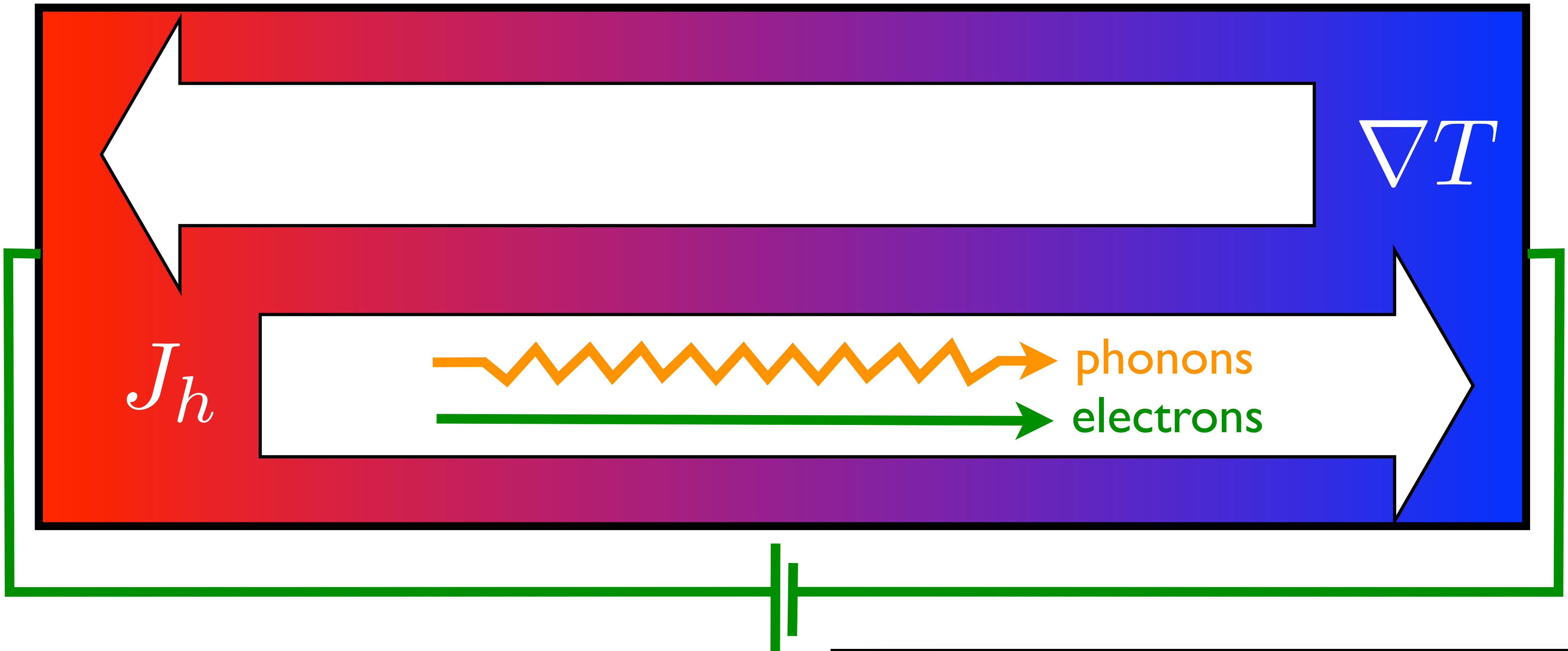
IPAM Workshop "Energy Conservation and Waste Heat Recovery" – 18th-22nd November 2013

Thermal Transport from First Principles

Christian Carbogno and Matthias Scheffler

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

The Thermoelectric Effect



$$
\begin{aligned}
J_h &= -(\kappa_{ph} + \kappa_{el})\nabla T \\
\nabla U &= -S_{el}\nabla T \\
J_q &= -\sigma_{el}\nabla U
\end{aligned}
$$

Efficiency: ***figure of merit***

$$\Longrightarrow zT = \frac{S_{el}^2\,\sigma_{el}\,T}{\kappa_{ph} + \kappa_{el}}$$

Phonon-Glass-Electron-Crystal-Paradigm

G.A. Slack, *CRC Handbook of Thermoelectrics*, CRC Press (1995).

$$zT = \frac{S_{el}^2 \, \sigma_{el} \, T}{\kappa_{ph} + \kappa_{el}}$$

Minimize phonon heat conductivity,
but do not disturb electronic transport!

Nuclear Motion

Born-Oppenheimer Approximation ?

