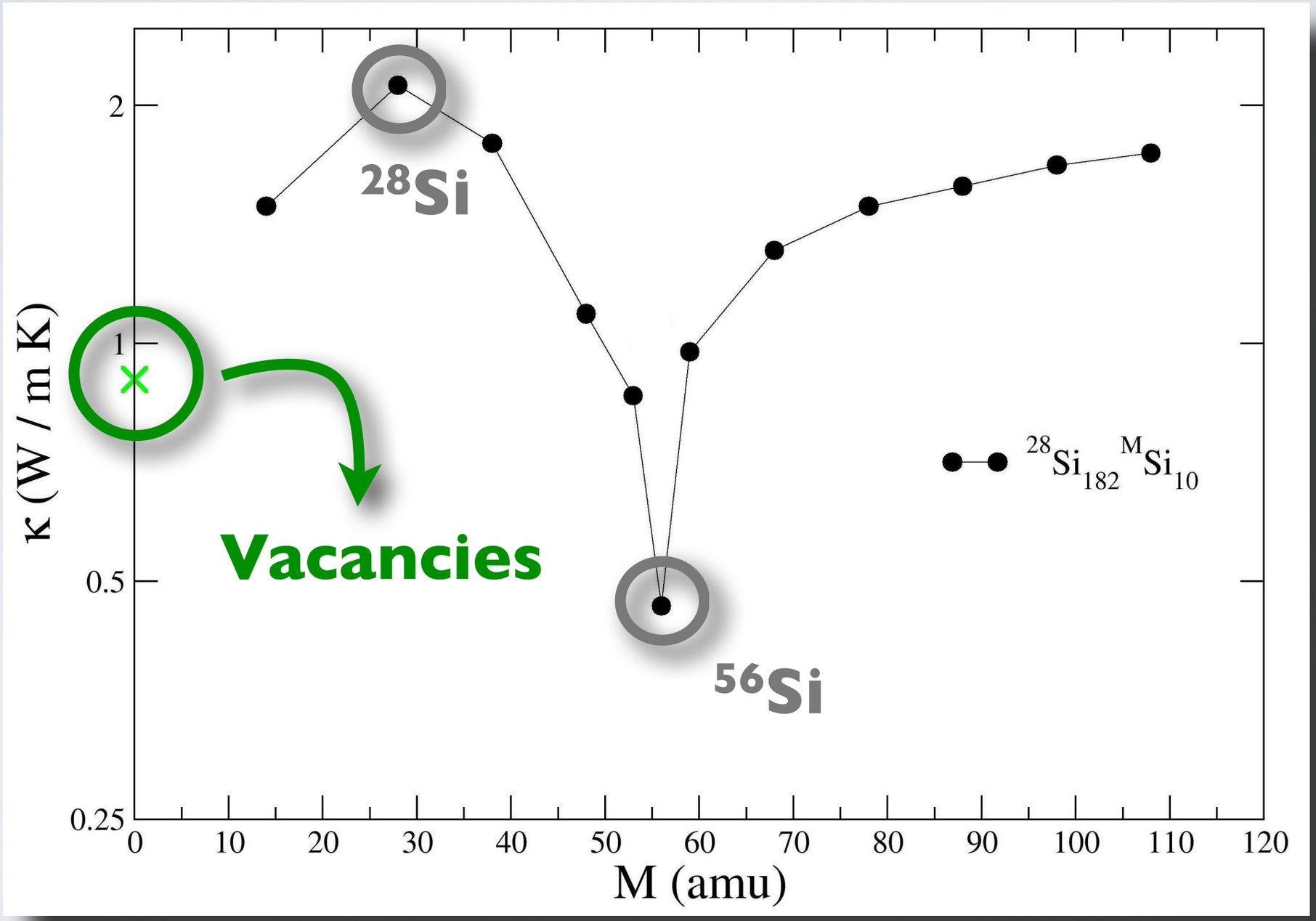


Si_{192} supercell containing **~5.2% impurities**

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

APPLICATION TO IMPURITIES IN SI

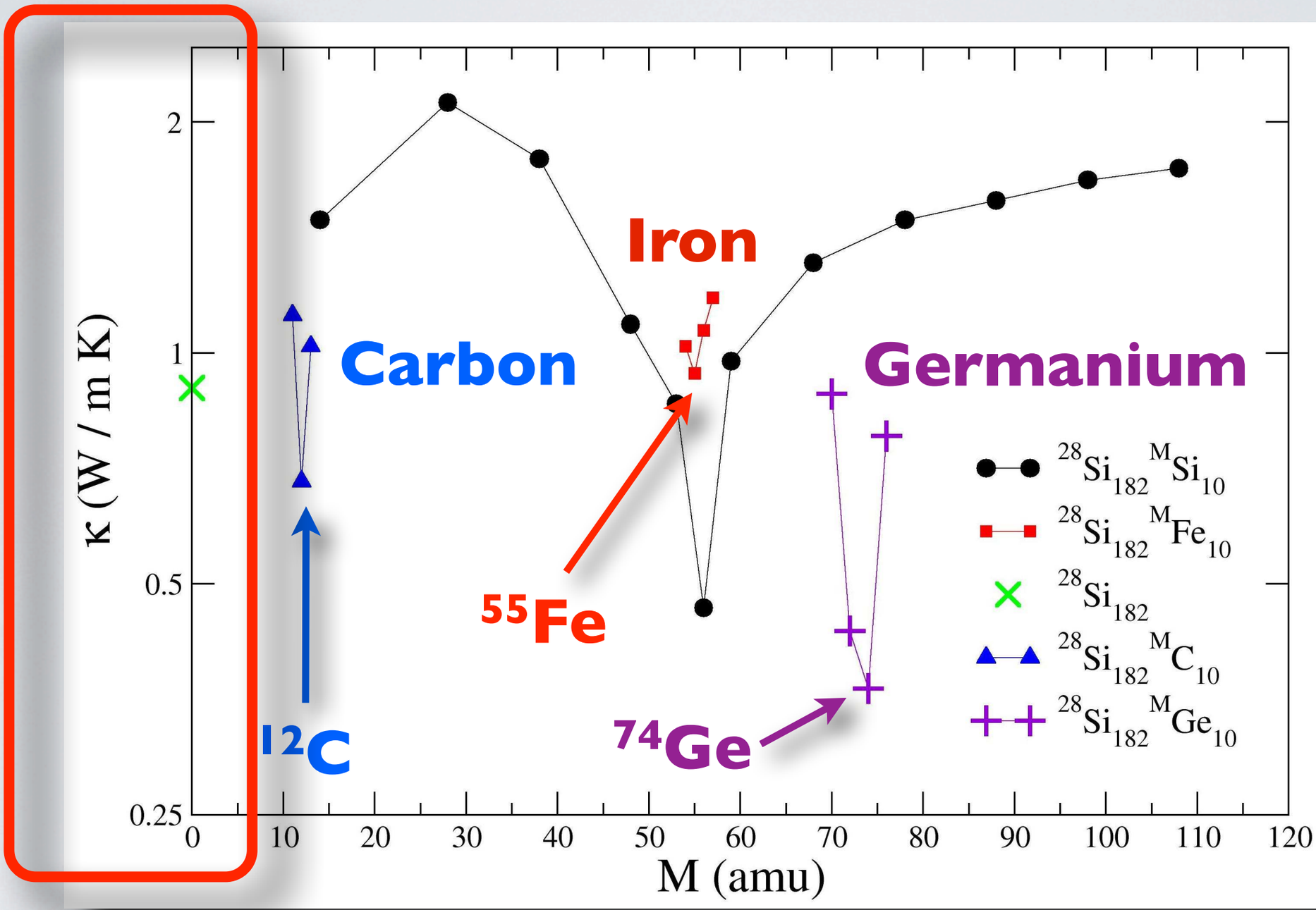
T. M. Gibbons and S. K. Estreicher, *Phys. Rev. Lett.* **102**, 255502 (2009).



Thermal conductivity can be controlled via the impurities‘ mass!

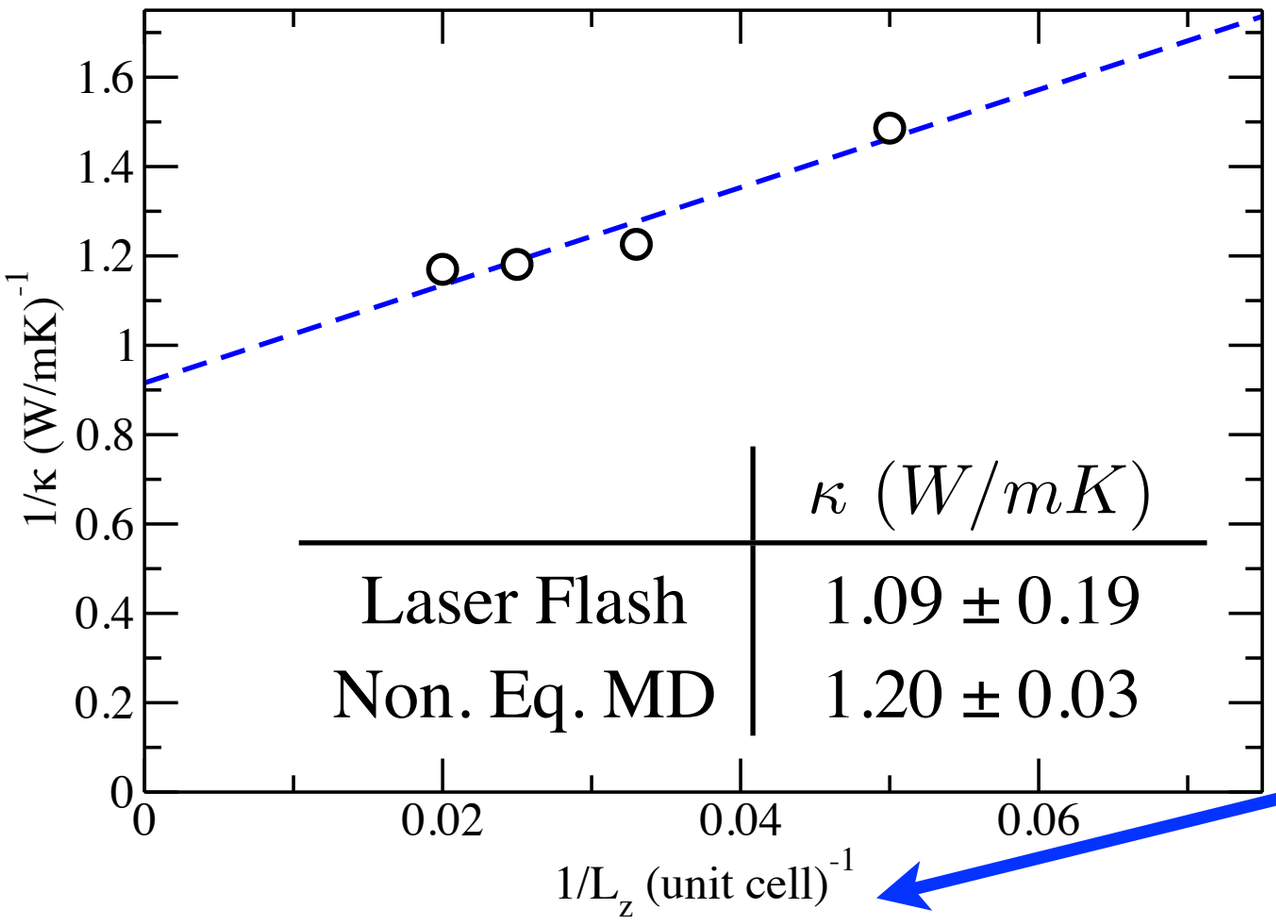
APPLICATION TO IMPURITIES IN SI

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



Finite Size Corrections

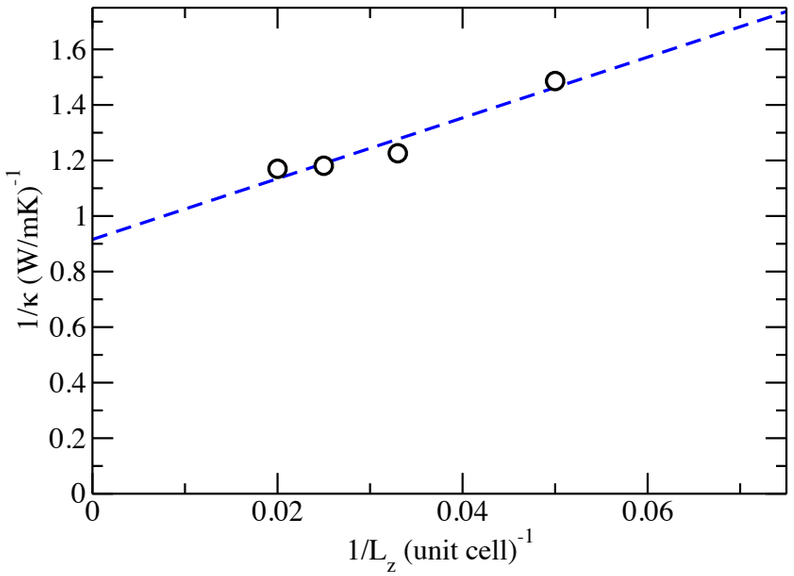
$$\frac{1}{\kappa} \sim \left(\frac{1}{l_\infty} + \frac{4}{L_z} \right)$$

mean free path

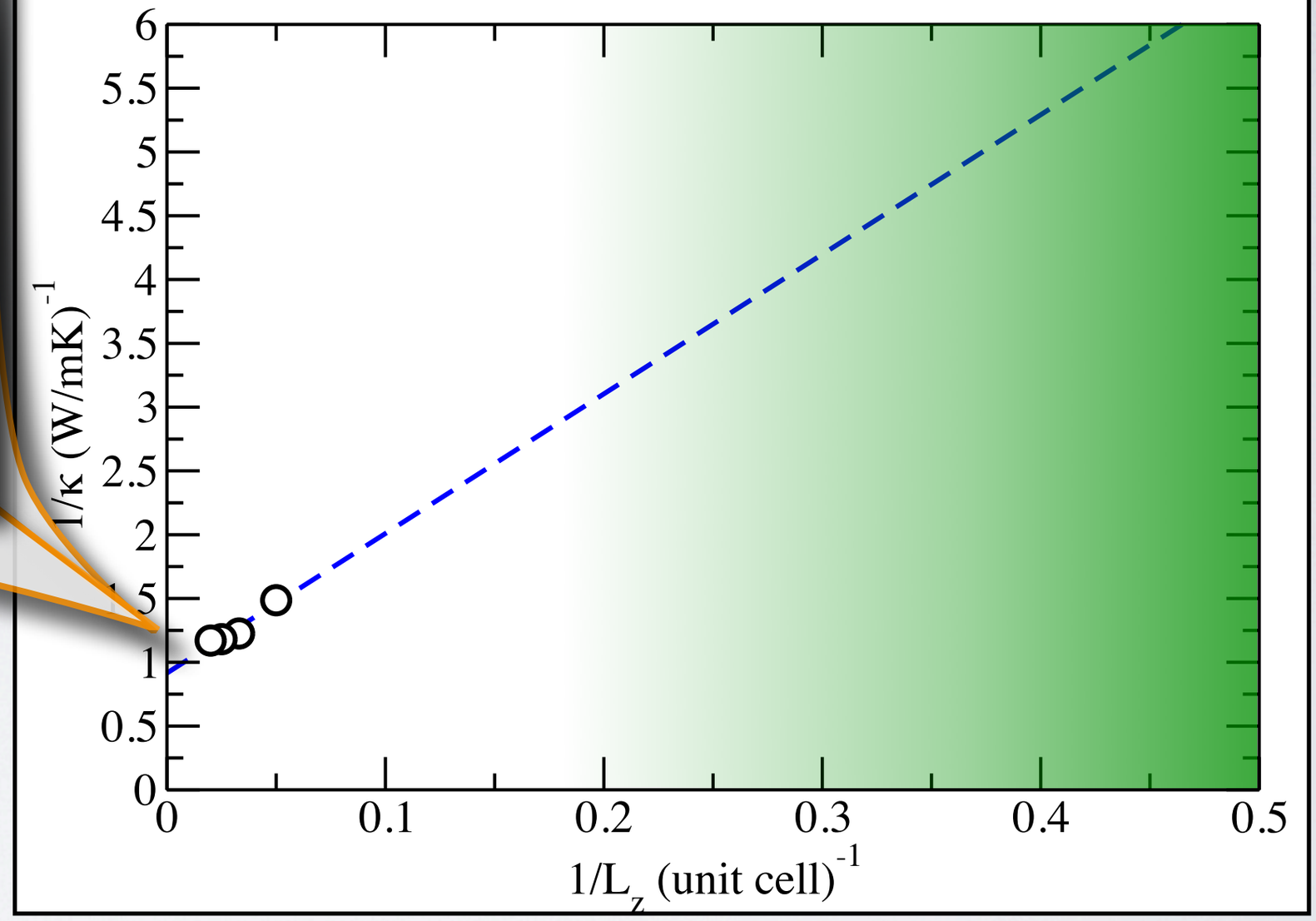
supercell length

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

FINITE SIZE EFFECTS

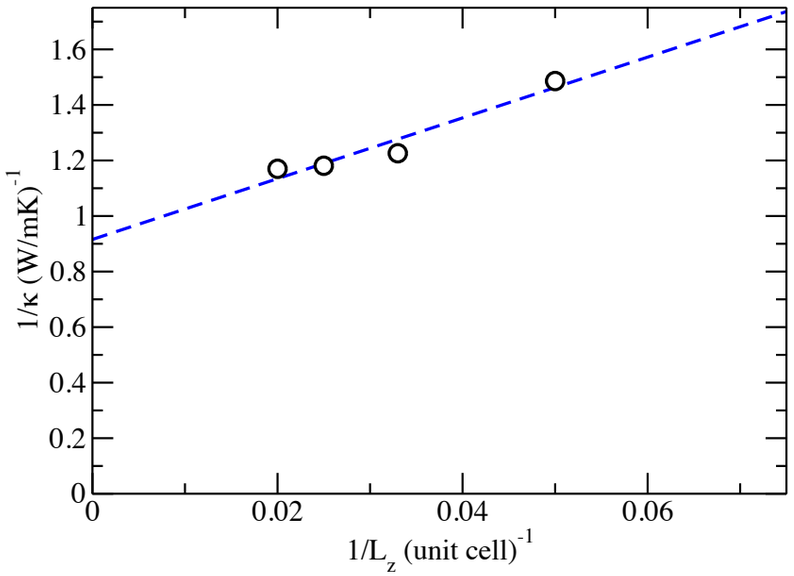


typical DFT/AIMD supercells

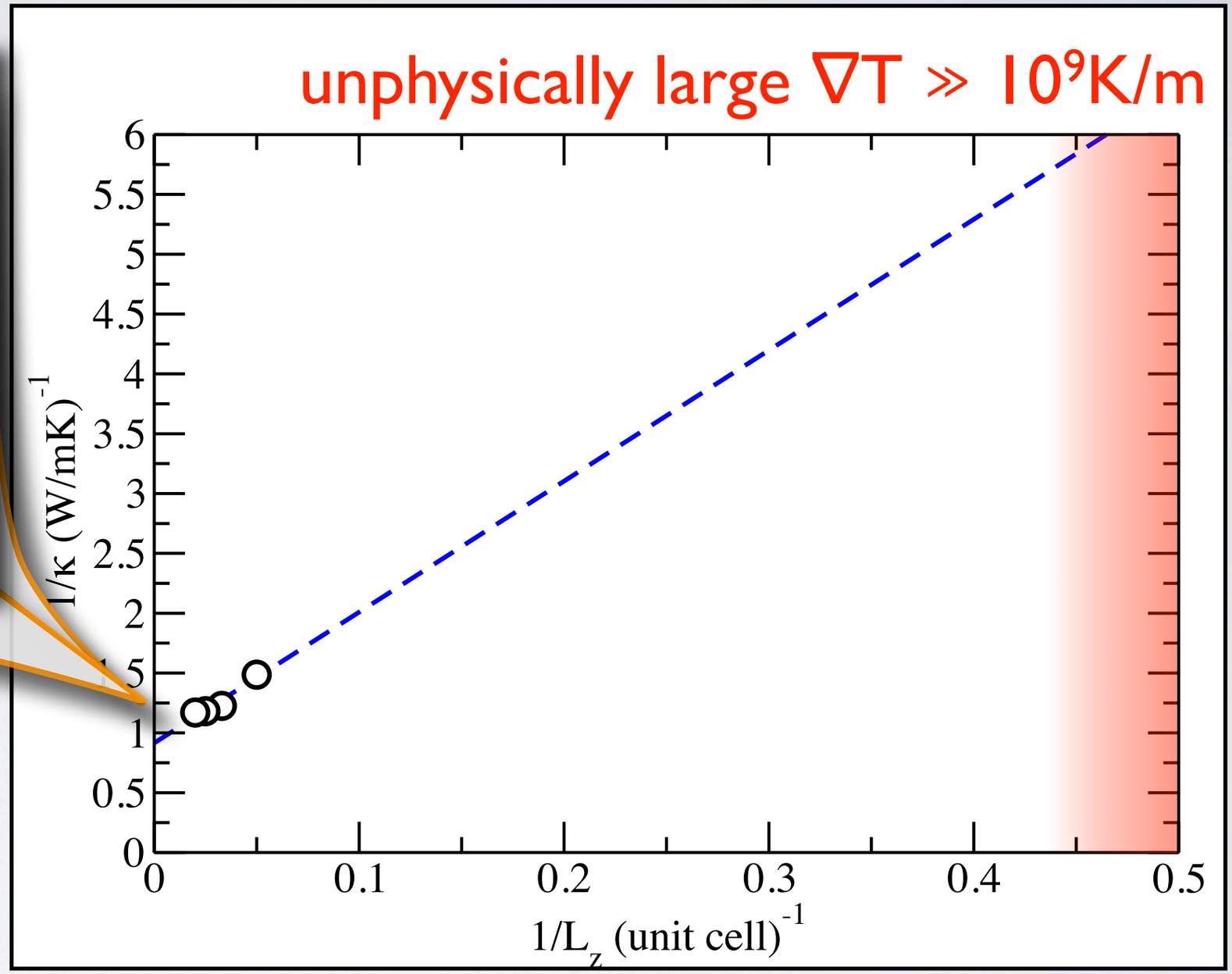


Laser-flash approach exhibits strong finite-size artifacts in supercells typically accessible within DFT/AIMD.

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				

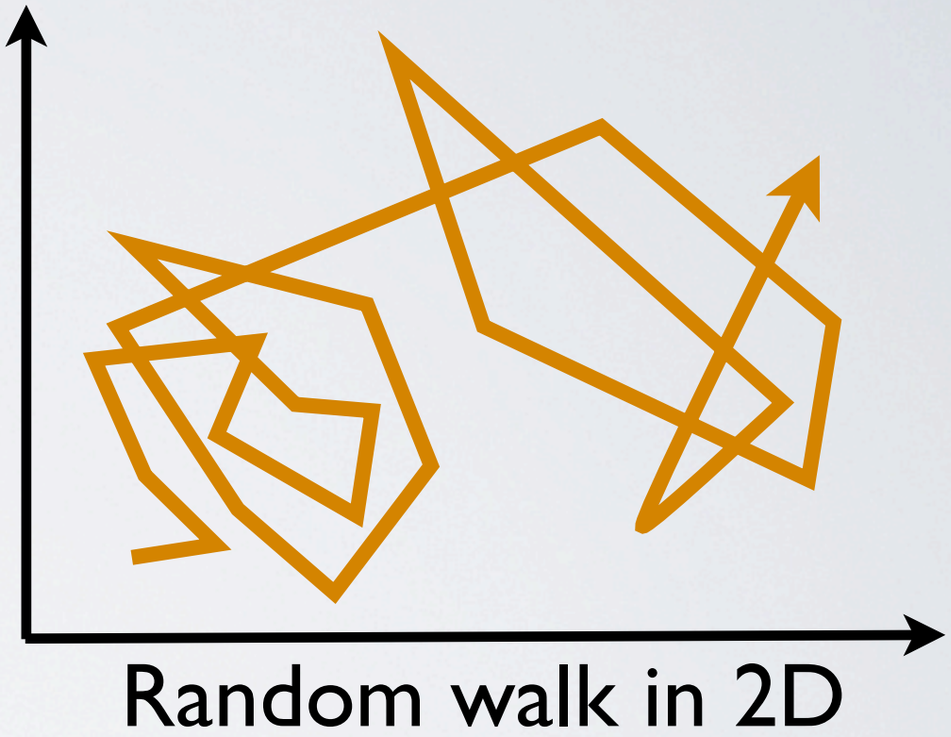
Laser-flash MD yields **accurate qualitative results** at **low temperatures** within **moderate computational costs**. **Quantitative** predictions require **finite size corrections**, though.

