Thermal Conductivity at High Temperatures from First Principles

Christian Carbogno[1,2], Ramamurthy Ramprasad[2,3], and Matthias Scheffler[1,2]

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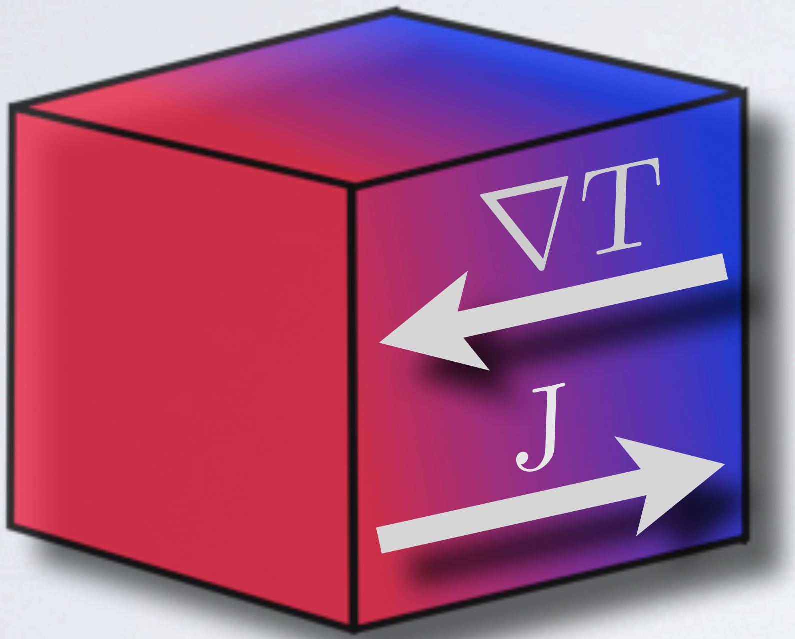
2: Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin

3: Chemical, Materials & Biomolecular Engineering, University of Connecticut, Storrs

HEAT TRANSPORT

Macroscopic Effect:



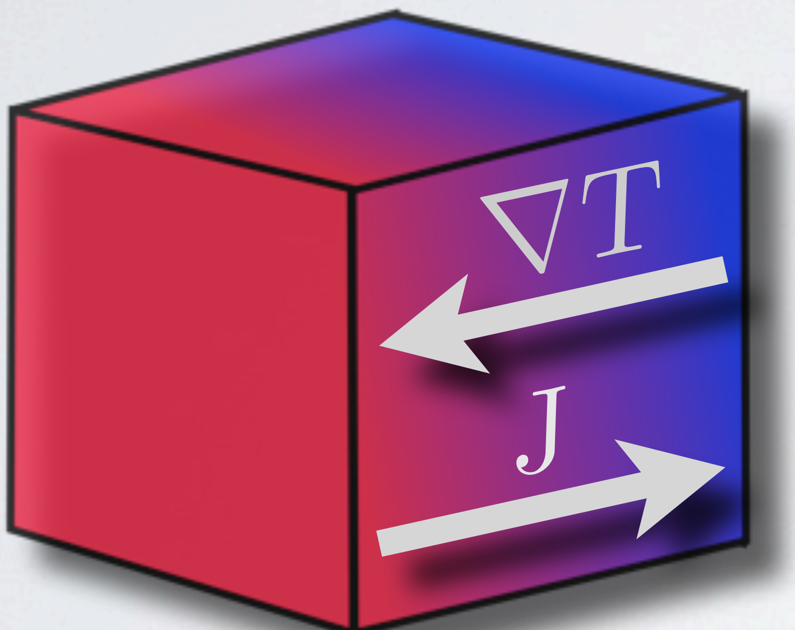
Fourier's Law:

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

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

HEAT TRANSPORT

Macroscopic Effect:



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

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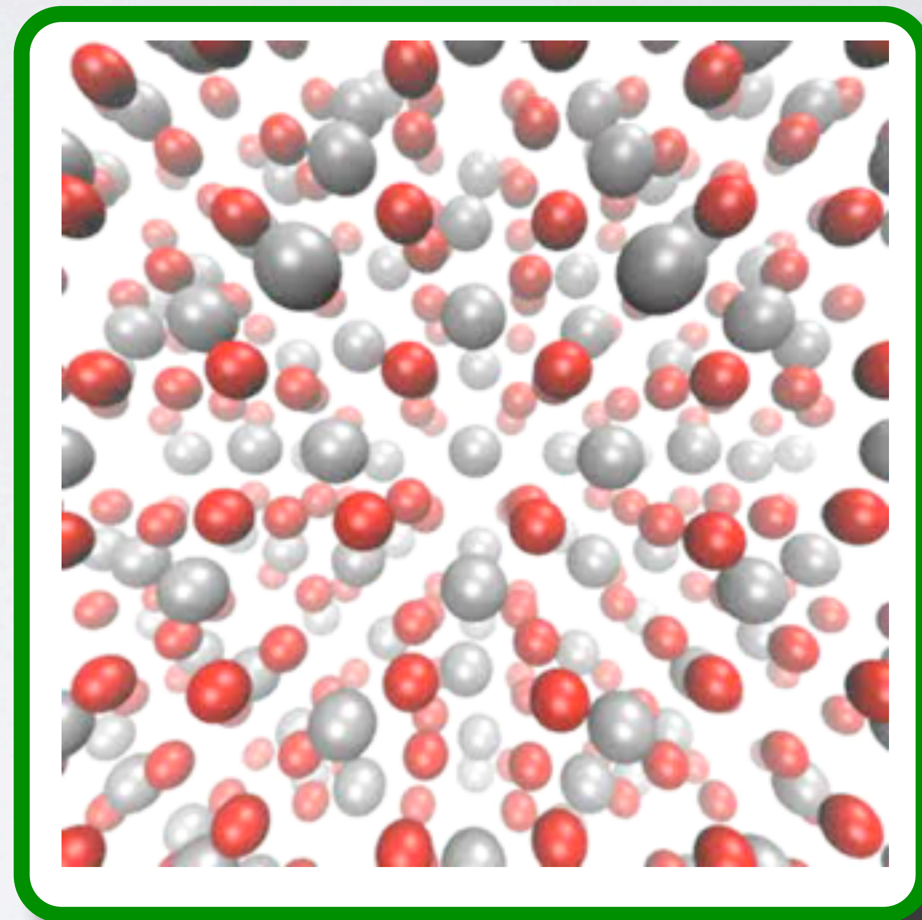
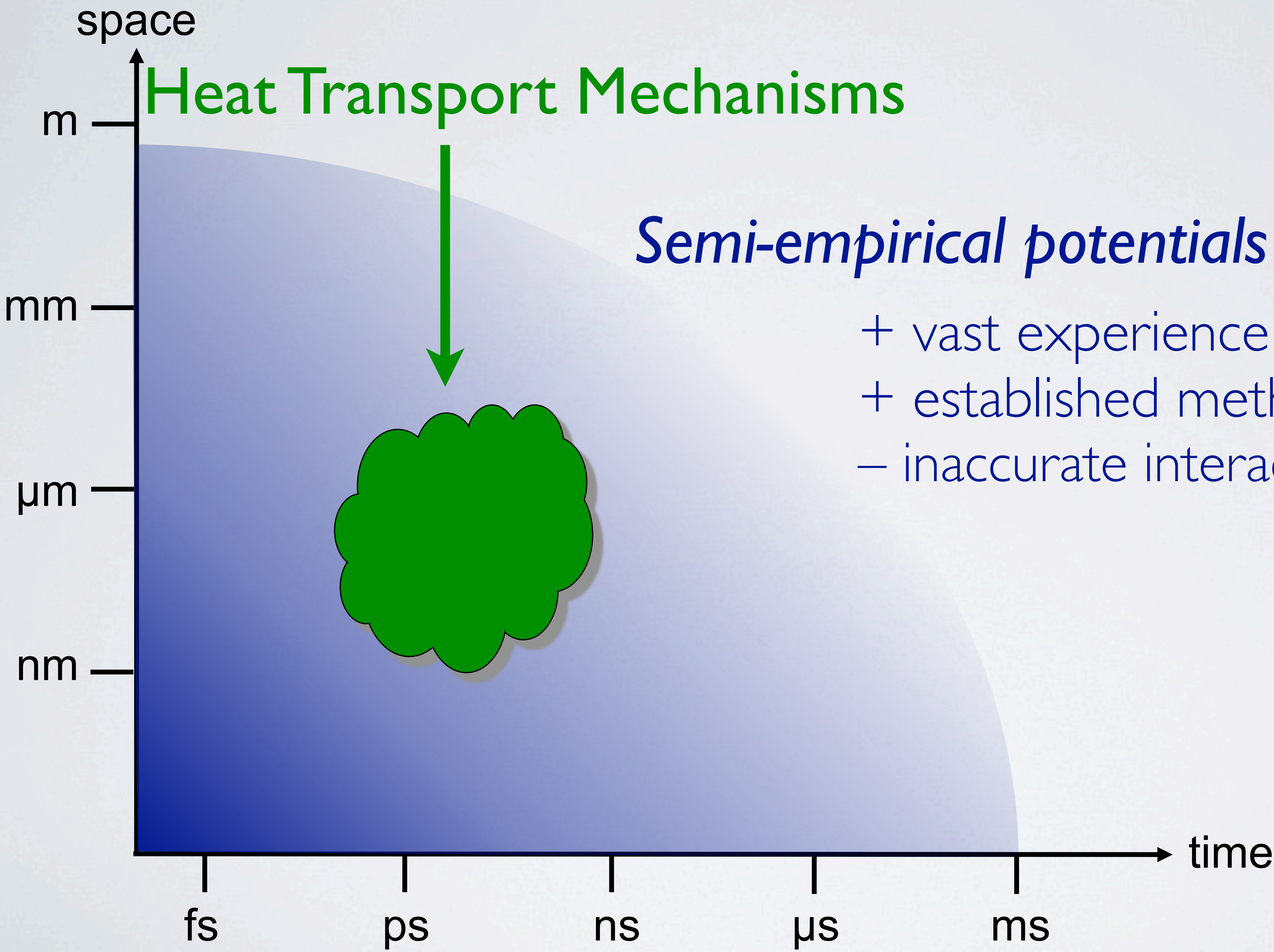