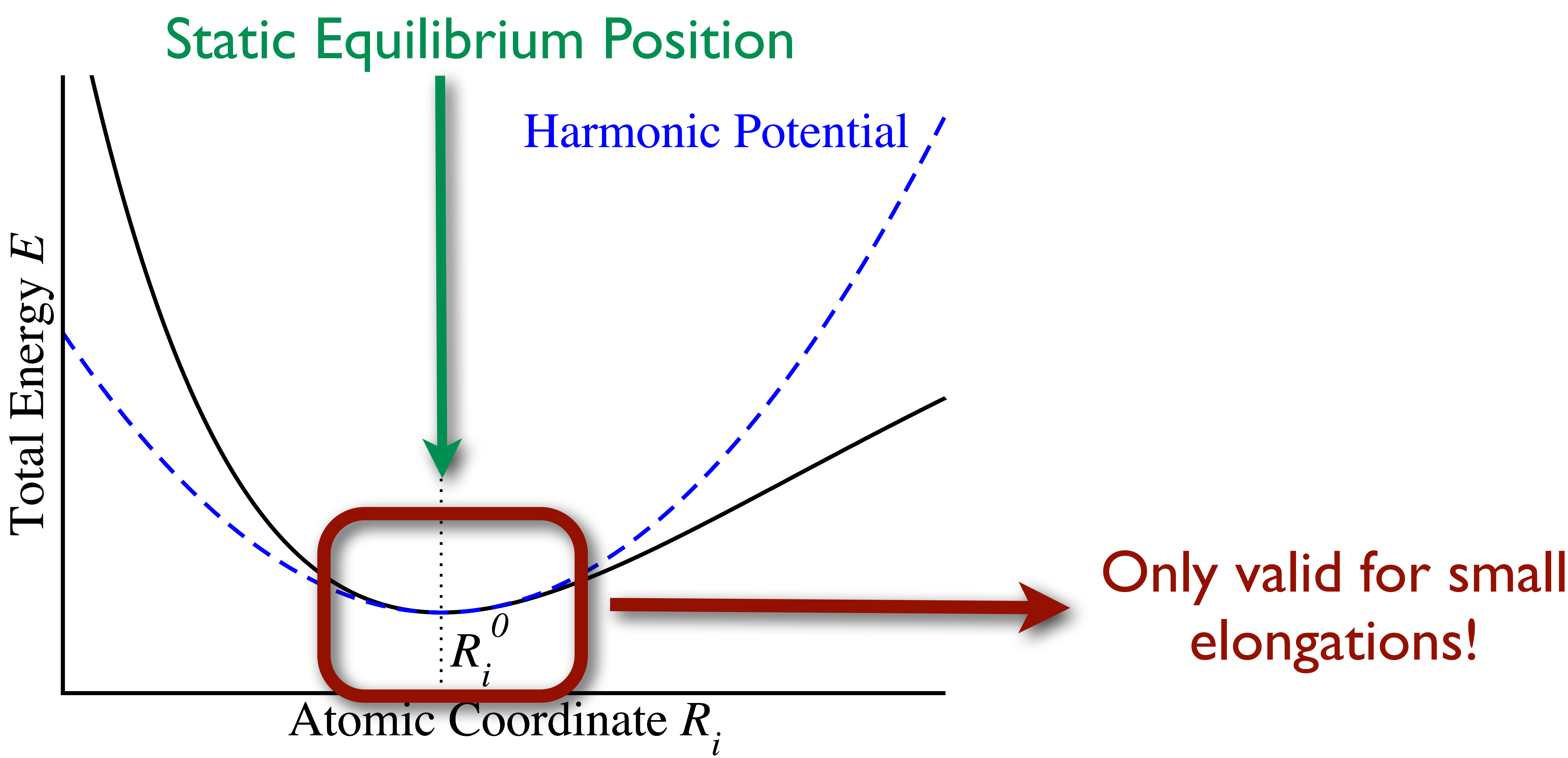
Molecular Dynamics

Perturbative Description

The Harmonic Approximation

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

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



The Harmonic Approximation

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

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 Approximation

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

Static Equilibrium Energy

Forces vanish at **$\mathbf{R}_0$**

Hessian Φ_{ij}

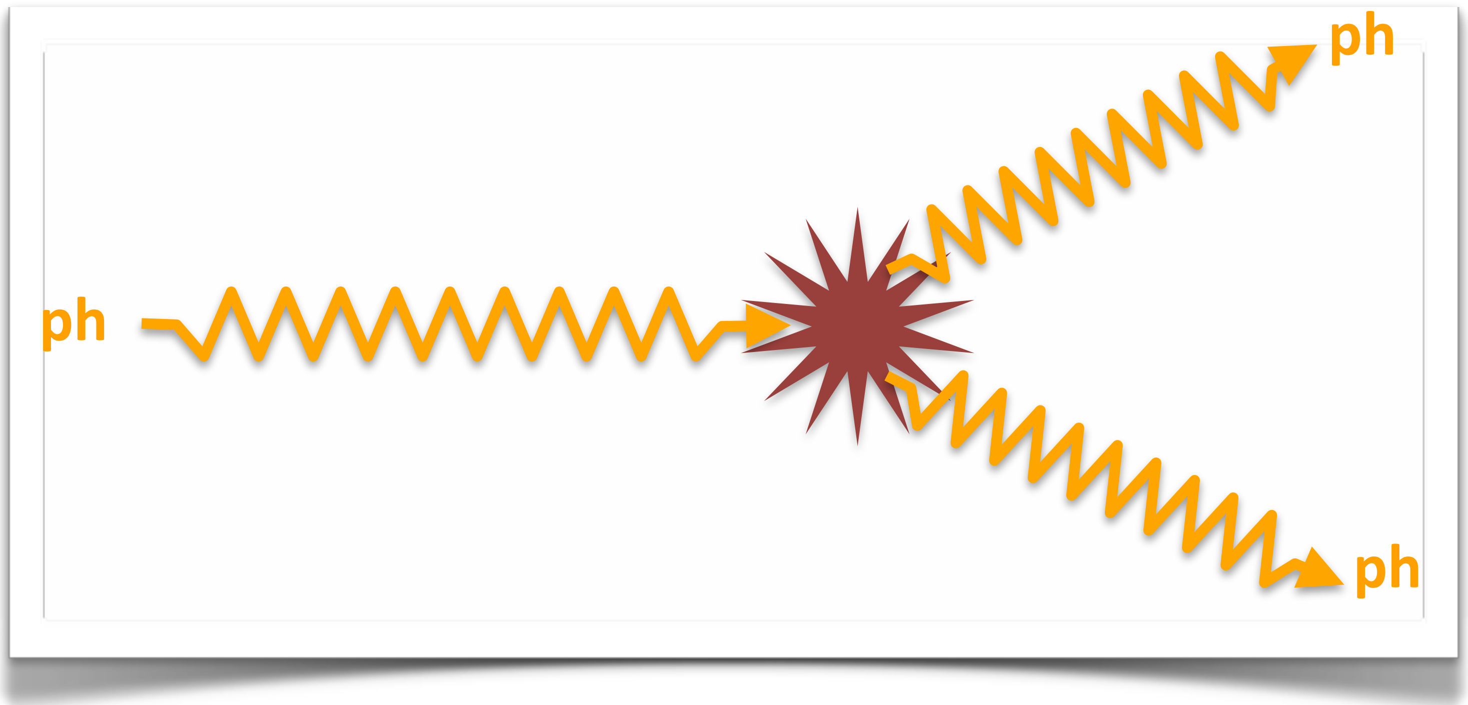
Solve *harmonic* Equation of Motion:

$$\left(\frac{1}{\sqrt{M_i M_j}} \left.\frac{\partial^2 E}{\partial \mathbf{R}_i \partial \mathbf{R}_j}\right|_{\mathbf{R}_0} \right) \nu = \omega \nu$$

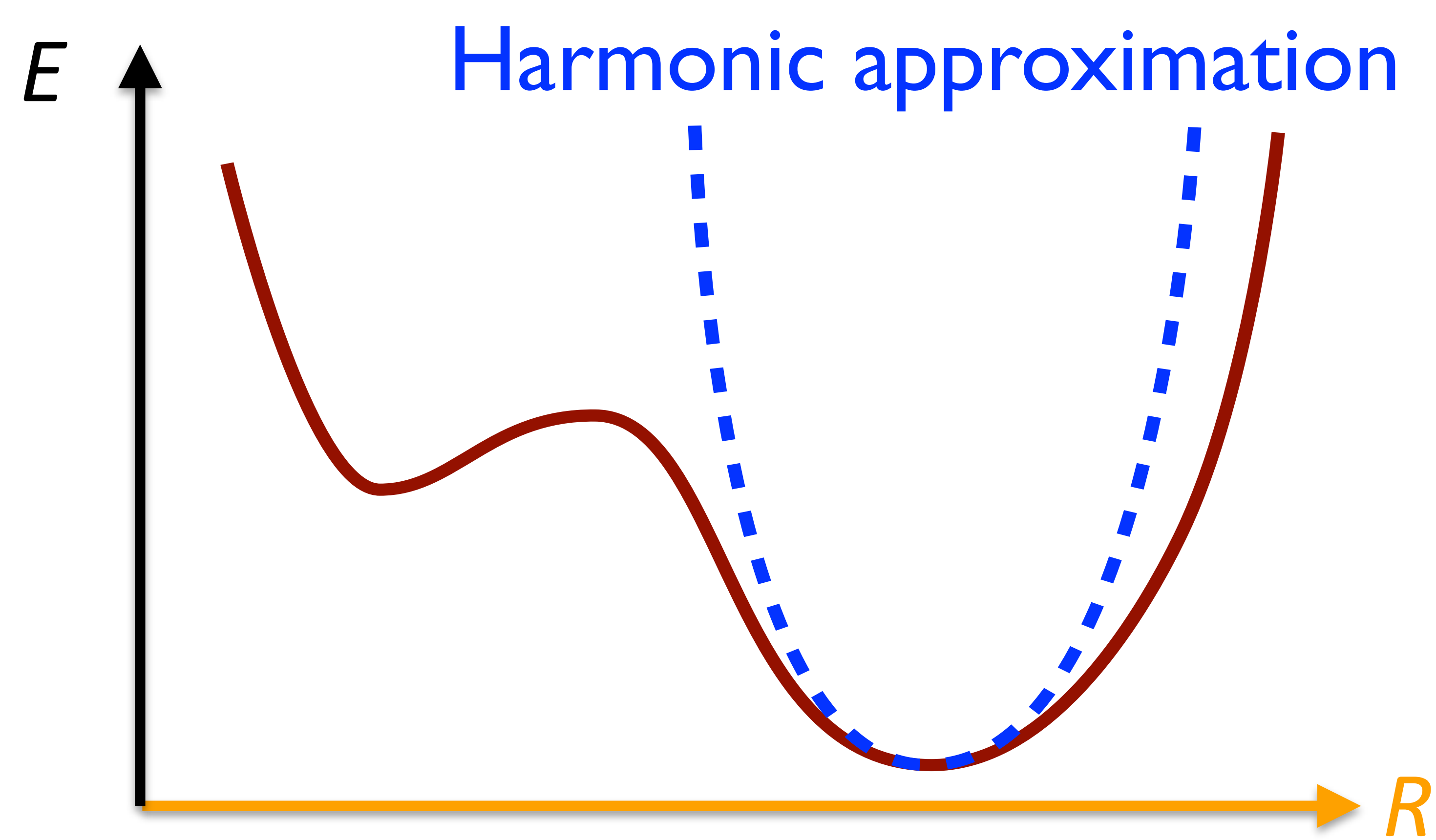
- *Approximative* vibrational band structures & DOS
- *Approximative* free energies, heat capacities, etc.

- **No** thermal expansion
- **No** thermal conductivity

Beyond the Harmonic Approximation



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



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

Phonon-Glass-Electron-Crystal-Paradigm

G.A. Slack, *CRC Handbook of Thermoelectrics*, CRC Press (1995).

$$zT = \frac{S_{el}^2 \, \sigma_{el} \, T}{\kappa_{ph} + \kappa_{el}}$$

Minimize phonon heat conductivity,
*but **do not disturb** electronic transport!*

Nuclear Motion

Born-Oppenheimer Approximation

Molecular Dynamics:
All anharmonic effects included!

Perturbative Description:
Requires contributions beyond the harmonic approximation.

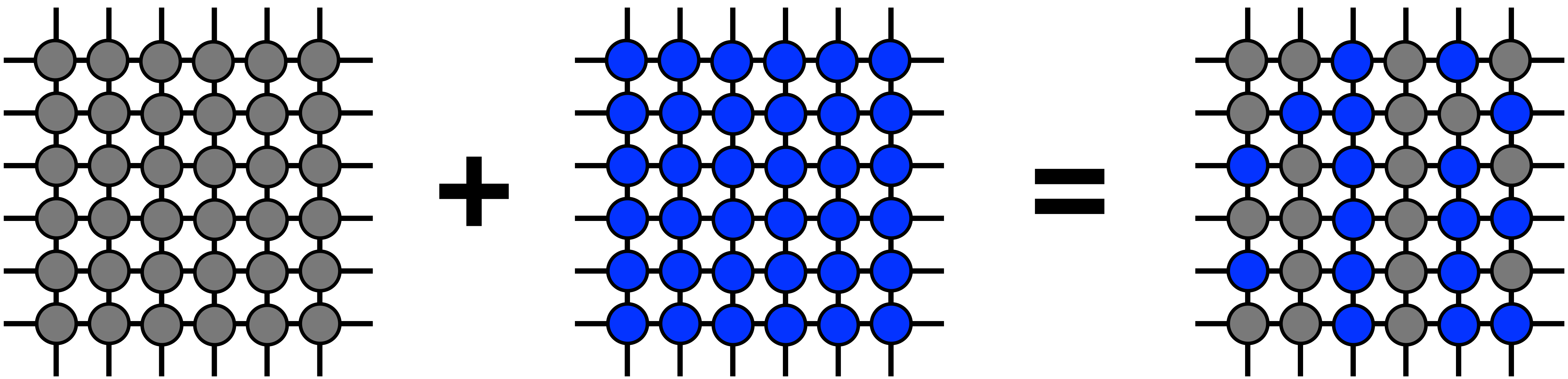
Phonon-Glass-Electron-Crystal-Paradigm

G.A. Slack, *CRC Handbook of Thermoelectrics*, CRC Press (1995).

$$zT = \frac{S_{el}^2 \, \sigma_{el} \, T}{\kappa_{ph} + \kappa_{el}}$$

*Minimize phonon heat conductivity, but **do not disturb** electronic transport!*