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

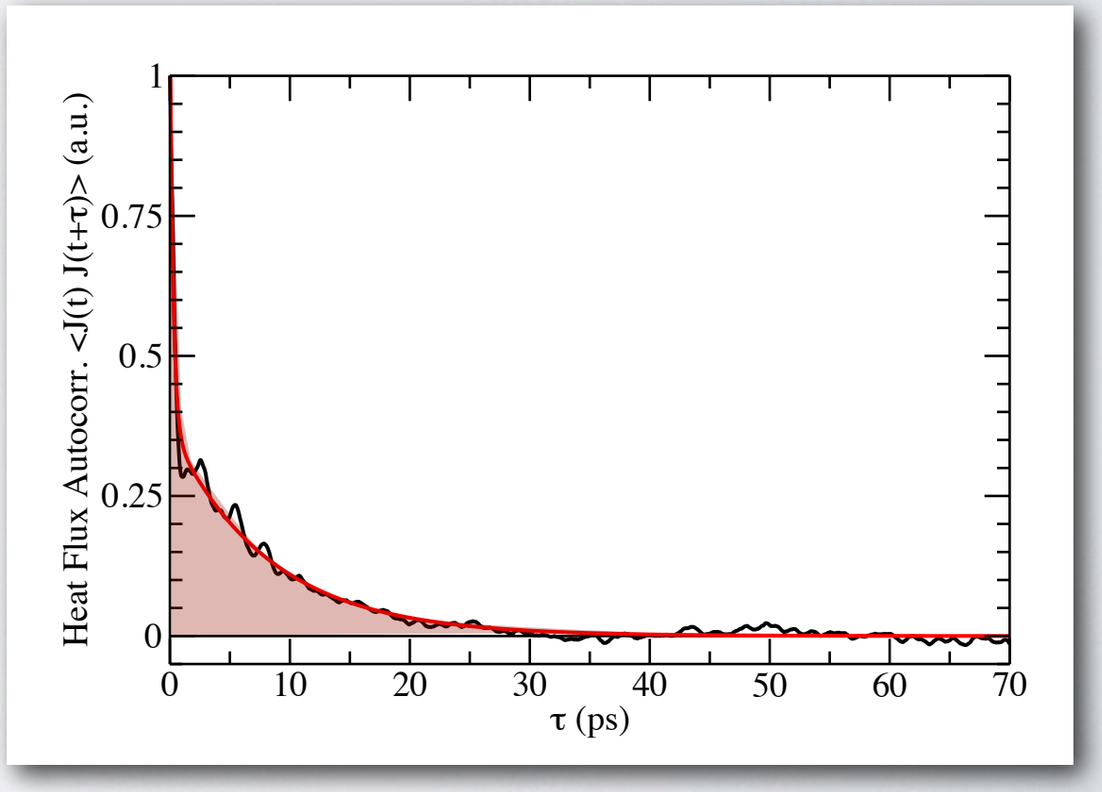
Simulations of the **thermodynamic equilibrium**

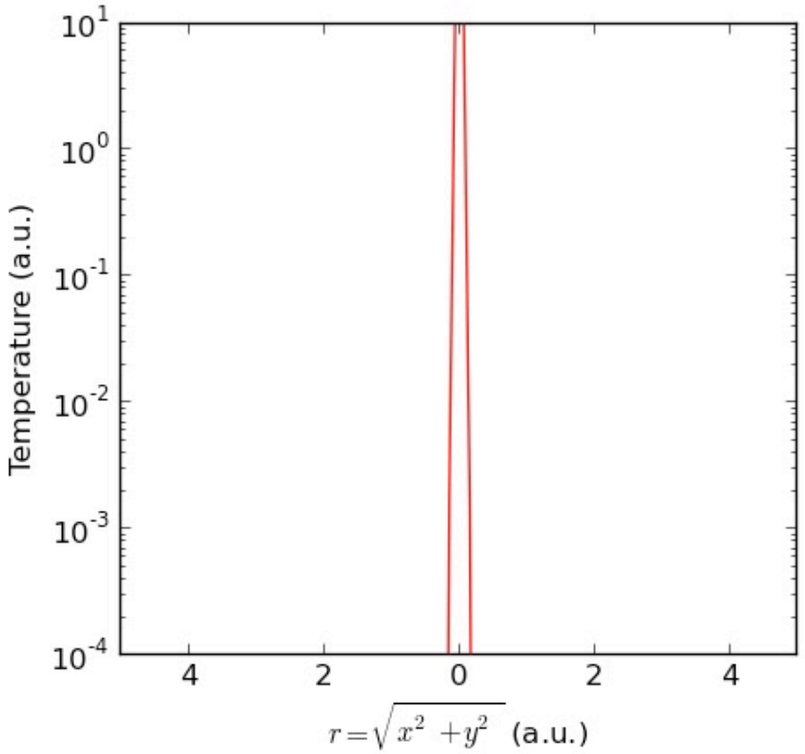
⇓ ⇓ ⇓

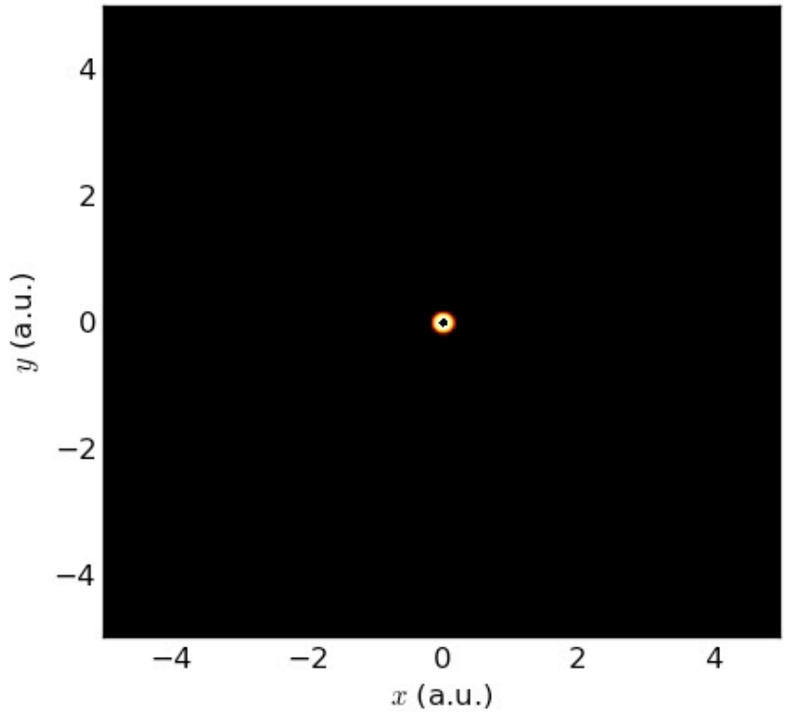
Information about **non-equilibrium processes**

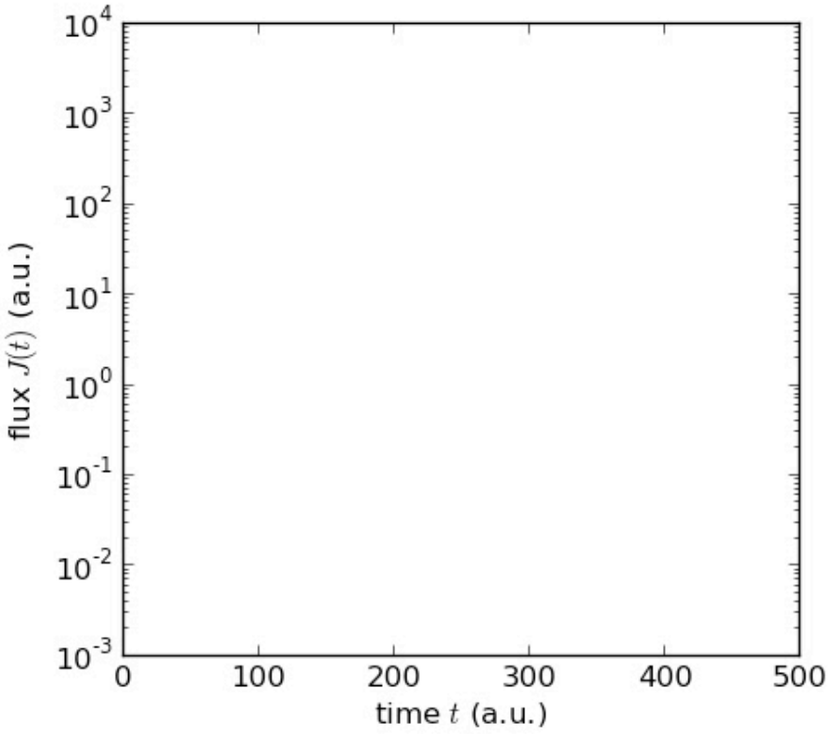
$$\kappa \sim \int_0^\infty d\tau \left\langle \mathbf{J}(0)\ \mathbf{J}(\tau) \right\rangle_{eq}$$

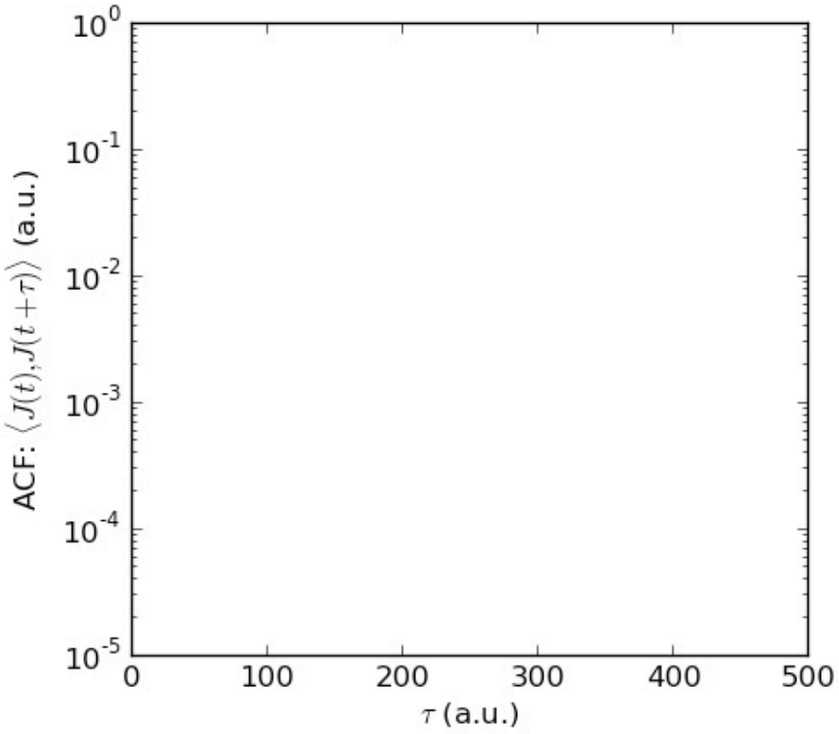
The **thermal conductivity** is related to the **autocorrelation function** of the **heat flux**



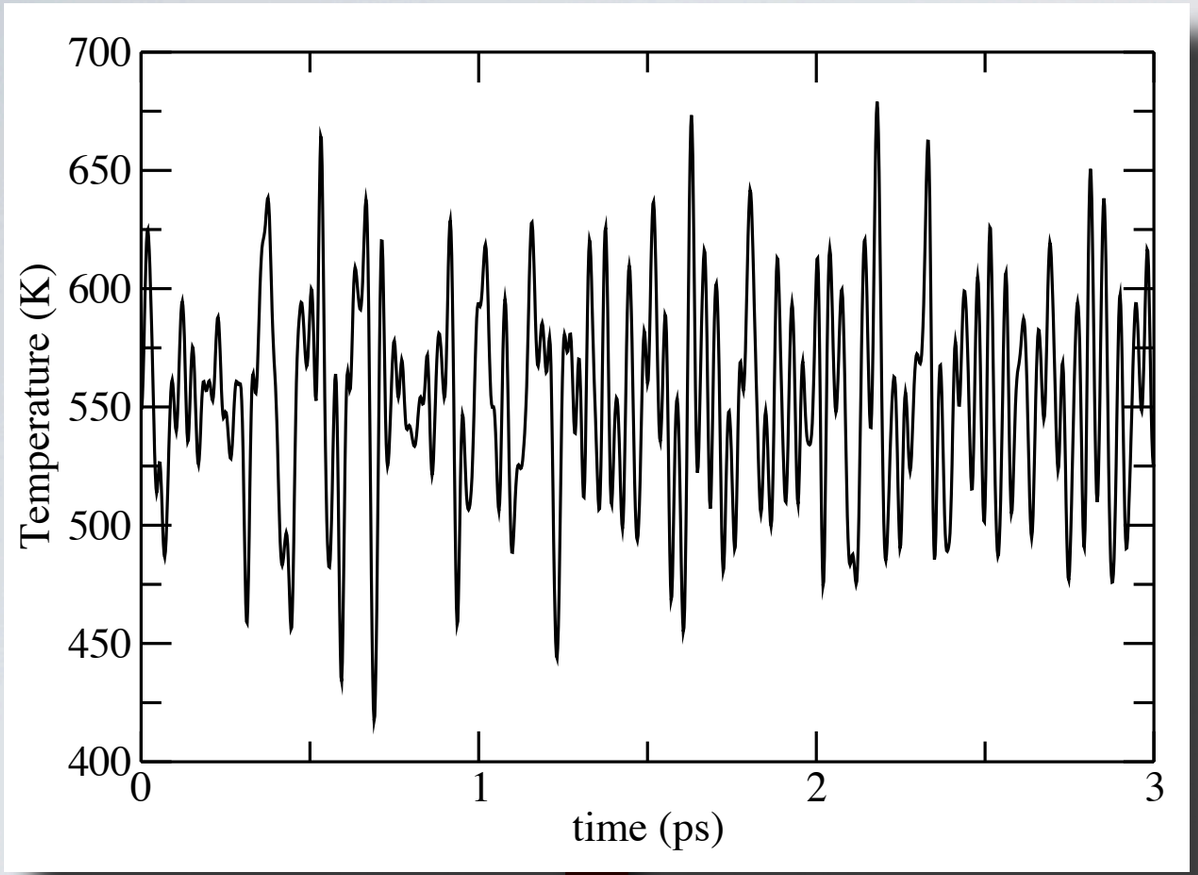


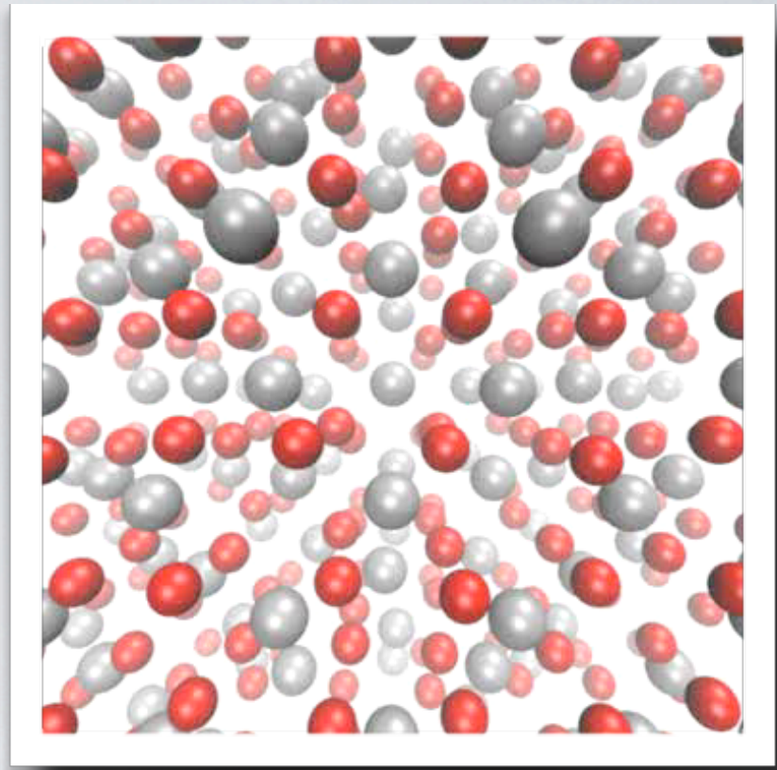


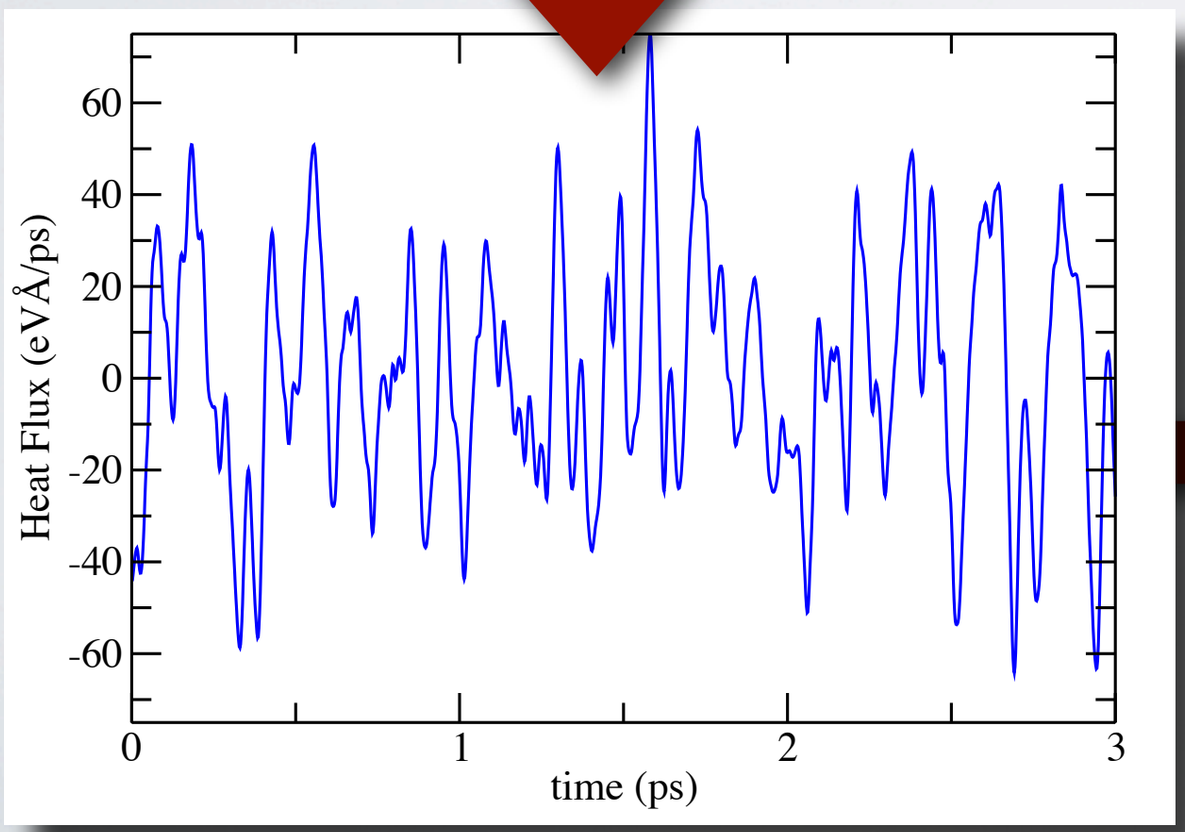


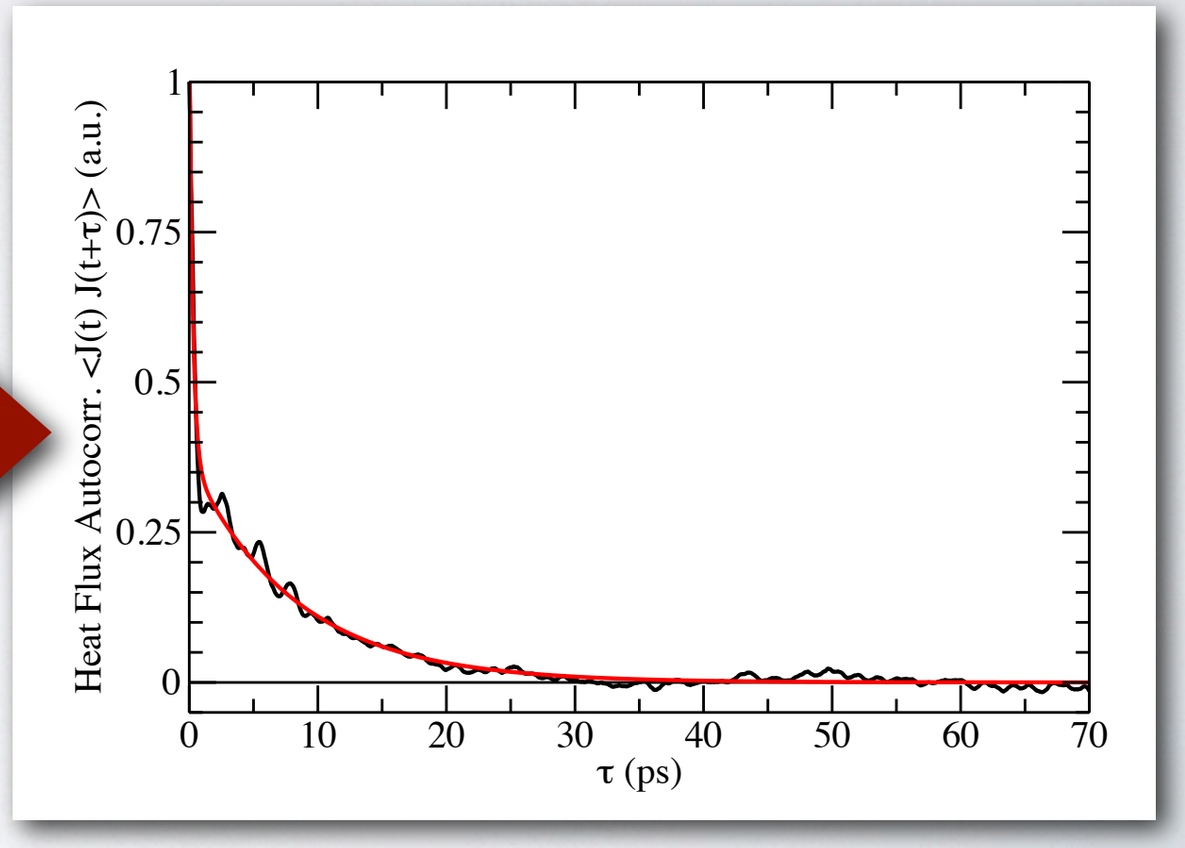


$$T(\mathbf{r}, t) = \frac{1}{(4\pi\kappa t)^{3/2}} \exp\left(-\frac{\mathbf{r}^2}{4\kappa t}\right) \quad \Rightarrow \quad \int \langle J(t), J(t+\tau) \rangle \, d\tau \quad \sim \kappa$$


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 $\boldsymbol{\varepsilon_i}$ 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).