Microscopic Mechanisms

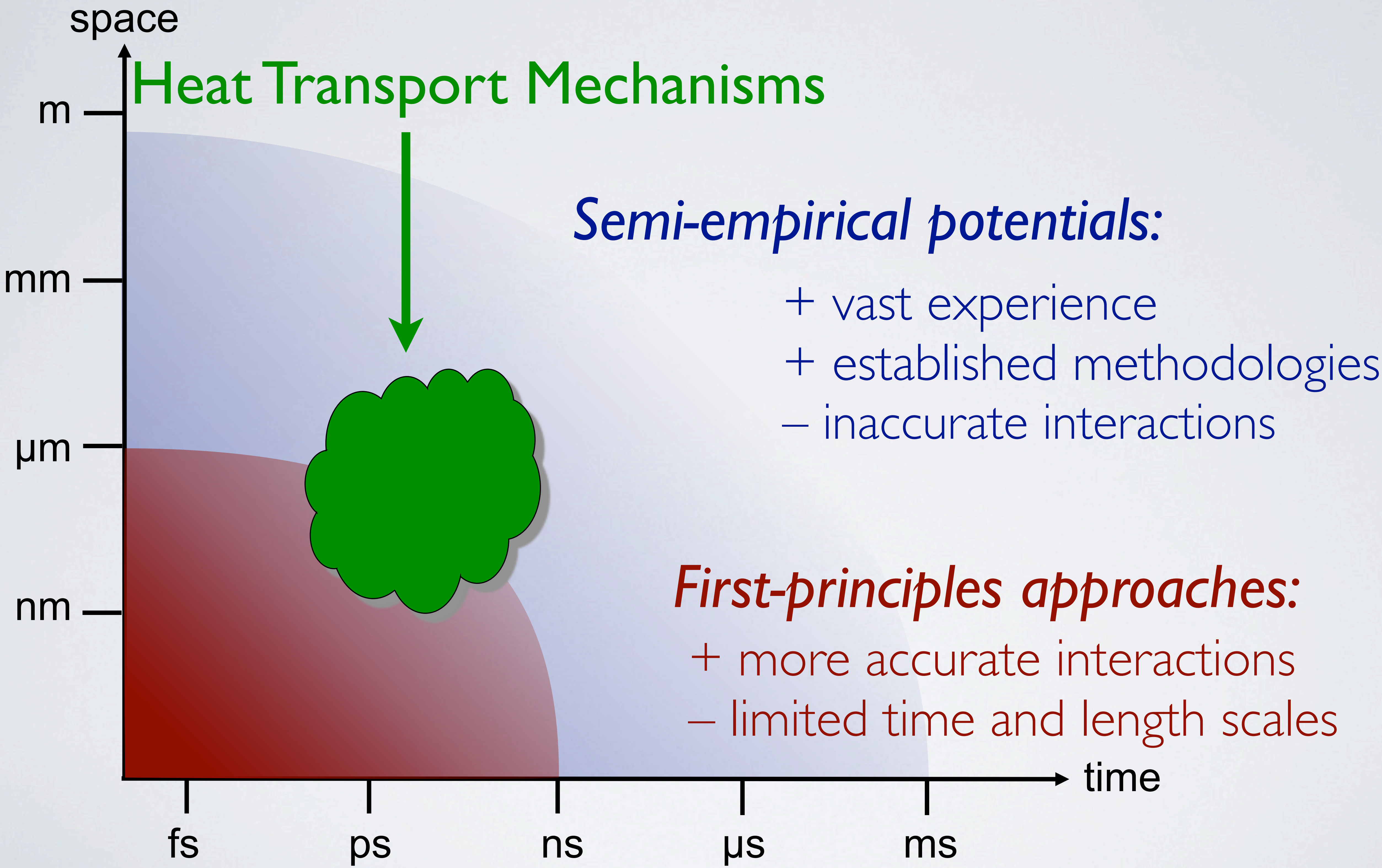
TIME AND LENGTH SCALES



Semi-empirical potentials

+ vast experience
+ established methodologies
– inaccurate interactions

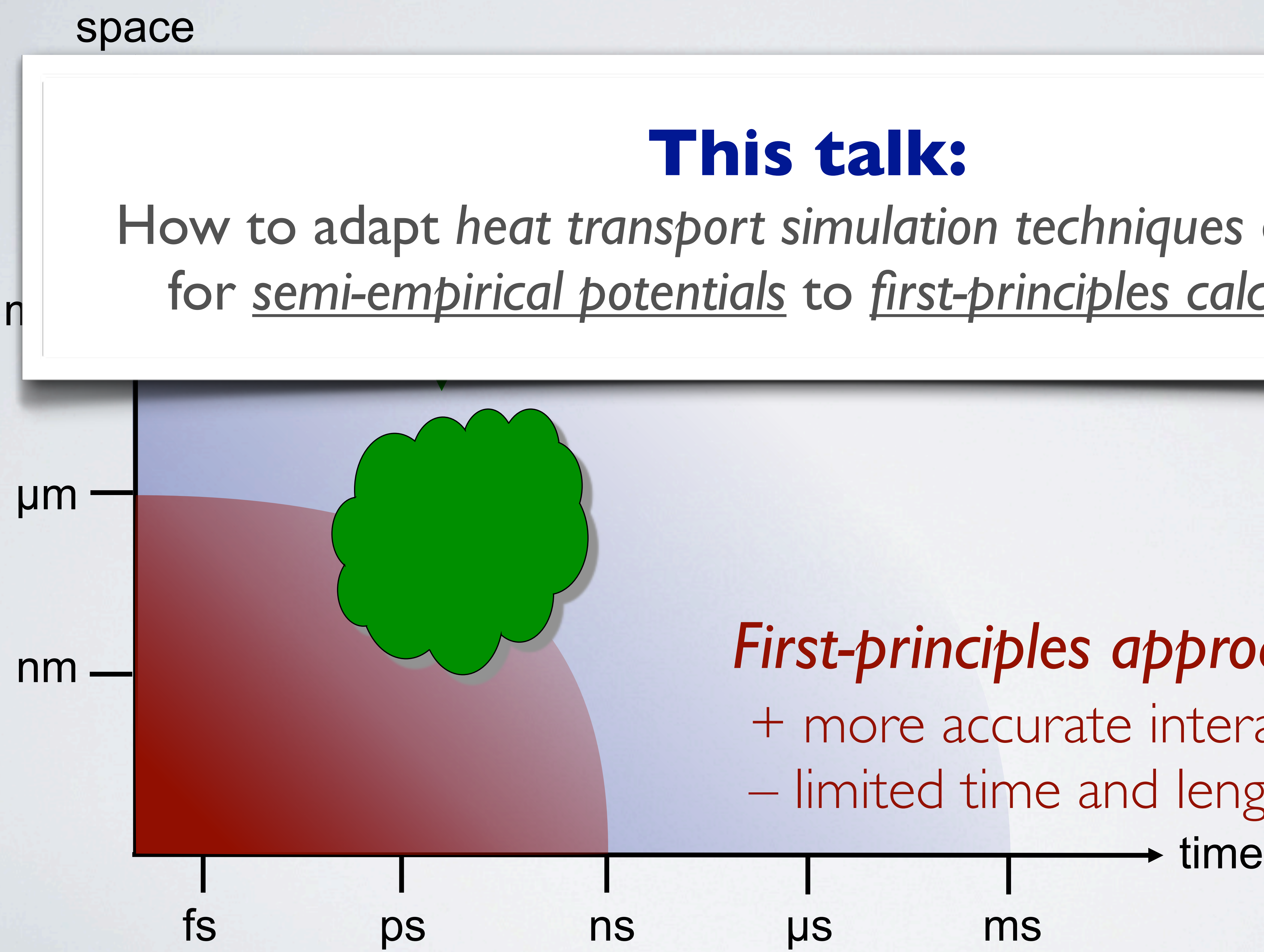
TIME AND LENGTH SCALES



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

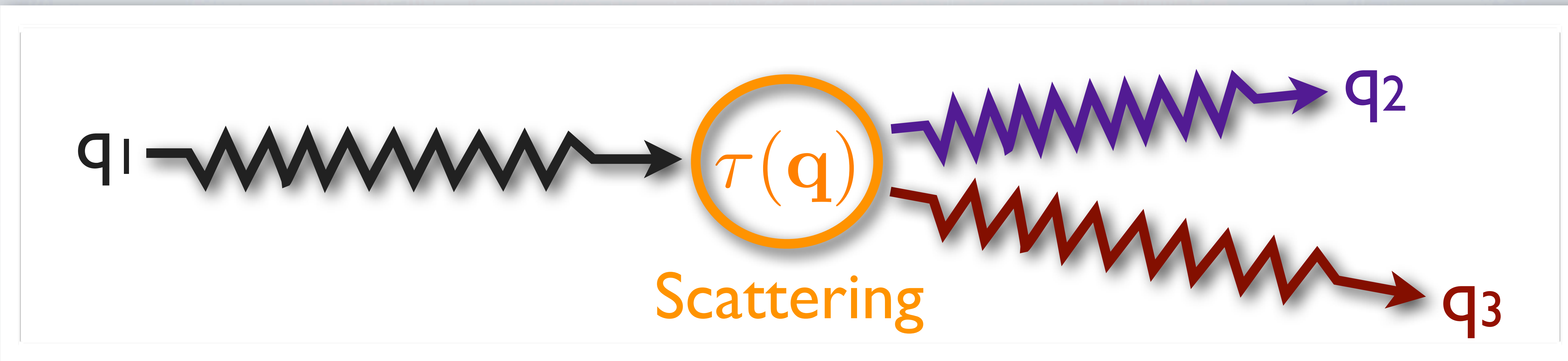
– limited time and length scales

FIRST-PRINCIPLES APPROACHES

	Order of interaction	Thermal Equilibrium	Finite Size Effects	Disorder
Boltzmann-Transport Eq.				
Non-Equilib. MD				
Laser-flash MD				
Green-Kubo MD				

BOLTZMANN TRANSPORT EQUATION

R. Peierls, *Ann. Phys.* **395**, 1055 (1929).



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

Group velocity (c_s^2)

Frequency (ω_s^2)

Equilibrium population ($n_s(n_s+1)$)

phonon lifetime (τ_s) **?**

Harmonic phonon theory

Phonon Lifetimes from First Principles

Primitive ("perfect") 0K - unit cell:

- from **Density Functional Perturbation Theory** ~$\mathcal{O}(r^3)$

  D. A. Broido *et al.*, *Appl. Phys. Lett.* **91**, 231922 (2007).

- from **fitting** the **forces** in ***ab initio MD*** ~$\mathcal{O}(r^3)$-$\mathcal{O}(r^4)$

  K. Esfarjani, and H. T. Stokes, *Phys. Rev. B* **77**, 144112 (2008).

- from **fitting** the **AIMD phonon spectrum** ~$\mathcal{O}(r^3)$

  N. De Koker, *Phys. Rev. Lett.* **103**, 125902 (2009).

"Disorder": Defects, Alloying, ...

- **Density Functional Theory** based **Modeling**

  J. Garg *et al.*, *Phys. Rev. Lett.* **106**, 045901 (2011).

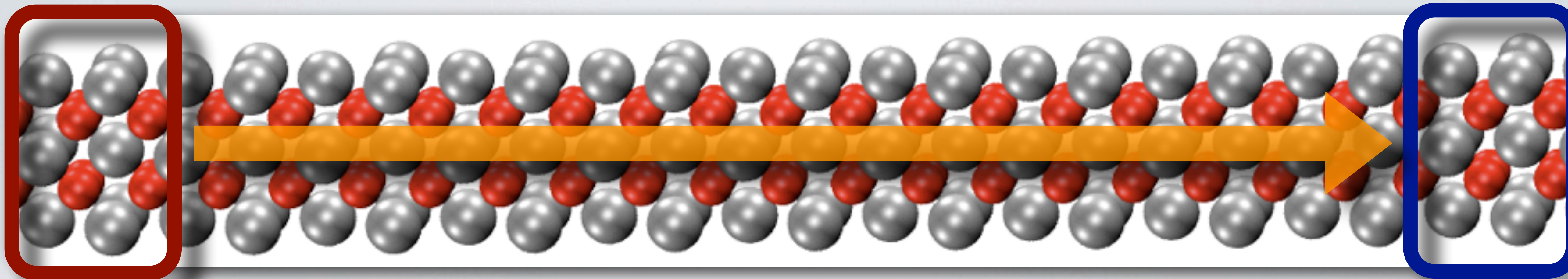
FIRST-PRINCIPLES APPROACHES

	Order of interaction	Validity & Applicability	Finite Size Effects	Disorder
Boltzmann-Transport Eq.	$\sim\mathcal{O}(r^3)$	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).



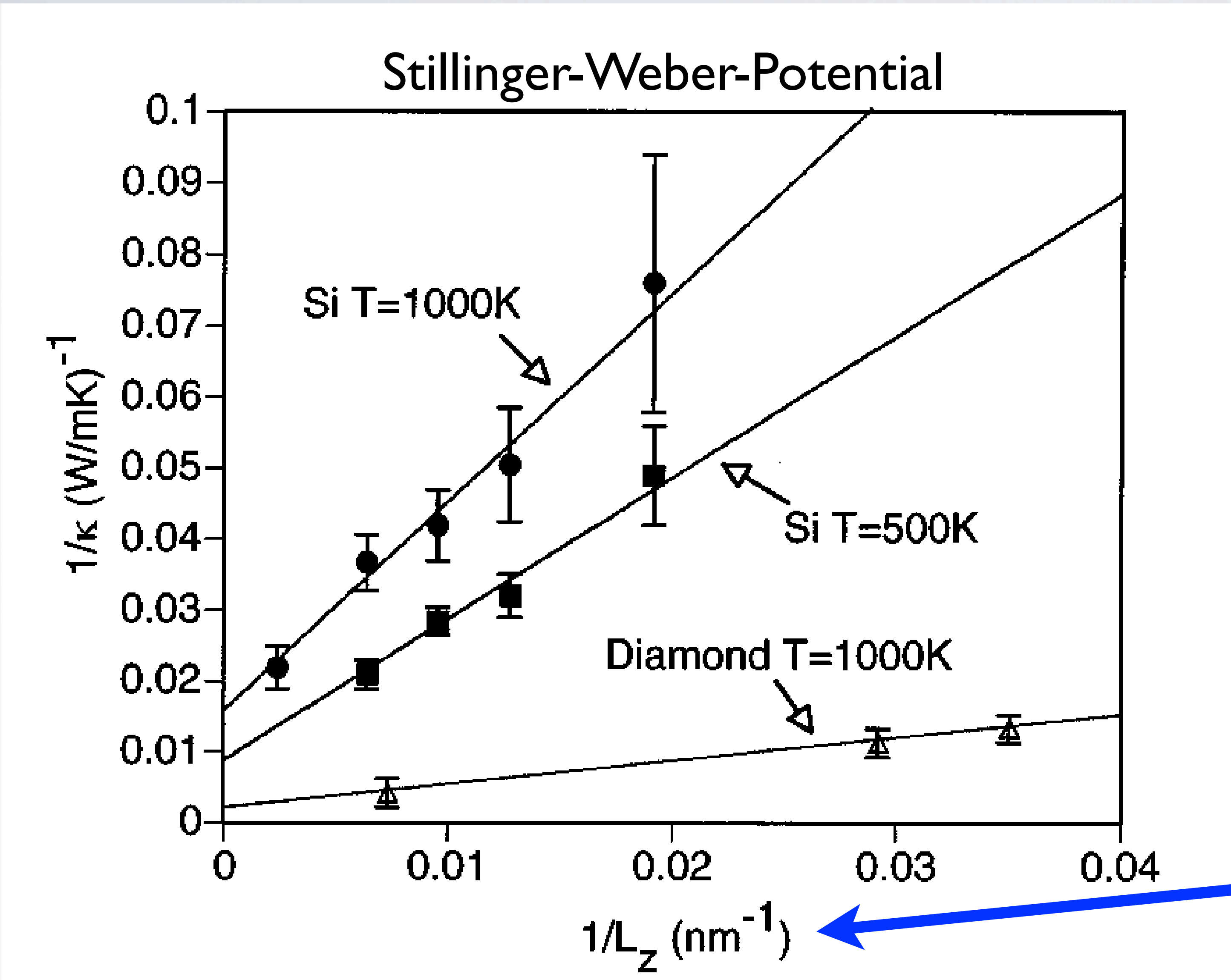
heat source → • Temperature gradient ∇T
• Stationary heat flux **J** → **heat sink**

⇓

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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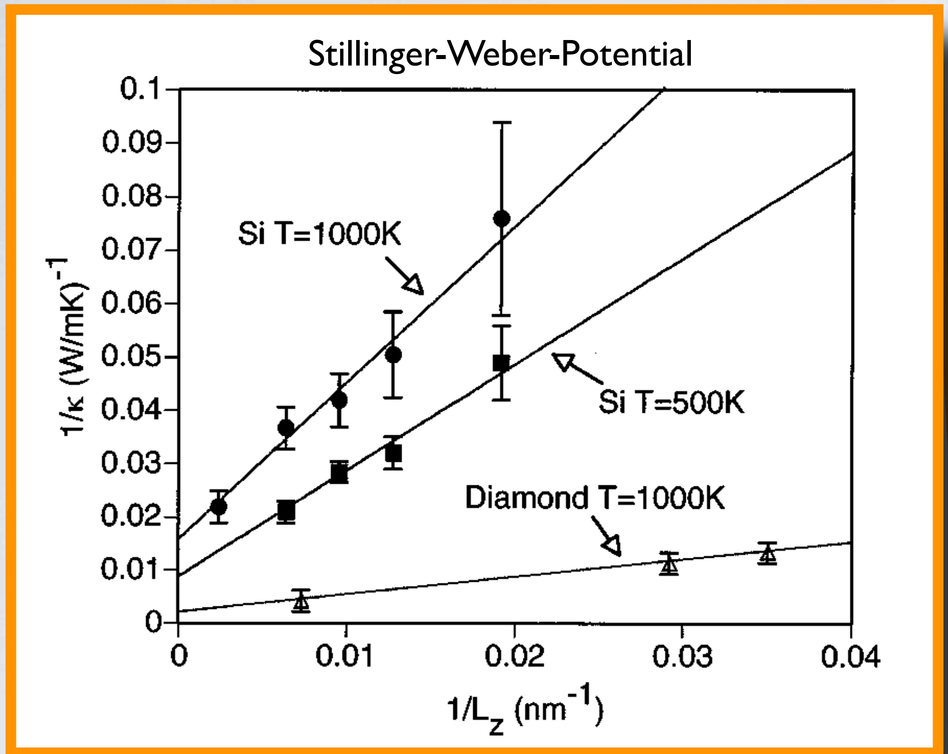