Example: $Si_x Ge_{(1-x)}$ Random Alloys



Silicon
$\kappa_{ph} \approx 130 \text{ W/mK}$

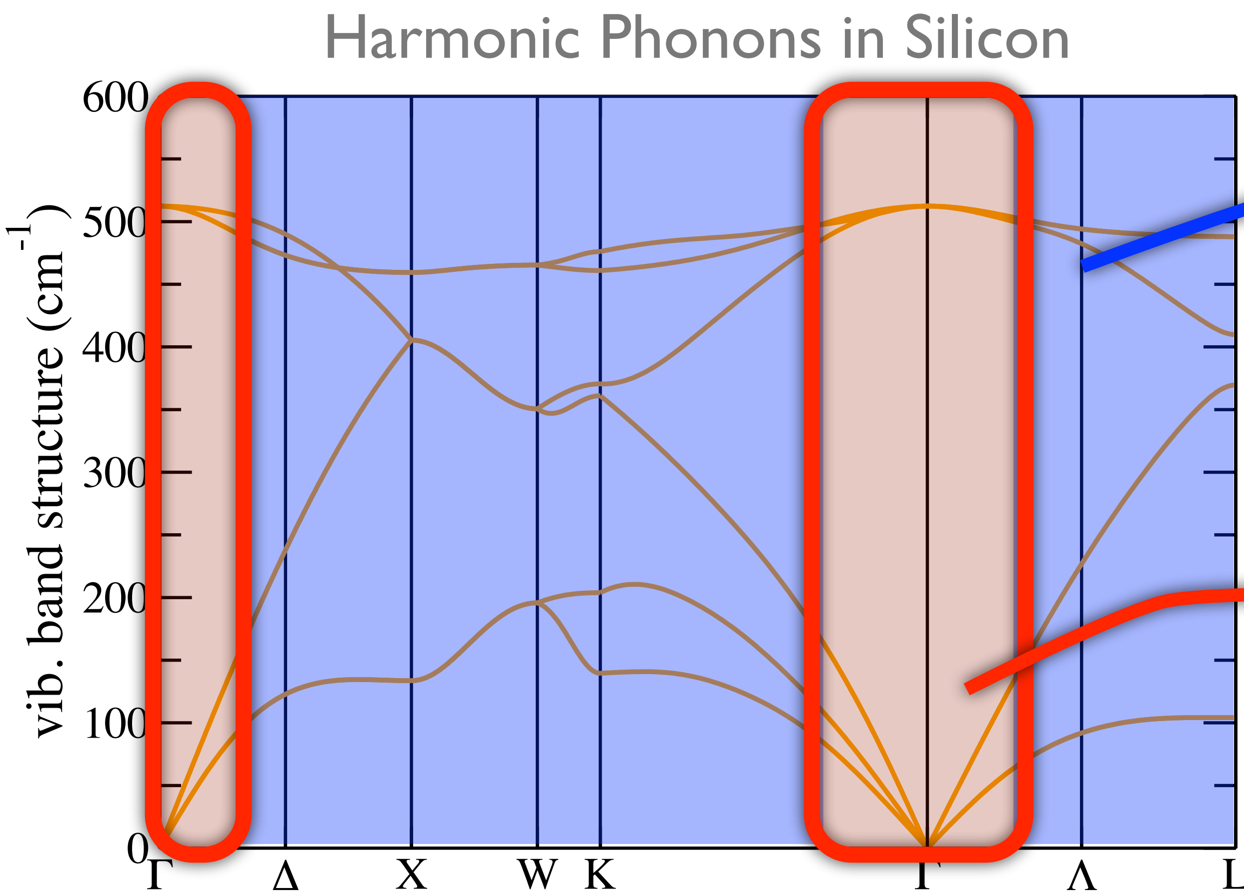
Germanium
$\kappa_{ph} \approx 55 \text{ W/mK}$

SiGe
$\kappa_{ph} \approx 10 \text{ W/mK}$

J. Garg, N. Bonini, B. Kozinsky, and N. Marzari, *Phys. Rev. Lett.* **106**, 045901 (2011).

Phonon-Glass-Electron-Crystal-Paradigm

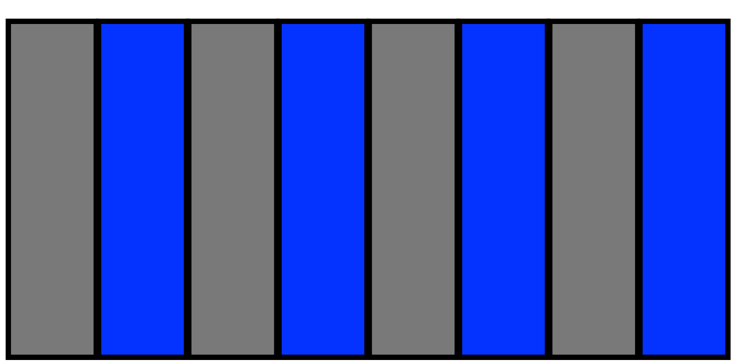
G.A. Slack, *CRC Handbook of Thermoelectrics*, CRC Press (1995).



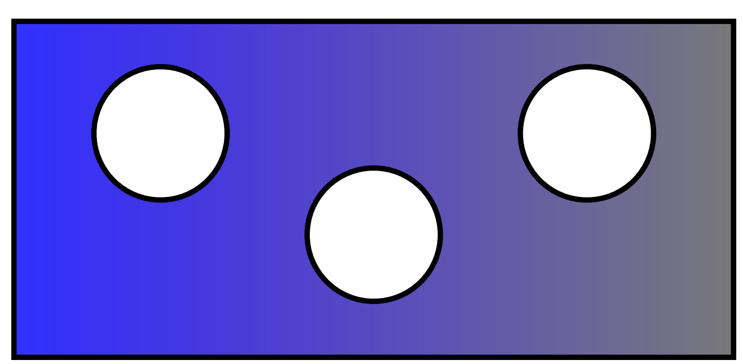
Alloying disturbs phonon transport **in the short range.**

Nano- and mesostructuring disturbs phonon transport **in the long range.**

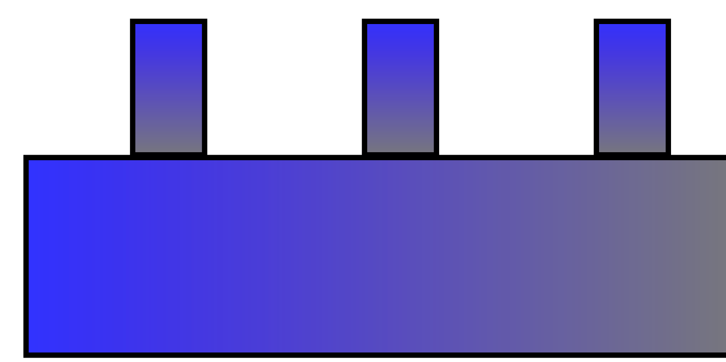
Superlattices



Nanoholes



Nanopillars



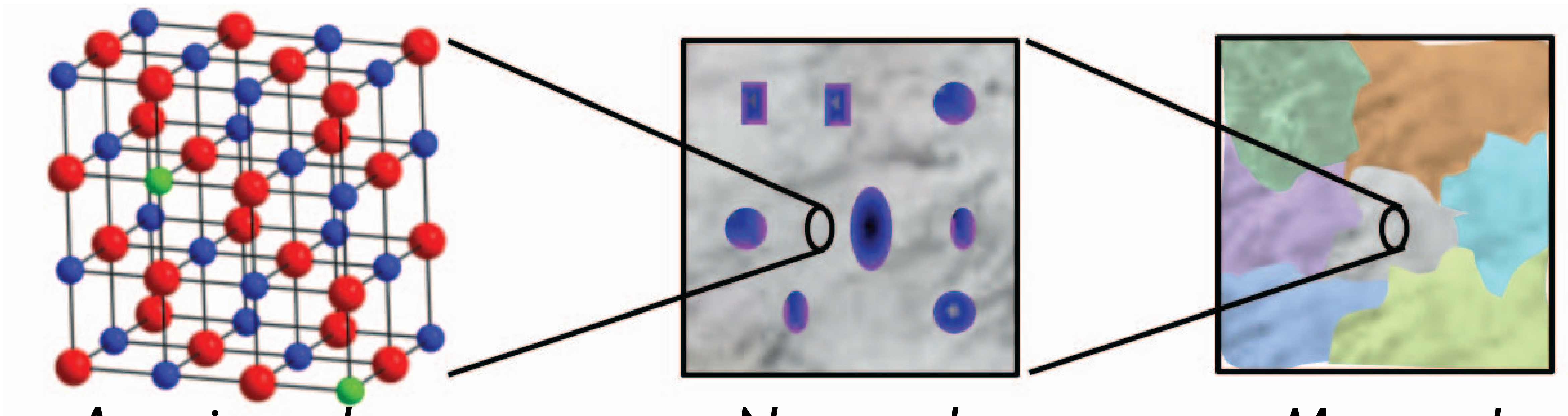
e.g., Y. He, D. Donadio, and G. Galli, *Nano Letters* **11**, 3608 (2011).