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

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

ASSESSING THE THERMAL CONDUCTIVITY

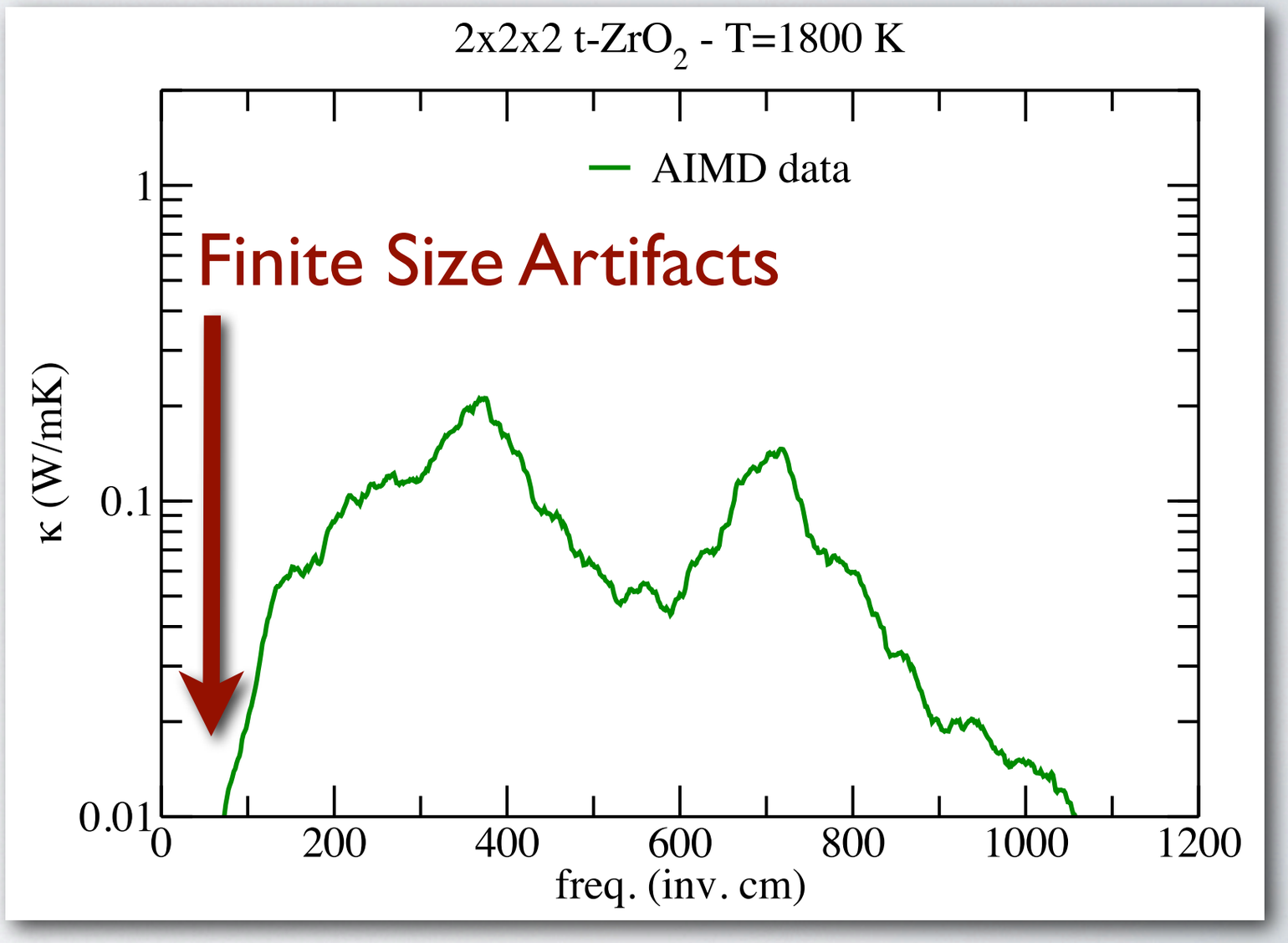
$$\kappa = \frac{V}{3k_B T^2} \int_0^\infty d\tau \, \langle \, \mathbf{J}(0) \, \mathbf{J}(\tau) \rangle_{eq}$$

Fourier Trans.

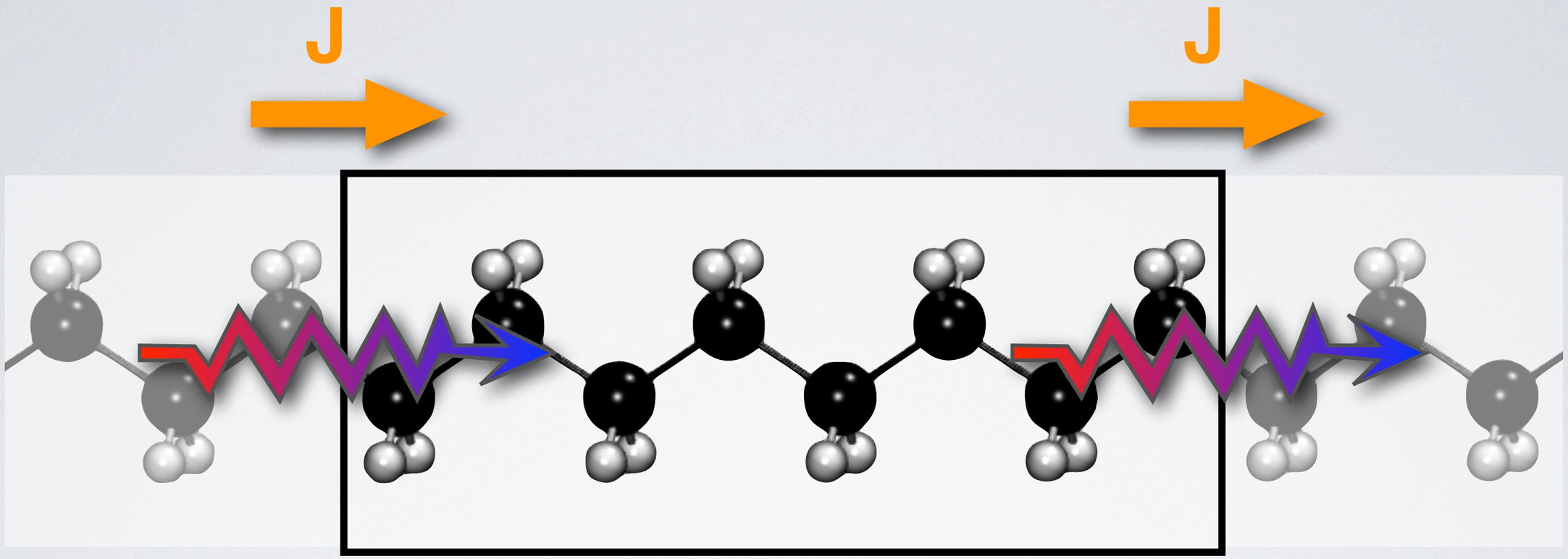
$$\kappa = \frac{V}{3k_B T^2} \lim_{\omega \to 0} |\mathbf{J}(\omega)|^2$$

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

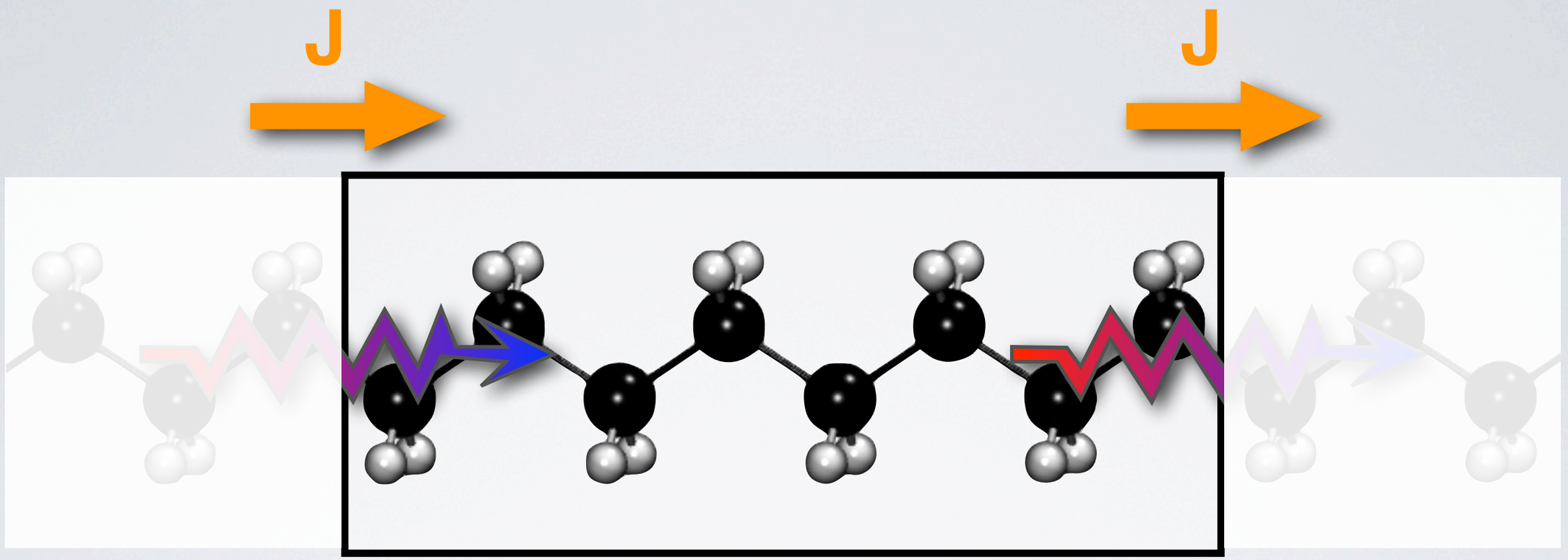
J. L. Feldman *et al.*,
Phys. Rev. B **48**, 12589 (1993).



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.**

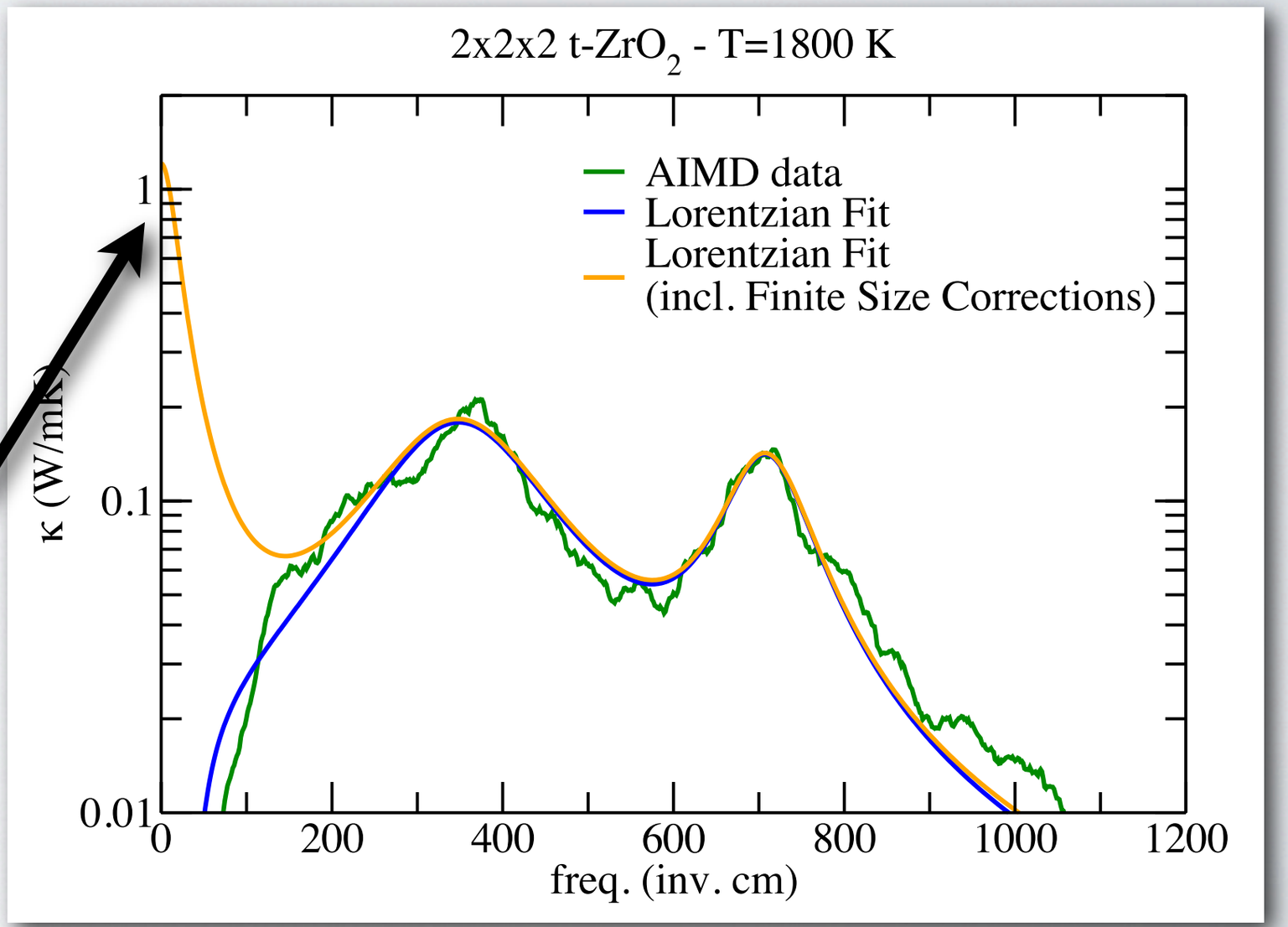
CORRECTING FOR FINITE SIZE EFFECTS

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

$$\kappa_{FS}(\omega) = \kappa(\omega) - \Theta_{FS}(\omega) = \sum_n \frac{\kappa_n}{1+\alpha_n\,\omega^2} - \frac{\kappa_{\rm art}}{1+\alpha_{\rm art}\,\omega^2}$$

Finite Size $\kappa_{FS}(\omega)$ is superposition of **bulk conductivity $\kappa(\omega)$** and **finite size effects $\Theta_{FS}(\omega)$!**

Finite Size corrected $\kappa(\omega)$!

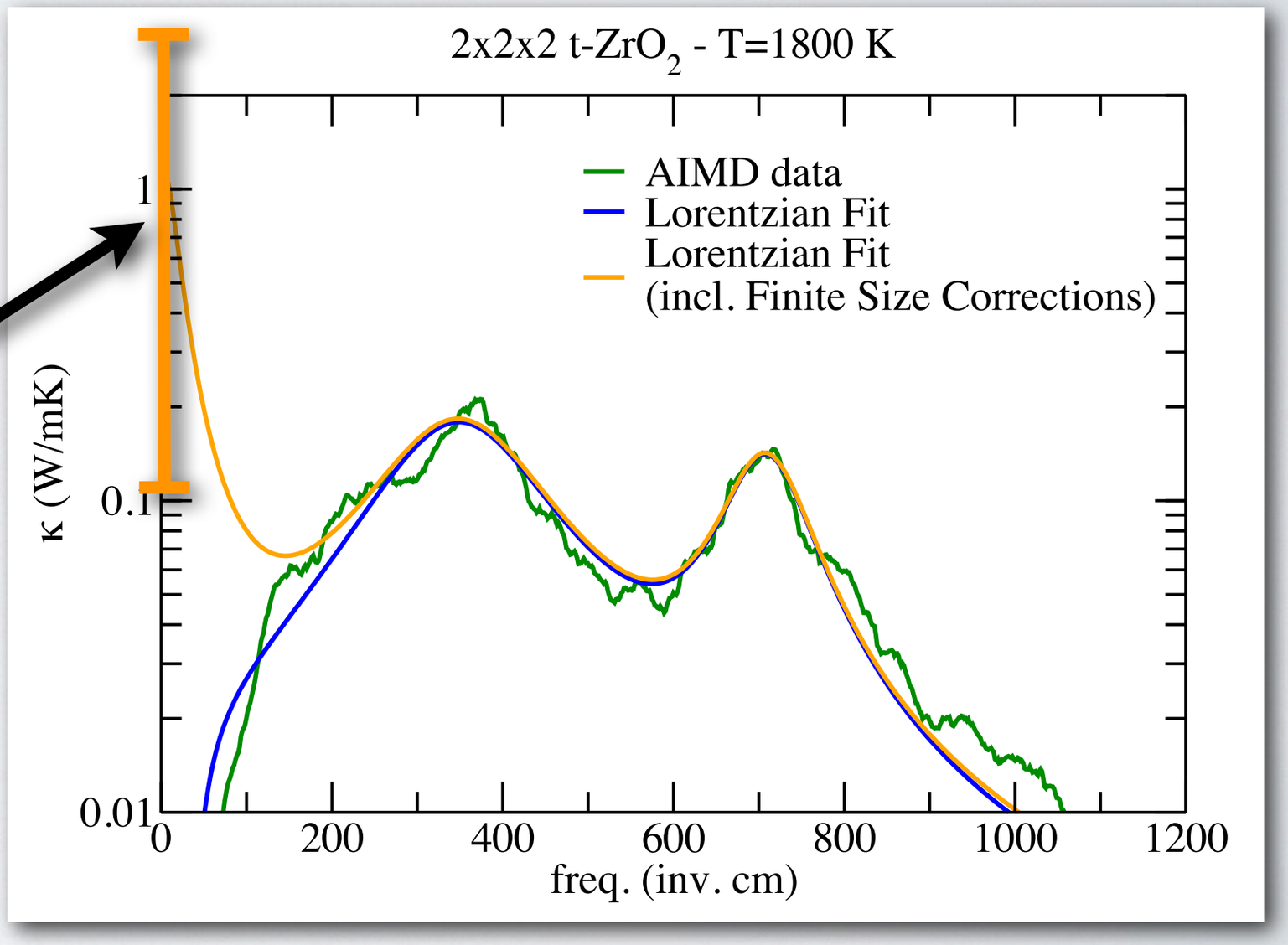


CORRECTING FOR FINITE SIZE EFFECTS

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

$$\kappa_{FS}(\omega) = \kappa(\omega) - \Theta_{FS}(\omega) = \sum_n \frac{\kappa_n}{1+\alpha_n\,\omega^2} - \frac{\kappa_{\mathrm{art}}}{1+\alpha_{\mathrm{art}}\,\omega^2}$$

Finite Size corrections however exhibit unacceptable "fitting uncertainty".



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).

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).

$\mathbf{J}(t)$

$t)$ $d\mathbf{r}$

Formulas for analytical stress

F. Knuth, FHI

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

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

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

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

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

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

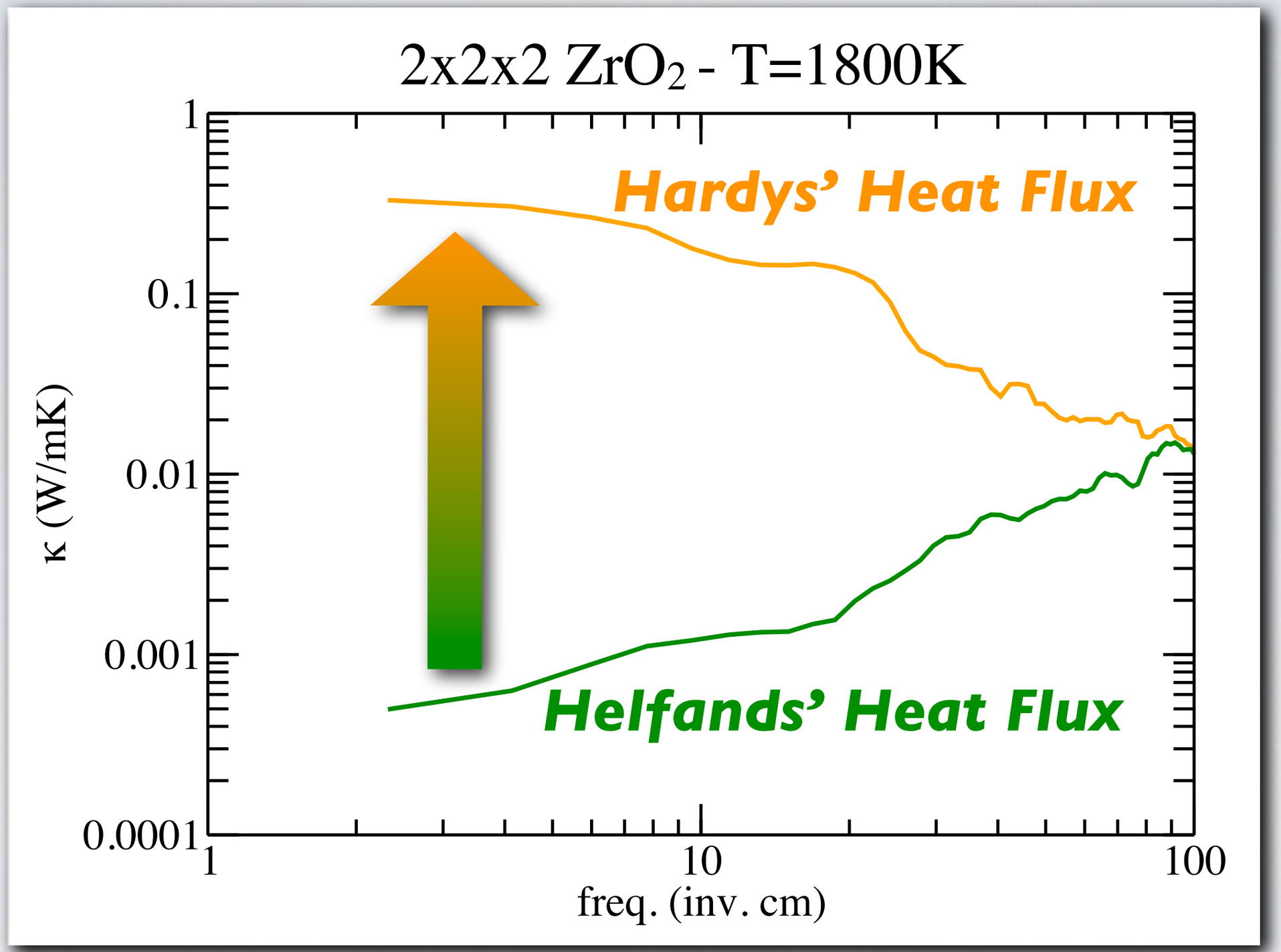
$$\sigma_{ij}^{\mathrm{Jac}} = \frac{1}{V} \delta_{ij} \left[E_{\mathrm{xc}}[n] - \int \mathrm{d}\mathbf{r}\, n(\mathbf{r}) v_{\mathrm{xc}}(\mathbf{r}) - \frac{1}{2} \int \mathrm{d}\mathbf{r}\, n_{\mathrm{MP}}(\mathbf{r}) v_{\mathrm{es,tot}}(\mathbf{r}) \right]$$

$\mathbf{J}$ (t)

sity

ELIMINATING THE FINITE SIZE ARTIFACTS

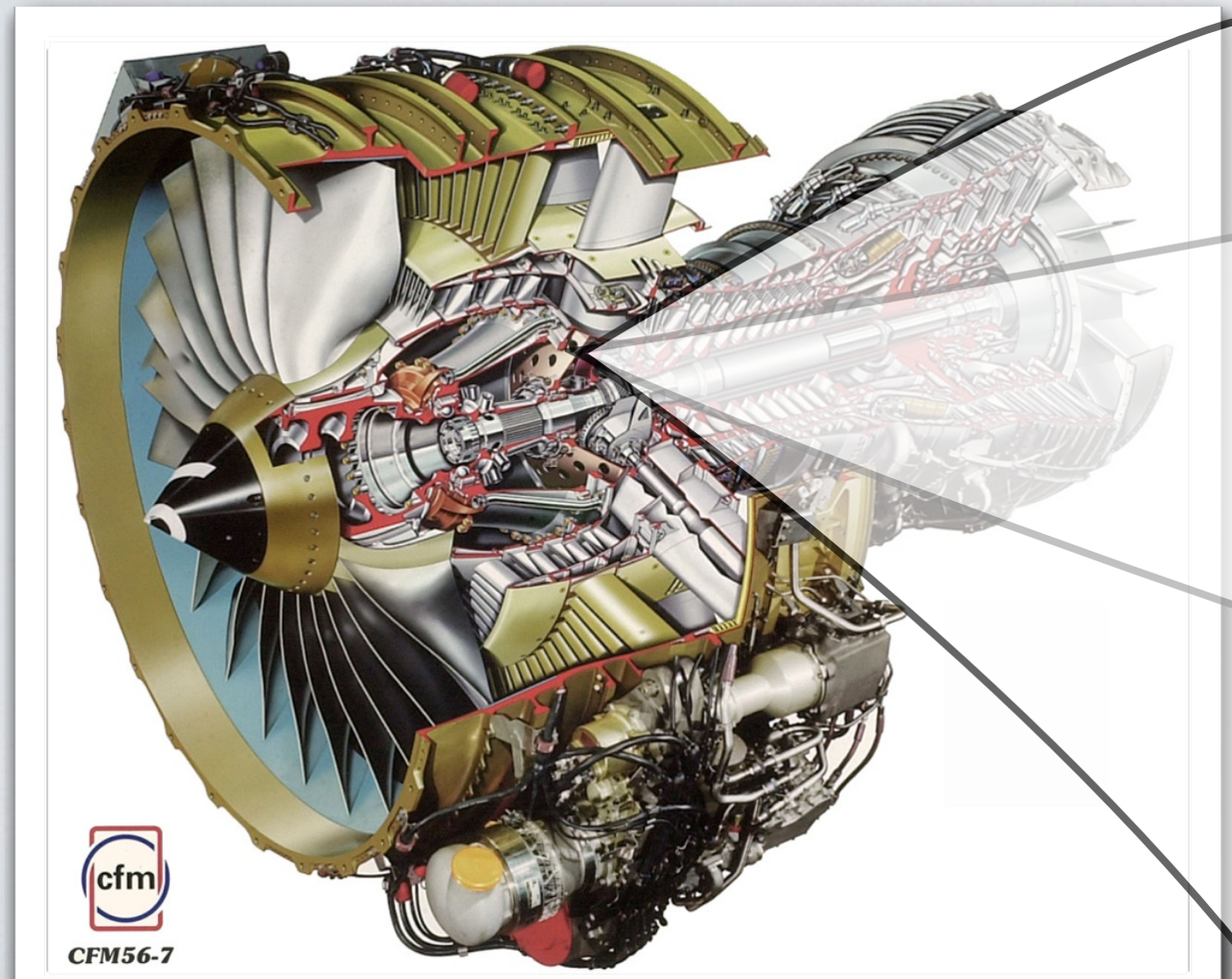
R. J. Hardy, *Phys. Rev.* **132**,168 (1963).



