Summer School of the Max-Planck-EPFL Center for Molecular Nanoscience & Technology

Thermal Conductivities from First Principles Molecular Dynamics

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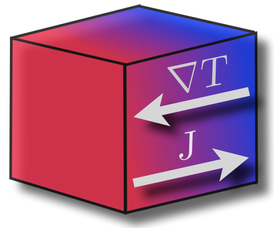
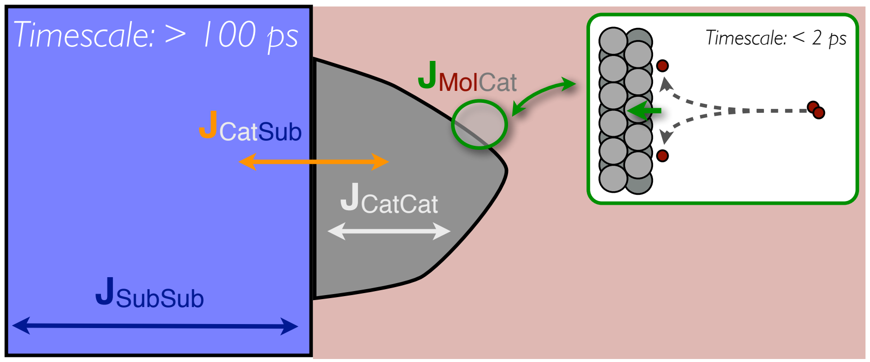
Heat Transport

Macroscopic Effect:

Fourier's Law: $\mathbf{J} = -\kappa \, \nabla T$



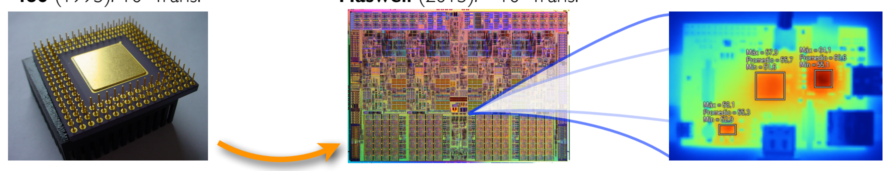
(A) Catalytic Reactors



Substrate Catalyst Gas phase

What are the **real** thermodynamic conditions at the **surface of the catalyst**?

(B) Semiconductor Technology

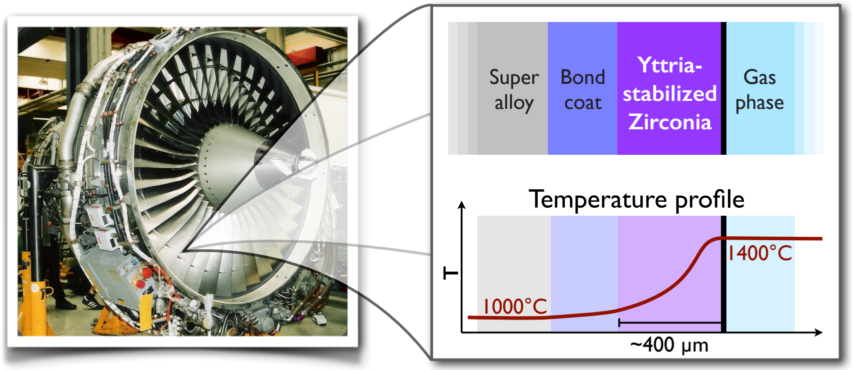


Miniaturization has lead **to enormous transistor densities**

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

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

(C) THERMAL BARRIER COATINGS



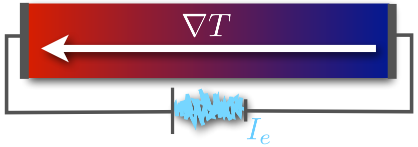
CFM 56-7 airplane engine

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

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

(D) Thermoelectric Elements

Conversion of **temperature gradient** into **electric current**.

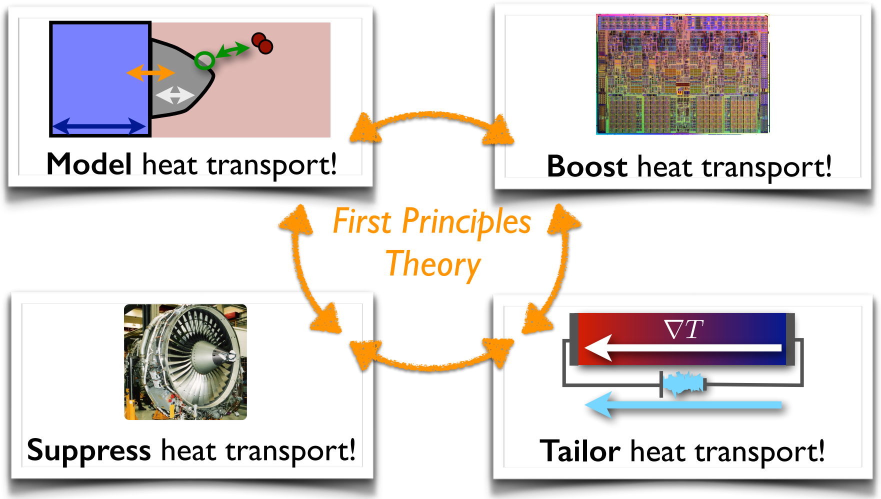


Efficiency roughly $\propto \frac{T}{\kappa}$

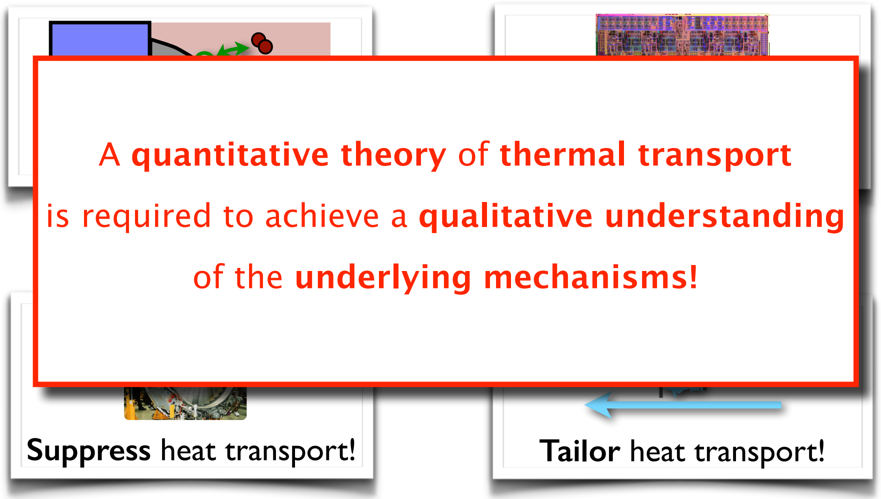
Potential *"waste heat recovery"* device!

Too low efficiency inhibits a large scale, economically attractive deployment of **thermoelectric devices.**

Technological Applications

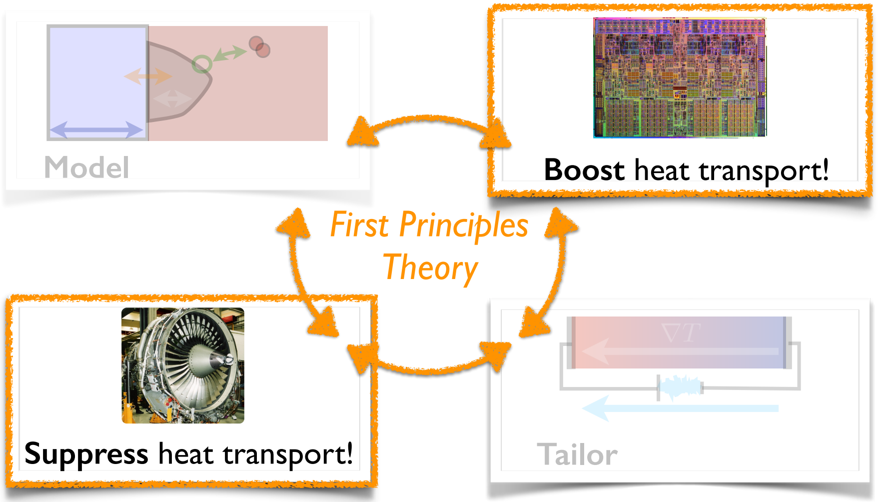


Technological Applications



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

Technological Applications



Heat Transport

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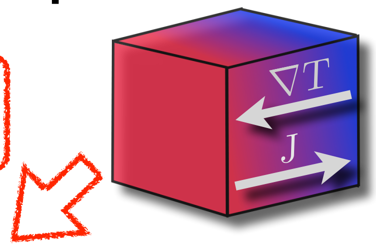


T > *T* > *T* > *T* > *T* > *T* > *T* > *T* > *T*

Onsager Theory of Thermodynamic Non-Equilibrium:

Bulk **discretized** in smaller **units** that are…
(a) **large** enough to be described by **equilibrium** theory
(b) in **non-equilibrium** with respect to **each other**