I. Savić, D. Donadio, F. Gygi, and G. Galli *Appl. Phys. Lett.* **102** 073113 (2013)

Phonon-Glass-Electron-Crystal-Paradigm

G. A. Slack, *CRC Handbook of Thermoelectrics*, CRC Press (1995).

Hierarchically structured PbTe



Atomic scale:
Lattice disorder
ZT≈1.1

Nanoscale:
Precipitates
ZT≈1.7

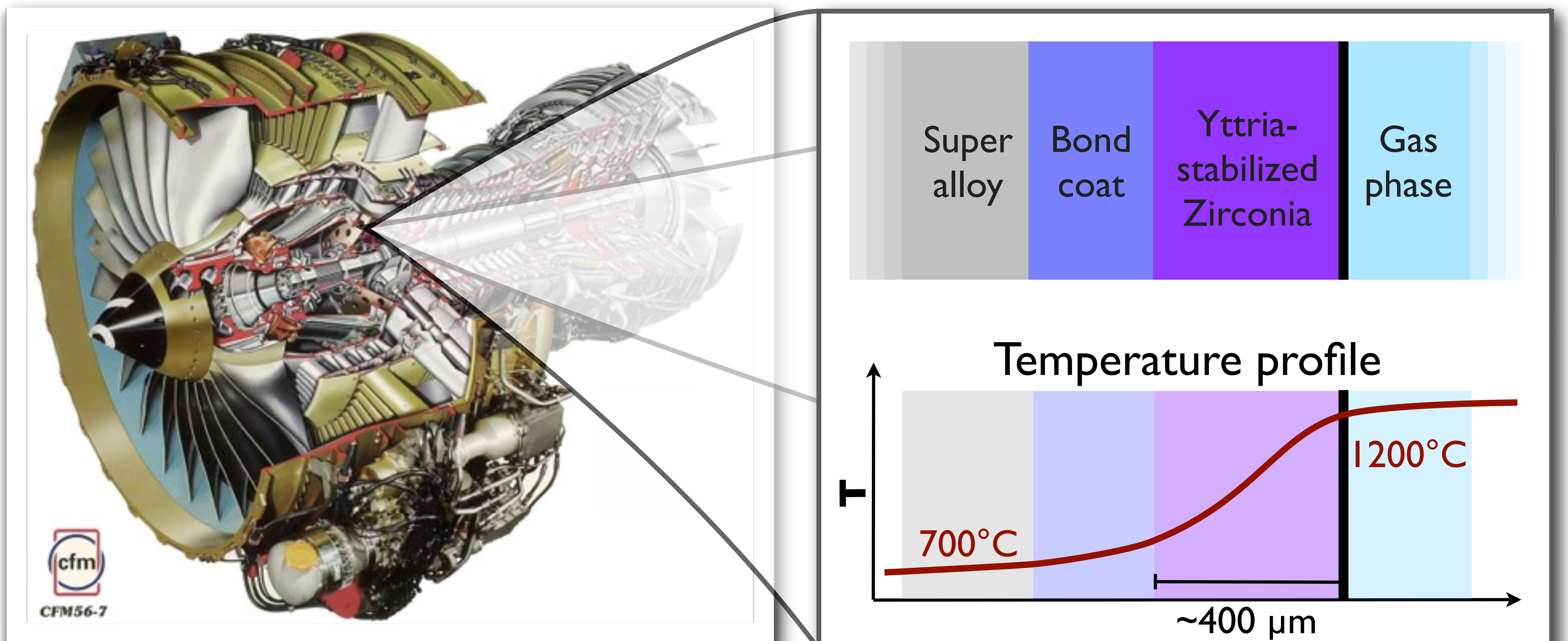
Mesoscale:
Grain boundaries
ZT≈2.2

K. Biswas, J. He, I. D. Blum, C.-I. Wu, T. P. Hogan, D. N. Seidman, V. P. Dravid, and M. G. Kanatzidis, *Nature* **489**, 414 (2012).

Is Nano- & Mesostructuring
the Answer?

YTTRIA-STABILIZED ZIRCONIA

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



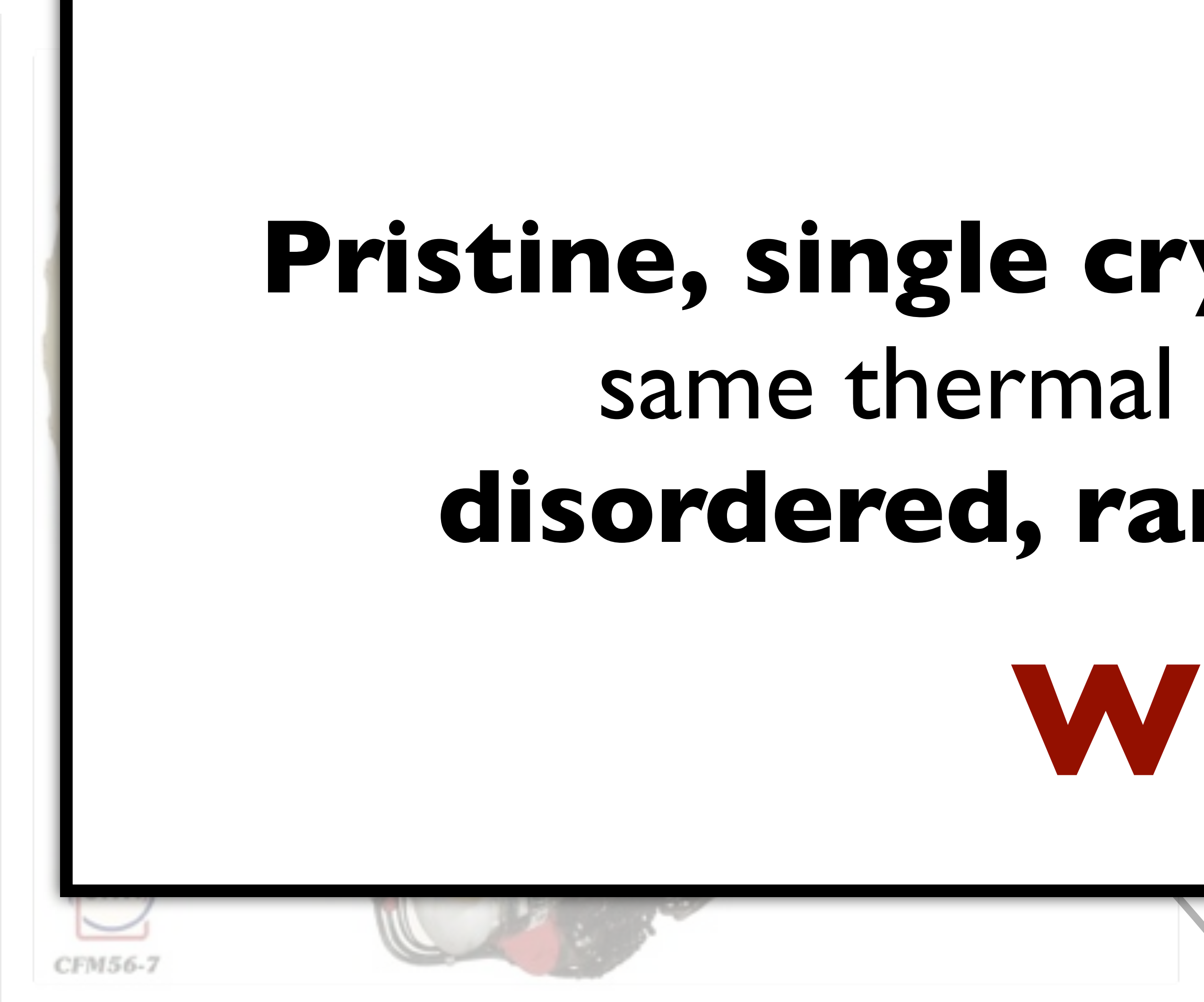
CFM 56-7 airplane engine

YTTRIA-STABILIZED ZIRCONIA

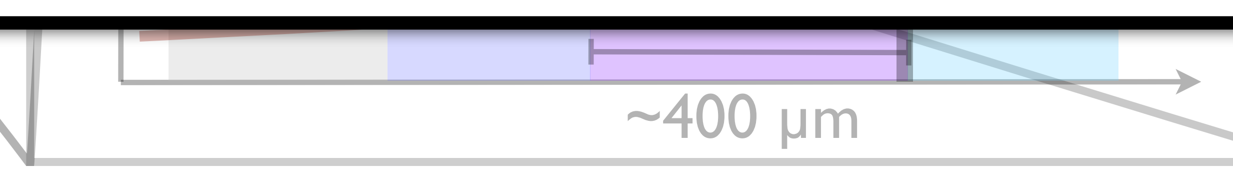
	Si	Ge	SiGe	YSZ	ZrO_2
κ (W/mK)	>100	>50	5–15	0.5–3.0	5–15

Pristine, single crystal ZrO_2 exhibits the same thermal conductivity as a **disordered, random SiGe alloy**.

Why?