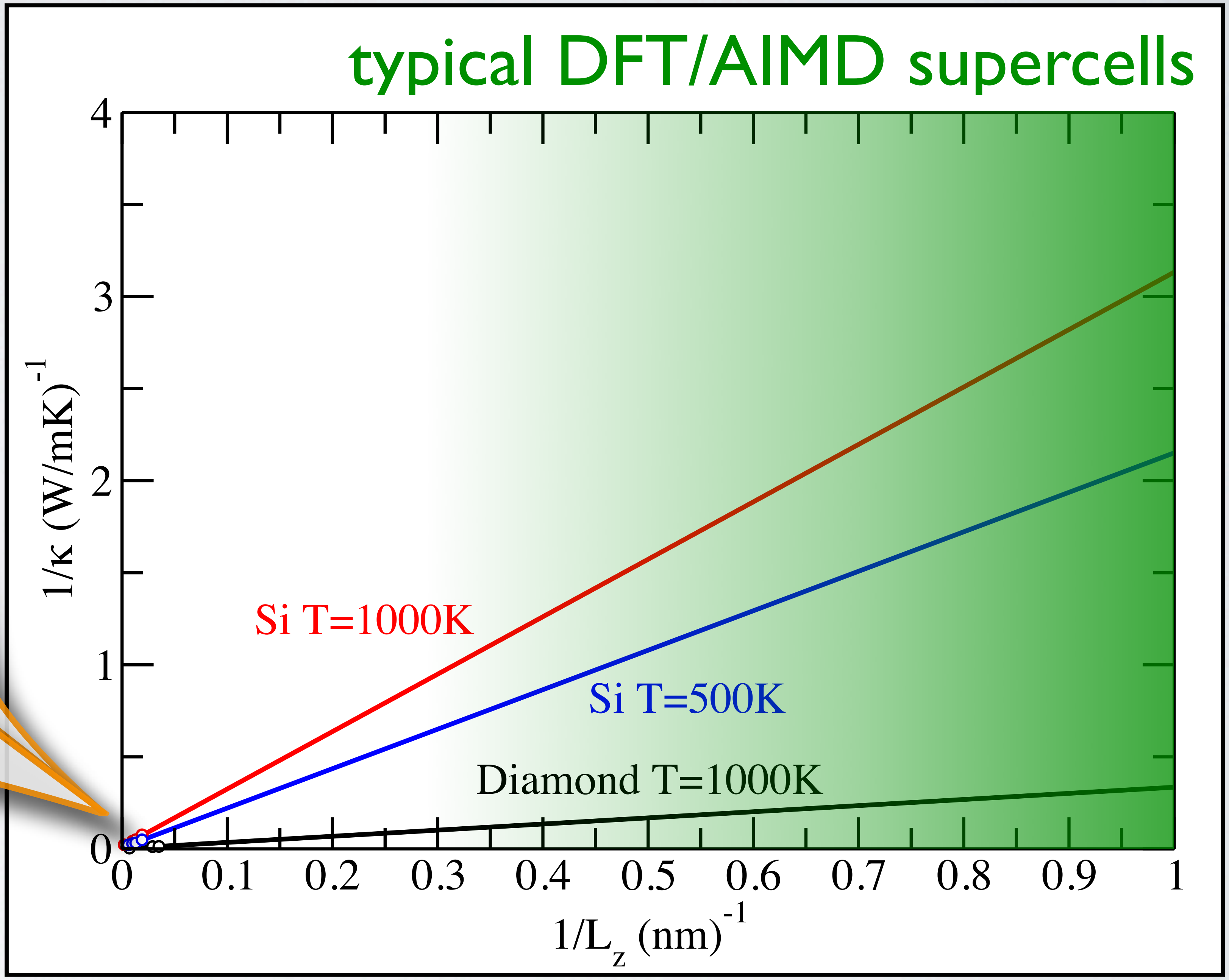

Non-equilibrium MD exhibits strong finite-size artifacts in supercells typically accessible within DFT/AIMD.

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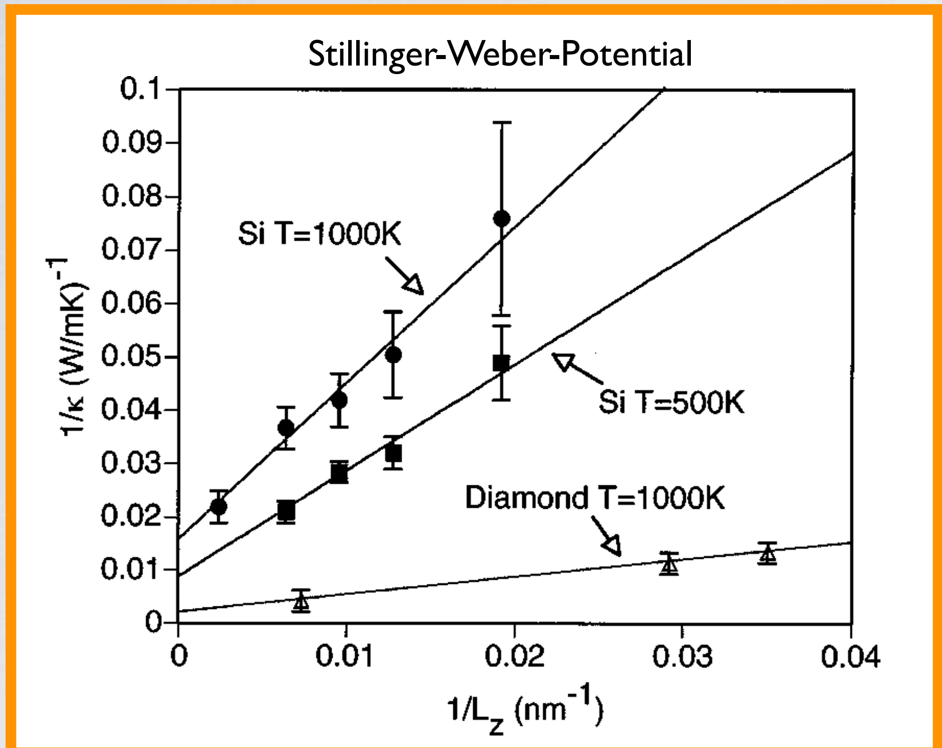

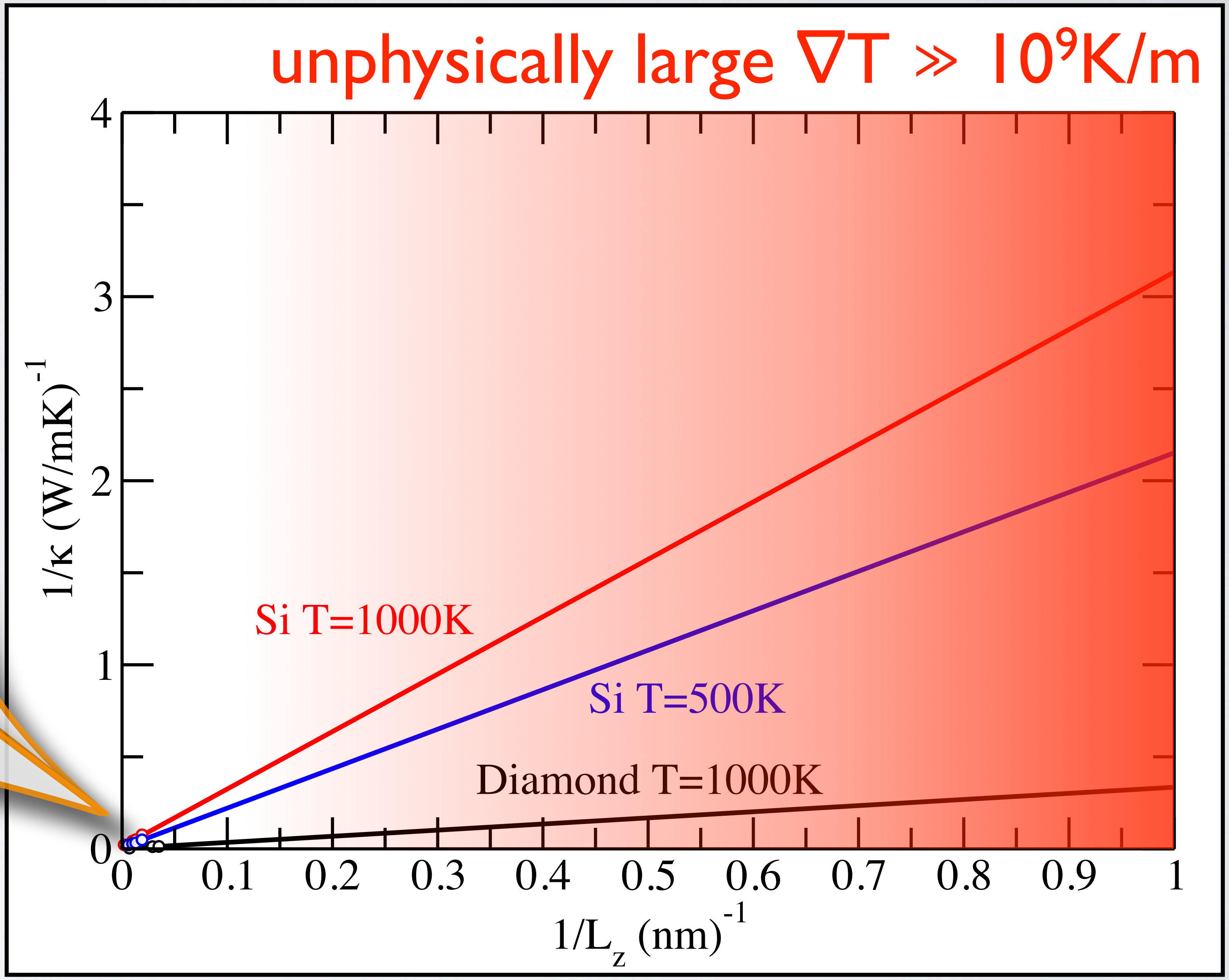

Non-equilibrium MD can suffer from **non-linear artifacts** in **supercells typically accessible within DFT/AIMD**.

FIRST-PRINCIPLES APPROACHES

	Order of interaction	Validity & Applicability	Finite Size Effects	Disorder
Boltzmann-Transport Eq.	$\sim\mathcal{O}(r^3)$	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).

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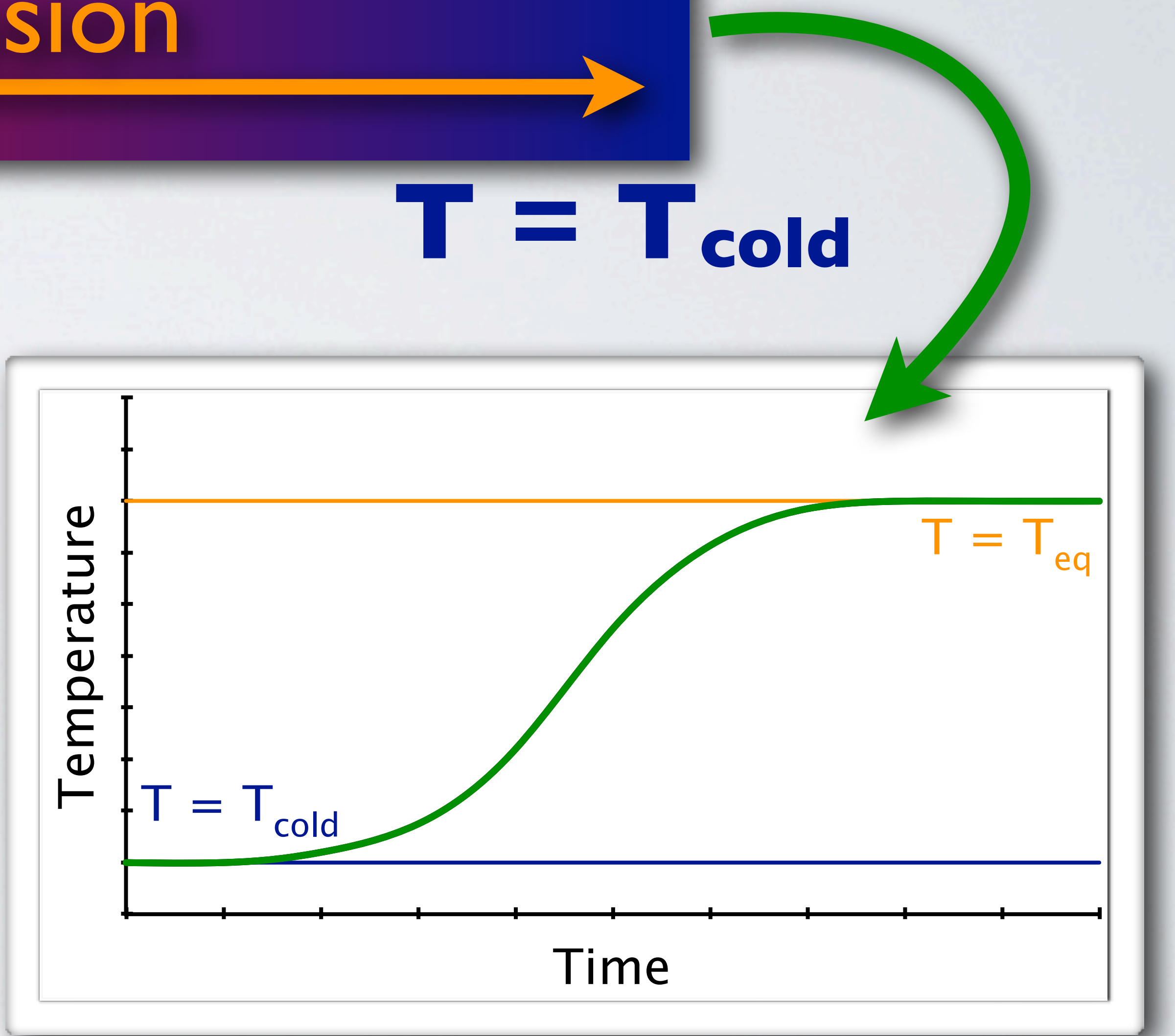
W. J. Parker *et al.*, *J. Appl. Phys.* **32**, 1679 (1961).