$T(r_1)$	$T(r_2)$	$T(r_3)$	$T(r_4)$	$T(r_5)$	$T(r_6)$	$T(r_7)$	$T(r_8)$	$T(r_9)$

Local Temperature *T(r)*

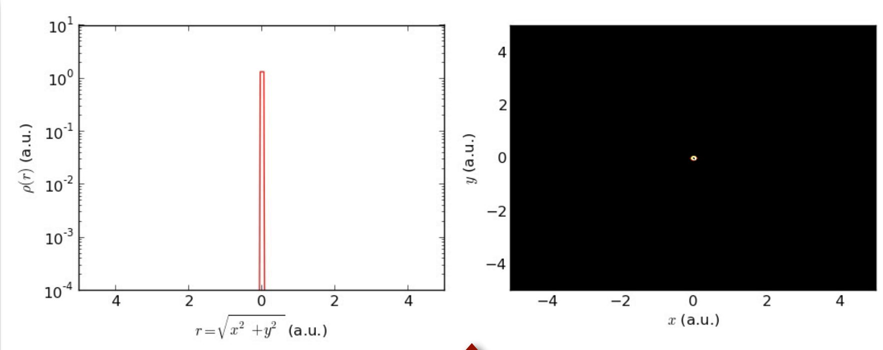
The Continuity Equation: $$\frac{\partial T(\mathbf{r},t)}{\partial t} + \nabla \cdot \mathbf{J}(\mathbf{r},t) = 0$$

Fourier's Law: $$\mathbf{J}(\mathbf{r},t) \;=\; -\kappa \, \nabla \mathbf{T}(\mathbf{r},t)$$

The **Diffusion** Equation: $$\frac{\partial T(\mathbf{r},t)}{\partial t} = \kappa \nabla^2 T(\mathbf{r},t)$$

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

Diffusive Transport



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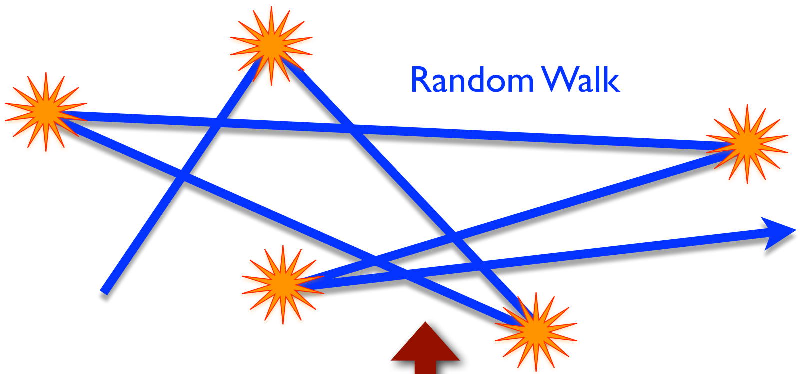
Diffusive Transport



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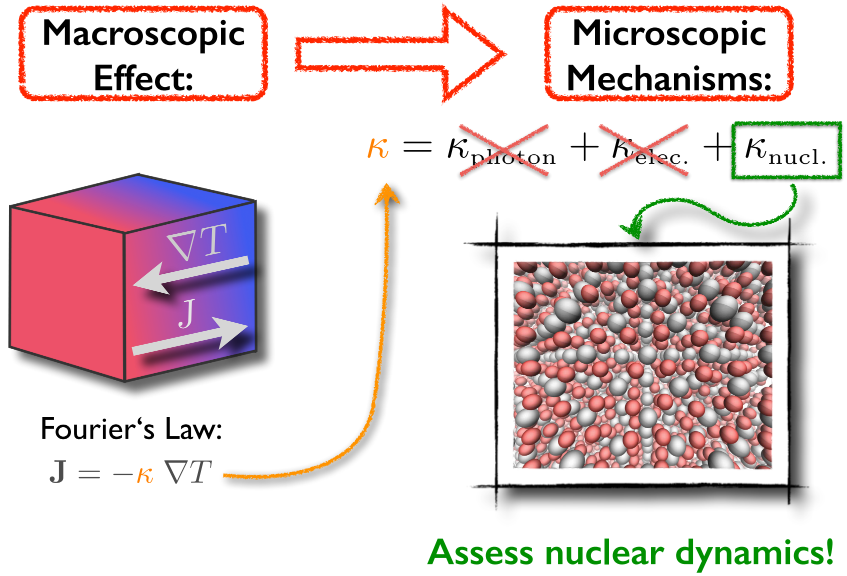
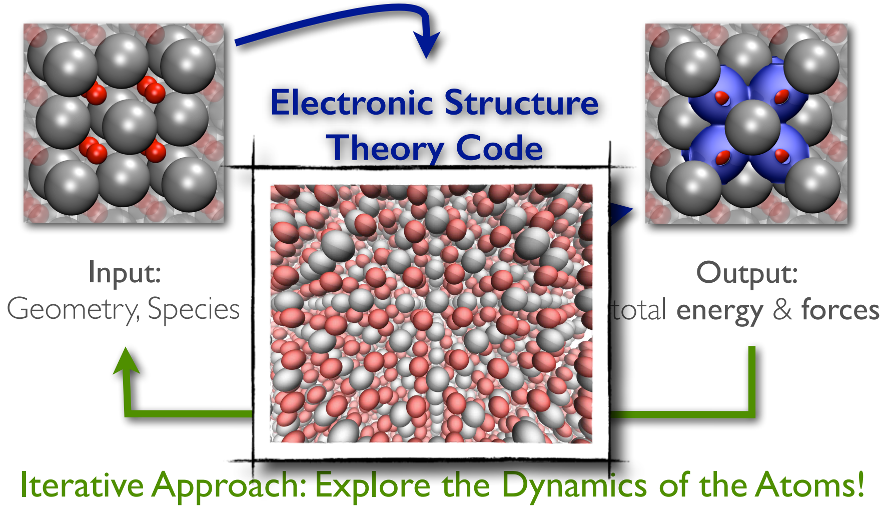
Heat Transport

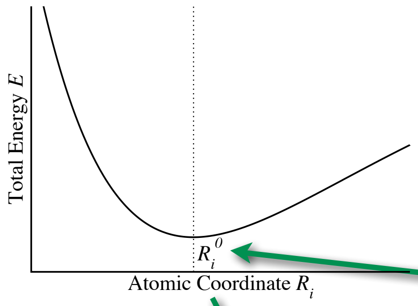


Ab initio Molecular Dynamics



I. THE HARMONIC CRYSTAL

THE HARMONIC APPROXIMATION



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

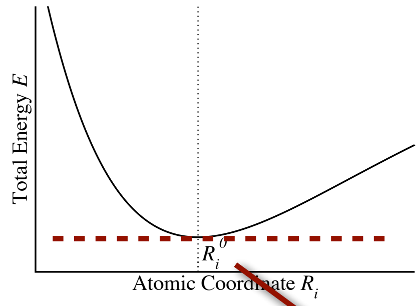
$$E = V\left(\mathbf{R}_1, \mathbf{R}_2, \cdots, \mathbf{R}_N\right)$$

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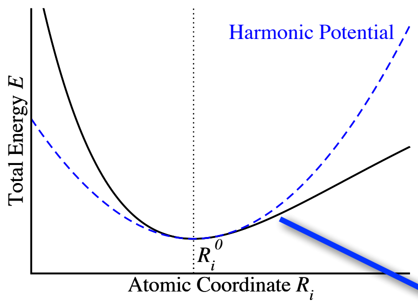
$$E\left(\{\mathbf{R}_0 + \Delta\mathbf{R}\}\right) \approx E\left(\{\mathbf{R}_0\}\right) + \sum_i \left.\frac{\partial E}{\partial \mathbf{R}_i}\right|_{\mathbf{R}_0} \Delta\mathbf{R}_i + \cdots$$

Forces vanish at $\mathbf{R_0}$

THE HARMONIC APPROXIMATION



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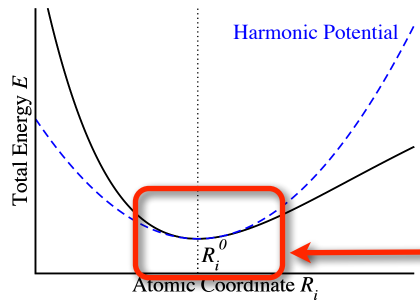
Hessian Φ_{ij}

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 ***R^0***!

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

THE HARMONIC APPROXIMATION

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Static Equilibrium Energy from DFT

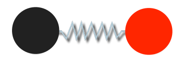
Hessian Φ_{ij}

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

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

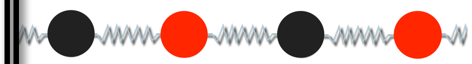
THE HARMONIC APPROXIMATION

...in Molecules:



N ... Number of atoms
⇓
Degrees of Freedom: *3N*
Dimension of Hessian: $9N^2$

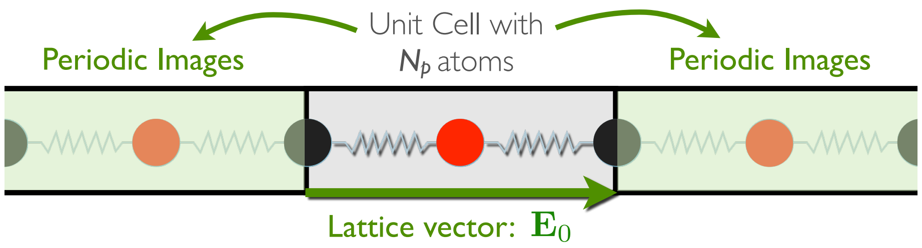
...in Crystalline Solids:



N ... Number of atoms
⇓
Degrees of Freedom: *3N*
Dimension of Hessian: $9N^2$

BUT:
$N \rightarrow \infty$

PERIODIC BOUNDARY CONDITIONS



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).