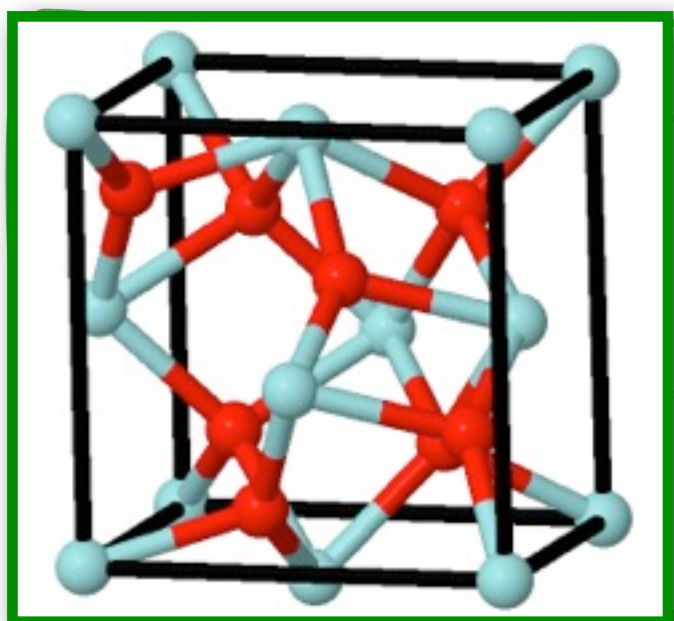
CFM 56-7 airplane engine



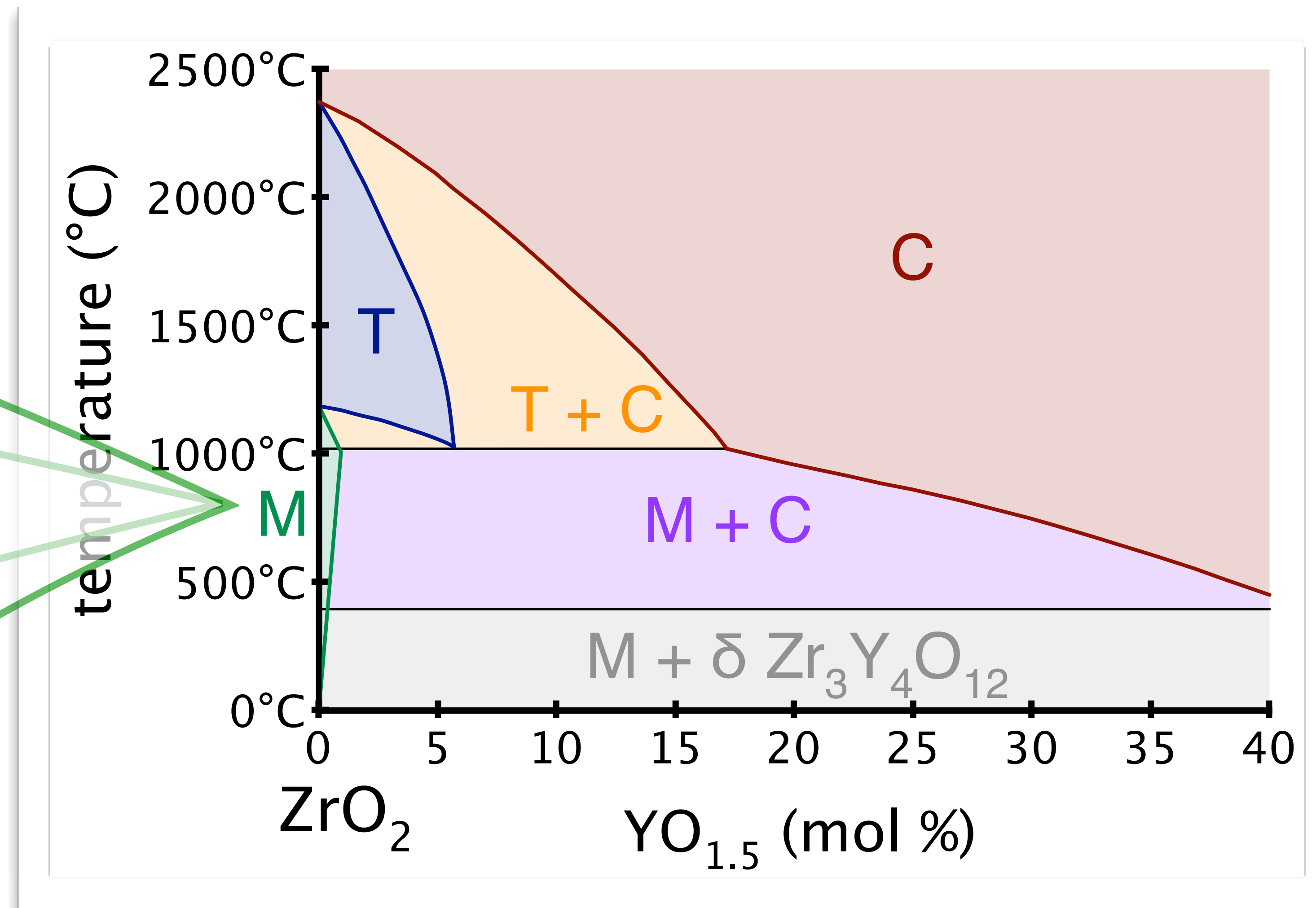
THE PHASE DIAGRAM

„Monoclinic"