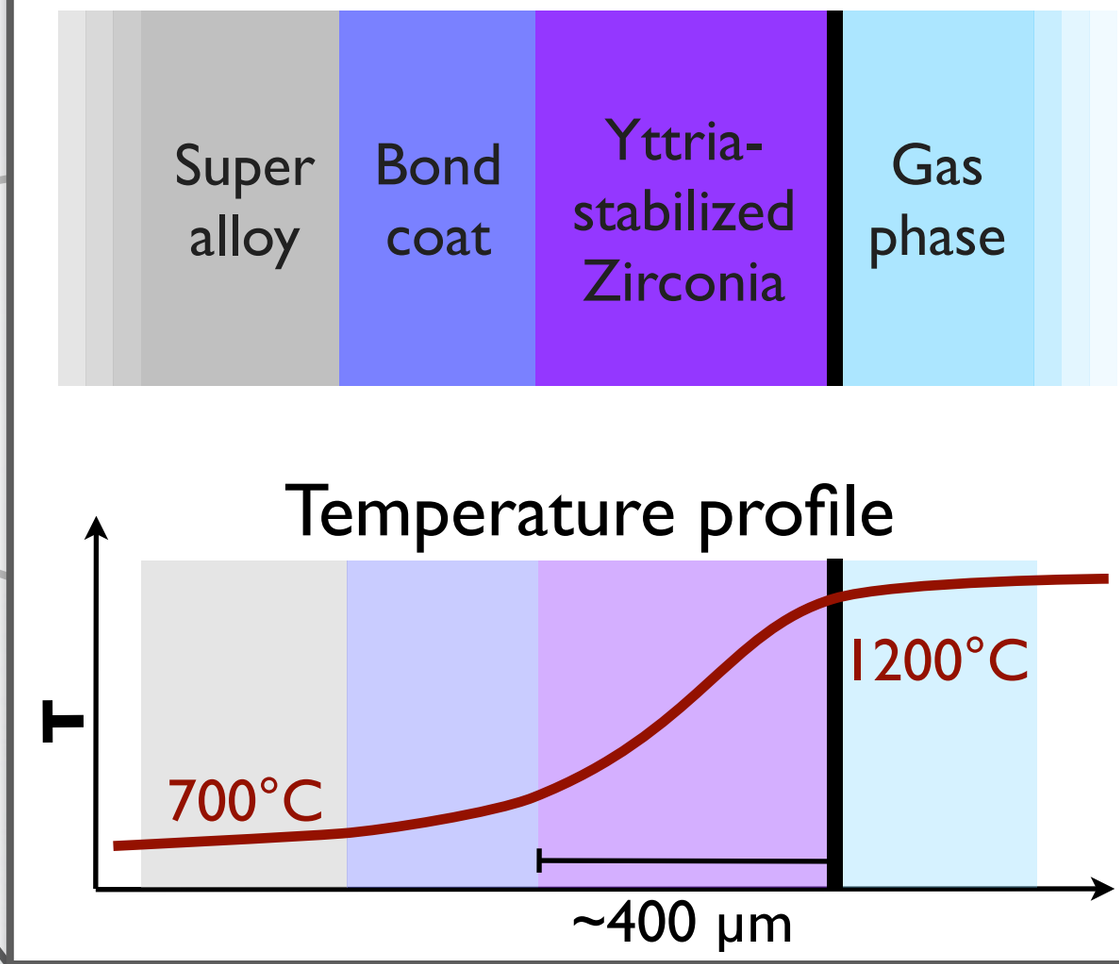
FINITE SIZE ARTIFACTS ELIMINATED!

YTTRIA-STABILIZED ZIRCONIA

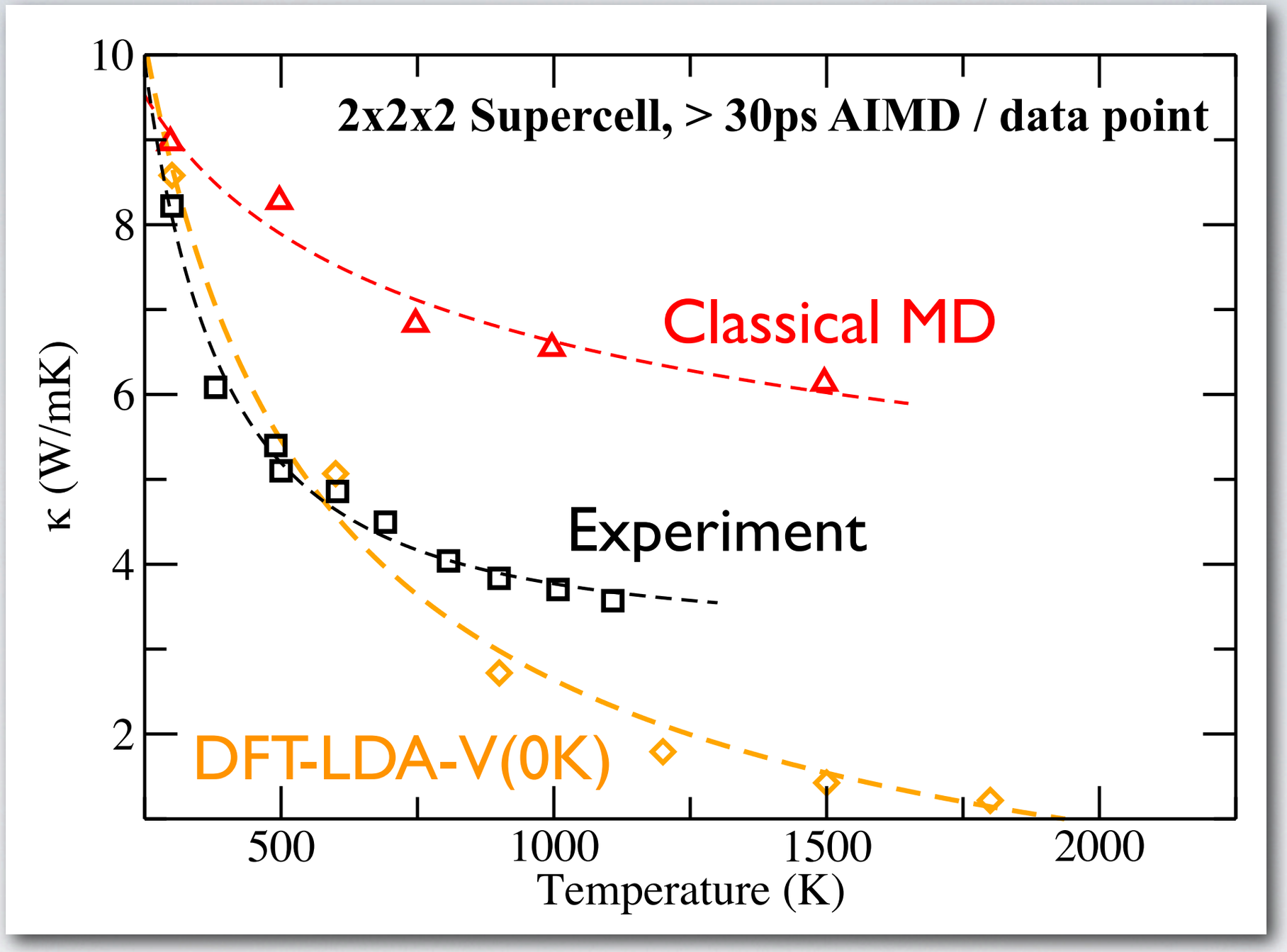
Yttria-stabilized Zirconia coatings play a crucial role in **high-temperature** applications.



CFM 56-7 airplane engine



APPLICATION TO ZIRCONIA



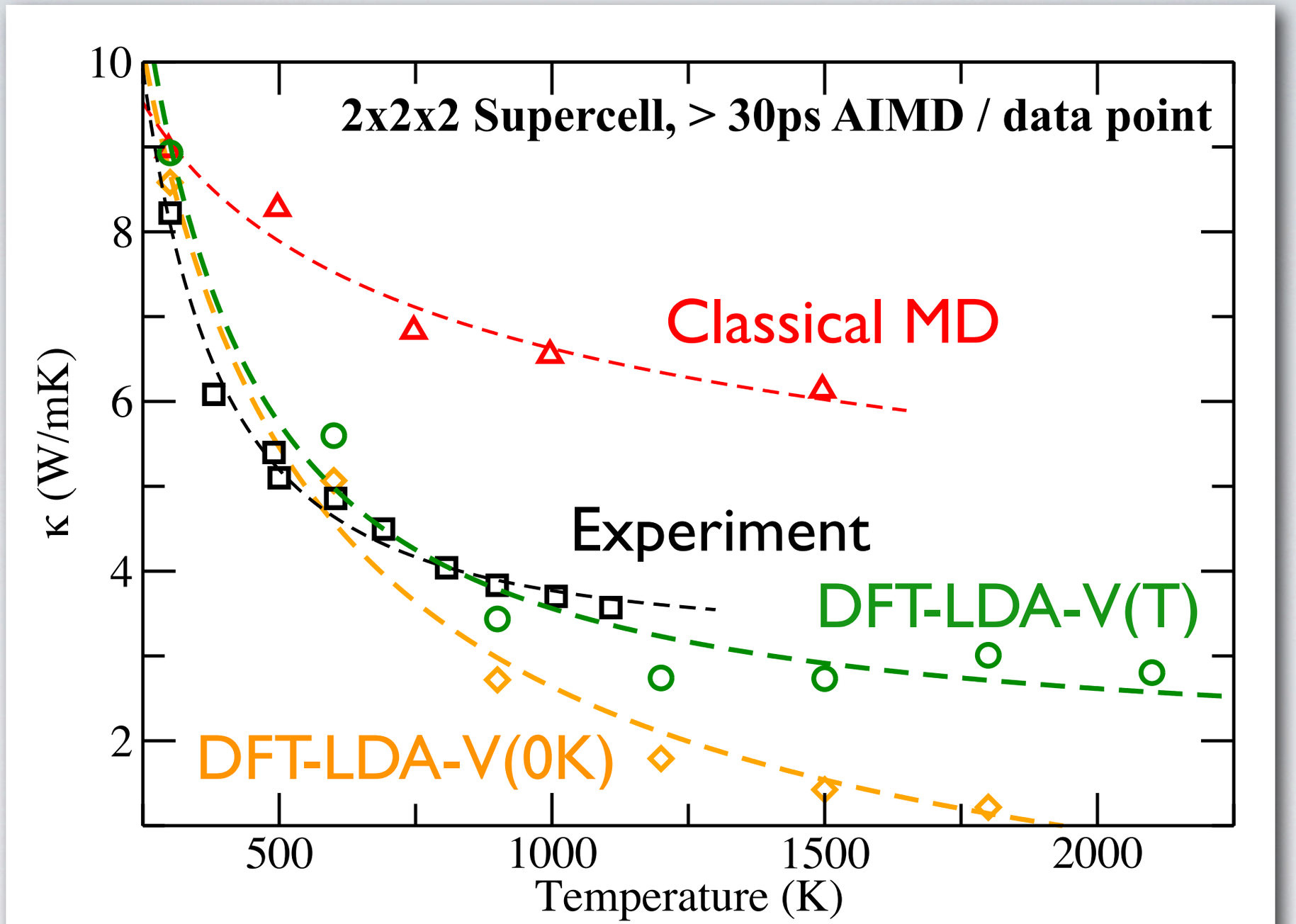
Experiment:

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).

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).

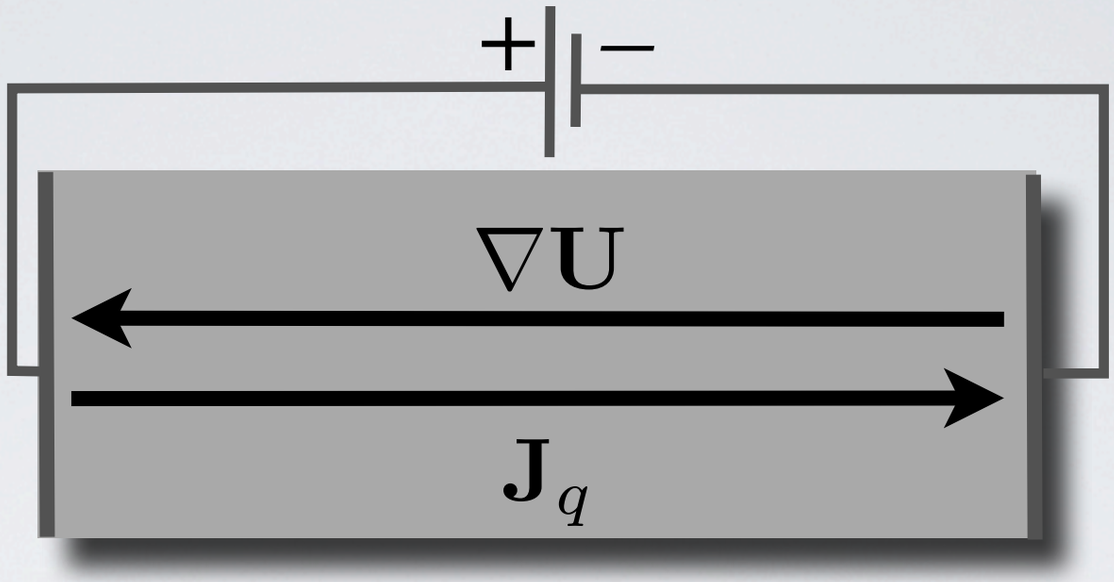
FIRST-PRINCIPLES APPROACHES

	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**!

III. CHARGE TRANSPORT

Macroscopic Electronic Transport Coefficients



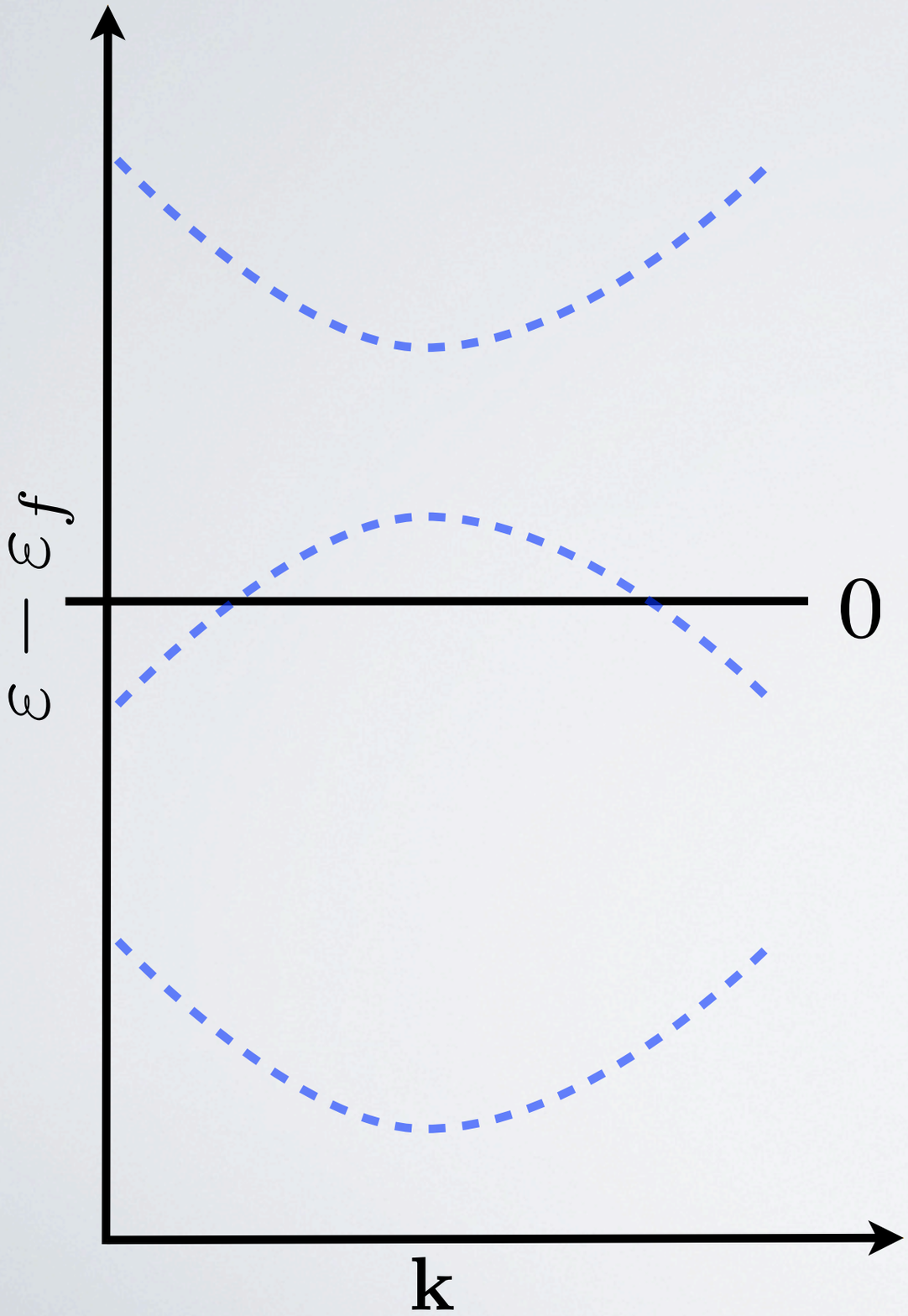
Charge Transport ⇔ *Electrical Conductivity* $J_q = -\sigma_{el}\nabla U$

Heat Transport ⇔ *Thermal Conductivity* $J_h = -\kappa_{el}\nabla T$

Coupling of Charge & Heat Transport
⇒**Thermopower** *(Seebeck Coefficient)* $\nabla U = -S\nabla T$

Conversion Efficiency
⇒**thermoelectric figure of merit** $zT = \dfrac{S^2\sigma T}{\kappa_{el} + \kappa_{nu}}$

ELECTRONS IN A PERIODIC POTENTIAL

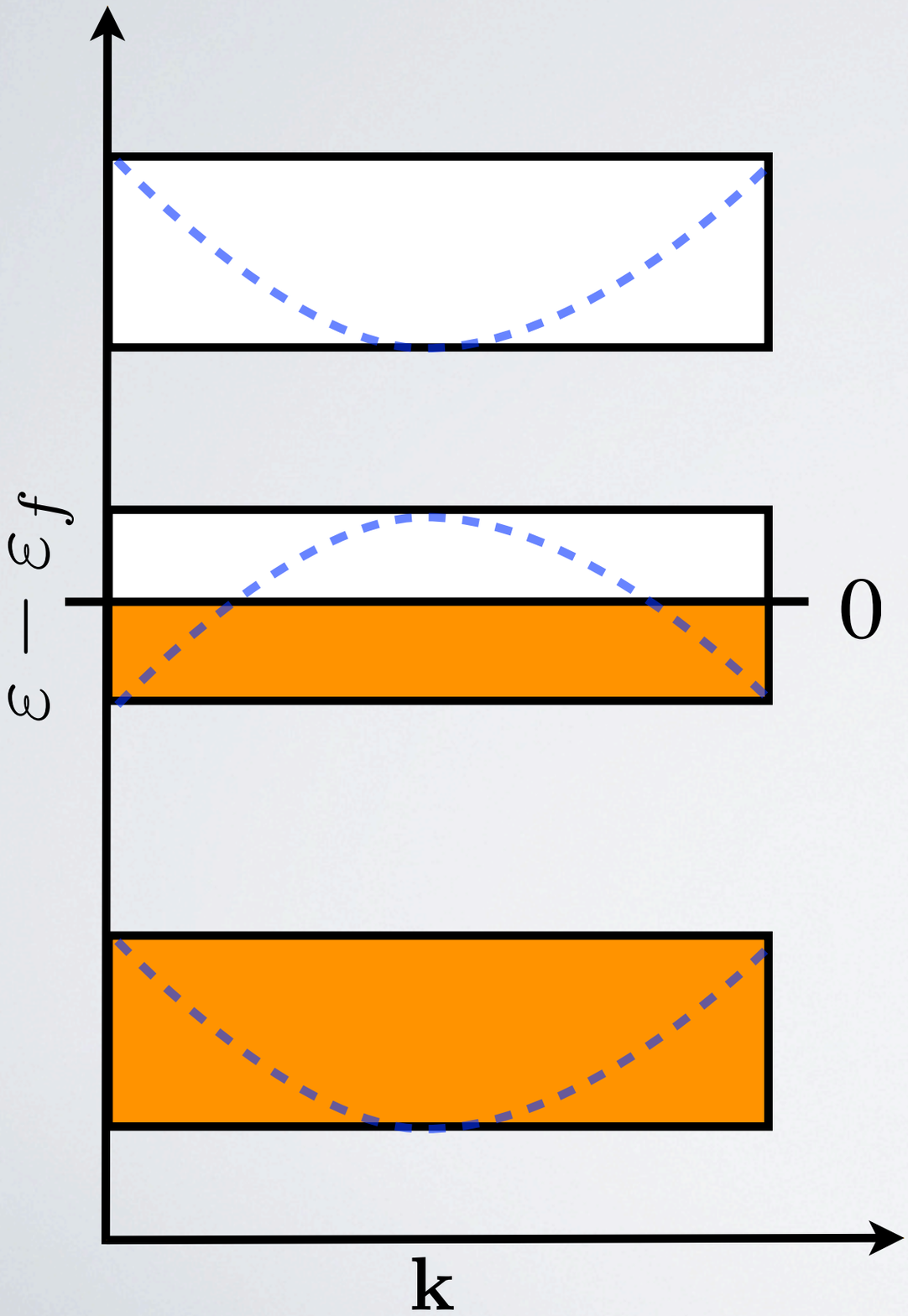


The Bloch Theorem:

F. Bloch, *Z. Physik* **52**, 555 (1929).

$$\Psi_{n\mathbf{k}}(\mathbf{r}) = u_{n\mathbf{k}}(\mathbf{r}) \cdot e^{i\mathbf{kr}}$$

ELECTRONS IN A PERIODIC POTENTIAL



The Bloch Theorem:

F. Bloch, *Z. Physik* **52**, 555 (1929).

$$\Psi_{n\mathbf{k}}(\mathbf{r}) = u_{n\mathbf{k}}(\mathbf{r}) \cdot e^{i\mathbf{kr}}$$

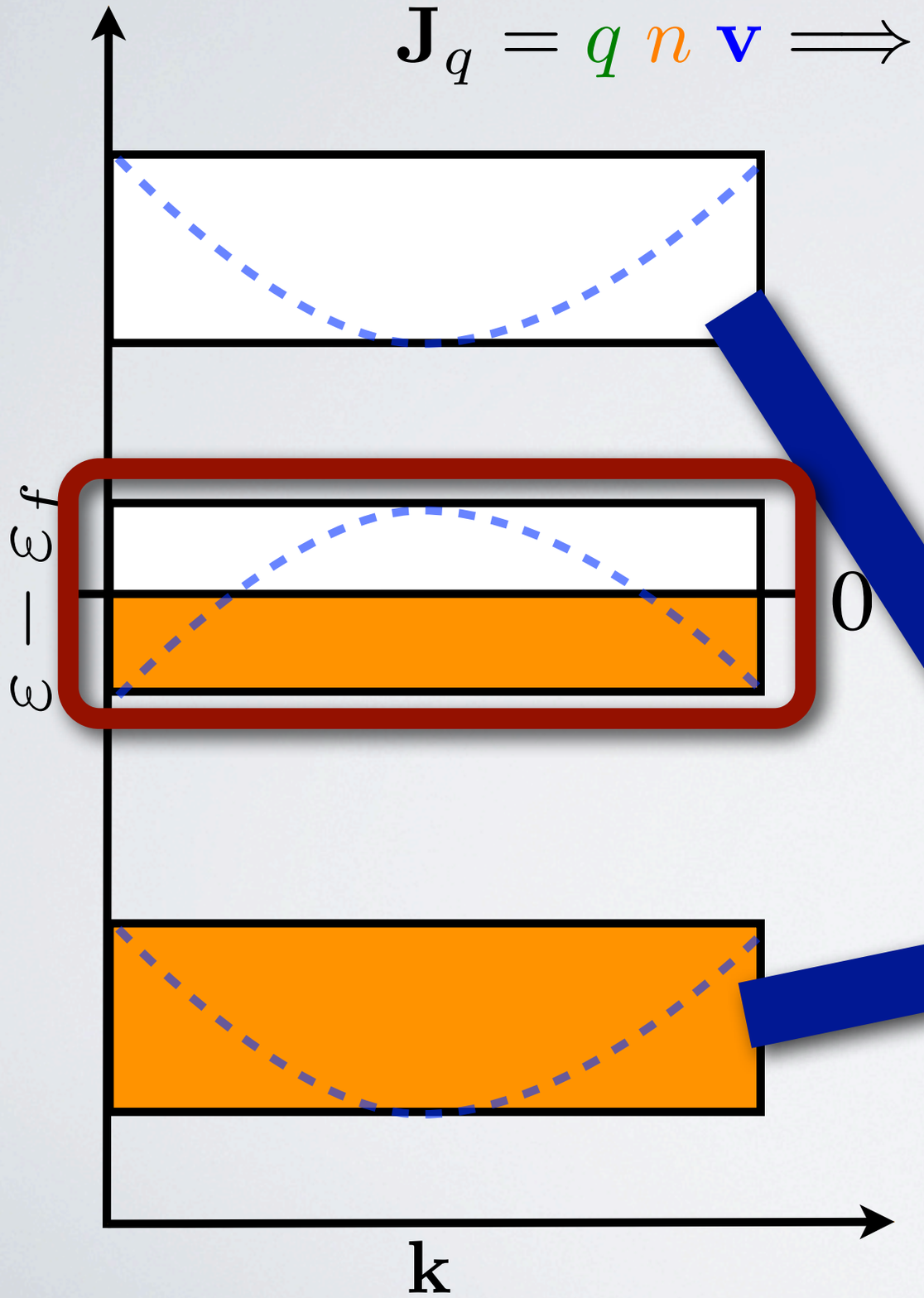
Fermi-Dirac Statistics:

E. Fermi, *Z. Physik* **36**, 902 (1926).
P. Dirac, *Proc. R. Soc. A* **112**, 661 (1926).

$$f(\varepsilon) = \frac{1}{1 + \exp\left(\frac{\varepsilon - \varepsilon_f}{k_B T}\right)}$$

ELECTRONS IN A PERIODIC POTENTIAL

$$\mathbf{J}_q = q\, n\, \mathbf{v} \Longrightarrow -e \sum_n \int \frac{d\mathbf{k}}{4\pi^3}\, f(\varepsilon_n(\mathbf{k}))\, \mathbf{v}_n(\mathbf{k})$$



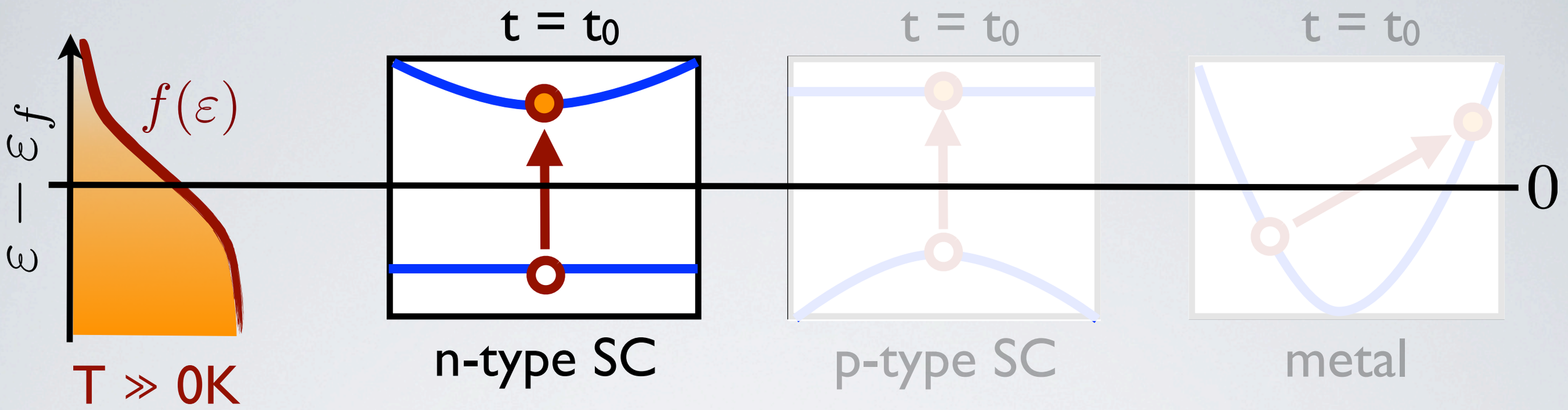
$$\mathbf{v}_n(\mathbf{k}) = \frac{1}{\hbar} \frac{\partial \varepsilon_n(\mathbf{k})}{\partial \mathbf{k}}$$

Each electron ***(n,k)*** has a constant avg. velocity $\mathbf{v}_n(\mathbf{k})$.

$$\int \frac{d\mathbf{k}}{4\pi^3}\, \mathbf{v}_n(\mathbf{k}) = 0$$

Fully filled and **empty** bands do not contribute to J_q

INSTANTANEOUS NON-EQUILIBRIUM

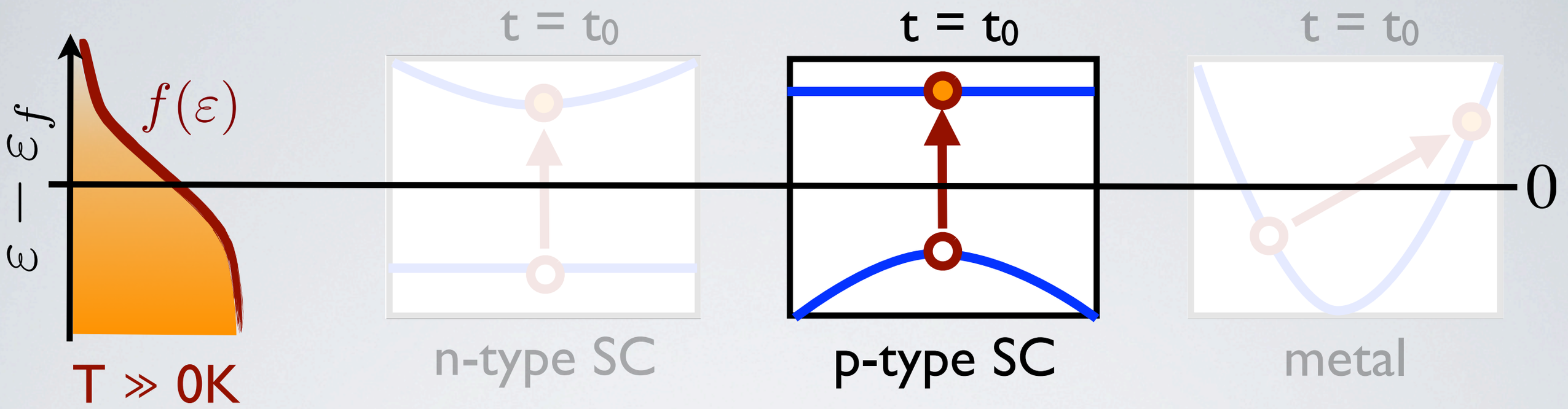


$$\mathbf{J}_q^{nk} = -e\ \mathbf{v}_n(\mathbf{k})$$

$$\mathbf{J}_e = -e\ \mathbf{v}_e(\mathbf{k_e}) \qquad \mathbf{J}_h = 0$$

In **n-type** semiconductors, **electrons** are the **majority charge carriers**.

INSTANTANEOUS NON-EQUILIBRIUM

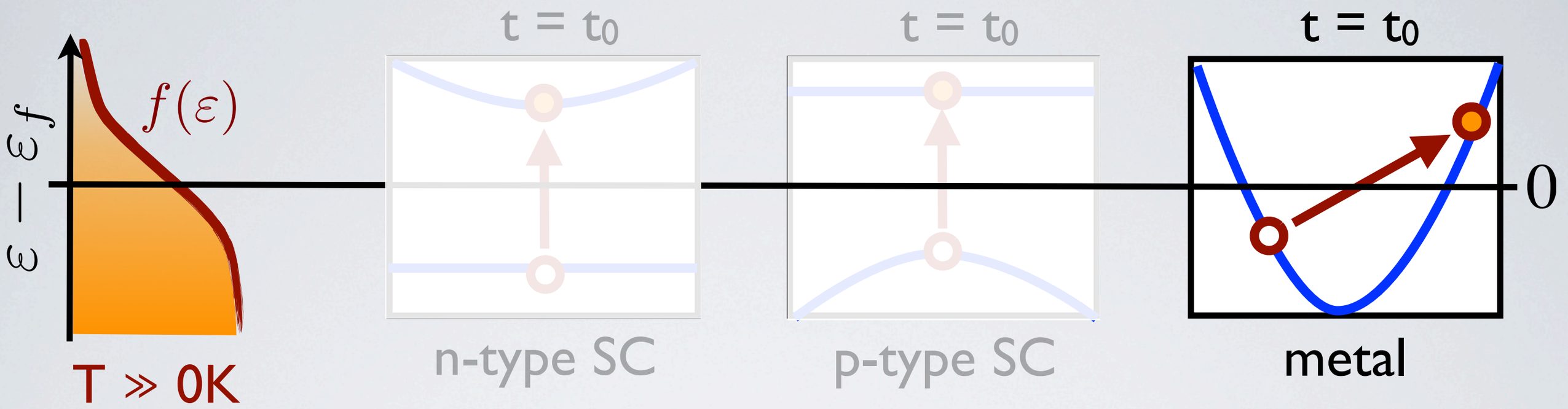


$$\mathbf{J}_q^{nk} = -e\ \mathbf{v}_n(\mathbf{k})$$

$$\mathbf{J}_e = 0 \qquad \mathbf{J}_h = +e\ \mathbf{v}_h(\mathbf{k_h})$$

In **p-type** semiconductors, **holes** are the **majority charge carriers**.

INSTANTANEOUS NON-EQUILIBRIUM



$$\mathbf{J}_q^{nk} = -e\ \mathbf{v}_n(\mathbf{k})$$

$$\mathbf{J}_e = -e\ \mathbf{v}_e(\mathbf{k_e}) \qquad \mathbf{J}_h = +e\ \mathbf{v}_h(\mathbf{k_h})$$

In typical **metals** with $\mathbf{v_e} > \mathbf{v_h}$,
electrons are the **majority charge carriers**.

BOLTZMANN TRANSPORT EQUATION

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

$$\sigma = -e^2 \sum_n \int \frac{d\mathbf{k}}{4\pi^3} \, \mathbf{v}_n(\mathbf{k}) \, \mathbf{v}_n(\mathbf{k}) \left(\frac{\partial f(\varepsilon_n)}{\partial \varepsilon_n} \right) \tau_{n\mathbf{k}}$$

$$S = -\frac{e k_B}{\sigma} \sum_n \int \frac{d\mathbf{k}}{4\pi^3} \, \mathbf{v}_n(\mathbf{k}) \, \mathbf{v}_n(\mathbf{k}) \left(\frac{\partial f(\varepsilon_n)}{\partial \varepsilon_n} \right) \tau_{n\mathbf{k}} \left(\frac{\varepsilon_n - \varepsilon_F}{k_B T} \right)$$

$$\kappa_{el} = -k_B^2 \sum_n \int \frac{d\mathbf{k}}{4\pi^3} \, \mathbf{v}_n(\mathbf{k}) \, \mathbf{v}_n(\mathbf{k}) \left(\frac{\partial f(\varepsilon_n)}{\partial \varepsilon_n} \right) \tau_{n\mathbf{k}} \left(\frac{\varepsilon_n - \varepsilon_F}{k_B T} \right)^2$$

Group velocity

Eq. population

scattering time

Band structure calculation

?

BOLTZMANN TRANSPORT EQUATION

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Electron-electron scattering

BOLTZMANN TRANSPORT EQUATION

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

$$\sigma = -e^2 \sum_n \int \frac{d\mathbf{k}}{4\pi^3} \, \mathbf{v}_n(\mathbf{k}) \, \mathbf{v}_n(\mathbf{k}) \left(\frac{\partial f(\varepsilon_n)}{\partial \varepsilon_n} \right) \tau_{n\mathbf{k}}$$

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~~Electron-electron scattering~~

Electron-nuclei scattering

defects

phonons

BOLTZMANN TRANSPORT EQUATION

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

$$\sigma = -e^2 \sum_n \int \frac{d\mathbf{k}}{4\pi^3} \mathbf{v}_n(\mathbf{k})\, \mathbf{v}_n(\mathbf{k}) \left(\frac{\partial f(\varepsilon_n)}{\partial \varepsilon_n} \right) \tau_{n\mathbf{k}}$$

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~~Electron-electron scattering~~

Electron-nuclei scattering

- defects
- phonons

SINGLE RELAXATION TIME APPROXIMATION

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

$$\sigma = -e^2 \tau \sum_n \int \frac{d\mathbf{k}}{4\pi^3} \mathbf{v}_n(\mathbf{k}) \mathbf{v}_n(\mathbf{k}) \left(\frac{\partial f(\varepsilon_n)}{\partial \varepsilon_n} \right)$$

$$S = -\frac{e k_B}{\sigma} \tau \sum_n \int \frac{d\mathbf{k}}{4\pi^3} \mathbf{v}_n(\mathbf{k}) \mathbf{v}_n(\mathbf{k}) \left(\frac{\partial f(\varepsilon_n)}{\partial \varepsilon_n} \right) \left(\frac{\varepsilon_n - \varepsilon_F}{k_B T} \right)$$

$$\kappa_{el} = -k_B^2 \tau \sum_n \int \frac{d\mathbf{k}}{4\pi^3} \mathbf{v}_n(\mathbf{k}) \mathbf{v}_n(\mathbf{k}) \left(\frac{\partial f(\varepsilon_n)}{\partial \varepsilon_n} \right) \left(\frac{\varepsilon_n - \varepsilon_F}{k_B T} \right)^2$$

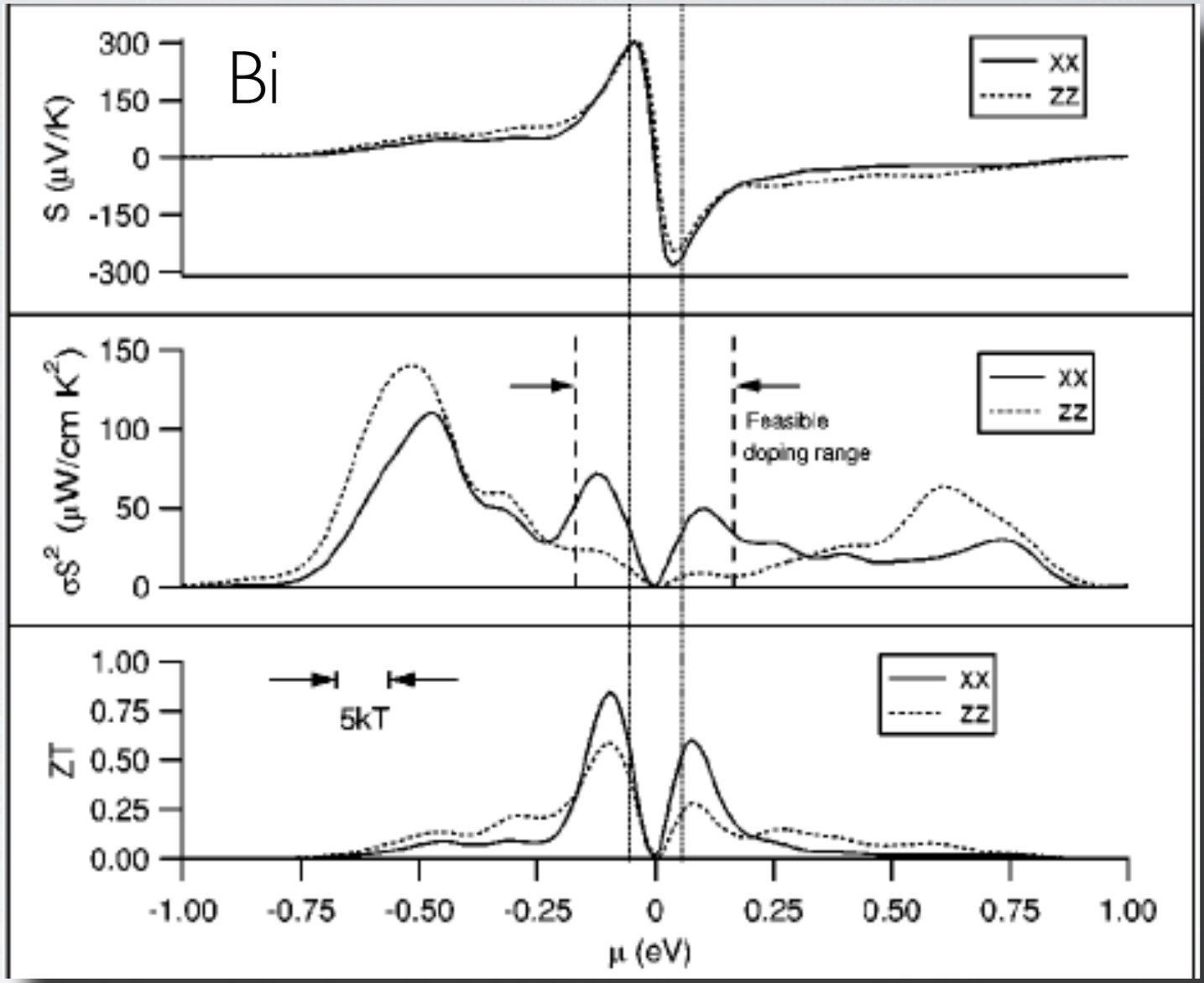
Energy and Crystal Momentum independent scattering time

SRTA **does not** facilitate the *first principles assessment*.