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

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

Hessian Φ_{ij} with finite number of non-zero entries → **Dynamical Matrix $D_{i'j'}(q)$ known for the whole *reciprocal space***

VIBRATIONS IN A CRYSTAL 101

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

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:

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

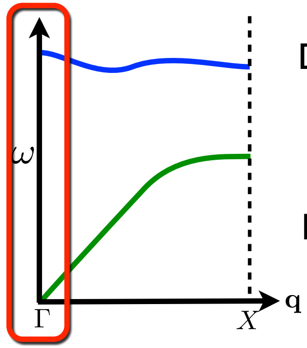
Analytical Solution in Real Space:

Superposition of Harmonic Oscillations

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

VIBRATIONS IN A CRYSTAL 101

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



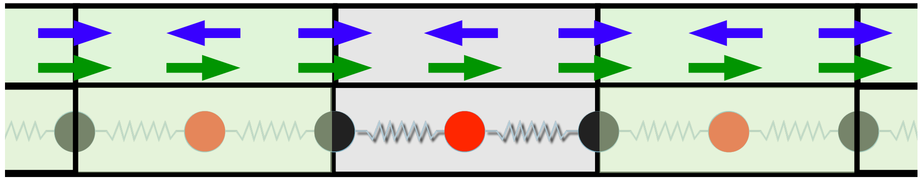
Dynamical matrix:

=1

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

Eigenvalue problem:

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



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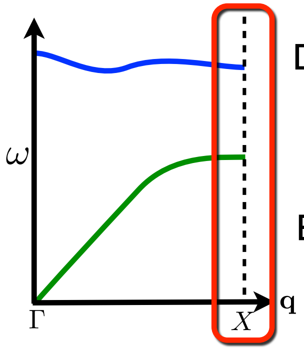
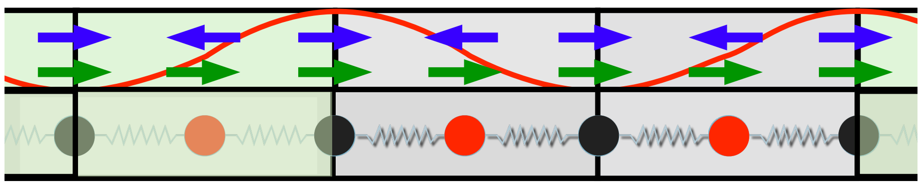


Dynamical matrix:

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

Eigenvalue problem:

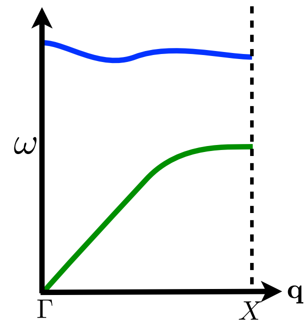
$$\mathbf{D}(X)\;[\nu(X)] = \omega^2(X)\;[\nu(X)]$$



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:



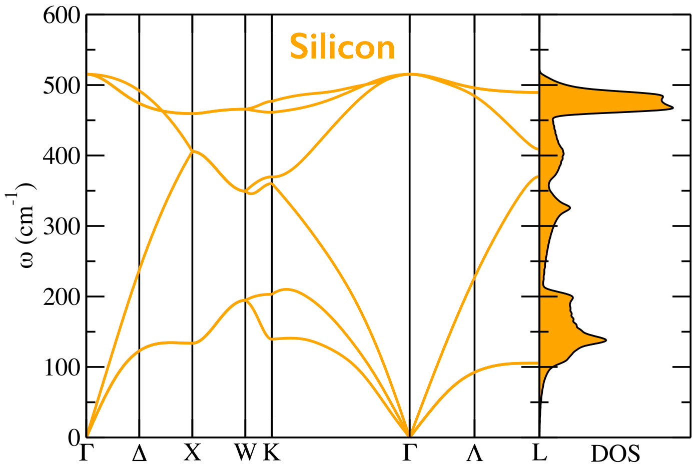
3 Acoustic modes:

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

($3N_p$ - 3) Optical modes:

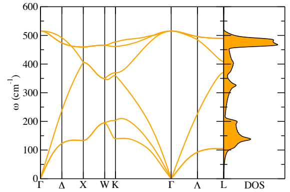
- Atoms in unit cell out-of-phase
- ω > 0 at $\boldsymbol{\Gamma}$ (and everywhere else)
- Weak dispersion

VIBRATIONAL BAND STRUCTURE

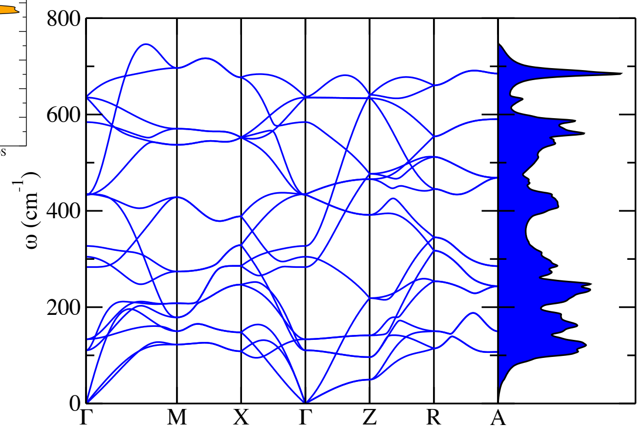


DOS: $g(\omega) = \sum_s \int \frac{d\mathbf{q}}{(2\pi)^3} \delta(\omega - \omega(\mathbf{q})) = \sum_s \int_{\omega(\mathbf{q})=\omega} \frac{dS}{(2\pi)^3} \frac{1}{|\nabla\omega(\mathbf{q})|}$

VIBRATIONAL BAND STRUCTURE



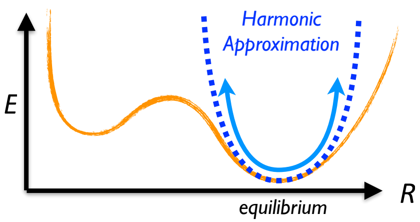
tetragonal Zirconia



Complex materials not always follow conventional wisdom.

Heat Transport Theory 101

Real Space Representation



Reciprocal Space Representation

Decoupled Normal Modes

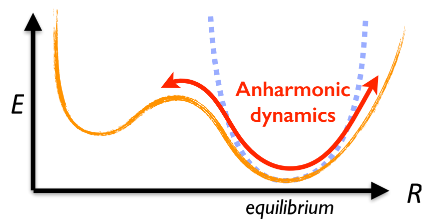
Infinite Phonon Lifetime

Harmonic Approximation:

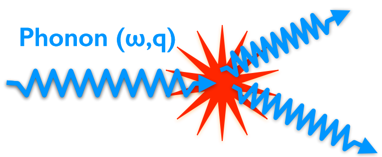
Second order Taylor expansion of the **potential energy surface** around **equilibrium**

Heat Transport Theory 101

Real Space Representation



Reciprocal Space Representation



Anharmonicity

Electron-Phonon Coupling

Phonon Scattering

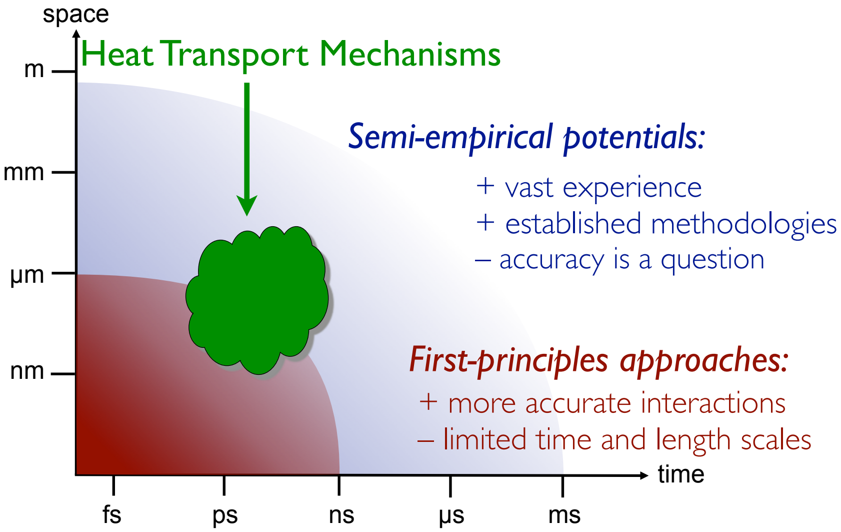
Theory Toolbox

Molecular Dynamics

Electronic Structure Theory

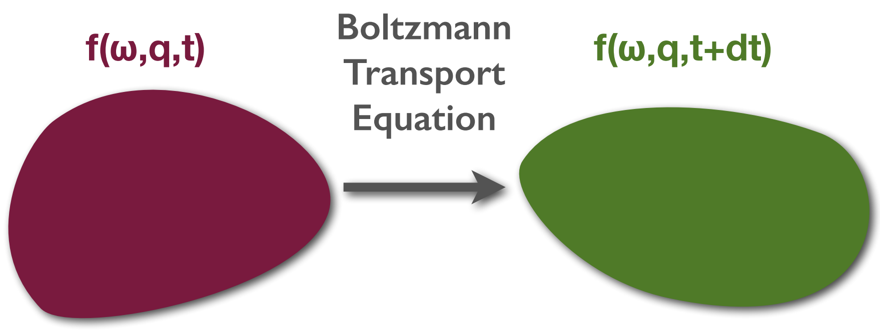
Perturbation Theory

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).