Baddeleyite Structure



T < 1200°C

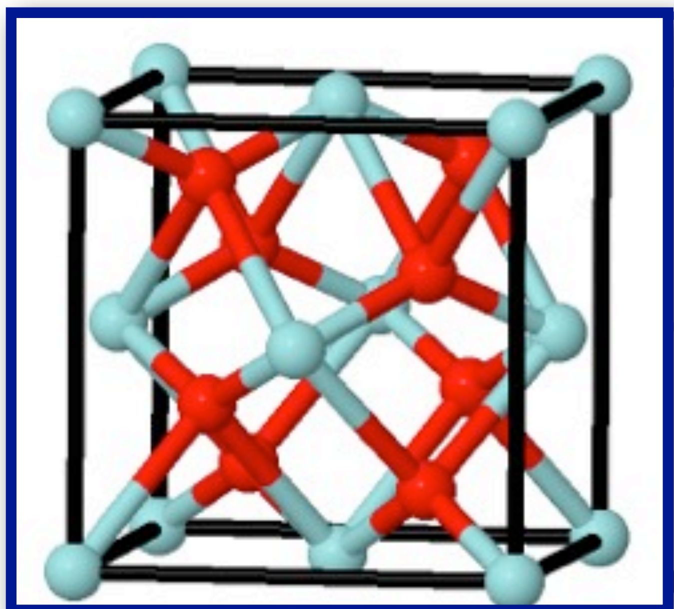


D. R. Clarke and C. G. Levi, *Annu. Rev. Mat. Res.* **33**, 383 (2003).

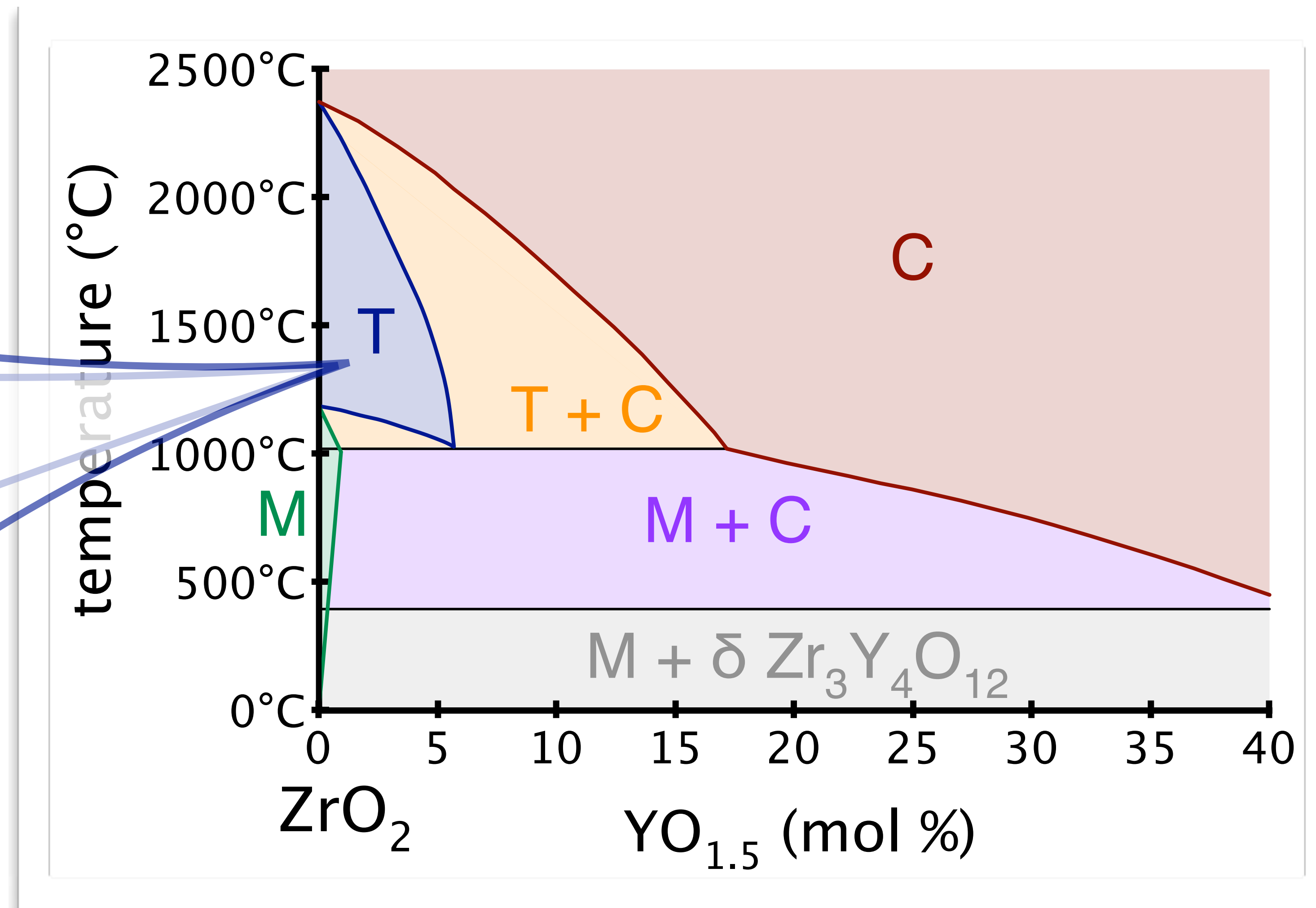
THE PHASE DIAGRAM

„Tetragonal“

$P4_2/nmc$ Structure



$1200°C < T < 2400°C$

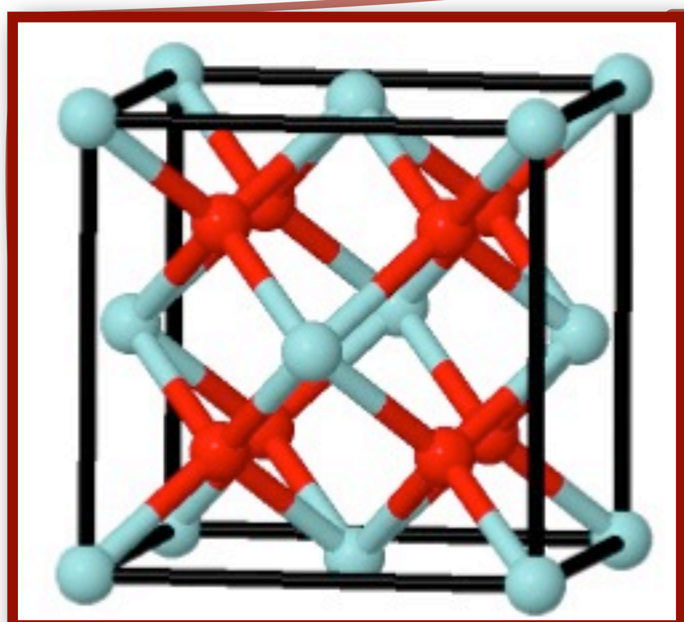


D. R. Clarke and C. G. Levi, *Annu. Rev. Mat. Res.* **33**, 383 (2003).

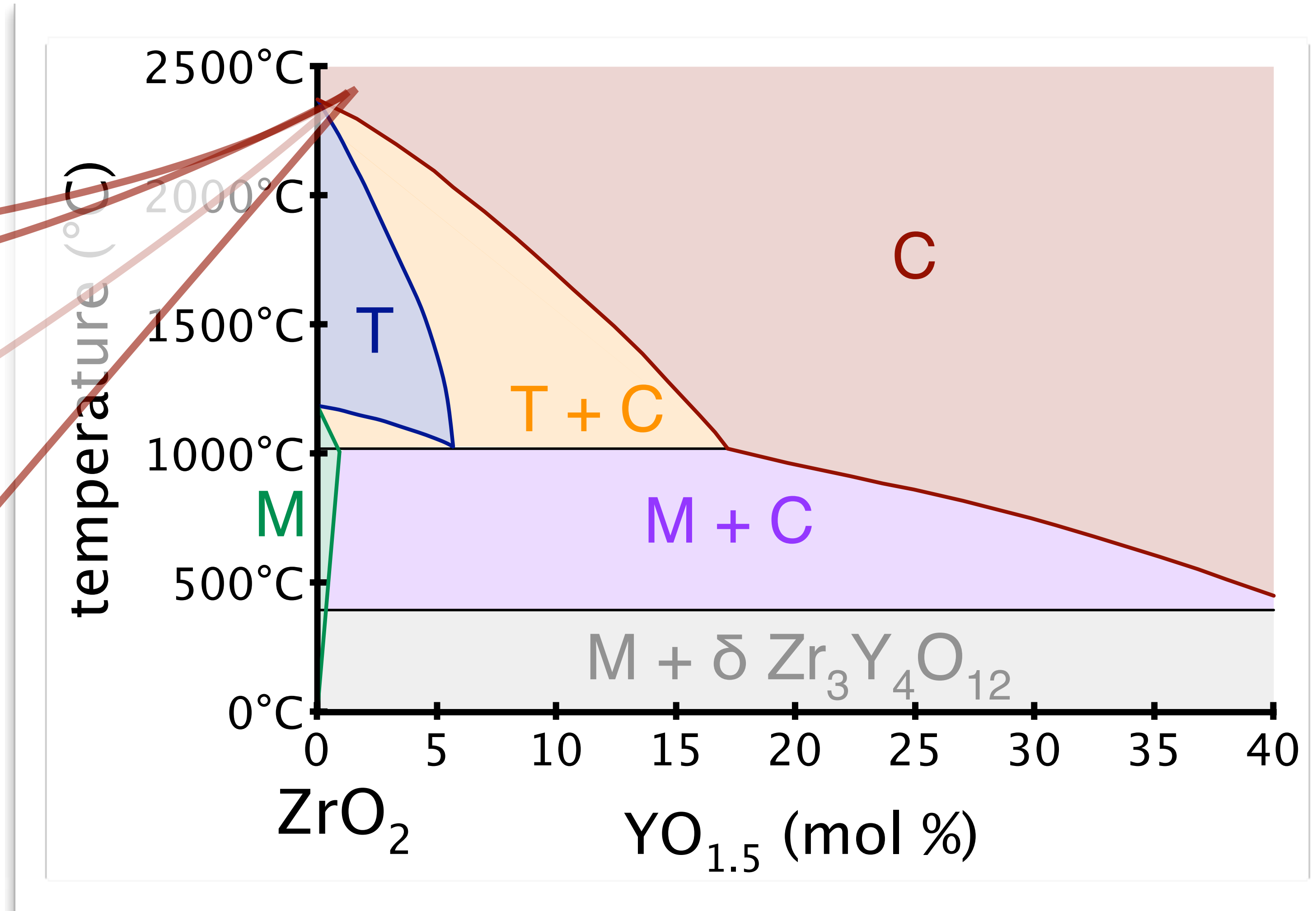
THE PHASE DIAGRAM

„Cubic“

Fluorite Structure



T > 2400°C

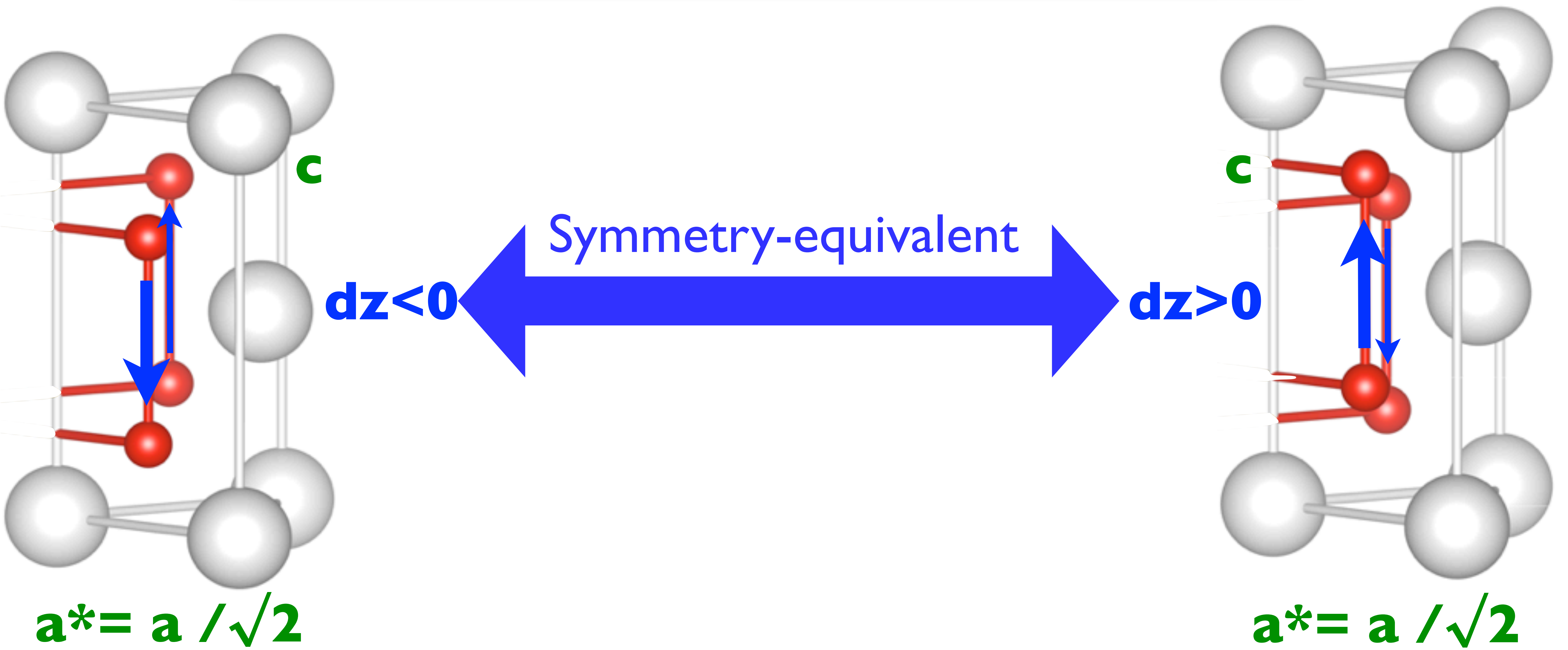


D. R. Clarke and C. G. Levi, *Annu. Rev. Mat. Res.* **33**, 383 (2003).

The Dynamics of Zirconia

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

The tetragonal phase of Zirconia



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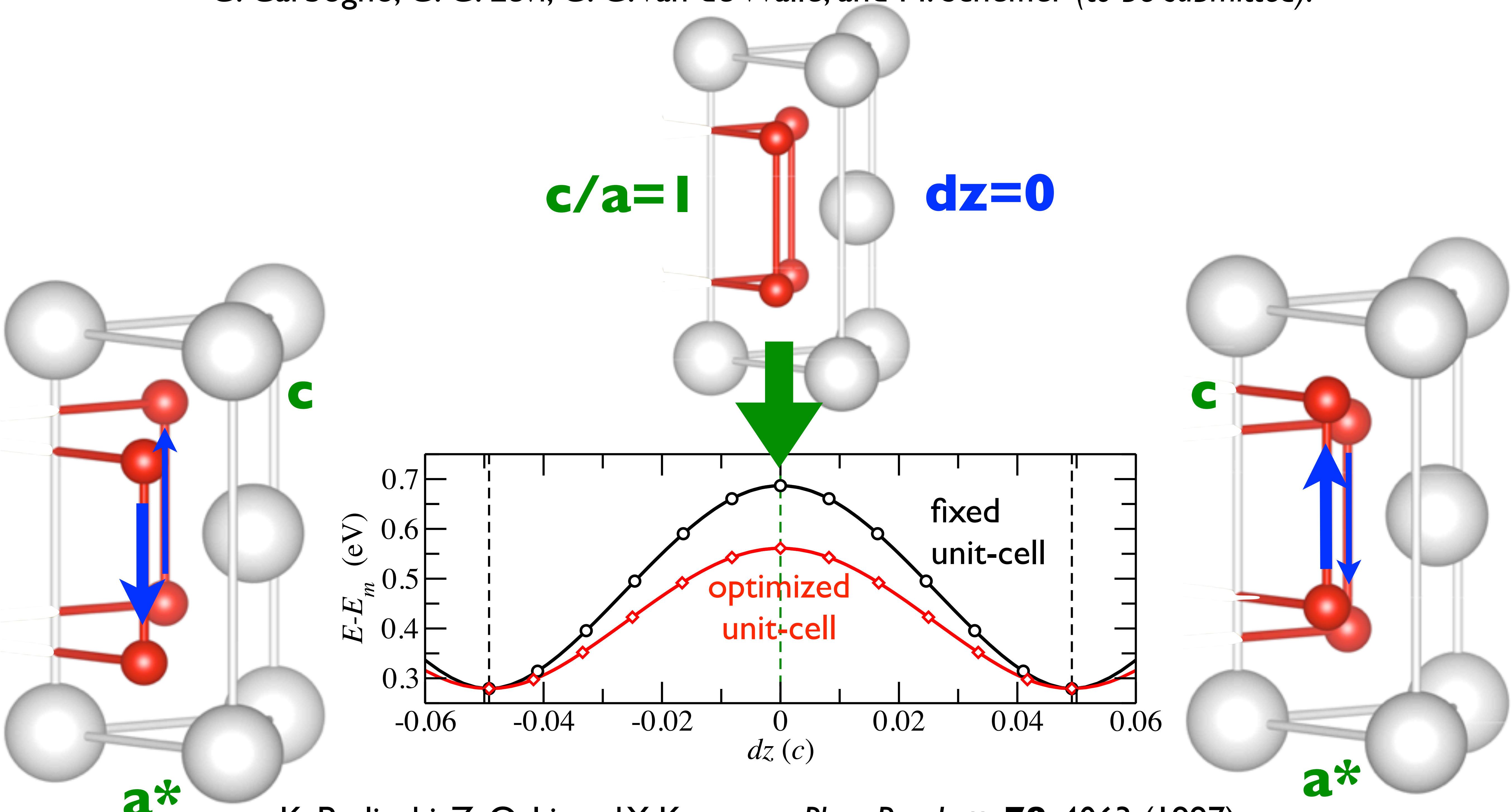

K. Parlinski, Z. Q. Li, and Y. Kawazoe, *Phys. Rev. Lett.* **78**, 4063 (1997).
S. Fabris, A. T. Paxton, and M. W. Finnis, *Phys. Rev. B* **61**, 6617 (2000).
S. Fabris, A. T. Paxton, and M. W. Finnis, *Phys. Rev. B* **63**, 094101 (2001).
M. Sternik and K. Parlinski, *J. Chem. Phys.* **123**, 204708 (2005).