SRTA allows **parametrical studies**

SINGLE RELAXATION TIME APPROXIMATION

- Accurate **band structure**
- *"Reasonable" relaxation time*
- *Lattice thermal conductivity* requires *separate calculation*



Transport Coefficients

T. Thonhauser, T. J. Scheidemantel, and J. O. Sofo, *Appl. Phys. Lett.* **85**, 588 (2004).

T. J. Scheidemantel, *et al.* *Phys. Rev. B* **68**, 125210 (2003)

SINGLE RELAXATION TIME APPROXIMATION

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

The **conductivity** is intrinsically related to the **effective mass**:

$$\sigma = -e^2\tau \sum_n \int \frac{d\mathbf{k}}{4\pi^3}\, \mathbf{v}_n(\mathbf{k})\, \mathbf{v}_n(\mathbf{k}) \left(\frac{\partial f(\varepsilon_n)}{\partial \varepsilon_n} \right)$$

$$= -e^2\tau \sum_n \int \frac{d\mathbf{k}}{4\pi^3}\, f(\varepsilon_n) \frac{1}{\hbar^2} \frac{\partial^2 \varepsilon}{\partial \mathbf{k}\, \partial \mathbf{k}}$$

The **AC conductivity** does not depend on the **relaxation time τ** for **ωτ** ≫ 1

$$\sigma(\omega) = -\frac{e^2\tau}{1 - i\omega\tau} \sum_n \int \frac{d\mathbf{k}}{4\pi^3}\, f(\varepsilon_n) \frac{1}{\hbar^2} \frac{\partial^2 \varepsilon}{\partial \mathbf{k}\, \partial \mathbf{k}}$$

$$\xrightarrow{\omega\tau \gg 1} \frac{e^2}{i\omega} \sum_n \int \frac{d\mathbf{k}}{4\pi^3}\, f(\varepsilon_n) \frac{1}{\hbar^2} \frac{\partial^2 \varepsilon}{\partial \mathbf{k}\, \partial \mathbf{k}}$$

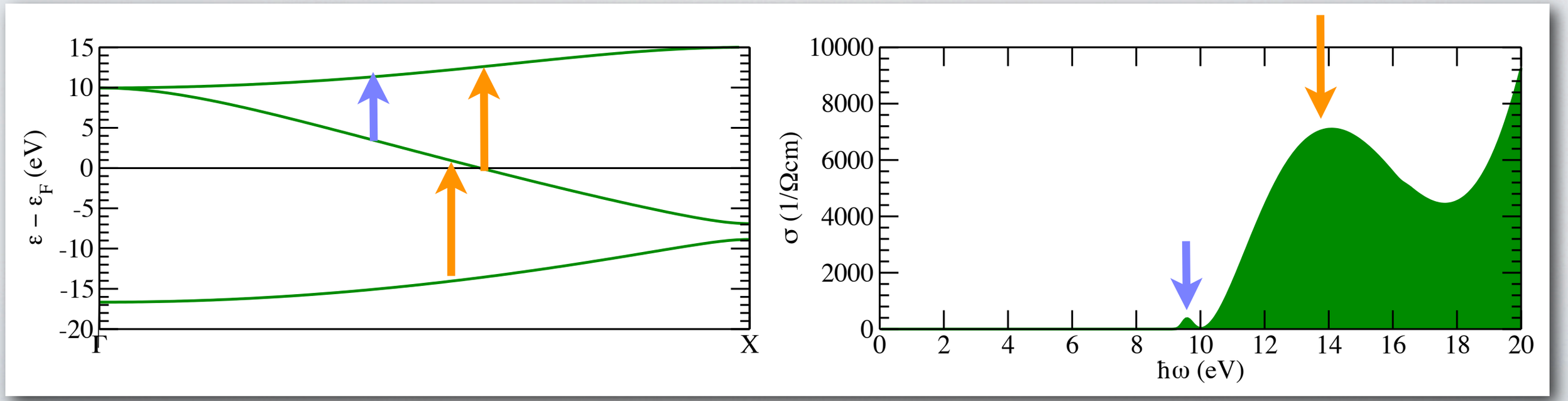
OPTICAL CONDUCTIVITY

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

Using **perturbation theory,** we can thus compute the **AC (optical) conductivity** (in the independent particle approximation).

$$\sigma(\omega) \xrightarrow{\omega\tau \gg 1} \frac{e^2}{i\omega} \sum_n \int \frac{d\mathbf{k}}{4\pi^3} f(\varepsilon_n) \frac{1}{\hbar^2} \frac{\partial^2 \varepsilon}{\partial \mathbf{k}\, \partial \mathbf{k}}$$

$$= \frac{e^2\hbar^2}{i\omega m_e^2} \sum_{n,m\neq n} \int \frac{d\mathbf{k}}{4\pi^3} \left[f(\varepsilon_n) - f(\varepsilon_m)\right] \frac{|\langle nk|\, \nabla\, |mk\rangle|^2}{\varepsilon_n - \varepsilon_m - \hbar\omega}$$

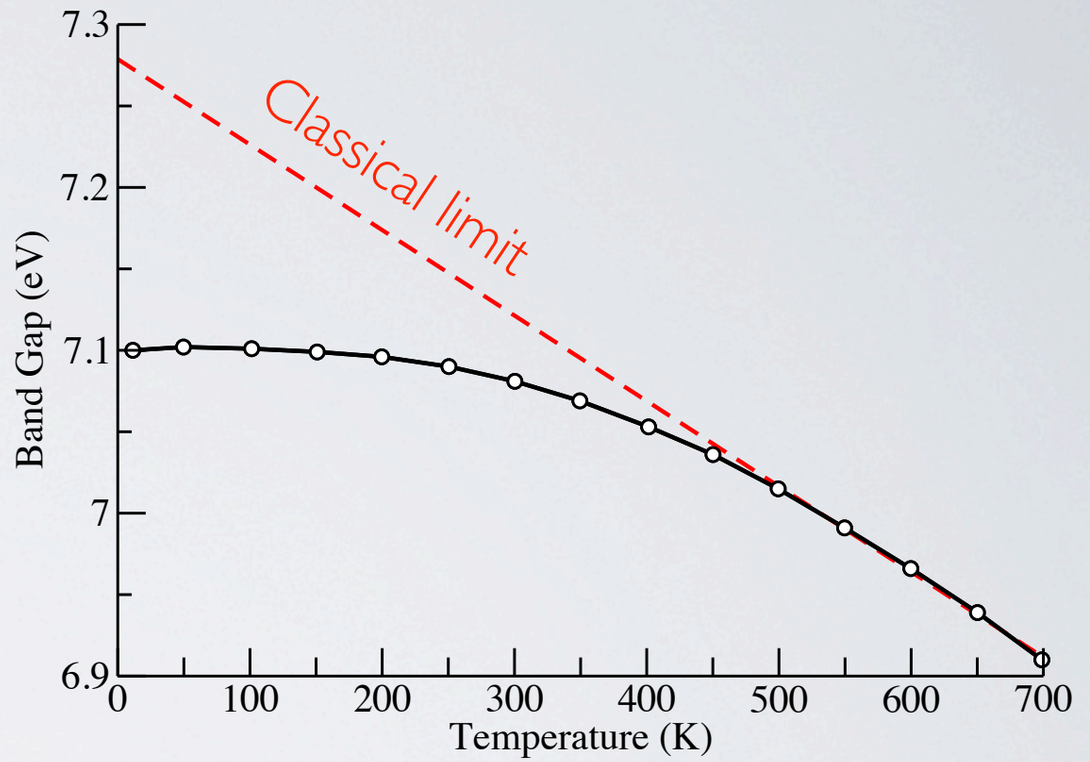


ficticious sc-Aluminum along X direction

PROBLEMS OF THE BTE/SRTA

(a) Rigid band approximation:

The BTE/SRTA relies on a rigid (or perturbative) definition of the band structure.



Band gap renormalization in diamond
F. Giustino, S. G. Louie, and M. L. Cohen,
Phys. Rev. Lett. **105**, 265501 (2010).

(b) Nature of the scattering:

The **main complexity** of the conductivity is still hidden in the **relaxation time τ**

Parametrical studies of **τ** do not allow predictions.

Computational assessment of **τ** still topic of research.

P. Boulet, *et al., Comp. Mater Sci* **50**, 847 (2011).

GREENWOOD-KUBO FORMALISM

D. A. Greenwood, *Proc. Phys. Soc.* **71**, 585 (1958).

Kubo's Linear Response:

$$\sigma(\omega) = \frac{1}{V} \left\langle \lim_{\varepsilon \to 0} \int_0^\infty dt\, e^{i(\omega + i\varepsilon)t} \int_0^{(k_B T)^{-1}} d\tau\, \mathbf{Tr}\left[\hat{\rho}_0\, \mathbf{j}_c(t - i\hbar\tau) \cdot \mathbf{j}_c(t)\right] \right\rangle_T$$

Independent Particle Picture:

$$\mathbf{j}_c = -\frac{e}{\hbar} \frac{\partial \varepsilon_n(\mathbf{k})}{\partial \mathbf{k}}$$

Heisenberg picture

$$\mathbf{j}_c(t)$$

$$\sigma(\omega) = \frac{e^2\hbar^2}{m_e^2 \omega} \frac{2\pi}{V} \left\langle \sum_{n, n \neq m} \sum_{\mathbf{k}} w_k \left[f(\varepsilon_n) - f(\varepsilon_m)\right] \left|\langle n\mathbf{k}| \nabla |m\mathbf{k}\rangle\right|^2 \delta\left(\varepsilon_n - \varepsilon_m - \hbar\omega\right) \right\rangle_T$$

B. Holst, M. French, and R. Redmer, *Phys. Rev. B* **83**, 235120 (2011).

GREENWOOD-KUBO FORMALISM

D. A. Greenwood, *Proc. Phys. Soc.* **71**, 585 (1958).

For **ω ≠ 0**, the **electrical conductivity** can be computed from the ***thermodynamic average*** $\langle\rangle_T$:

$$\sigma(\omega) = \frac{e^2\hbar^2}{m_e^2\omega}\frac{2\pi}{V}\left\langle \sum_{n,n\neq m}\sum_{\mathbf{k}} w_k \left[f(\varepsilon_n) - f(\varepsilon_m)\right] \left|\langle n\mathbf{k}|\nabla|m\mathbf{k}\rangle\right|^2 \delta\left(\varepsilon_n - \varepsilon_m - \hbar\omega\right)\right\rangle_T$$

(a) Thermodynamic average of the band structure is sampled
⇒ no rigid band approximation

(b) Full adiabatic electron-phonon coupling is accounted for if the thermodynamic average is perfomed via ab initio MD
⇒ no perturbative approximation

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Compare: Optical conductivity in **SRT approximation**

$$\sigma(\omega) \xrightarrow{\omega\tau \gg 1} \frac{e^2\hbar^2}{m_e^2\omega}\sum_{n,m\neq n}\int \frac{d\mathbf{k}}{4\pi^3}\left[f(\varepsilon_n) - f(\varepsilon_m)\right]\frac{\left|\langle nk|\nabla|mk\rangle\right|^2}{\varepsilon_n - \varepsilon_m - \hbar\omega}$$

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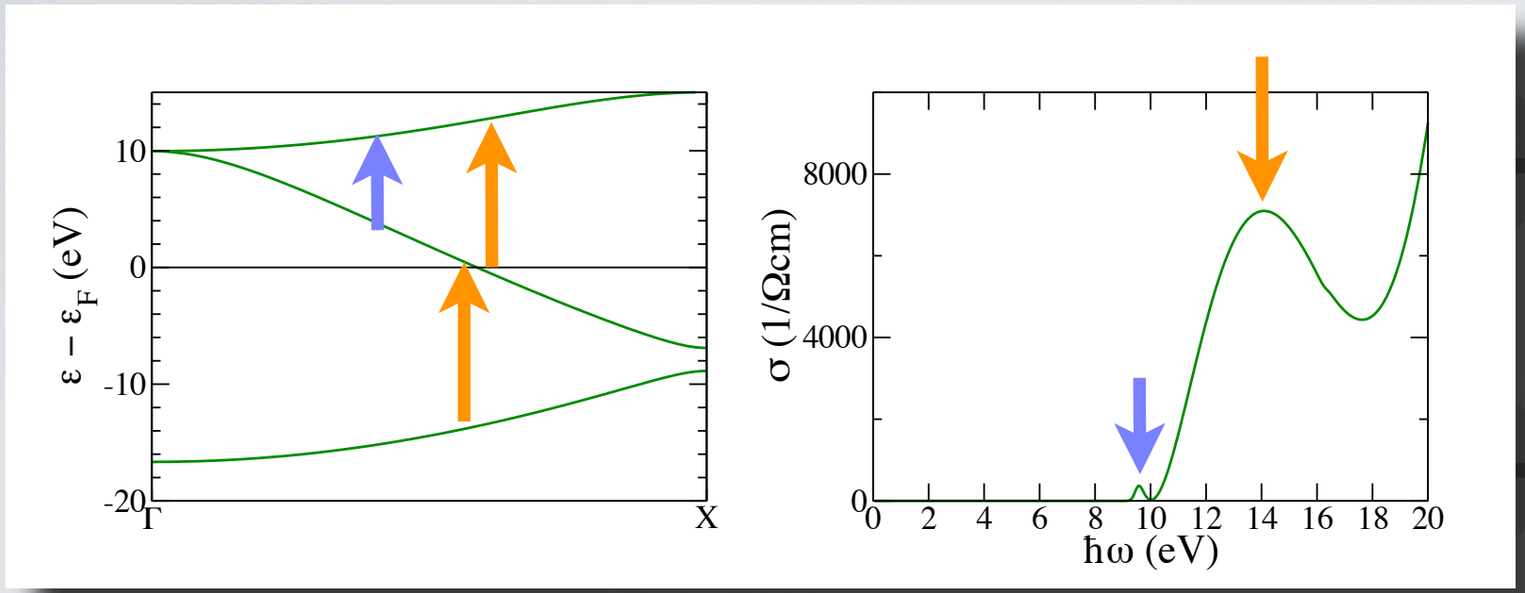
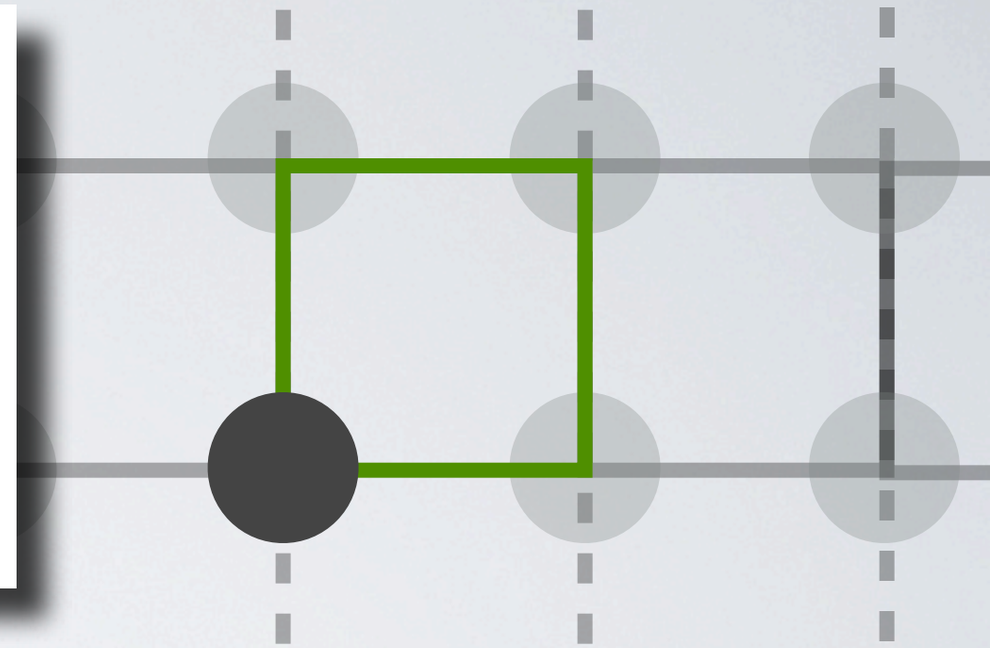
D. A. Greenwood, *Proc. Phys. Soc.* **71**, 585 (1958).





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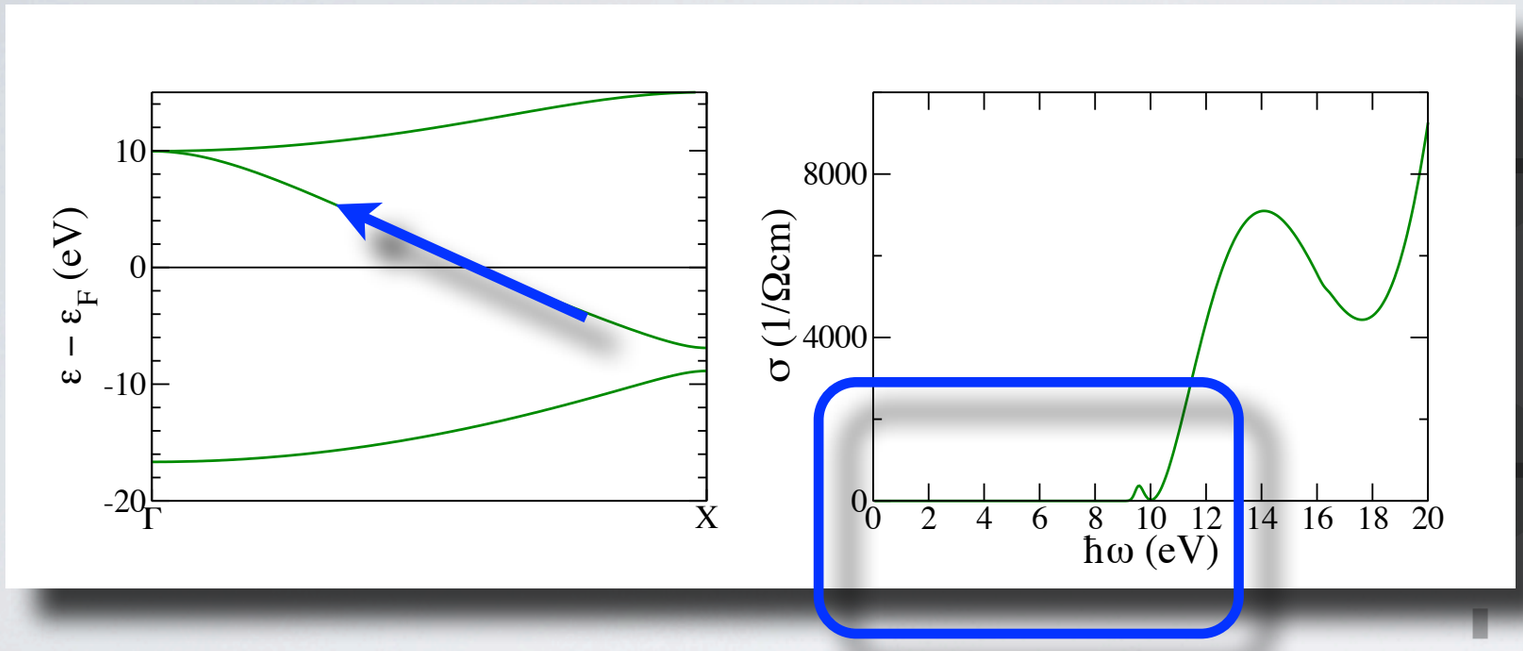
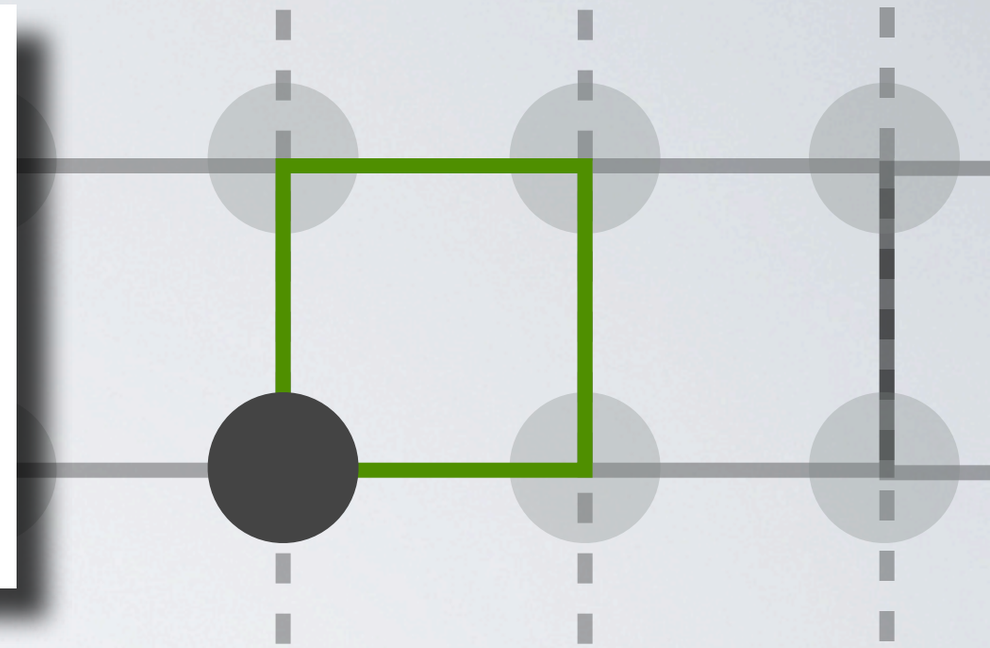
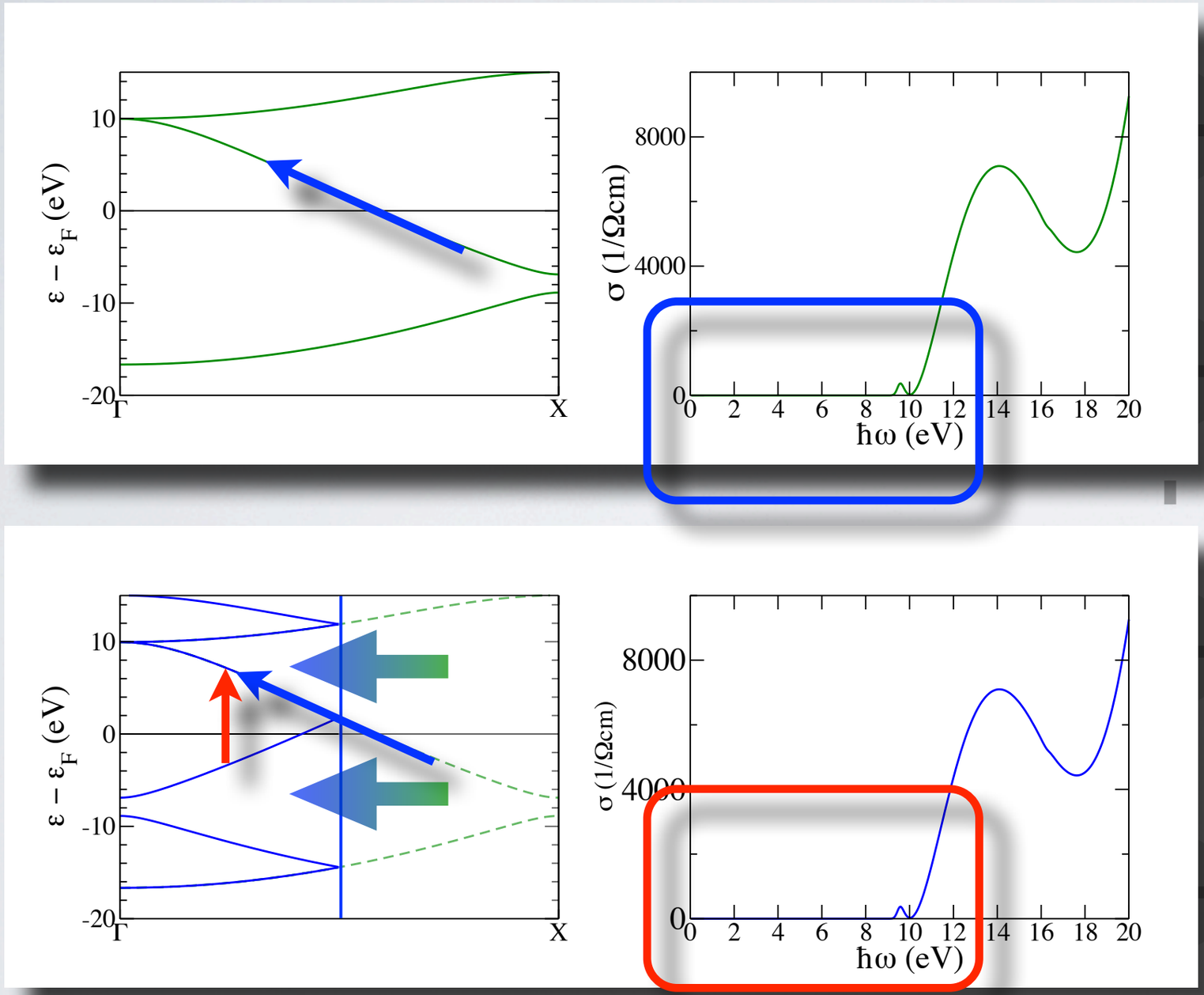