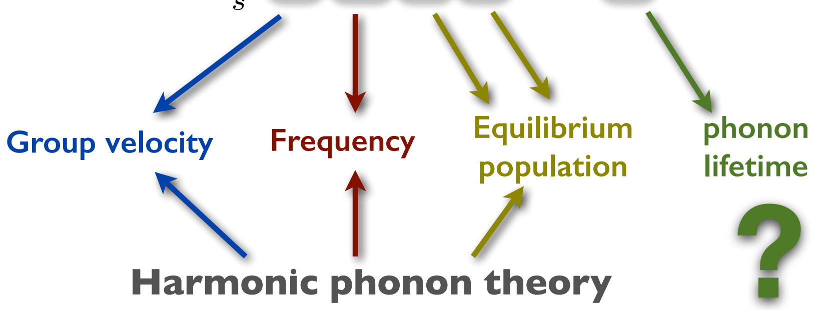
Boltzmann-Peierls-Transport-Equation describes the evolution of the **phonon** phase space distribution **f(ω,q,t)**.

(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

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



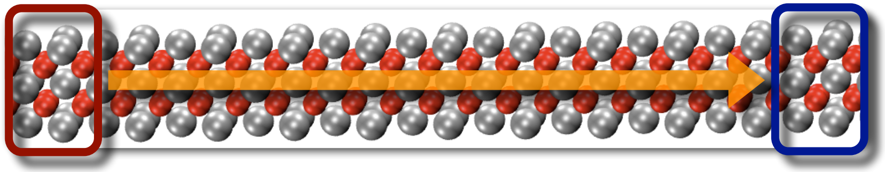
FIRST-PRINCIPLES APPROACHES

	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 $\mathbf{J}$

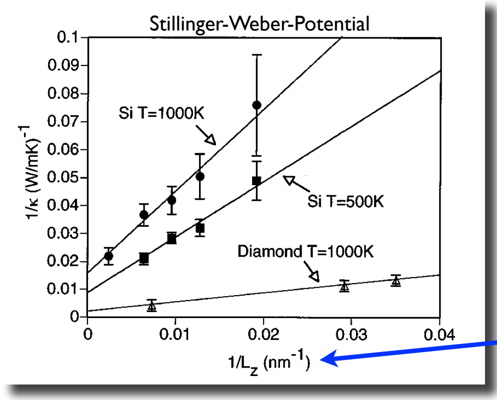
→ **heat sink**

⇓

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).

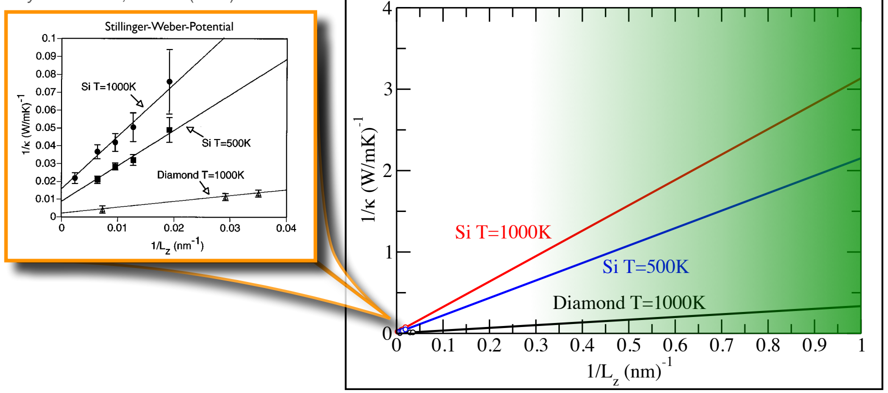
Finite Size Corrections

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

mean free path

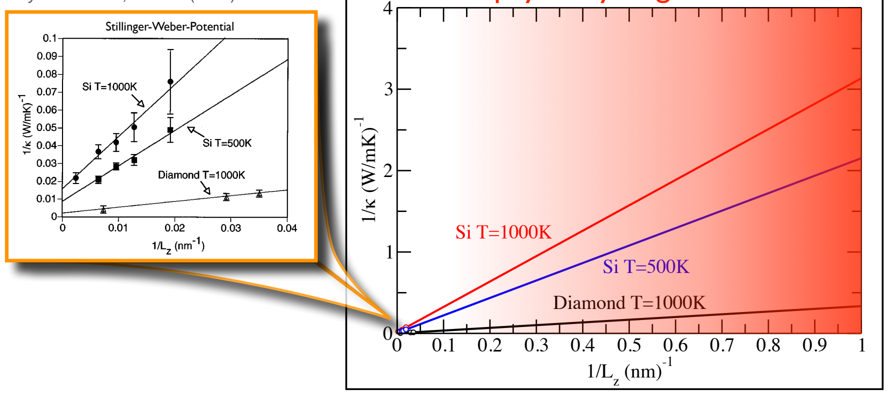
supercell length

FINITE SIZE EFFECTS



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

FINITE SIZE EFFECTS



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				

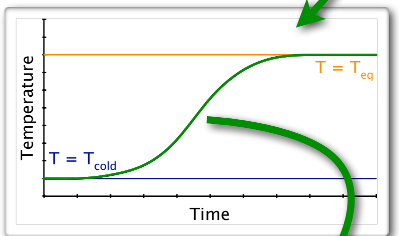
Non-Equilibrium MD approaches are **in principle exact**, in **DFT** however **prohibitively costly** to converge **accurately**.

„LASER FLASH" MEASUREMENTS

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

„LASER FLASH" MEASUREMENTS

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



Heat Diffusion Equation:

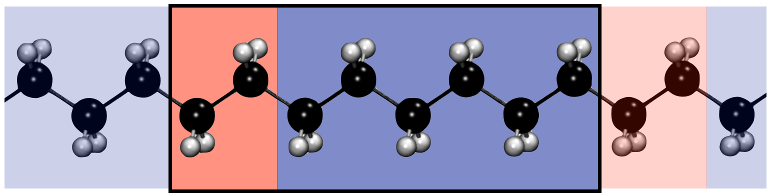
$$\frac{\partial T(x,t)}{\partial t} + \alpha \frac{\partial^2 T(x,t)}{\partial x^2} = 0$$

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 $\mathbf{e}_s$.

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

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

Maxwell-Boltzmann distributed amplitudes

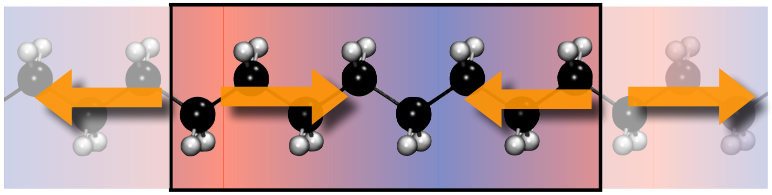
random phase

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***:

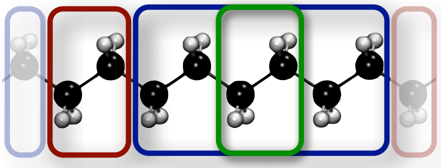


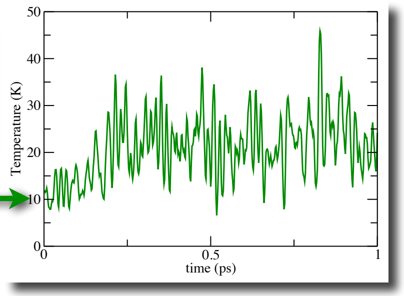
(A) **Prepare two supercells:** a **small hot** one and a **large cold** one.

(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); C. Carbogno, *Phys. Rev. B* **84**, 035317 (2011).