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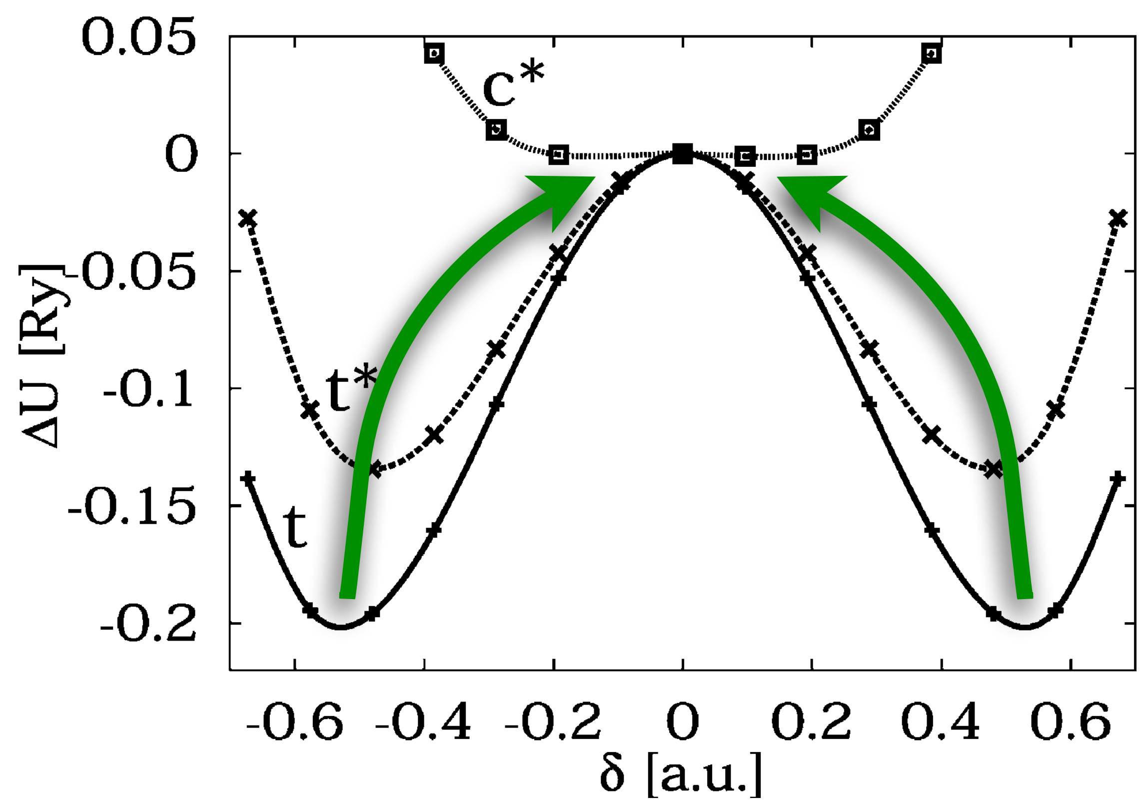
S. Fabris, A. T. Paxton, and M. W. Finnis,
Acta Materialia **50**, 5171 (2002).



increasing F^{2+} concentration

G. Stapper, M. Bernasconi, N. Nicoloso, and M. Parrinello, *Phys. Rev. B* **59**, 797 (1999).
A. Eichler, *Phys. Rev. B* **64**, 174103 (2001).
H. Ding, A. V. Virkar, and F. Liu, *Solid State Ionics* **215**, 16 (2012).

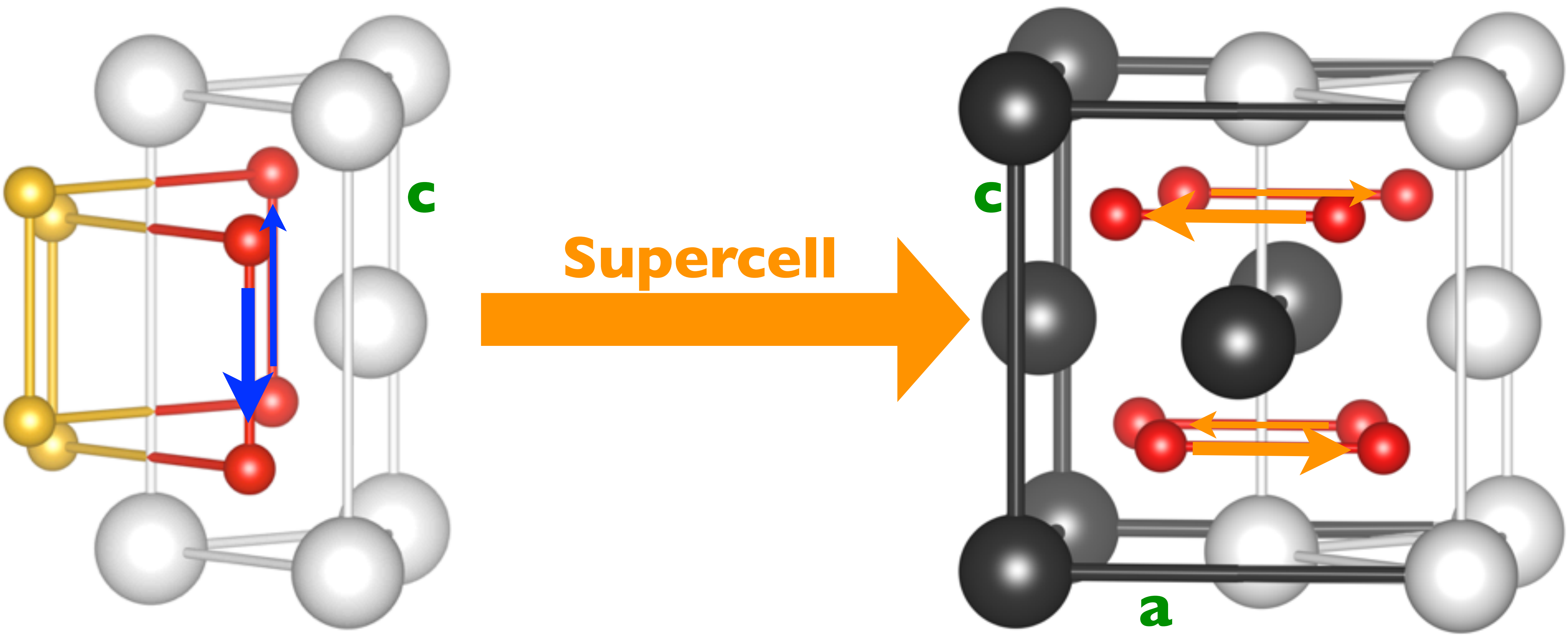
...and many more!

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

The Dynamics of Zirconia

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

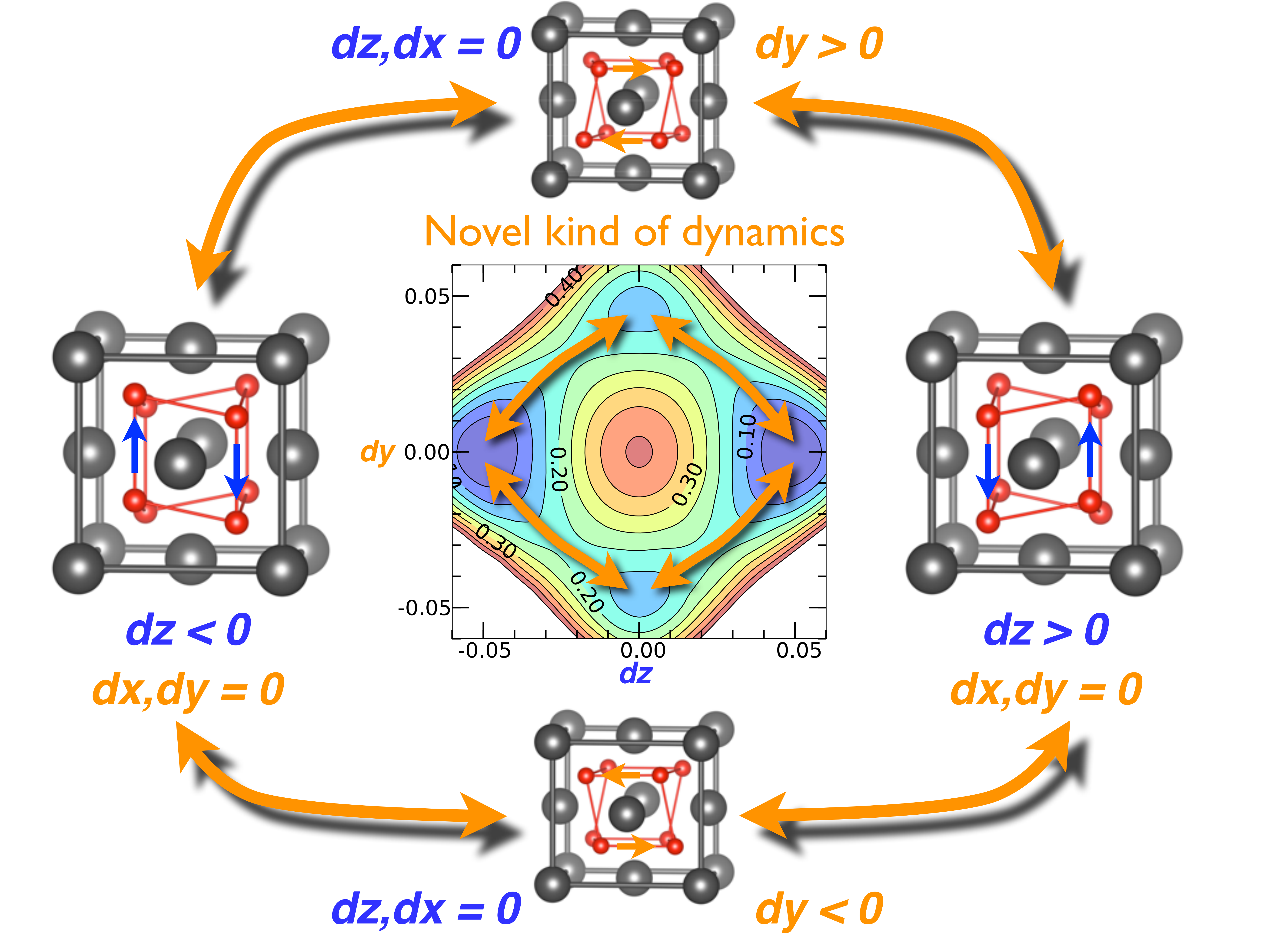
Primitive Unit-cell Artificially Constrains the Dynamics!