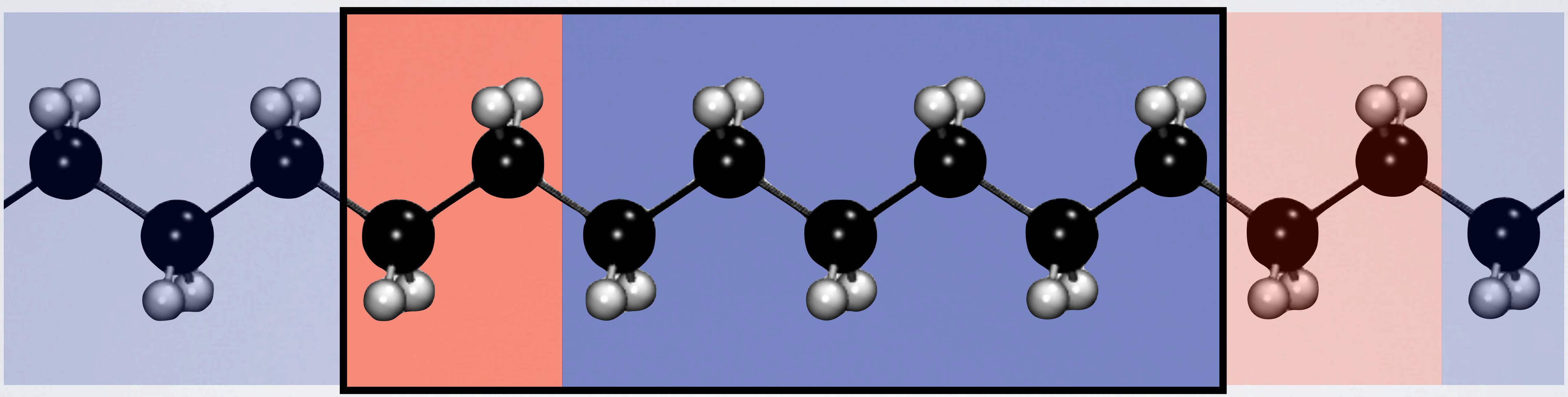
Heat Diffusion Equation:

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

„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 **quasi-harmonic approximation**, the **positions r_i** and the **velocities v_i** are related to the **vibrational eigenfrequencies ω_s** and -vectors **e_s**.

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

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

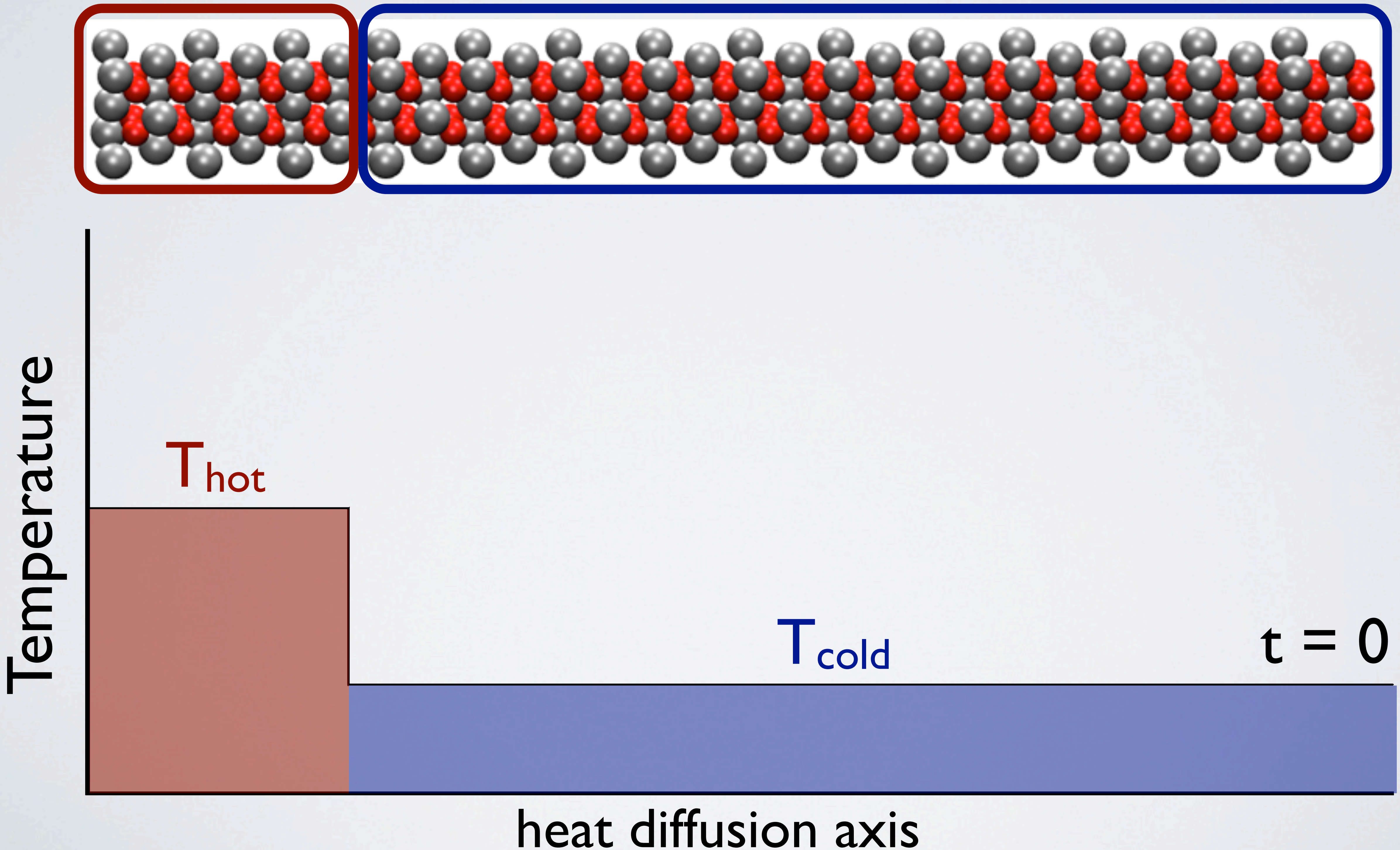
Maxwell-Boltzmann distributed amplitudes

random phase

harmonic approximation

SUPERCELL PREPARATION

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



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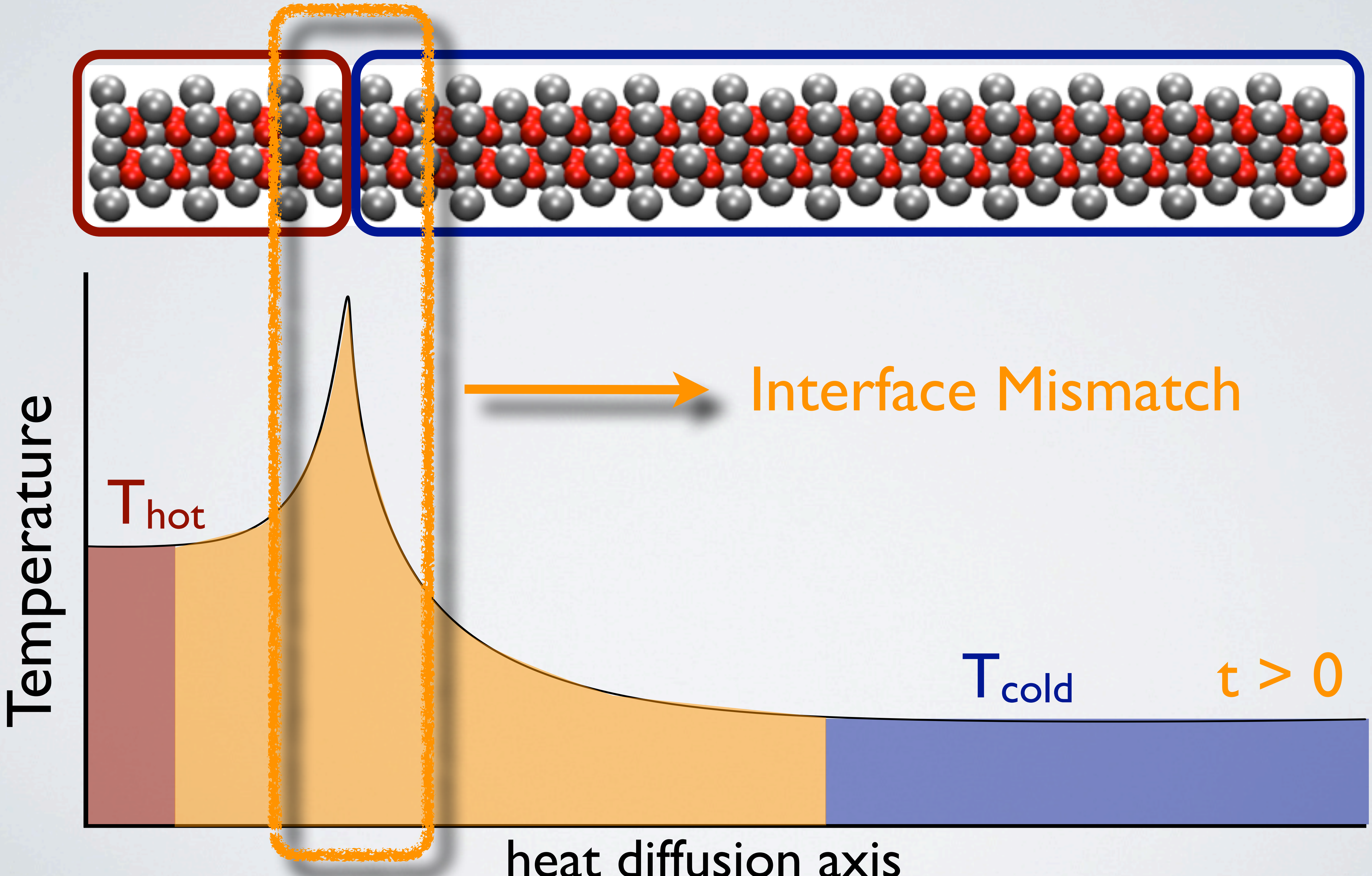


PHASE MATCHING

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

The cartesian displacements **r**$_i$ are related to the eigenfrequencies **ω**$_s$ and -vectors **e**$_s$ of the *dynamical matrix*.

$$\Delta \mathbf{r}_i = \frac{1}{\sqrt{M_i}} \sum_s A_s(T) \cos\left(\Phi_s + \omega_s t\right) \cdot \mathbf{e}_s$$

Maxwell-Boltzmann distributed amplitudes

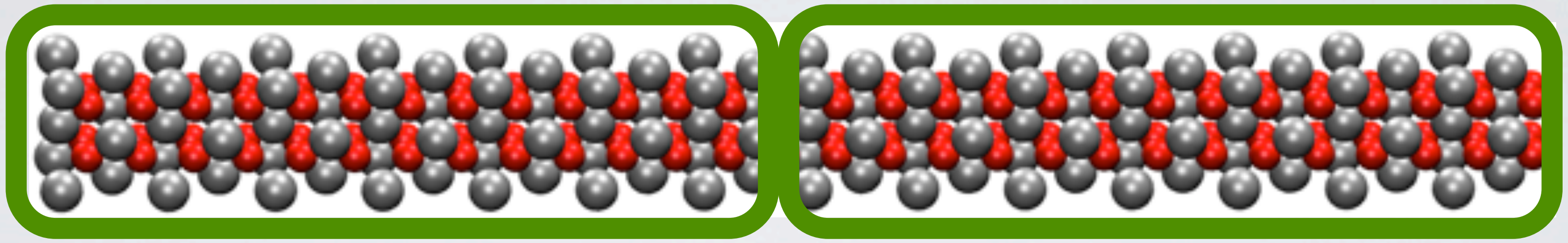
random phase

harmonic approximation

Enforce **consistent boundary conditions** at the interface!