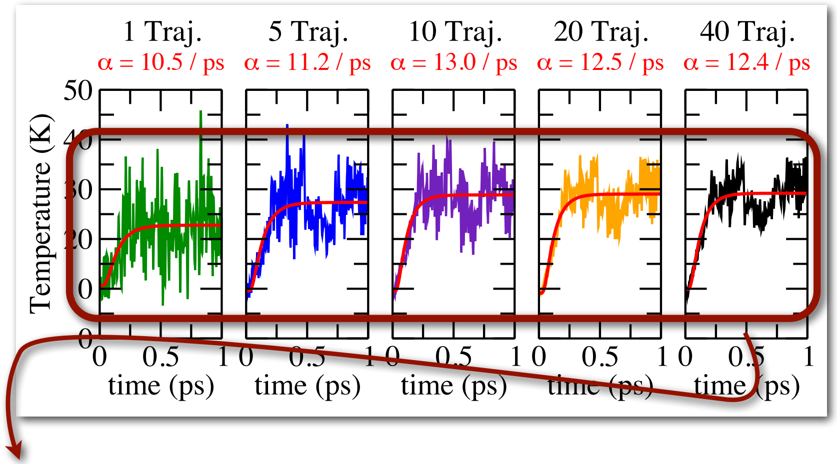


Monitor temperature of the central cell

The finite number of atoms leads to large **temperature fluctuations**.

„LASER FLASH" SIMULATIONS

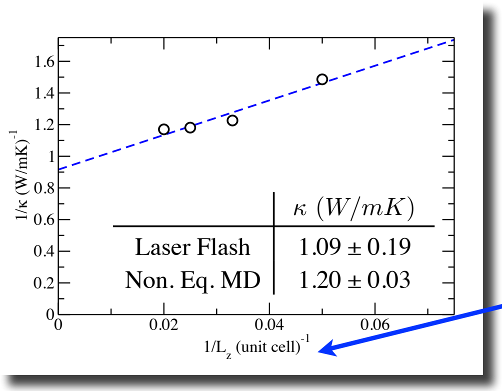
T. M. Gibbons and S. K. Estreicher, *Phys. Rev. Lett.* **102**, 255502 (2009); C. Carbogno, *Phys. Rev. B* **84**, 035317 (2011).



Fit to

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

FINITE SIZE EFFECTS



Finite Size Corrections

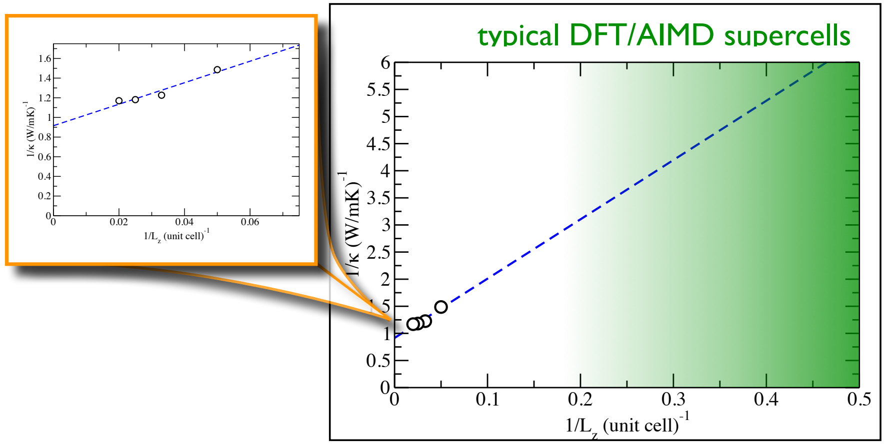
$$\frac{1}{\kappa} \sim \left(\frac{1}{l_\infty} + \frac{4}{L_z} \right)$$

mean free path

supercell length

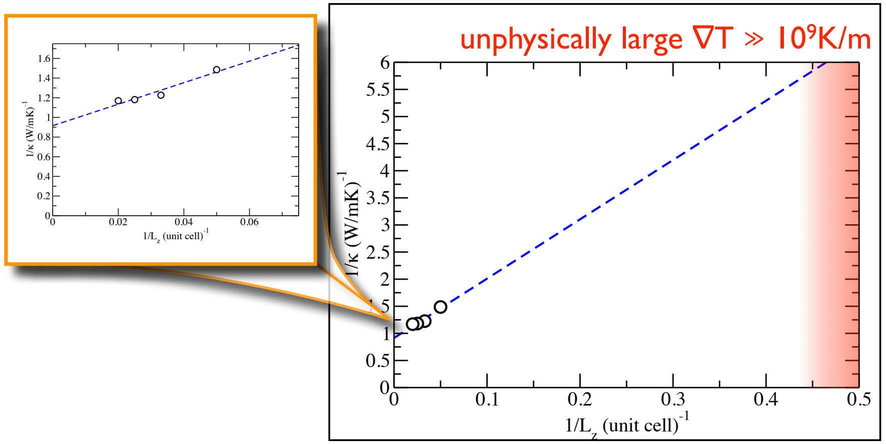
SiGe, Stillinger-Weber Potential,
Courtesy of Philip Howell, Siemens AG

FINITE SIZE EFFECTS



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

FINITE SIZE EFFECTS



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.	~$\mathcal{O}(r^3)$	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				

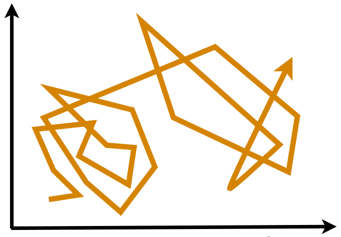
Laser-flash MD yields **accurate qualitative results** at **low temperatures** within **moderate computational costs.** **Quantitative** predictions require **finite size corrections**, though.

FLUCTUATION-DISSIPATION THEOREM

Brownian Motion:

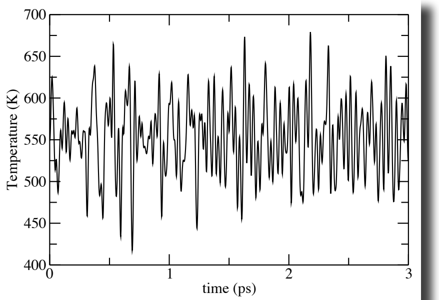
A. Einstein, *Ann. Phys.* **322**, 549 (1905).

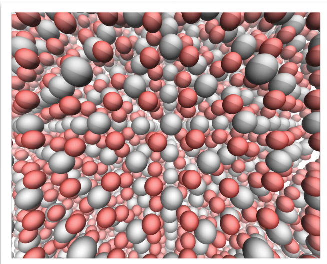
The erratic motion of the particles is closely related to frictional force under perturbation.

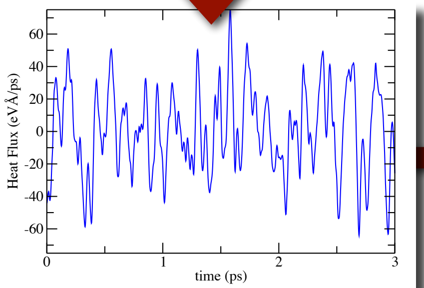


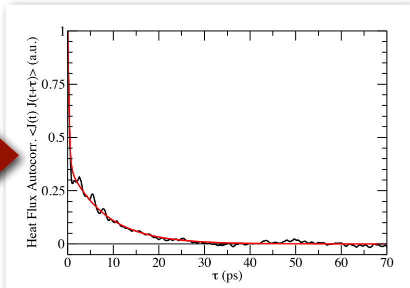
Random walk in 2D

> 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

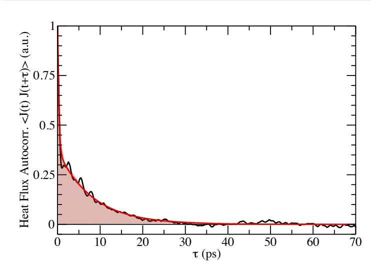
Simulations of the **thermodynamic equilibrium**

⇓ ⇓ ⇓

Information about **non-equilibrium processes**

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

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



THE ATOMISTIC HEAT FLUX

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

Continuity Equation:

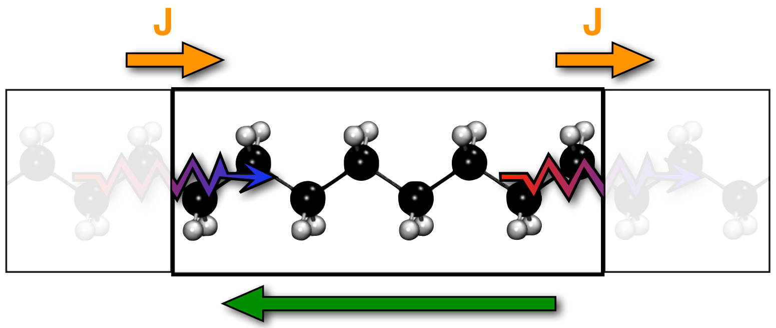
$$\frac{\partial E(\mathbf{r})}{\partial t} + \nabla \cdot \mathbf{j}(\mathbf{r}) = 0 \qquad \mathbf{J}(t) = \int \mathbf{j}(\mathbf{r}) \, d\mathbf{r}$$

Energy decomposition | *Heat flux*

$$E(\mathbf{r}) = \sum_i E_i \, \delta(\mathbf{r} - \mathbf{R}_i) \quad \Rrightarrow \quad \mathbf{J}(t) = \frac{d}{dt}\left(\sum_i \mathbf{R}_i E_i \right)$$

⇒ Barycenter not well defined in periodic boundary conditions!