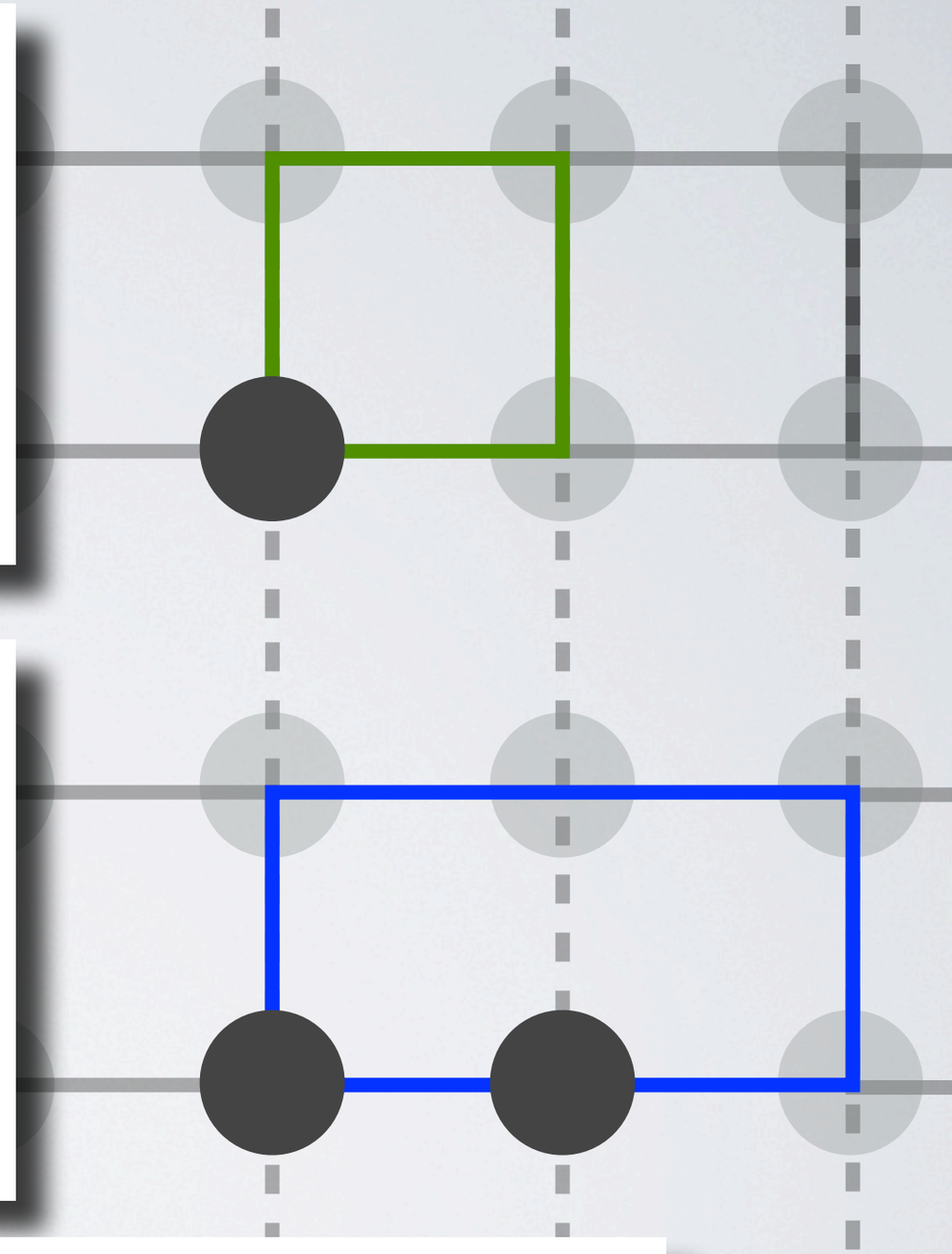


Crystal Momentum Conservation:
Non-vertical transitions require **phonons**

GREENWOOD-KUBO FORMALISM

D. A. Greenwood, *Proc. Phys. Soc.* **71**, 585 (1958).





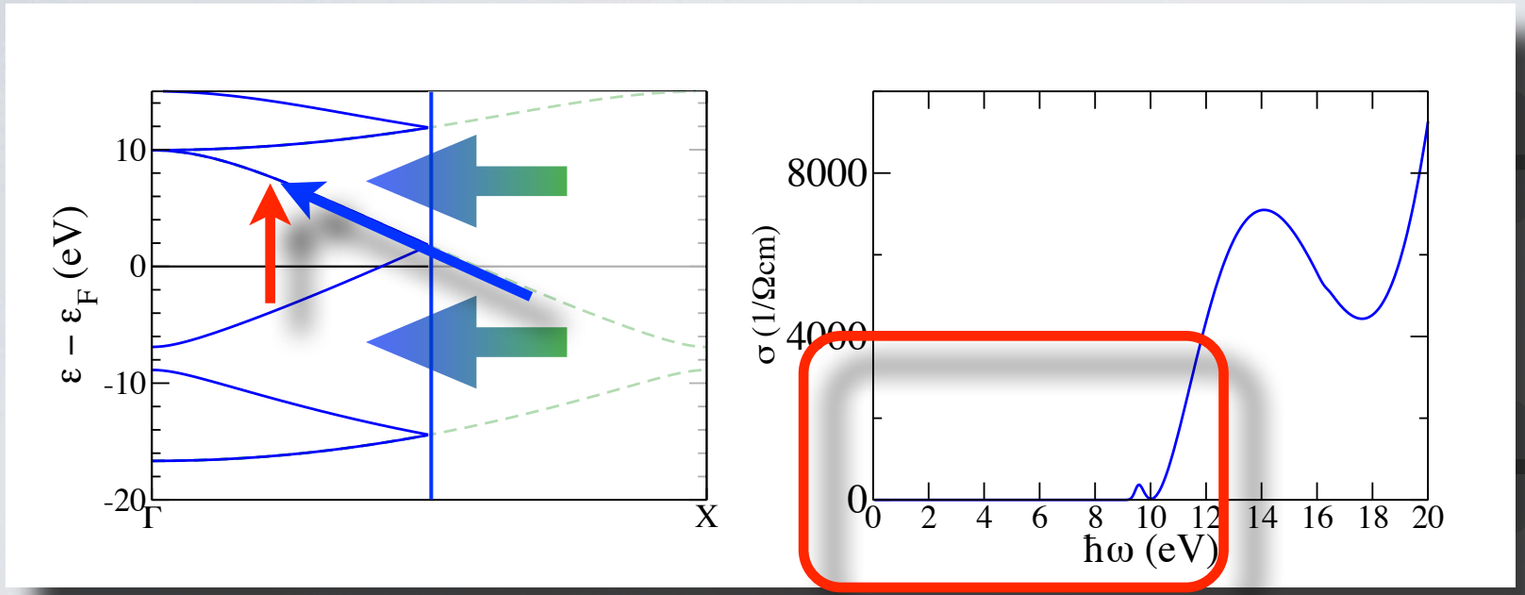
Brillouin zone folding:

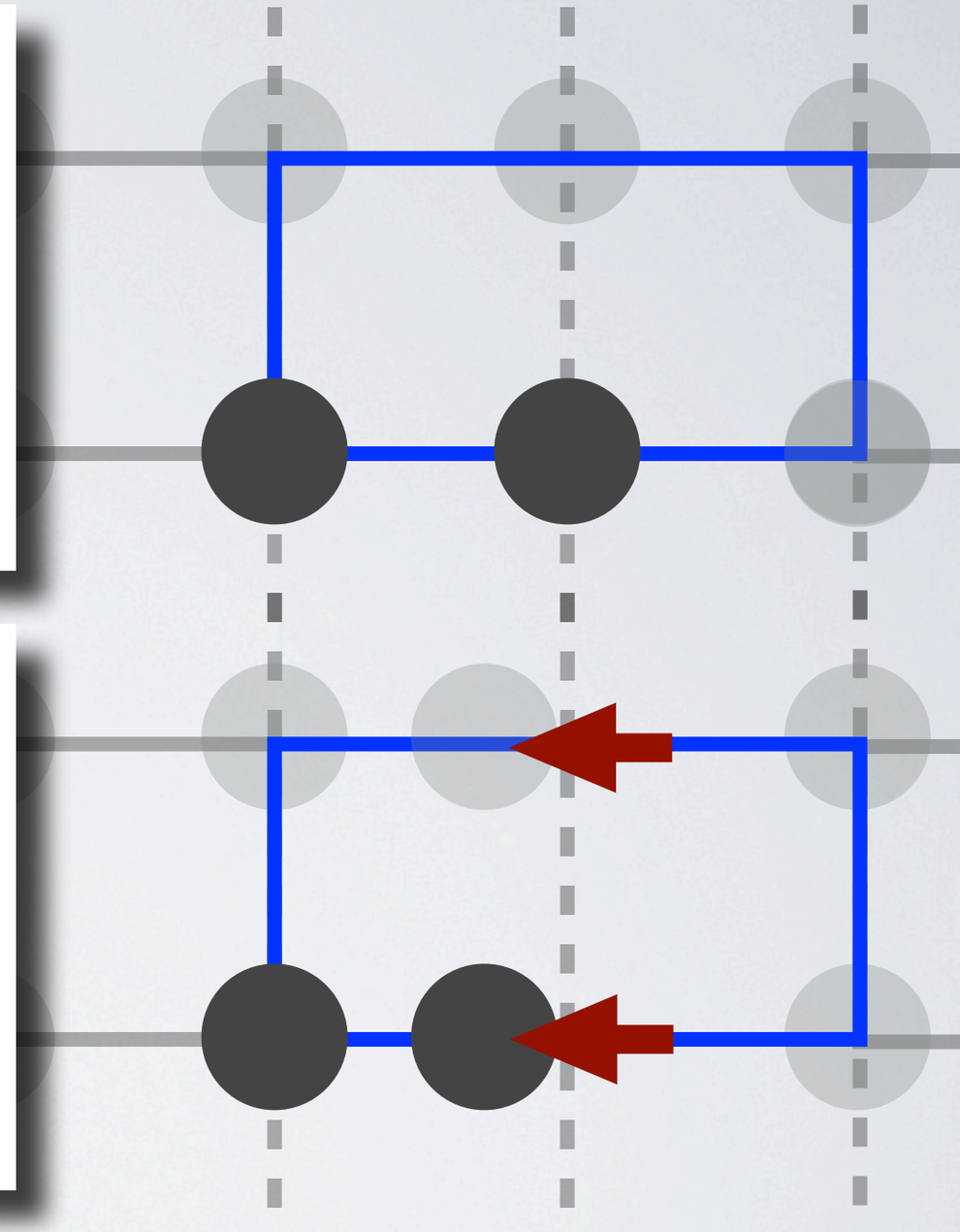
Larger supercells allow for **direct transitions**

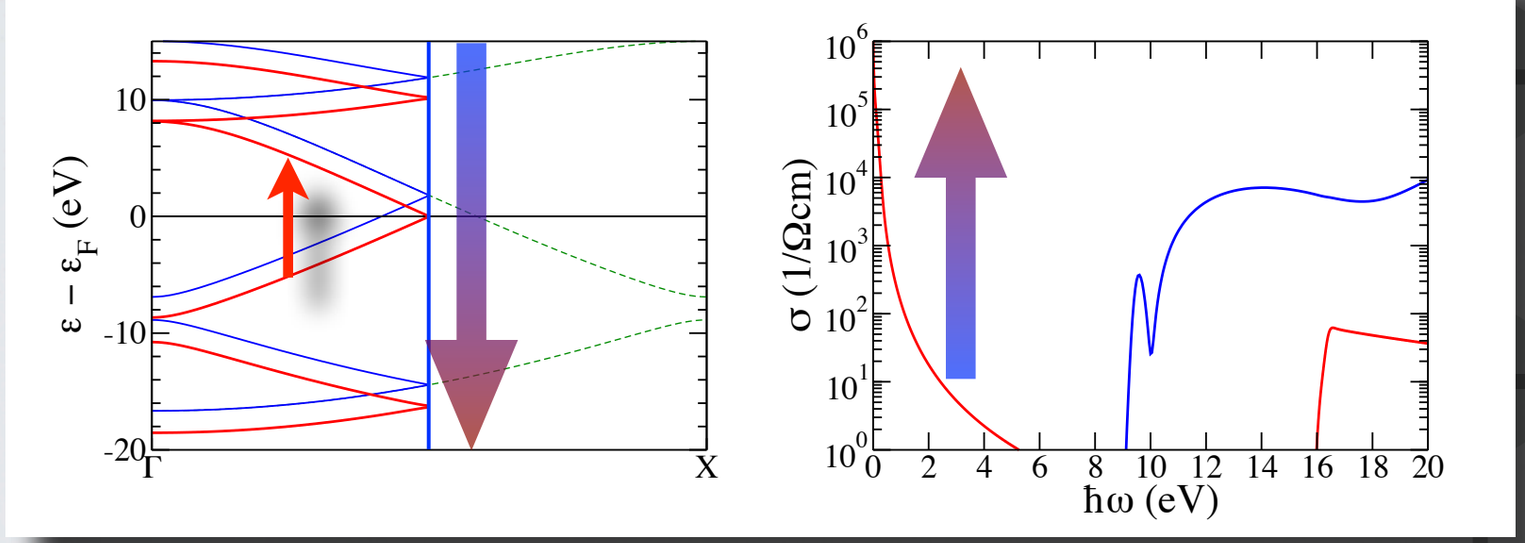
that are however suppressed by **symmetry**.

GREENWOOD-KUBO FORMALISM

D. A. Greenwood, *Proc. Phys. Soc.* **71**, 585 (1958).





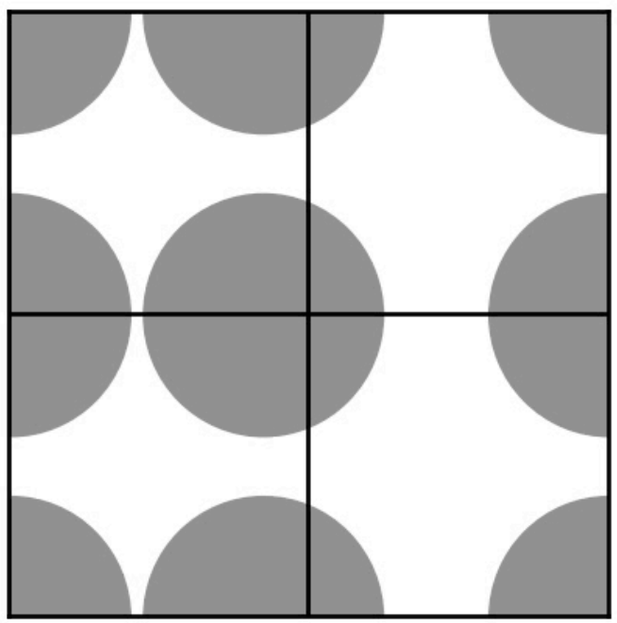


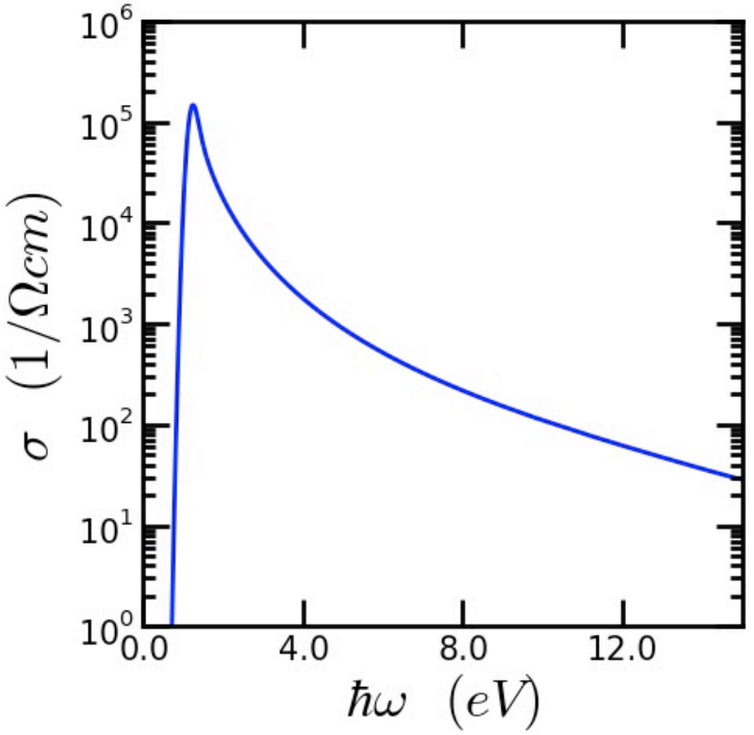
Thermal Motion of the nuclei:

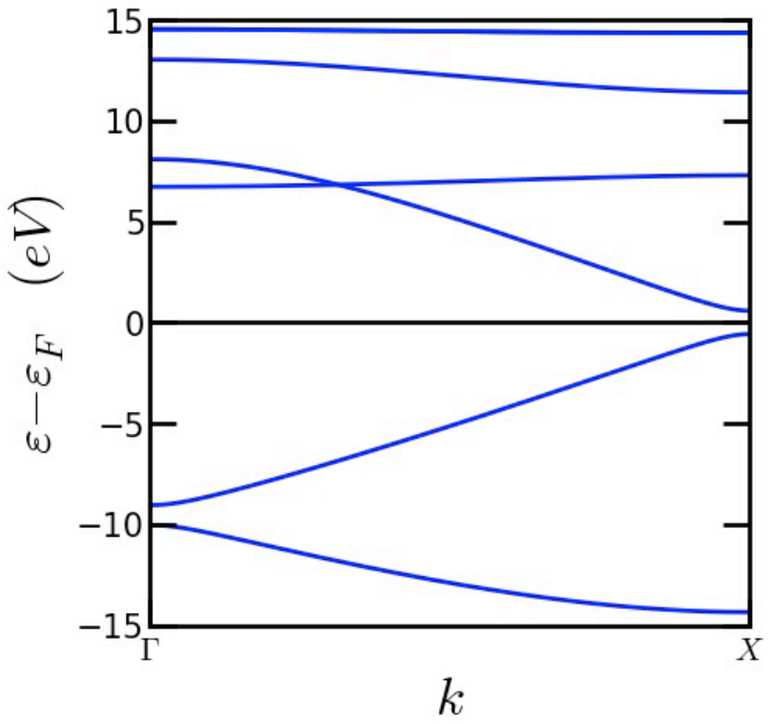
Phonons momentarily break the **symmetry** and thus allow the **direct transitions** to become **active**.

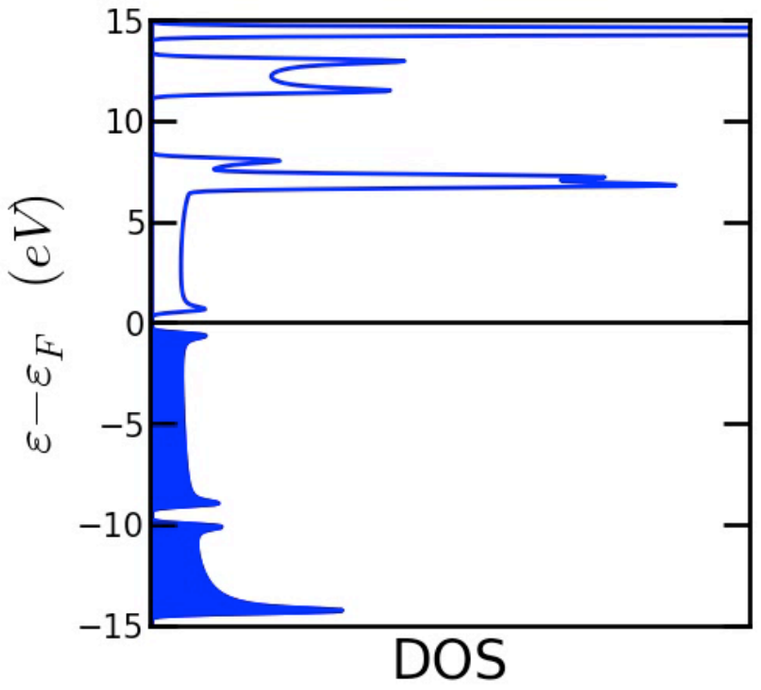
GREENWOOD-KUBO FORMALISM

D. A. Greenwood, *Proc. Phys. Soc.* **71**, 585 (1958).









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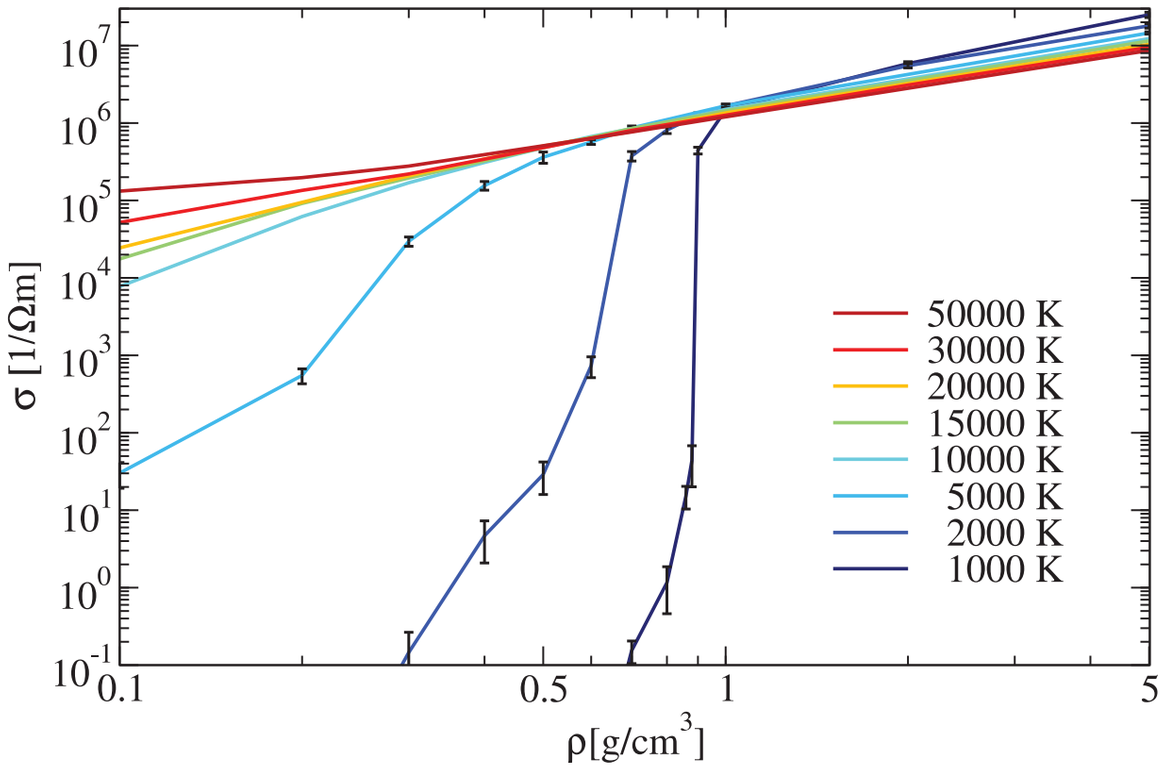
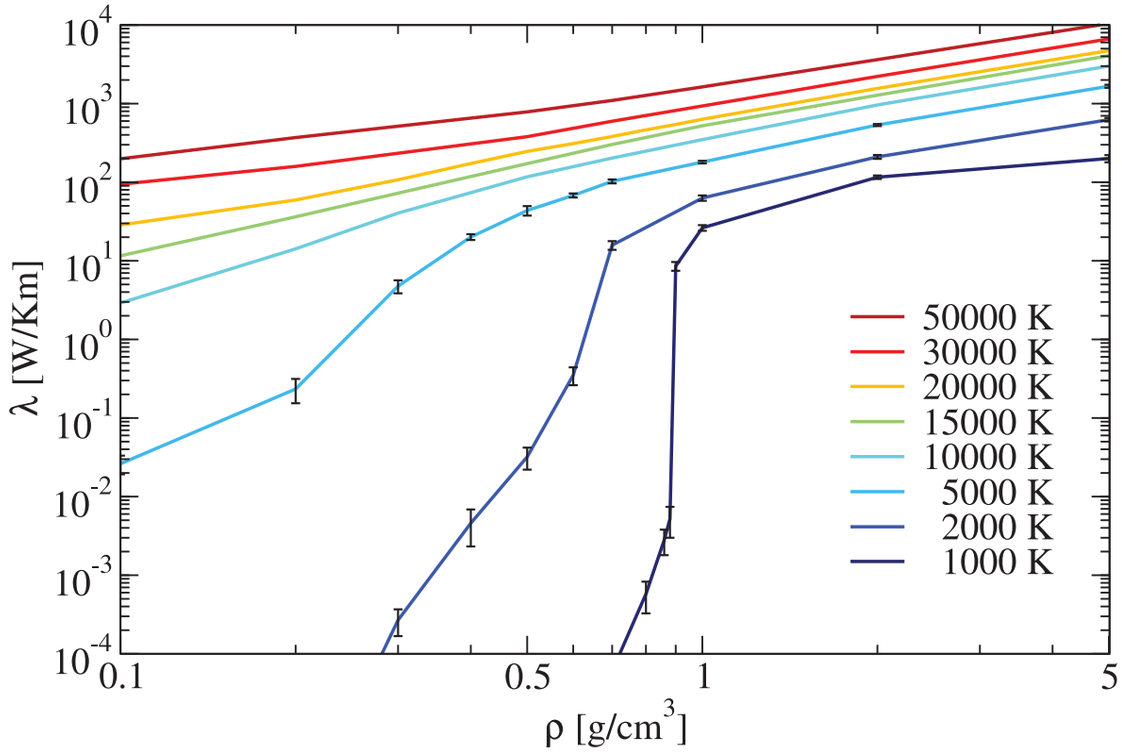
Electrical cond.