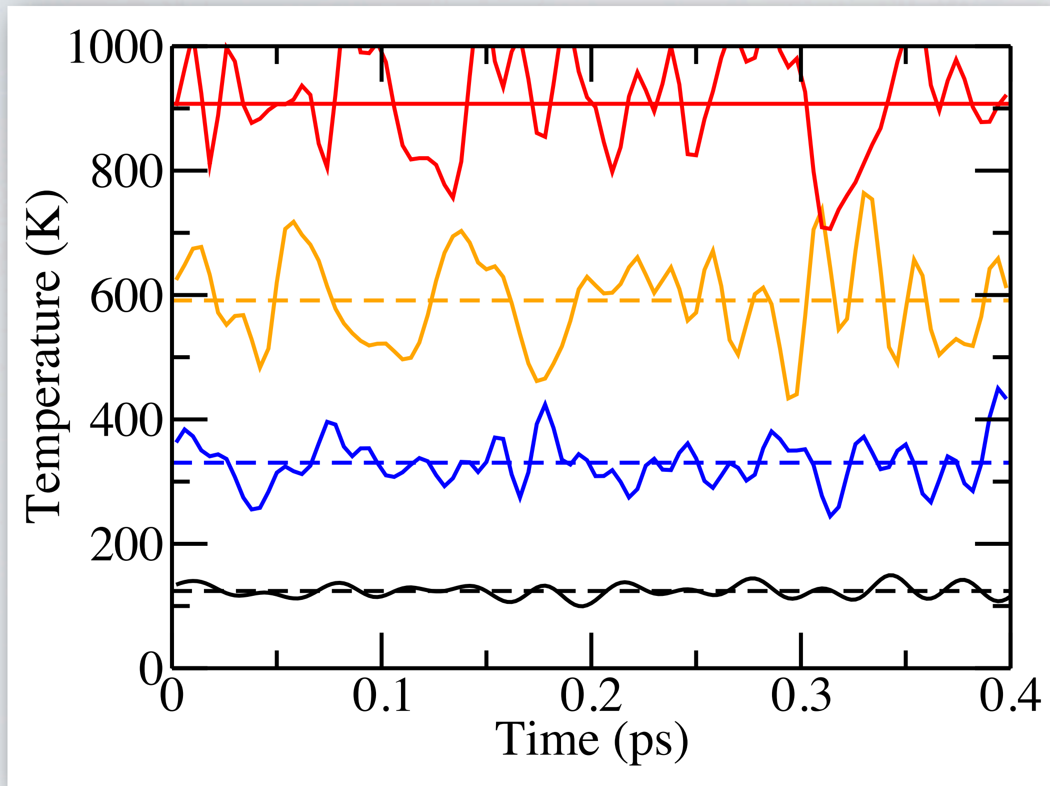
PHASE MATCHING

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



$T=T_1=T_2$

Random Phases



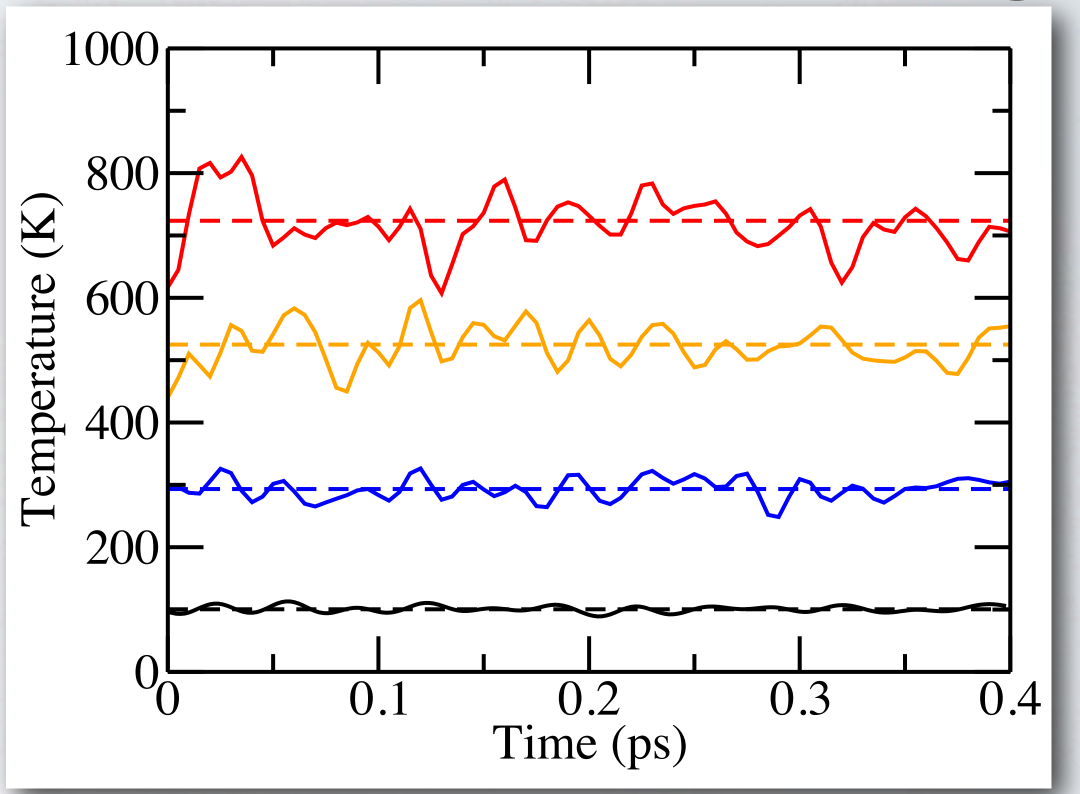
T=700 K

T=500 K

T=300 K

T=100 K

Phase Matching

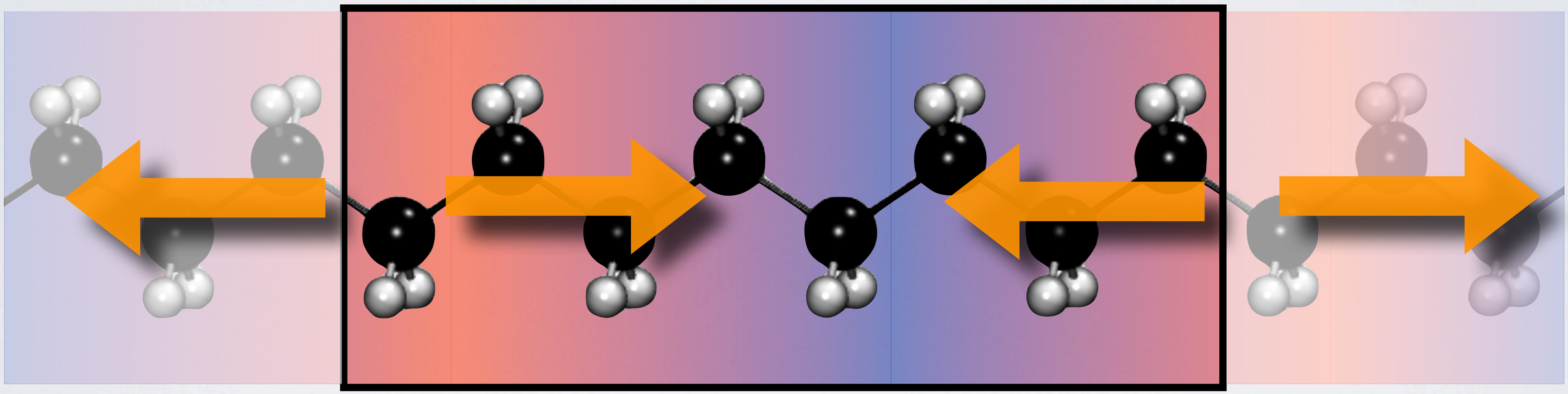


„Phase matching" reduces the artifacts by **two orders** of magnitude.

„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***:

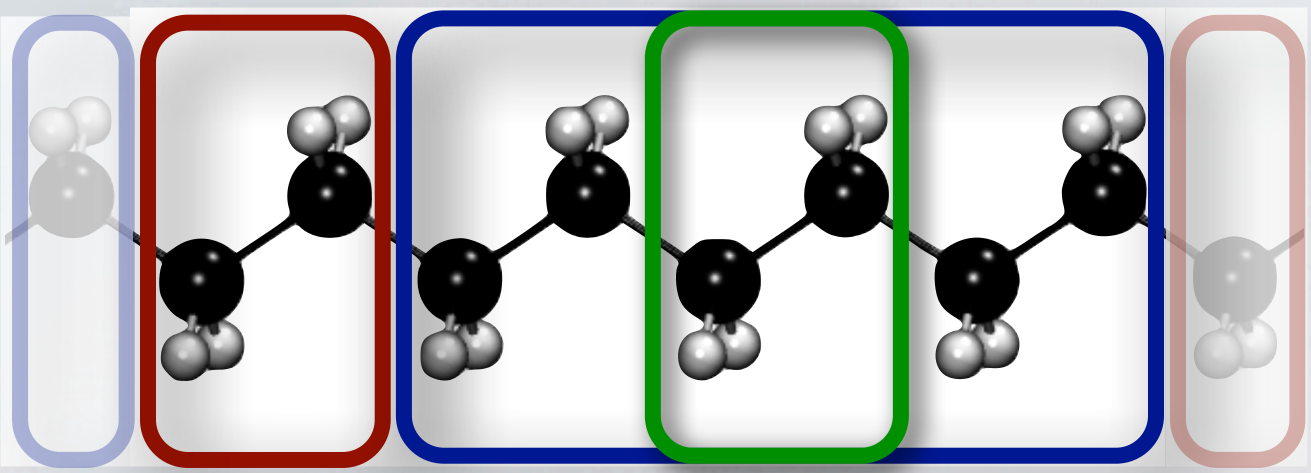


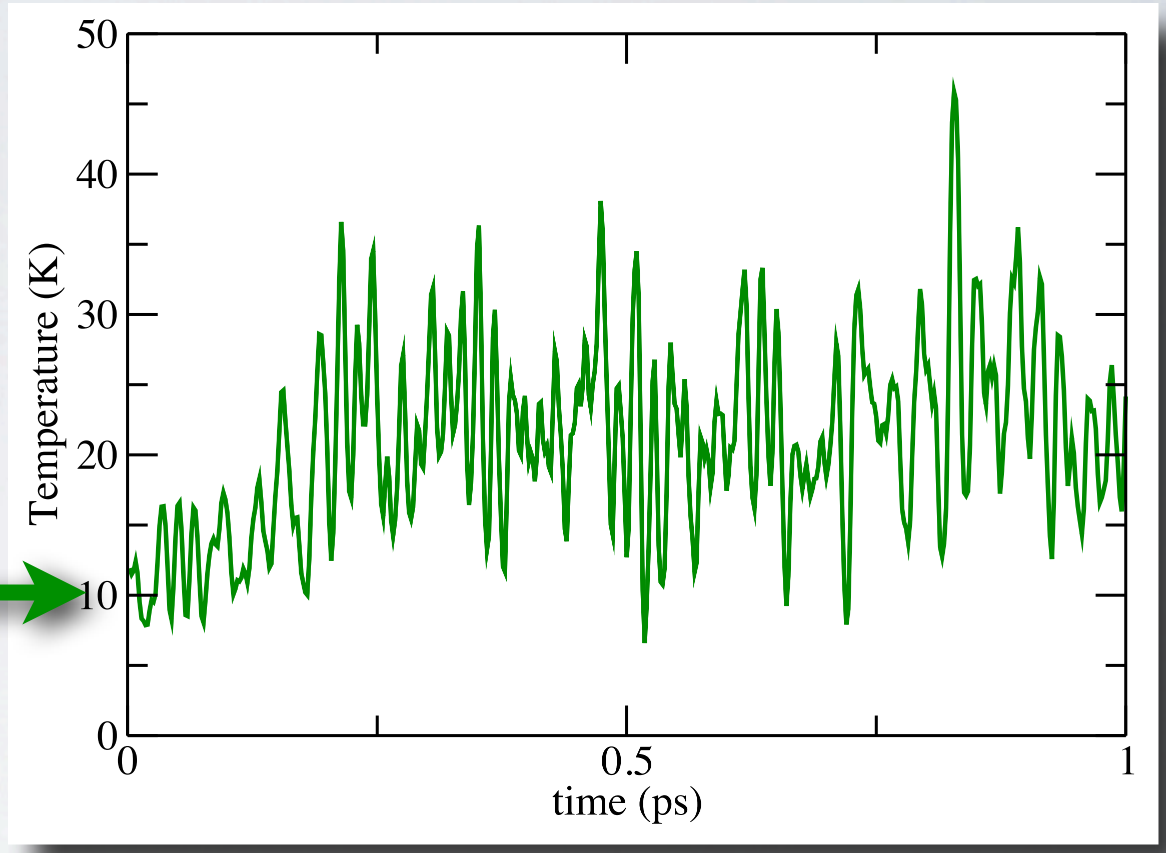
(A) **Prepare two supercells:** a **small hot** one and a **large cold** one.

(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).



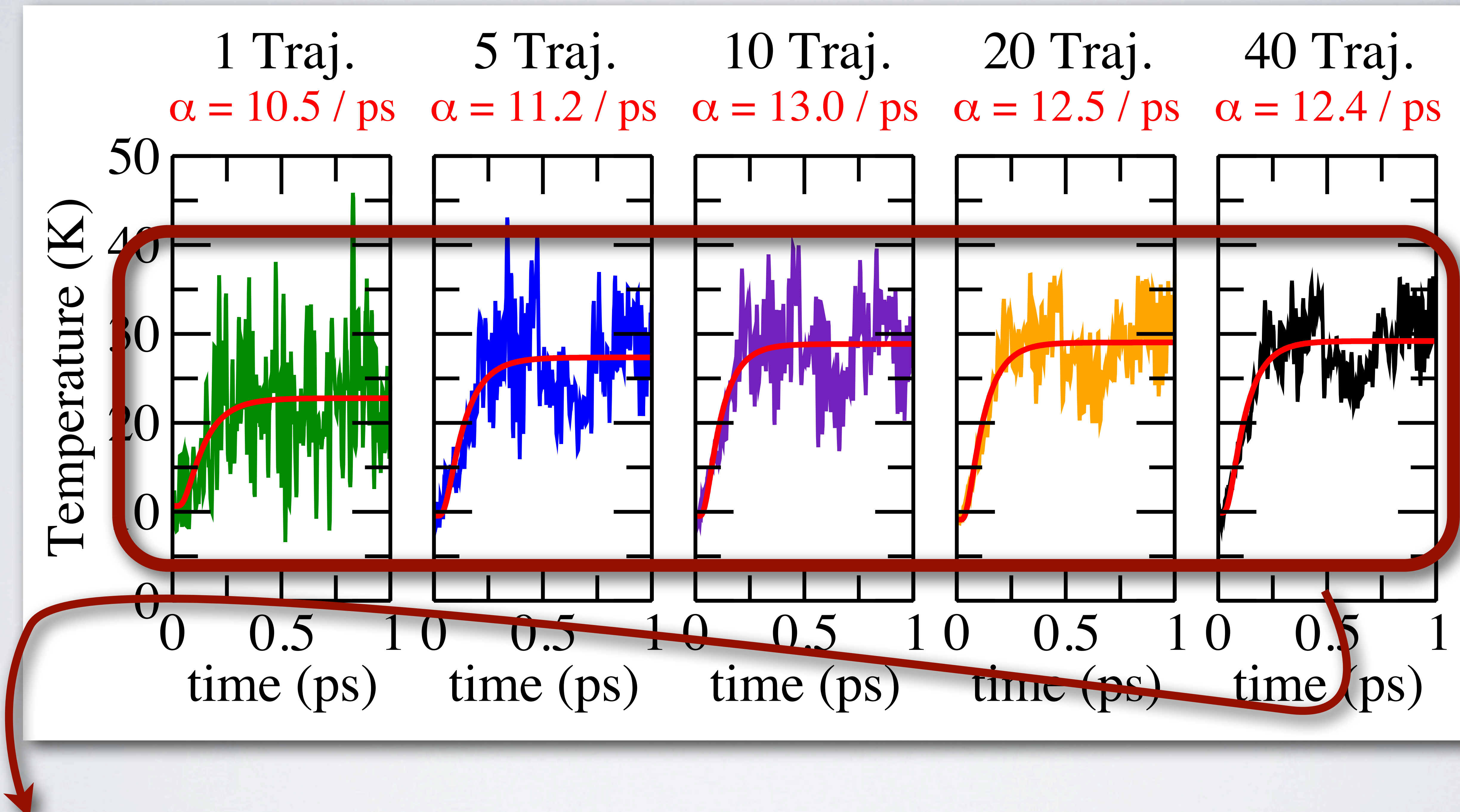


Monitor temperature of the central cell

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).