PERIODIC BOUNDARY CONDITIONS



$$\mathbf{J}(t) = \frac{d}{dt}\left(\sum_i \mathbf{R}_i E_i\right)$$

Small heat flux through boundaries
leads to huge change in energy barycenter.
⇒ **Artifical scattering at the cell's boundaries!**

THE ATOMISTIC HEAT FLUX

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

Continuity Equation: $\frac{\partial E(\mathbf{r})}{\partial t} + \nabla \cdot \mathbf{j}(\mathbf{r}) = 0$ $\mathbf{J}(t) = \int \mathbf{j}(\mathbf{r})\, d\mathbf{r}$

Energy decomposition *Heat flux*

~~$E(\mathbf{r}) = \sum_i E_i\, \delta(\mathbf{r} - \mathbf{R}_i) \Rightarrow \mathbf{J}(t) = \frac{d}{dt}\left(\sum_i \mathbf{R}_i E_i\right)$~~

$$E(\mathbf{r}) = \sum_i \left(\sum_j E_{ij}\right) \delta(\mathbf{r} - \mathbf{R}_i) \Longrightarrow \mathbf{J}(t) = \frac{d}{dt}\left(\sum_{i>j} (\mathbf{R}_i - \mathbf{R}_j)\, E_{ij}\right)$$

⇒ **Relative distances** are well defined in **periodic boundary conditions!**

THE ATOMISTIC HEAT FLUX

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

Continuity Equation: $\frac{\partial E(\mathbf{r})}{\partial t} + \nabla \cdot \mathbf{j}(\mathbf{r}) = 0$ $\mathbf{J}(t) = \int \mathbf{j}(\mathbf{r})\, d\mathbf{r}$

Energy decomposition *Heat flux*

~~$E(\mathbf{r}) = \sum_i E_i\, \delta(\mathbf{r} - \mathbf{R}_i) \Rightarrow \mathbf{J}(t) = \frac{d}{dt}\left(\sum_i \mathbf{R}_i E_i\right)$~~

$$E(\mathbf{r}) = \sum_i \left(\sum_j E_{ij}\right) \delta(\mathbf{r} - \mathbf{R}_i) \Longrightarrow \mathbf{J}(t) = \frac{d}{dt}\left(\sum_{i>j} (\mathbf{R}_i - \mathbf{R}_j)\, E_{ij}\right)$$

⇒ **Correct** heat flux definition requires an energy decompositions in **pairwise interactions.**

THE VIRIAL HEAT FLUX

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

Helfands' Heat Flux *Hardys' Heat Flux*

$$\mathbf{J}(t) = \frac{d}{dt}\left(\sum_{i>j} (\mathbf{R}_i - \mathbf{R}_j)\, E_{ij}\right) = \sum_i \mathbf{V}_i E_i + \frac{1}{2}\sum_{ij} (\mathbf{R}_i - \mathbf{R}_j)\, \frac{\partial E_j}{\partial \mathbf{R_i}} \mathbf{V_I}$$

~~*Convective Heat Flux*~~

Virial Heat Flux:

$$\sigma V = -\frac{1}{2}\sum_{ij} (\mathbf{R}_i - \mathbf{R}_j)\, \frac{\partial E_j}{\partial \mathbf{R_i}} = \frac{1}{2}\sum_{ij} (\mathbf{R}_i - \mathbf{R}_j)\, \mathbf{F}_{ij}$$

Virial Heat Flux closely related to stress tensor σ!

AN *AB INITIO* VIRIAL FOR THE NUCLEI

Ab initio: Interactions driven by **electrons**

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

$$= \langle\Psi(\mathbf{r})|\,T_{\mathbf{r}} + \int \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}' - \sum_j \frac{Z_j}{|\mathbf{r}-\mathbf{R}_j|} + \sum_{ij}\frac{Z_i Z_j}{|\mathbf{R}_i-\mathbf{R}_j|}\,|\Psi(\mathbf{r})\rangle$$

Forces on atoms still well defined!

$$\mathbf{F}_i = -\langle\Psi(\mathbf{r})|\,\frac{\partial\mathbb{H}(\mathbf{R})}{\partial\mathbf{R}_i}\,|\Psi(\mathbf{r})\rangle = -Z_i\left(\int d\mathbf{r}\; n(\mathbf{r})\frac{\mathbf{r}-\mathbf{R}_i}{|\mathbf{r}-\mathbf{R}_i|^3} - \sum_{j\neq i} Z_j \frac{\mathbf{R}_j-\mathbf{R}_i}{|\mathbf{R}_j-\mathbf{R}_i|^3}\right)$$

…and so is the virial!

$$\sigma_{\alpha\beta} = -Z_i\left(\int d\mathbf{r}\; n(\mathbf{r})\frac{(\mathbf{r}-\mathbf{R}_i)_\alpha}{|\mathbf{r}-\mathbf{R}_i|^3}(\mathbf{r}-\mathbf{R}_i)_\beta - \sum_{j\neq i} Z_j \frac{(\mathbf{R}_j-\mathbf{R}_i)_\alpha}{|\mathbf{R}_j-\mathbf{R}_i|^3}(\mathbf{R}_j-\mathbf{R}_i)_\beta\right)$$

ALL-ELECTRON FORMALISM FOR TOTAL ENERGY STRAIN DERIVATIVES

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

Formulas for analytical stress

F. Knuth, FHI

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

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

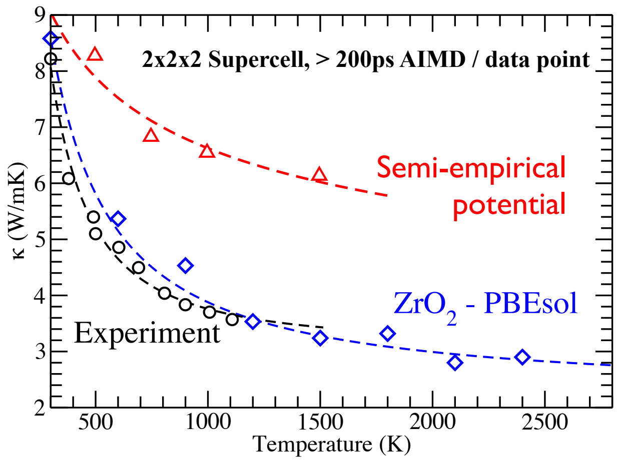
$$\sigma_{ij}^{\mathrm{MP}} = \frac{1}{V}\sum_\alpha\int_{\mathrm{UC}} d\mathbf{r}\left[n(\mathbf{r})-\frac{1}{2}n_{\mathrm{MP}}(\mathbf{r})\right]\frac{\partial v_\alpha^{\mathrm{es,tot}}(|\mathbf{r}-\mathbf{R}_\alpha|)}{\partial r_i}(\mathbf{r}-\mathbf{R}_\alpha)_j - \frac{1}{2V}\sum_\alpha\int_{\mathrm{UC}}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

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

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

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

APPLICATION TO ZIRCONIA



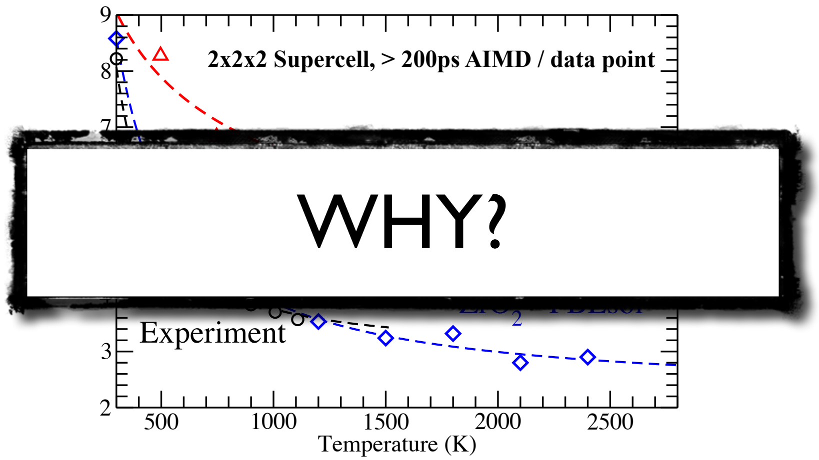
Experiment:

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

Semi-empirical MD:

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

APPLICATION TO ZIRCONIA



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Semi-empirical MD:

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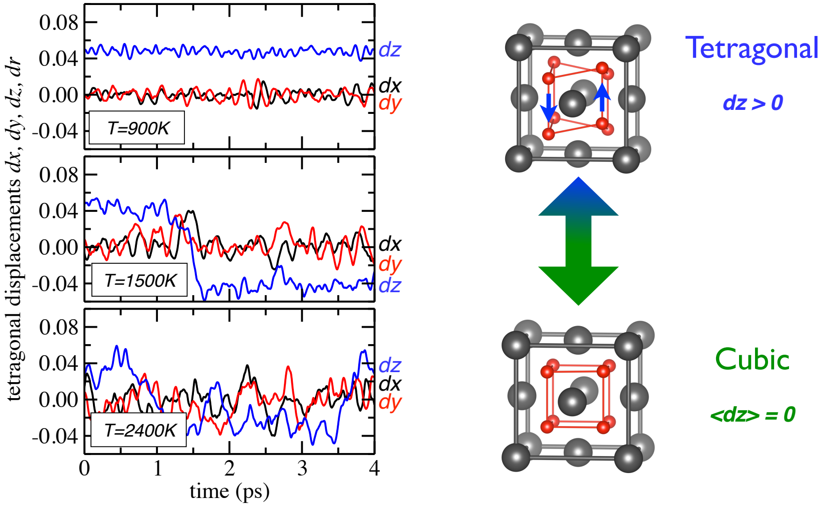
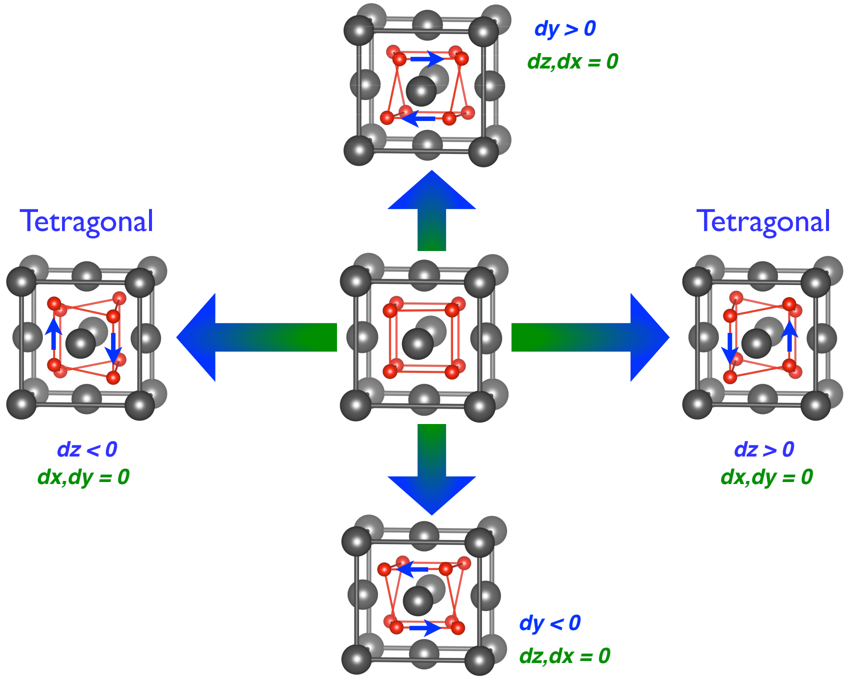
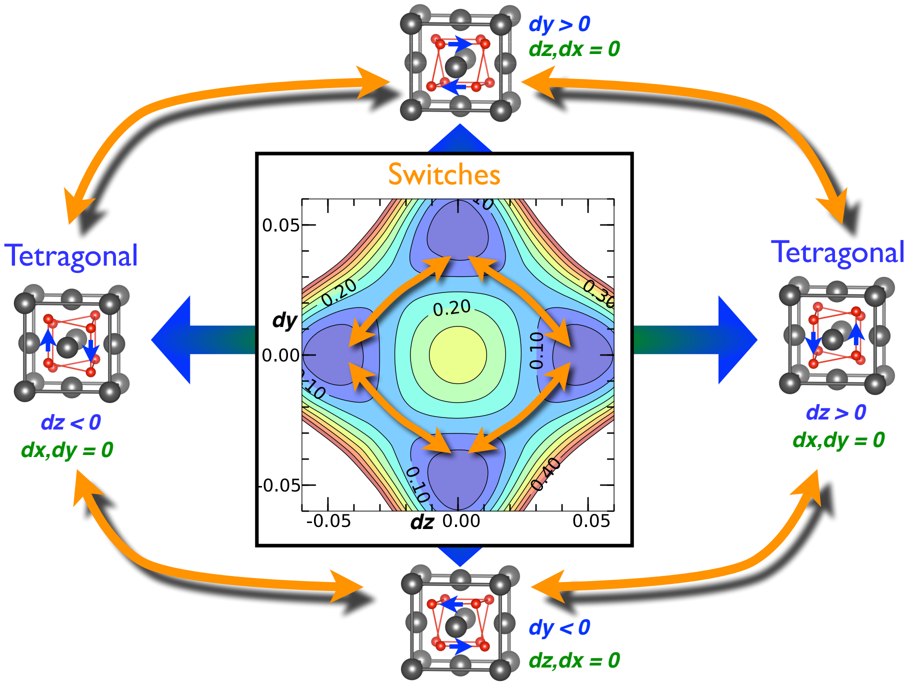
The Tetragonal-Cubic Phase Transition

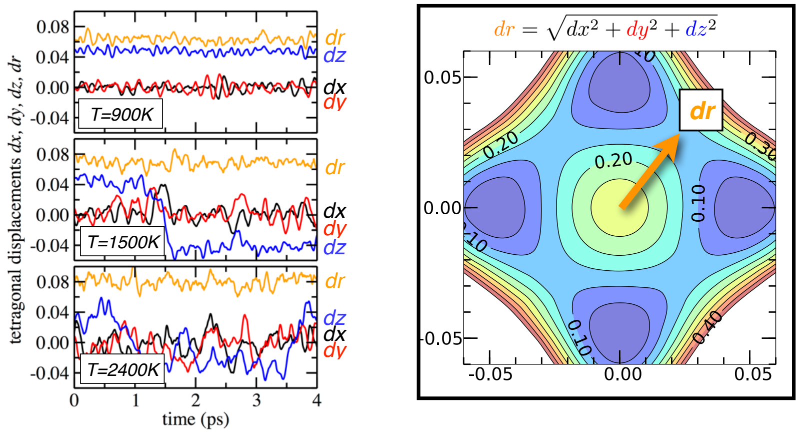


S. Fabris, A. T. Paxton, and M. W. Finnis, *Phys. Rev. B* **63**, 094101 (2001).
C. Carbogno, C. G. Levi, C. G. Van de Walle, and M. Scheffler, *Phys. Rev. B* **90**, 144109 (2014).