Elec. heat cond.



Non-metal to metal transition in dense liquid hydrogen

B. Holst, M. French, and R. Redmer, *Phys. Rev. B* **83**, 235120 (2011).

Also see Poster 10:

D. Cebulla, M. French, and R. Redmer,

"Ab initio simulations of MgO under extreme conditions"

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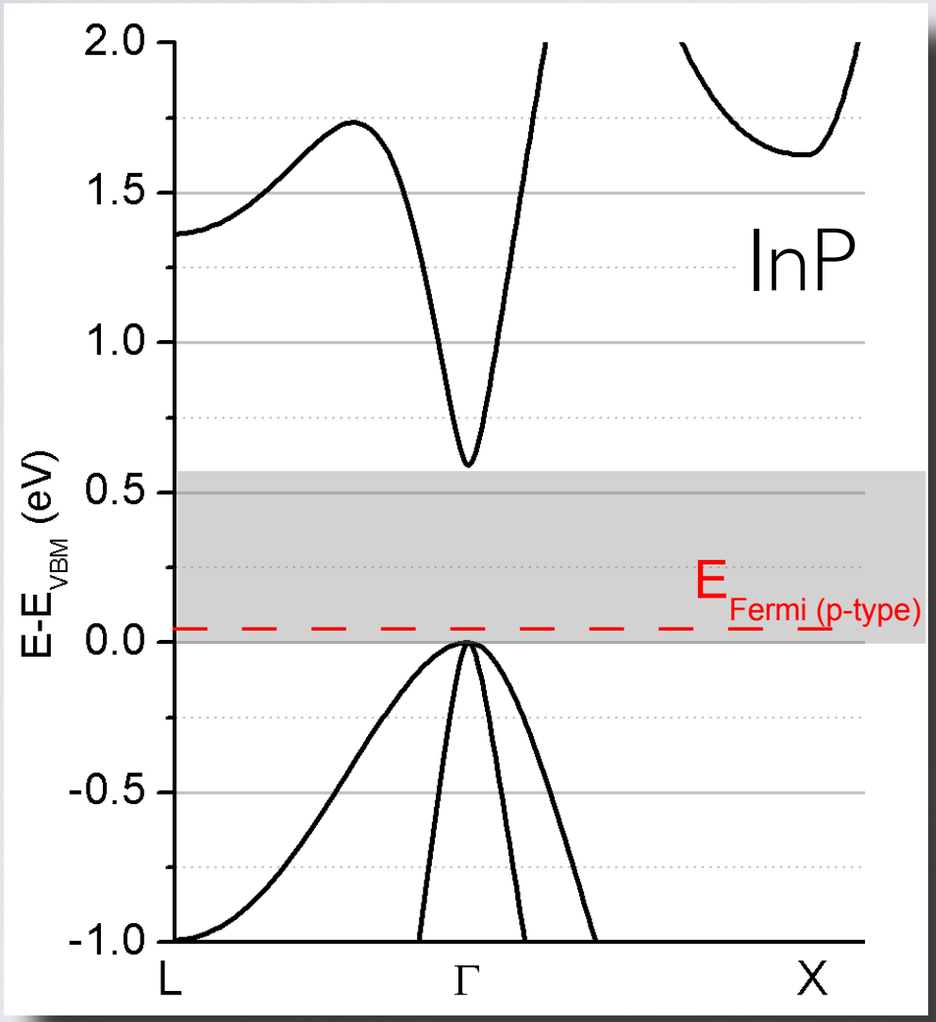

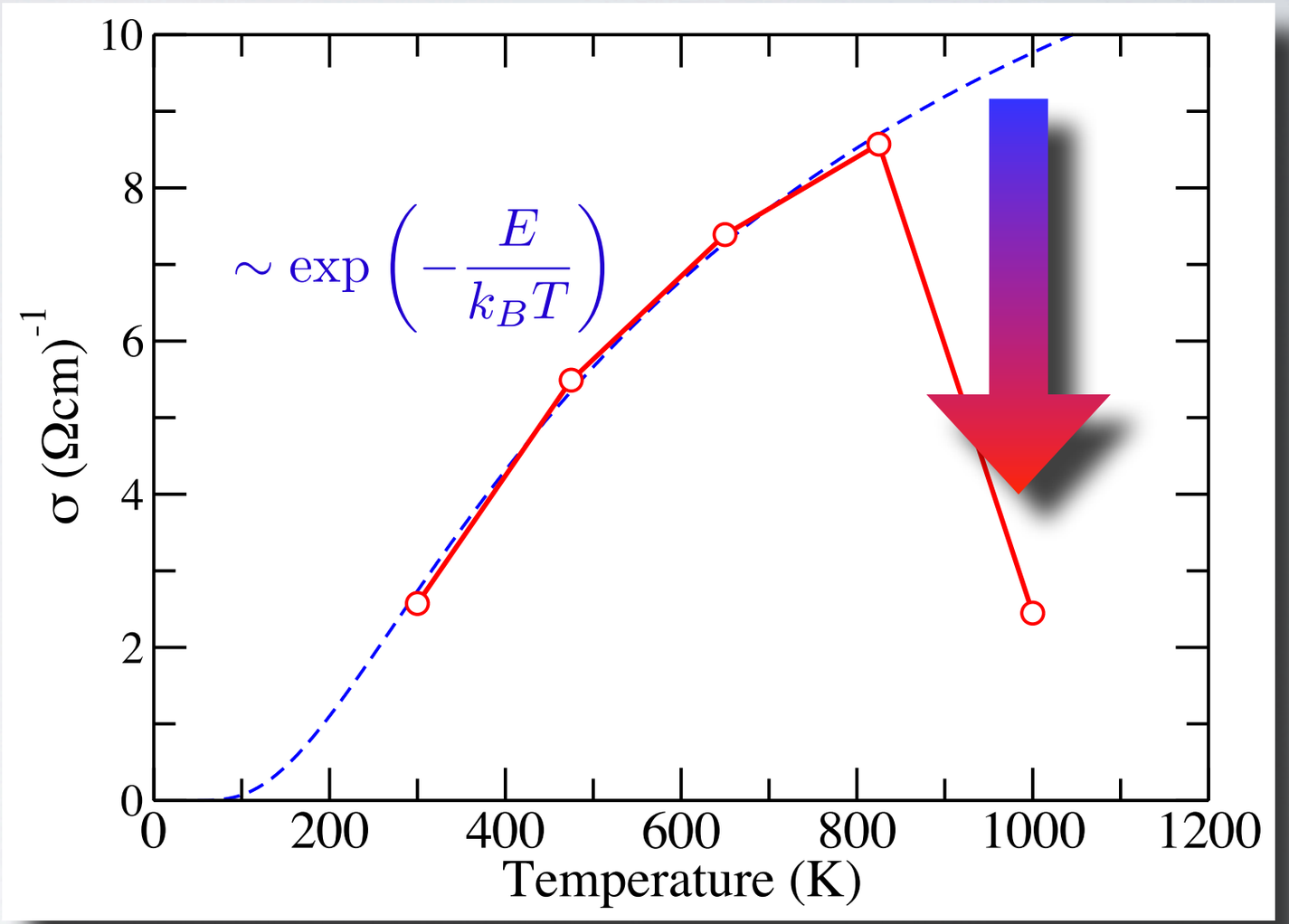

LDA-InP: Model for a direct band gap semiconductor

K. Rasim, B. Bieniek, C. Carbogno, and Matthias Scheffler *(in preparation)*.

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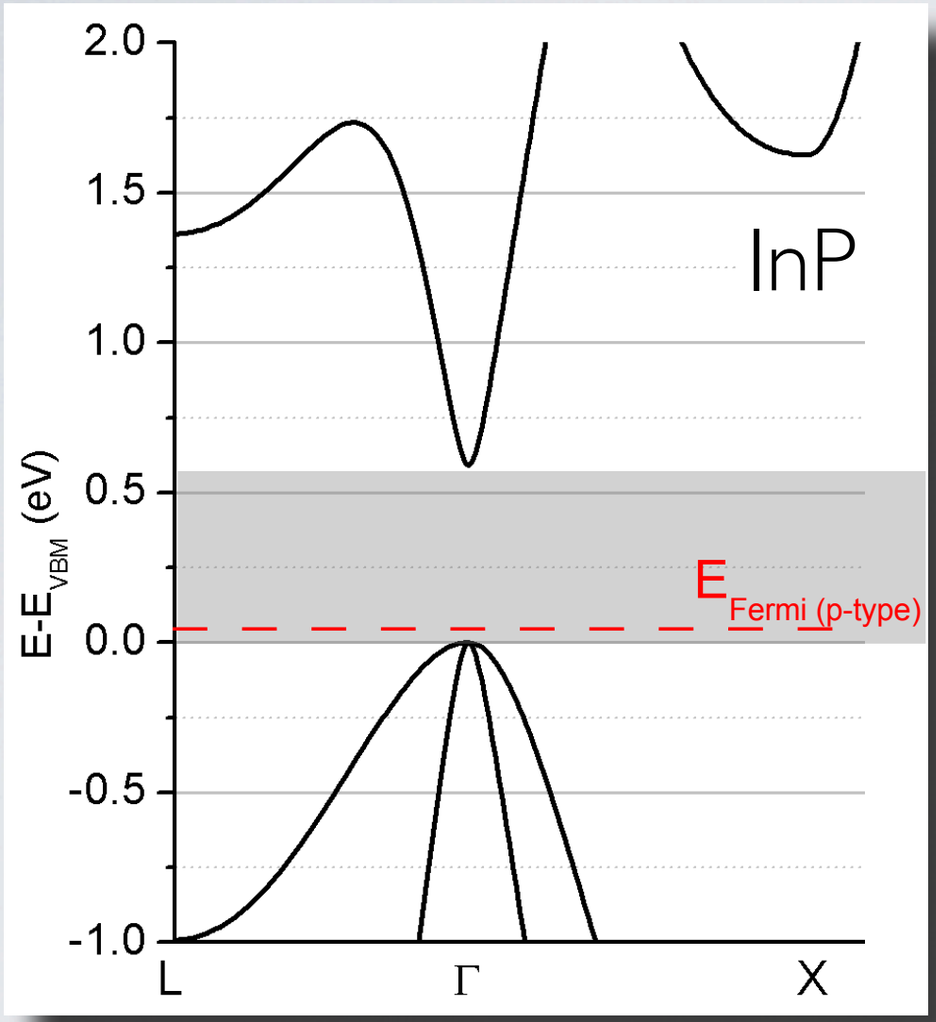

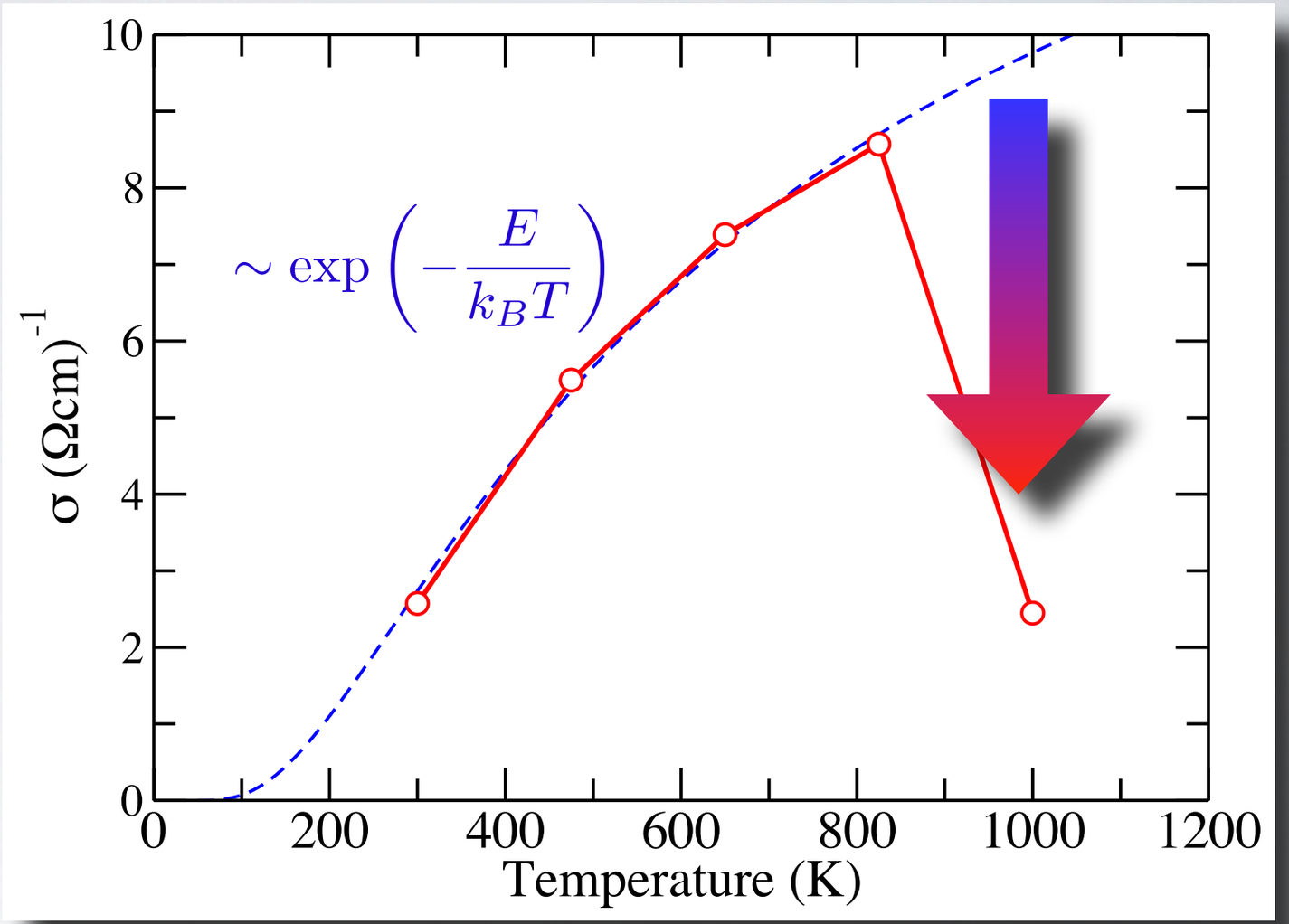

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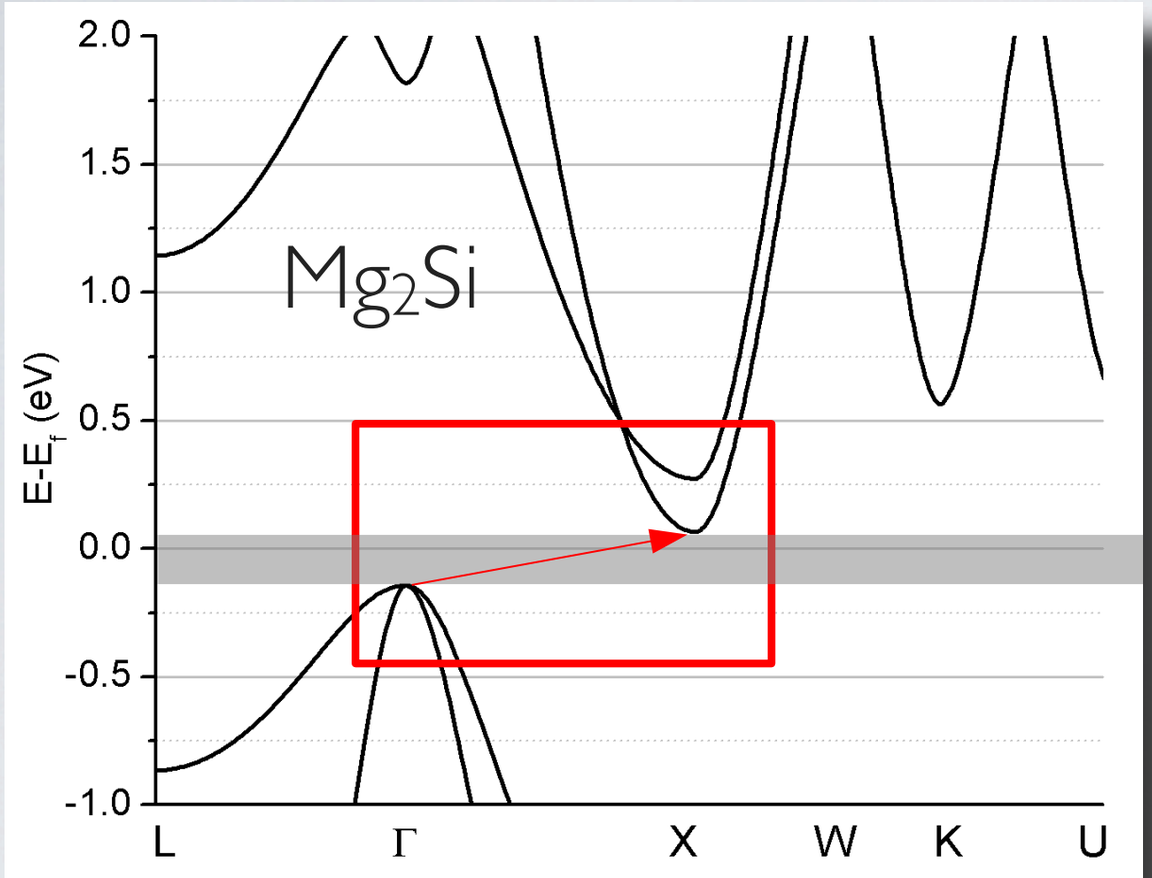

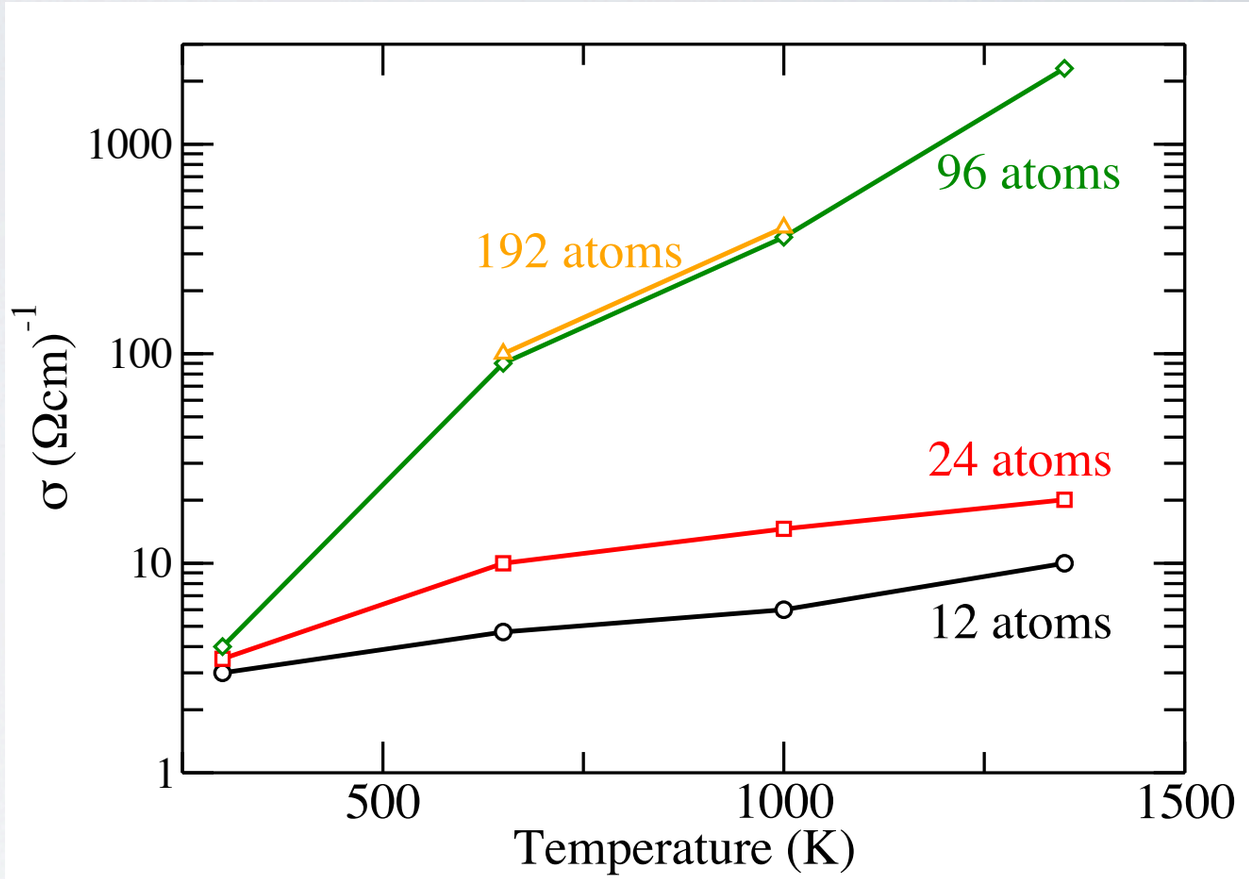

LDA-Mg_2Si: Model for an indirect band gap semiconductor

K. Rasim, B. Bieniek, C. Carbogno, and Matthias Scheffler *(in preparation)*.

CONCLUSION II

Boltzmann Transport Theory:

- ☑ **Rapid** one-shot **band structure calculation**
- ☐ **Rigid** band structure
- ☐ **Scattering** typically enters as a parameter

Greenwood-Kubo-Theory:

- ☑ **Transport coefficients** extracted from the **thermodynamic average** of the **optical conductivity**
- ☑ **Thermodynamic band structure changes** are inherently accounted for
- ☑ **First-principles** treatment of **adiabatic electron-phonon scattering**

CONCLUSIONS

- **Quality of the electronic structure:**
  Transport in **semiconductors** extremely **sensitive** to **band gap**
  ⟹ see *Patrick Rinke's* and *Sergey Levchenko's* talks
- **High-temperature limit:**
  Newtonian dynamics **not correct** at **low** temperatures.
  ⟹ see *Mariana Rossi's* talk
- **Electron-electron scattering neglected:**
  Can be accounted for by using **TDDFT** for the **ACF.**
  ⟹ see *Heiko Appel's* and *Stefano Baroni's* talks
- **"Band conductivity":**
  Different conductivities require
  a **different definition** of the **flux**
  ⟹ e.g. **Ionic conductivity**

M. French, S. Hamel, and R. Redmer, *Phys. Rev. Lett.* **107**, 185901 (2011).

SUMMARY

Nuclear Dynamics:
Harmonic Approximation: *Heat Capacities & Lattice Expansion*

Nuclear Heat Transport:
Thermal Conductivity from First Principles

Electronic Heat & Charge Transport:
Electronic Transport Coefficients from First Principles

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Karsten Rasim

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THANK YOU!