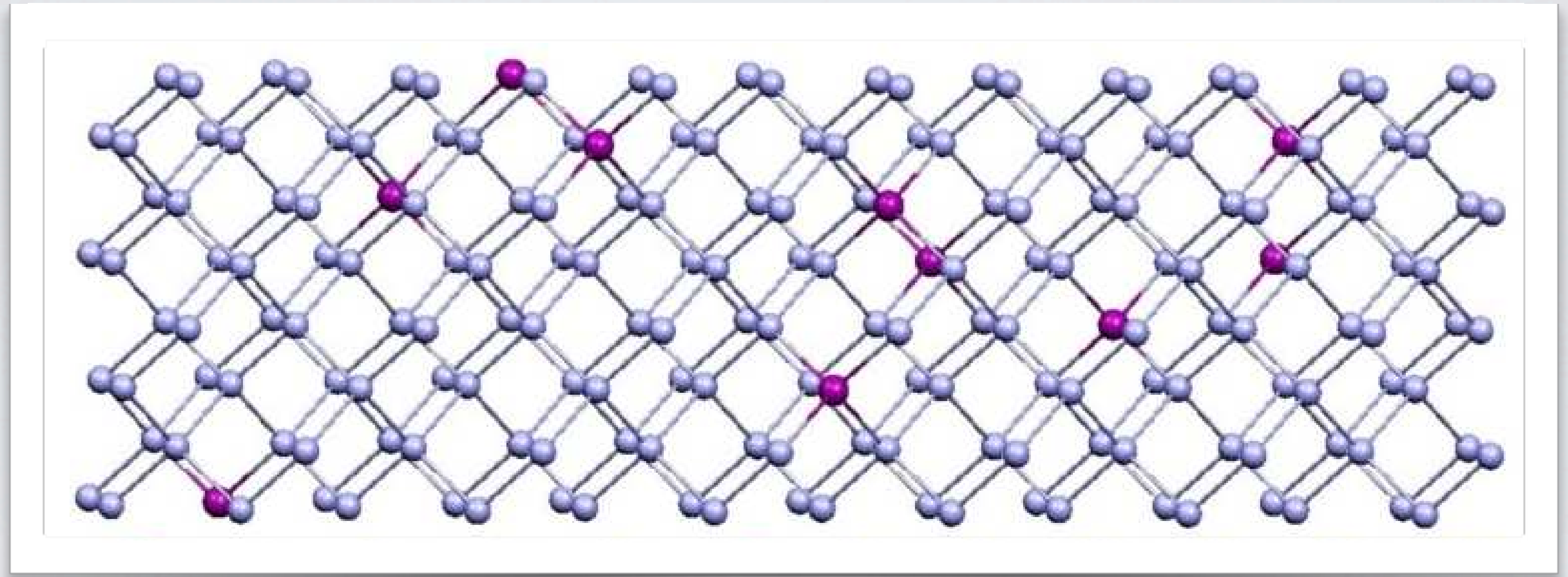


Fit to

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

APPLICATION TO IMPURITIES IN SI

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

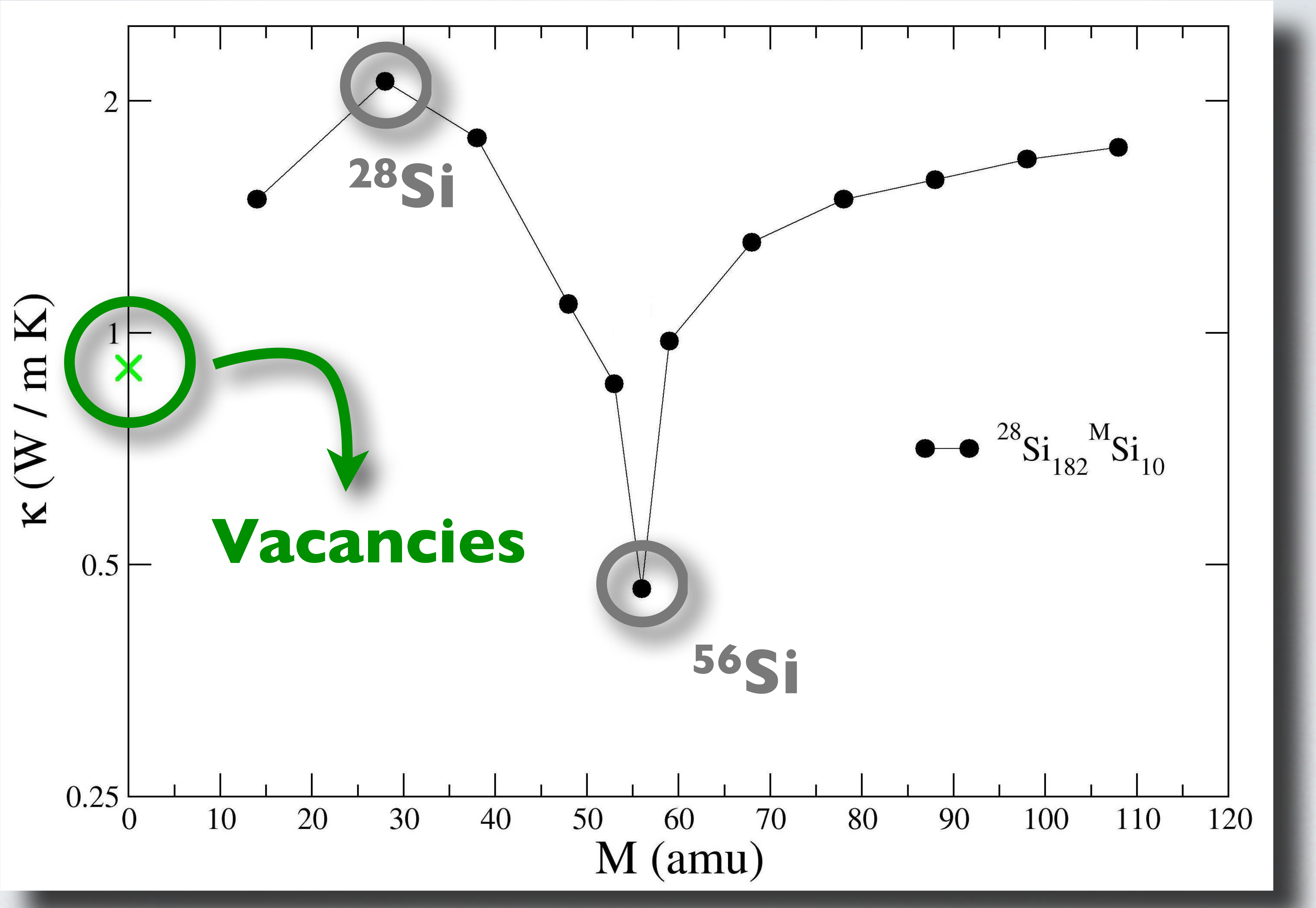


Si_{192} supercell containing **~5.2% impurities**

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

APPLICATION TO IMPURITIES IN SI

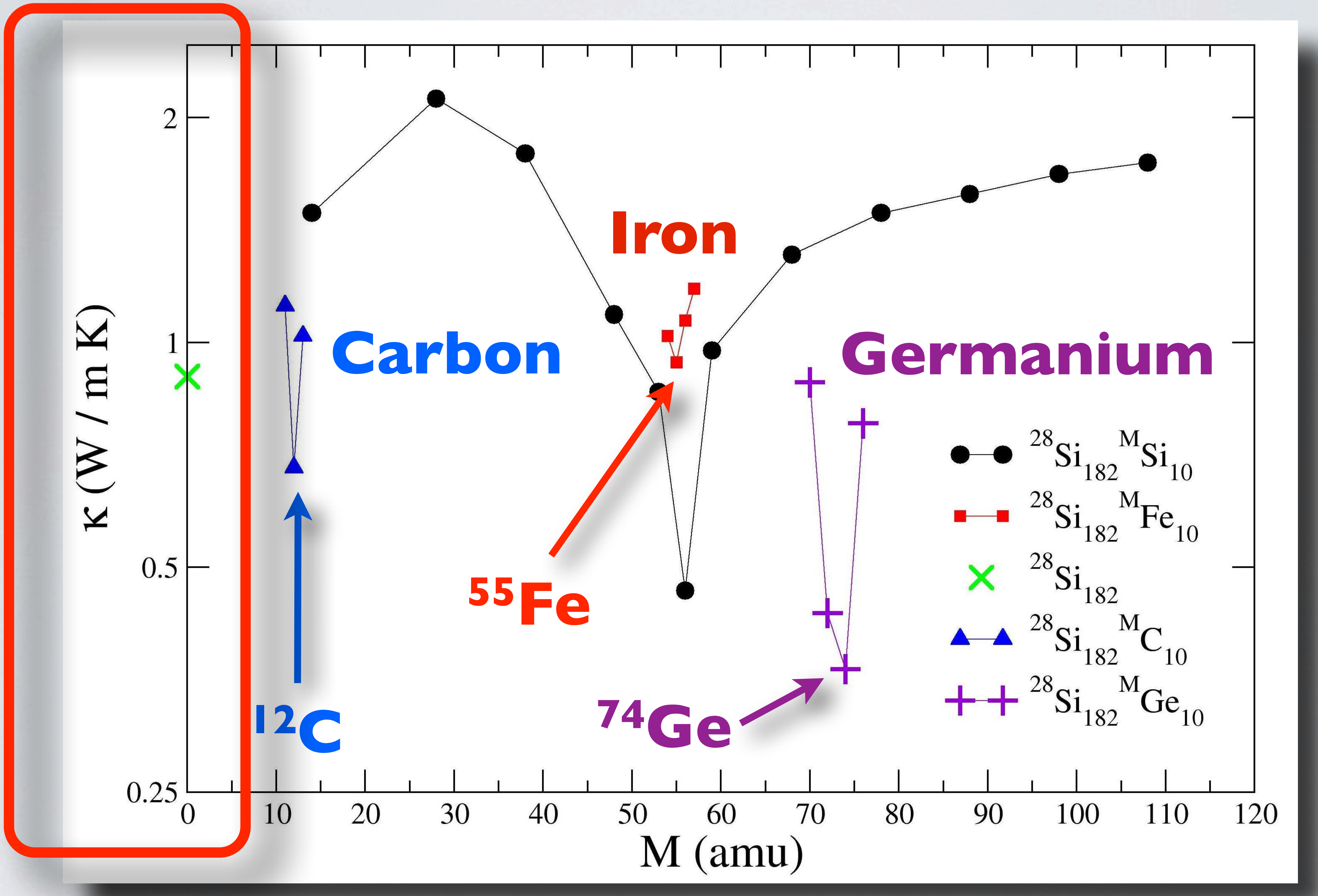
T. M. Gibbons and S. K. Estreicher, *Phys. Rev. Lett.* **102**, 255502 (2009).



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!

FIRST-PRINCIPLES APPROACHES

	Order of interaction	Validity & Applicability	Finite Size Effects	Disorder
Boltzmann-Transport Eq.	$\sim\mathcal{O}(r^3)$	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.

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**

$\Downarrow$ $\Downarrow$ $\Downarrow$

Information about **non-equilibrium processes**

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

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

THE ATOMISTIC HEAT FLUX

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

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

$\mathbf{r}_i \quad \cdots \quad$ Position of atom i

$\varepsilon_i \quad \cdots \quad$ 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).