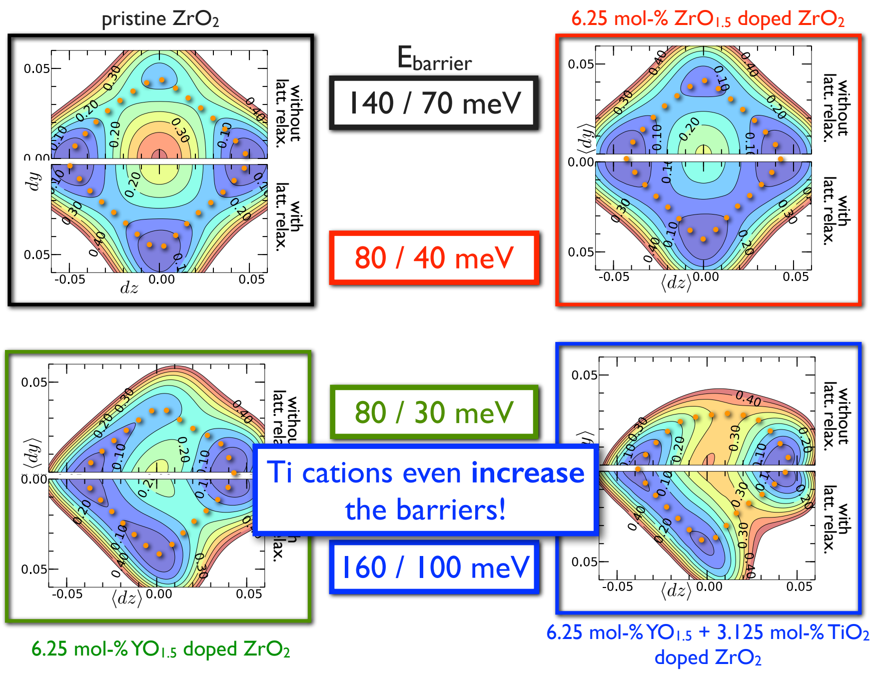


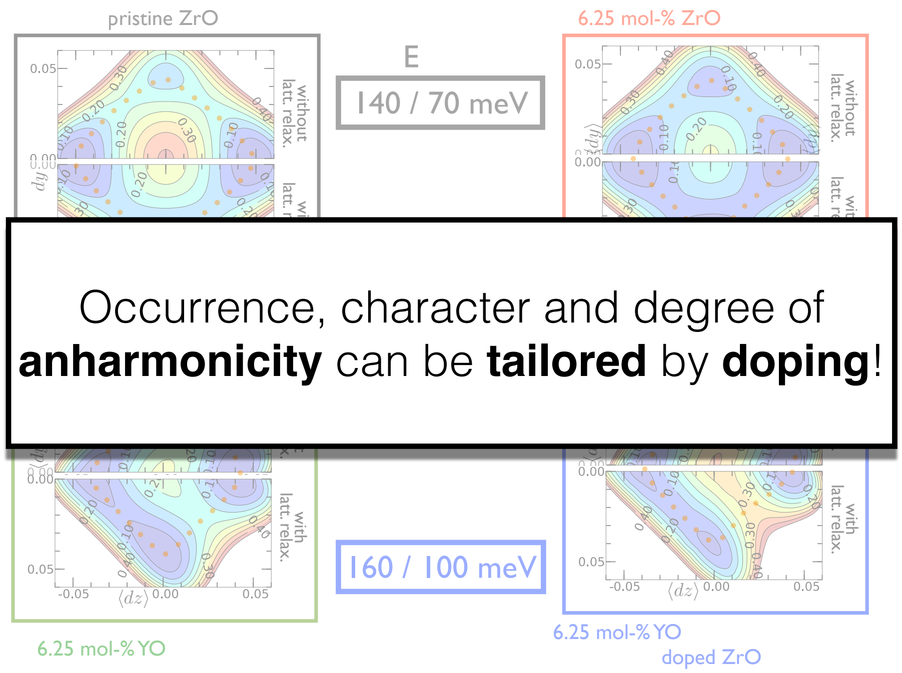
Ab initio MD Evidence



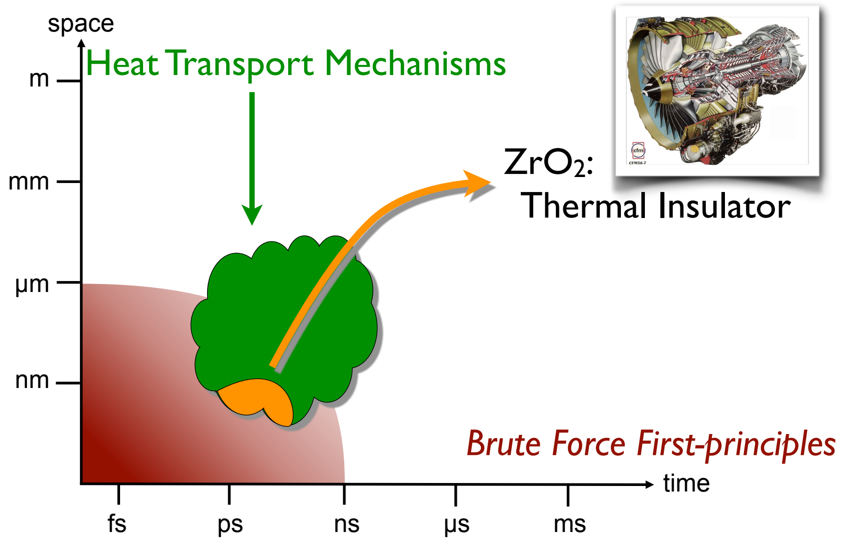
Distance ***dr*** finite at **all** temperatures!

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

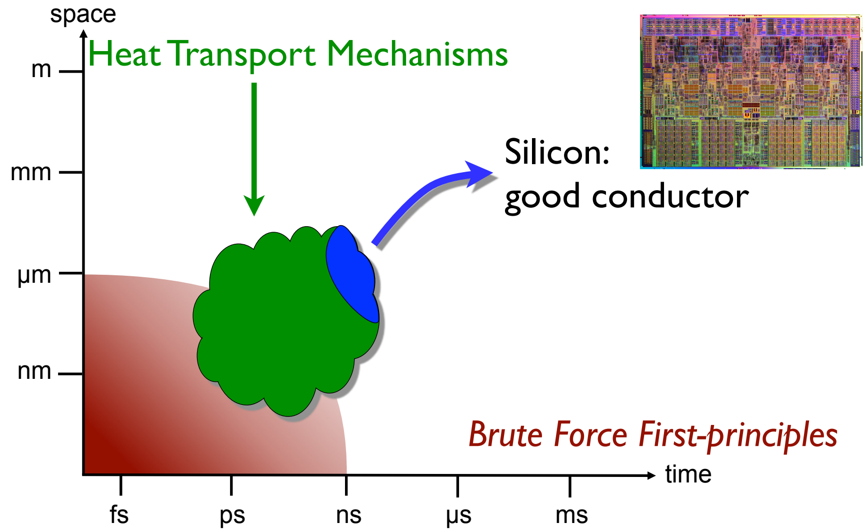




TIME AND LENGTH SCALES

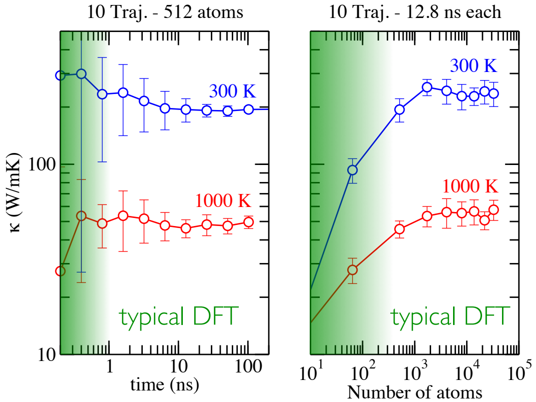


TIME AND LENGTH SCALES



CONVERGING THERMAL CONDUCTIVITIES

C. Carbogno, R. Ramprasad, and M. Scheffler *(in preparation)*.



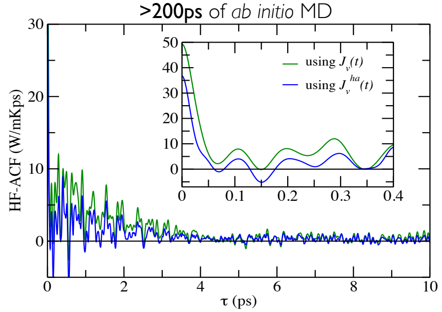
Computational Details:

- pristine Si (diamond)
- up to 1 million atoms
- up to 256 ns per trajectory
- average over 10 trajectories
- Tersoff potential
- LAMMPS code

Converging the **thermal conductivity of Silicon** requires **at least**
10 times **10 ns** of MD in a **512** atom cell.

HOW TO BOOST CONVERGENCE?

Si (diamond), **64** atoms, **1000K**,
>200ps of *ab initio* MD



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

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

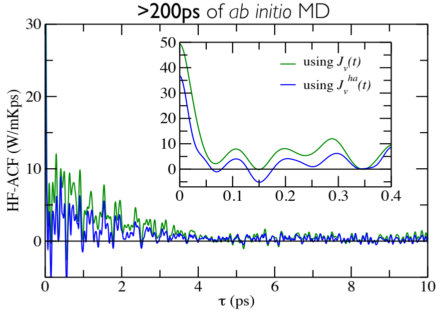
$$\langle J_v, J_v \rangle = \langle \Delta J_v, \Delta J_v \rangle + \langle J_v^{ha}, \Delta J_v \rangle + \langle \Delta J_v, J_v^{ha} \rangle + \langle J_v^{ha}, J_v^{ha} \rangle$$

Rapid Decay!

Slow Decay!

HOW TO BOOST CONVERGENCE?

Si (diamond), **64** atoms, **1000K**,
>200ps of *ab initio* MD



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

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

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

Can be (time + size!) converged independently since it solely depends on the force constants! ← **Slow Decay!**

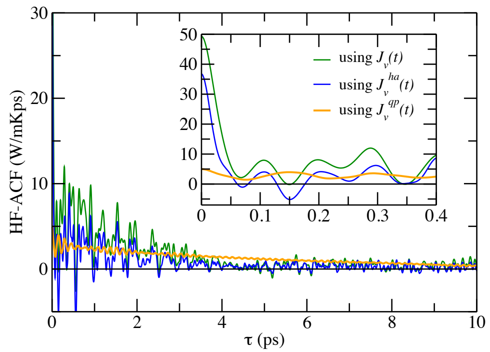
THE QUASI-PARTICLE PICTURE

Real Space

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

Reciprocal Space

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

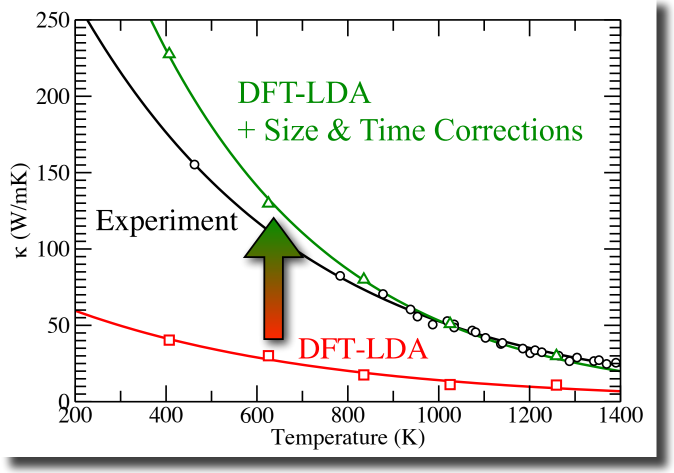


Real & Reciprocal space picture give exact same thermal conductivity!

Reciprocal space heat flux better suited for extrapolation!

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

EXTRAPOLATED CONDUCTIVITY



Extrapolation procedure yields satisfactory results!

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	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**!