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

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

ASSESSING THE THERMAL CONDUCTIVITY

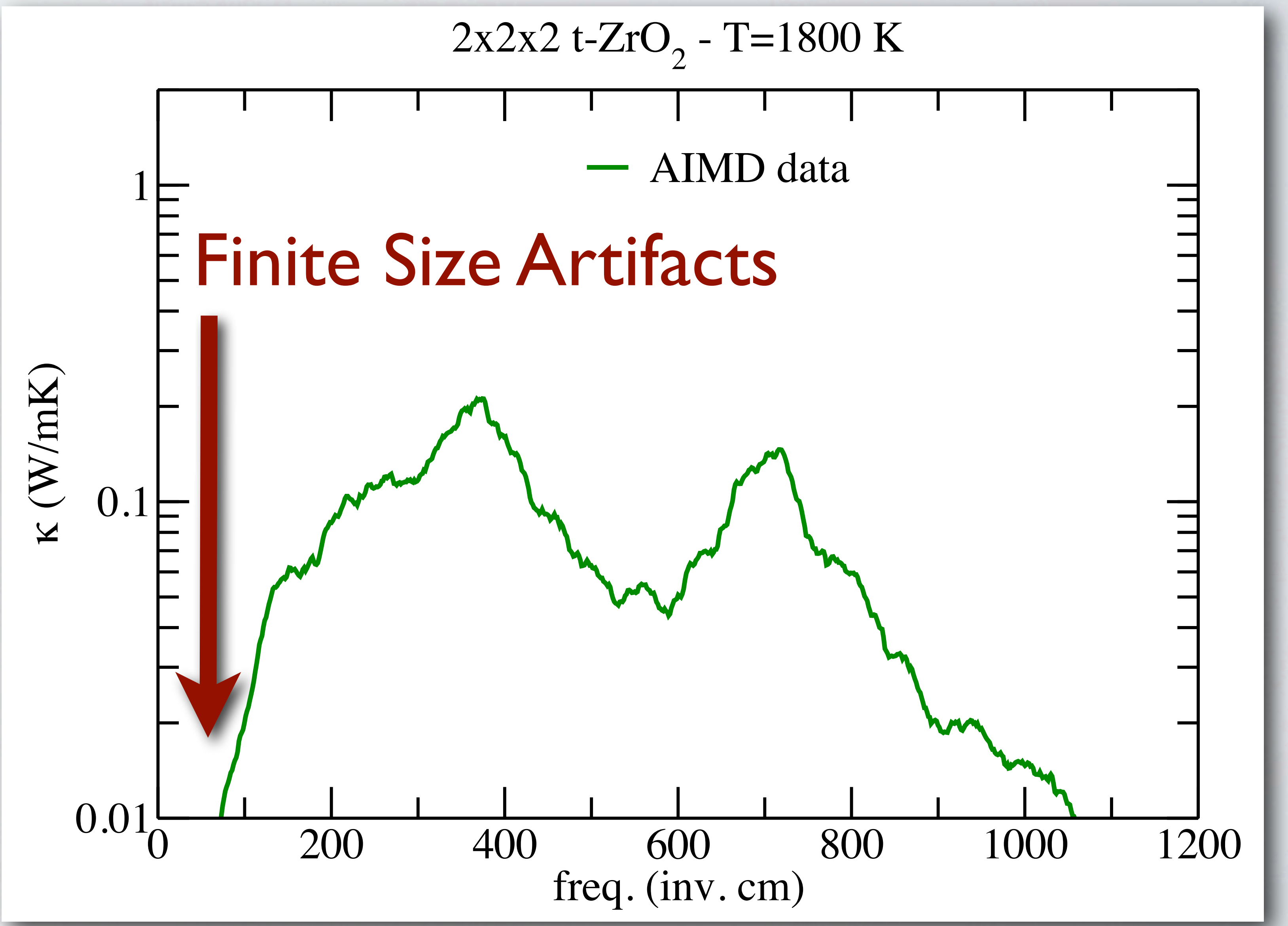
$$\kappa = \frac{V}{3k_BT^2}\int_0^\infty d\tau \,\langle\, \mathbf{J}(0)\,\mathbf{J}(\tau)\rangle_{eq}$$

Fourier Trans.

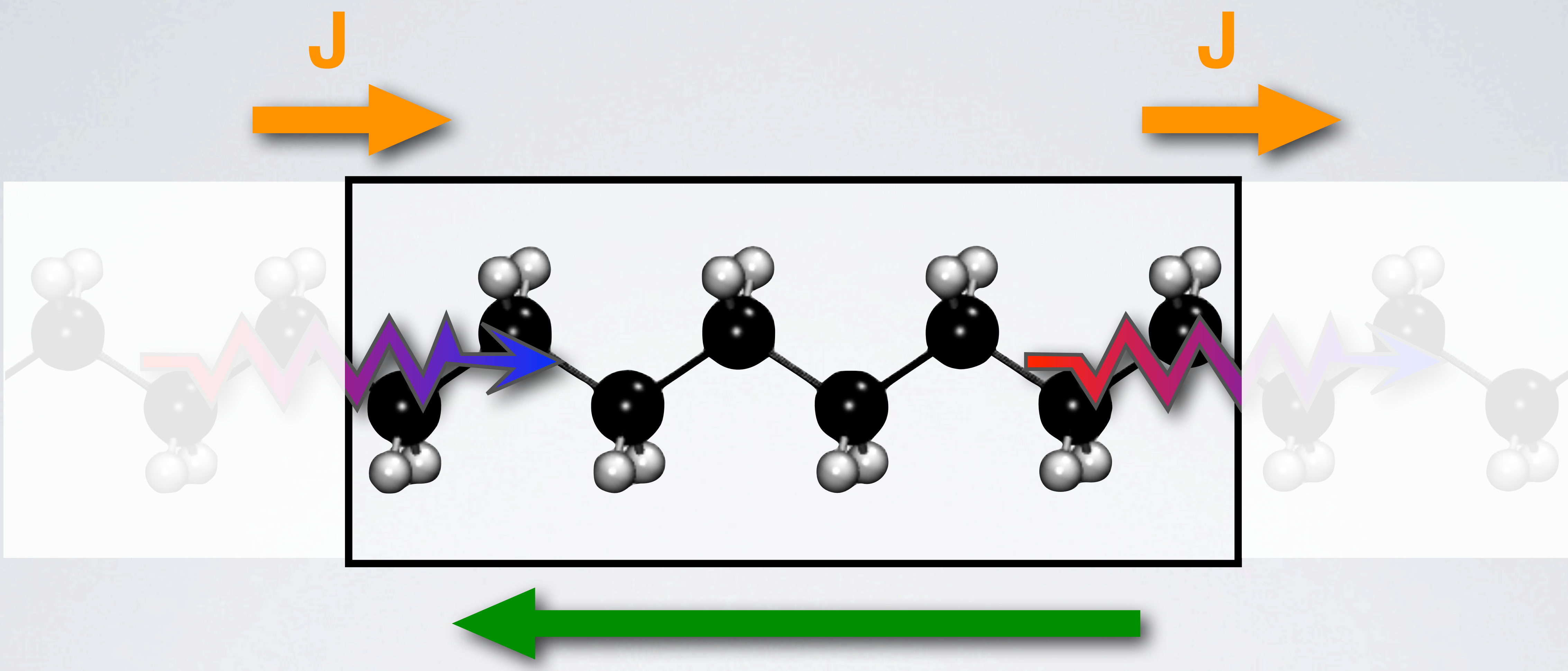
$$\kappa = \frac{V}{3k_BT^2}\lim_{\omega\to 0}|\mathbf{J}(\omega)|^2$$

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



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

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

CORRECTING FOR FINITE SIZE EFFECTS

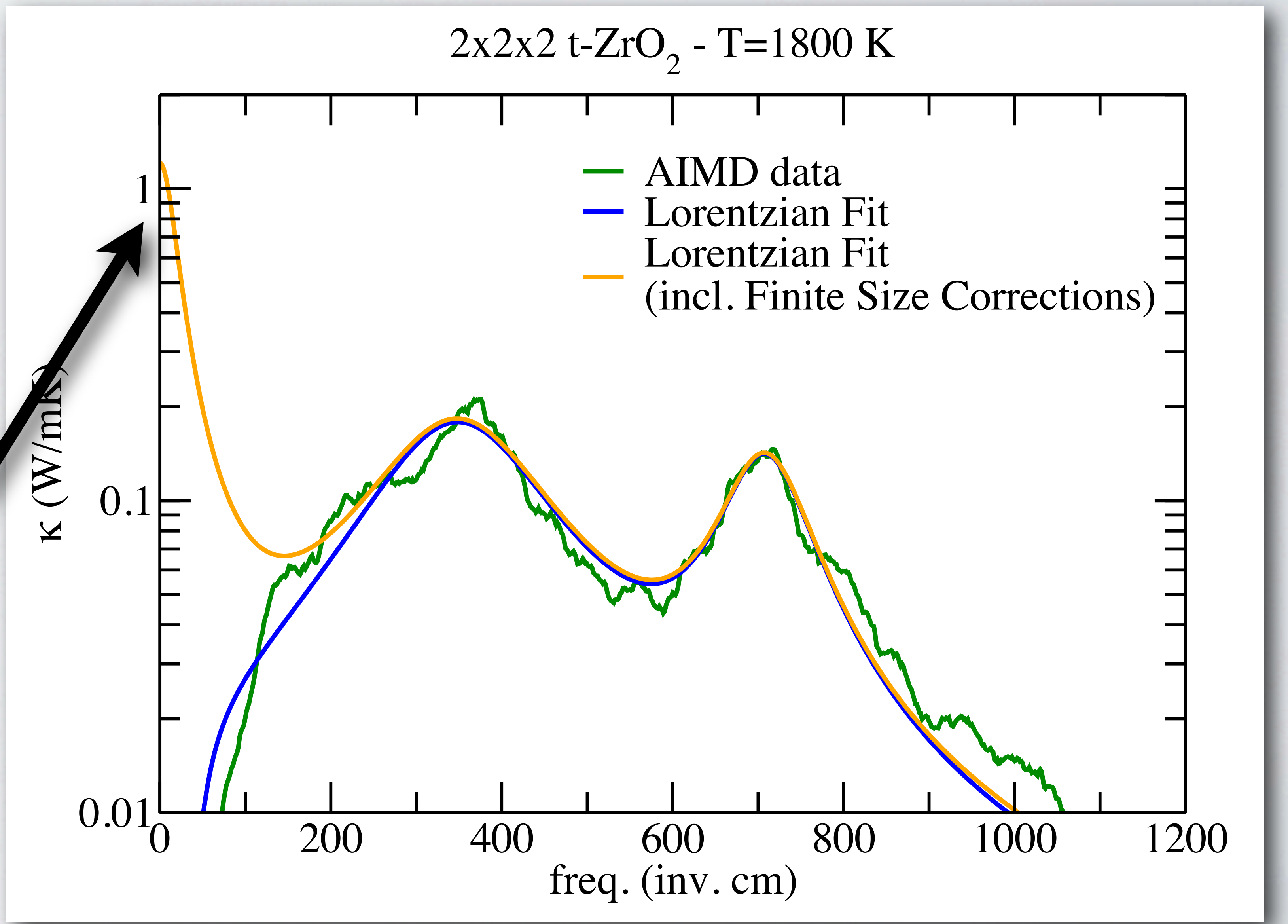
J. L. Feldman *et al.*, *Phys. Rev. B* **48**, 12589 (1993).

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

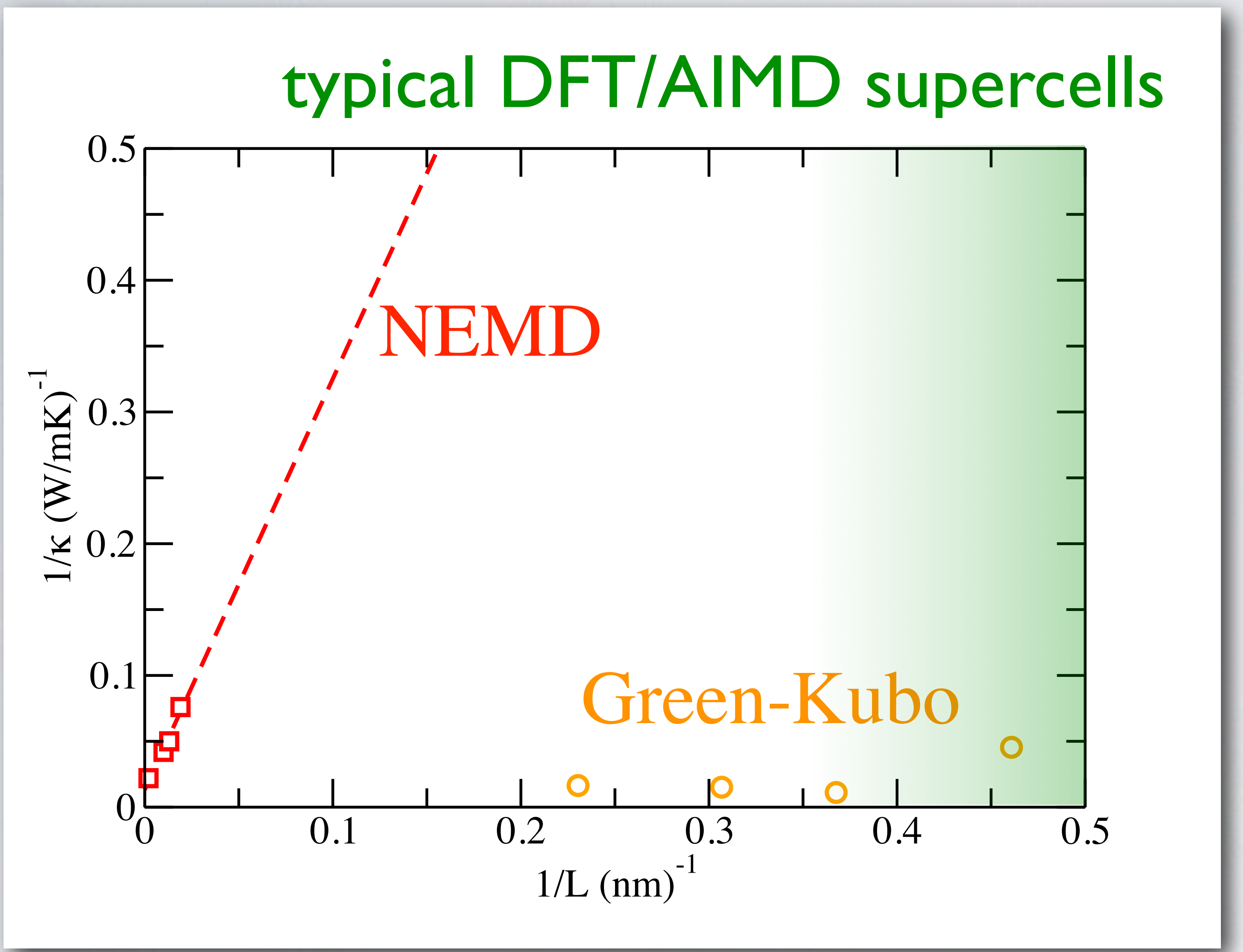
Finite Size $\kappa_{FS}(\omega)$ is superposition of bulk conductivity $\kappa(\omega)$ and finite size effects $\Theta_{FS}(\omega)$!

↓

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



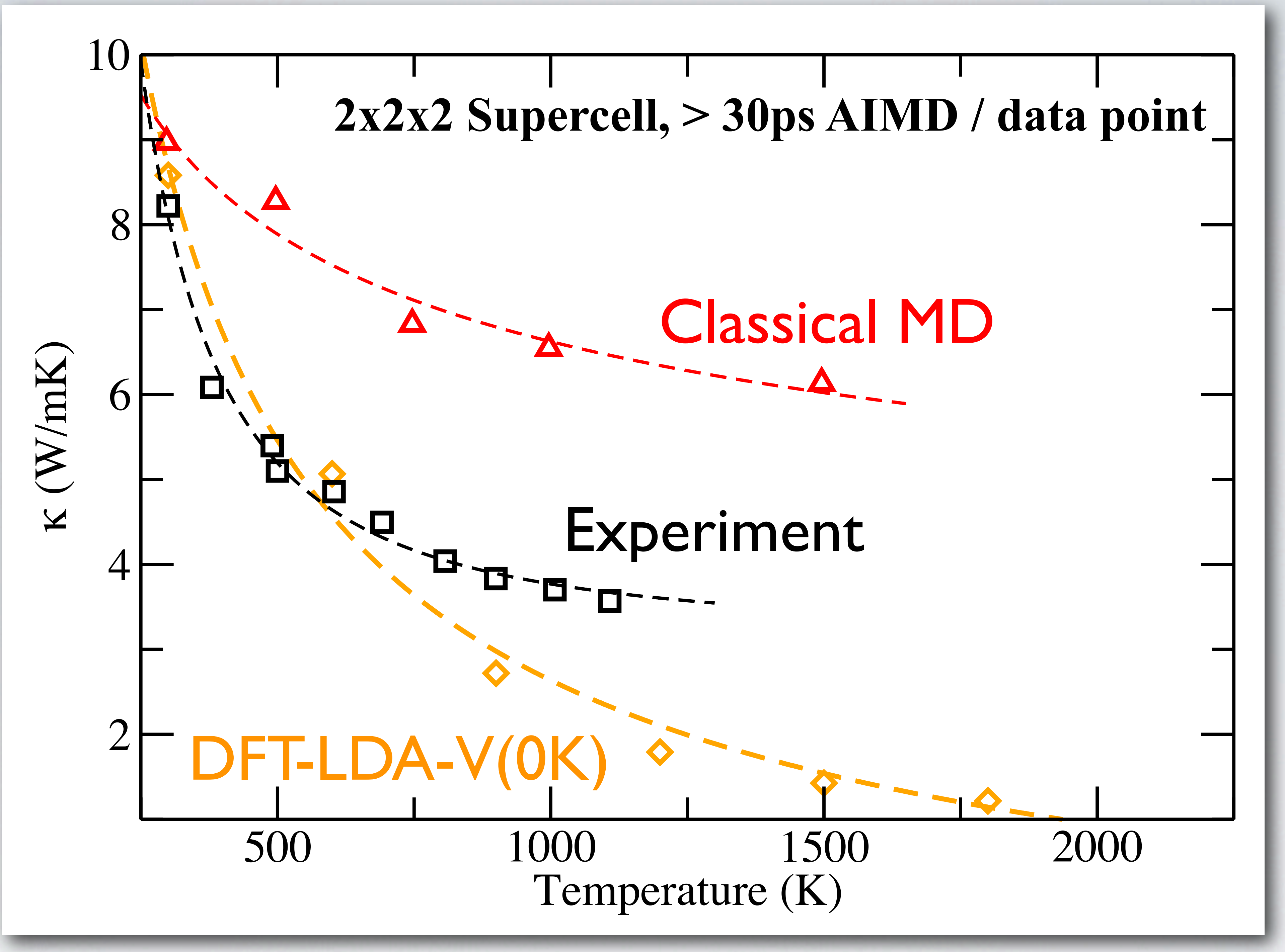
FINITE SIZE EFFECTS



First-principles Green Kubo Simulations $t\text{-}ZrO_2$ - T= 1800K	
Supercell Size	*(k)* [W/mK]
1x1x1	0.96
2x2x2	1.21
3x3x3	~1.27

Green-Kubo Simulations with Hardy's Heat Flux exhibit only small finite size effects.

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).

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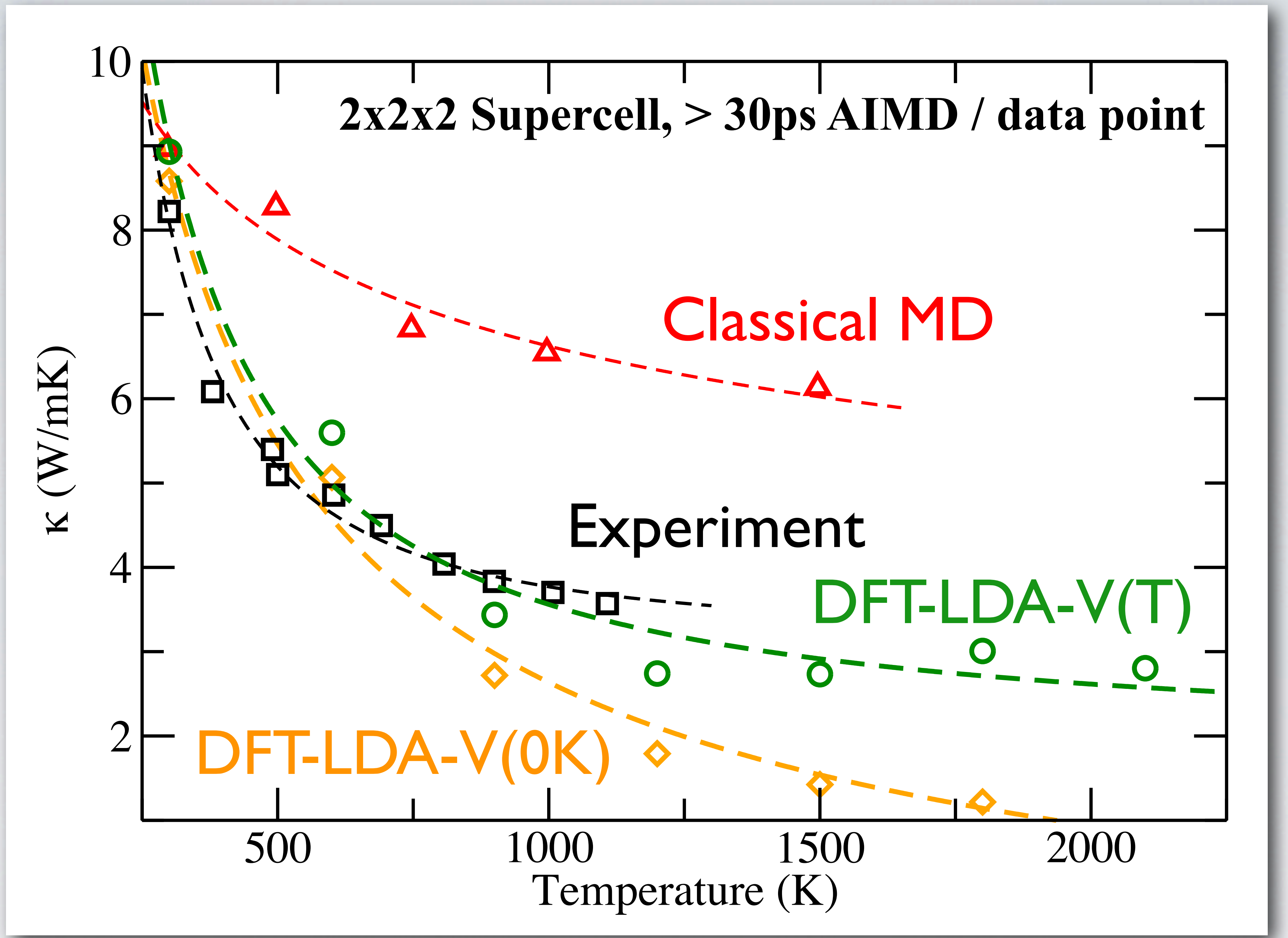

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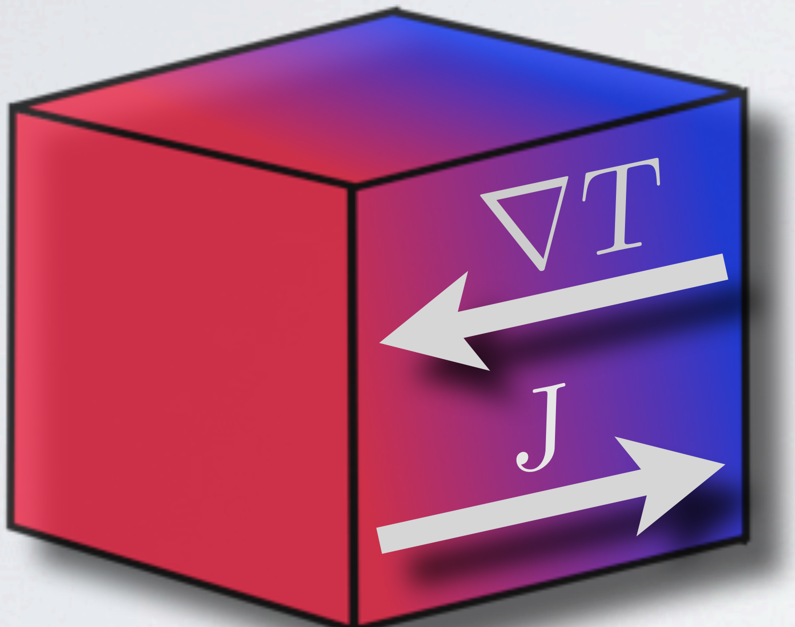
Laser-flash MD	Full	low T	Medium-Large	as in supercell
Green-Kubo MD	Full	all T	Small	as in supercell

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

CHALLENGES

Macroscopic Effect:



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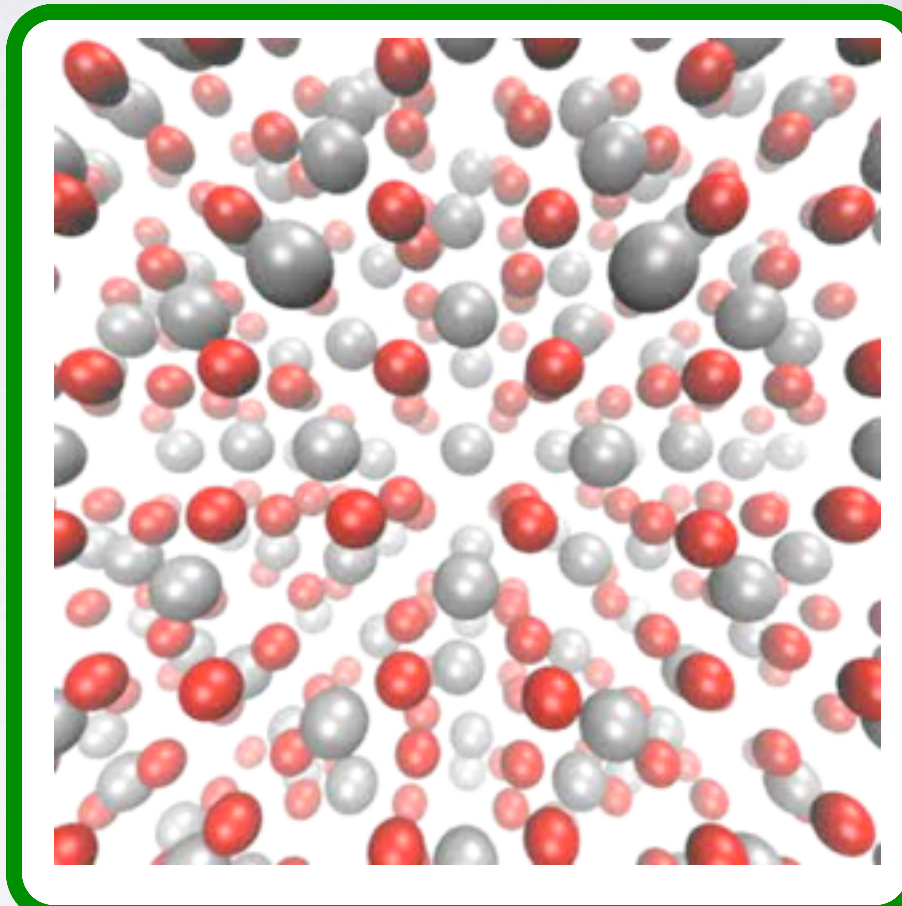
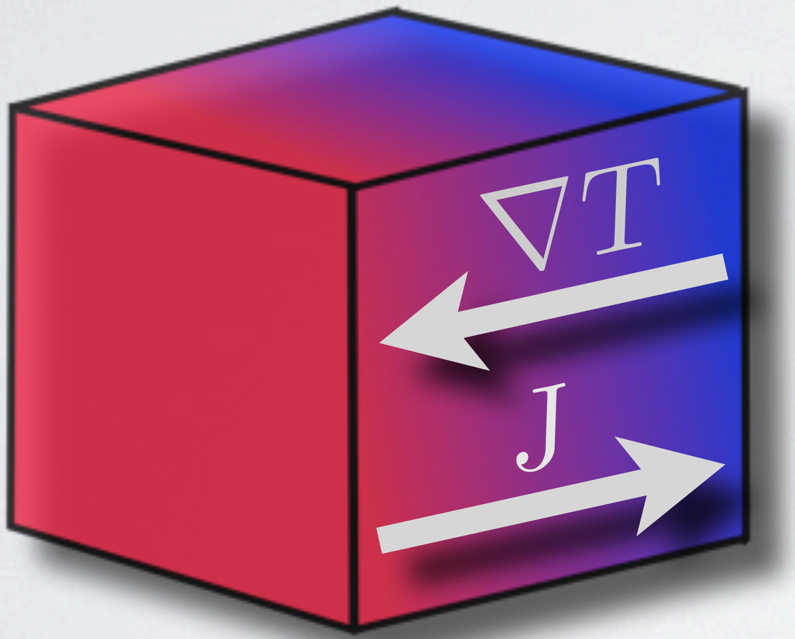
$$\kappa = \kappa_{\mathrm{photon}} + \kappa_{\mathrm{elec.}} + \kappa_{\mathrm{nucl.}}$$



Microscopic Mechanisms

CHALLENGES

Macroscopic Effect:



Fourier's Law:

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

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

Is the separation into *electronic* and *nuclear* thermal conductivities still valid at high temperatures?