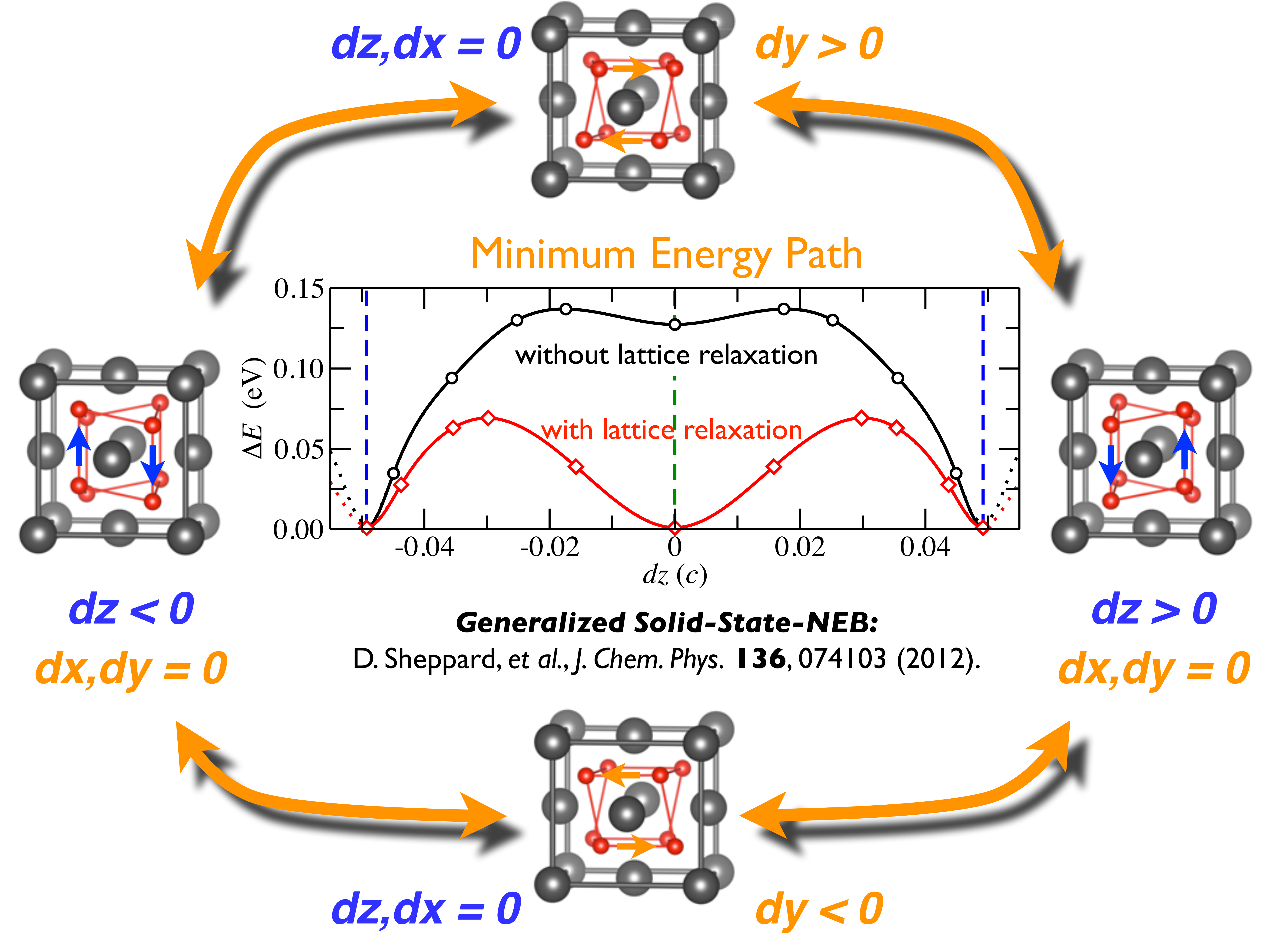
$a^* = a/\sqrt{2}$

dz<0
dx,dy=0

dx,dy > 0 become possible



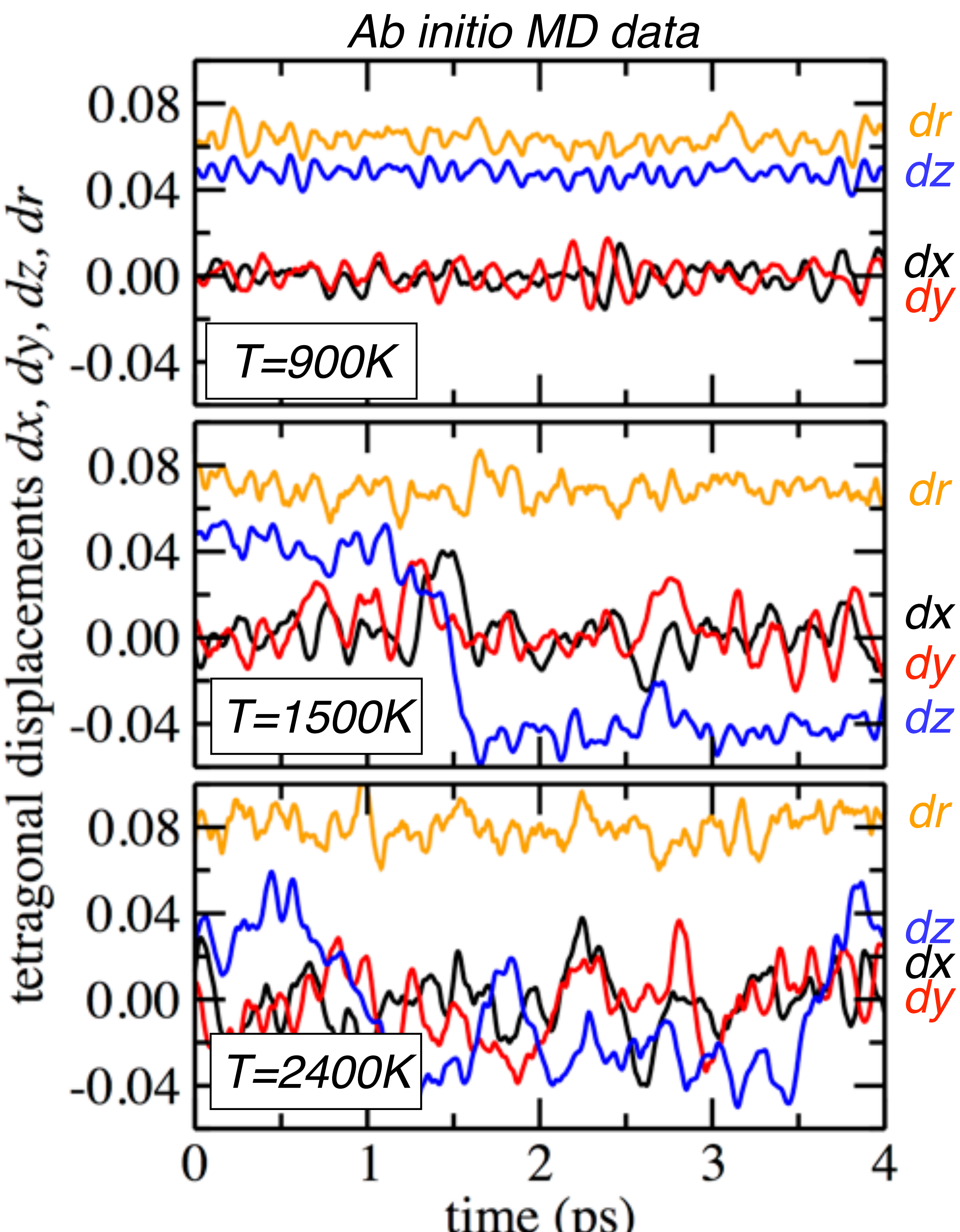
dz,dx = 0
dy > 0
Novel kind of dynamics
0.05
dy 0.00
-0.05
-0.05
0.00
0.05
dz
0.40
0.10
0.20
0.30
0.30
0.20
dz < 0
dx,dy = 0
dz > 0
dx,dy = 0
dz,dx = 0
dy < 0



Generalized Solid-State-NEB:
D. Sheppard, *et al.*, *J. Chem. Phys.* **136**, 074103 (2012).

The Dynamics of Zirconia

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



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

⇓

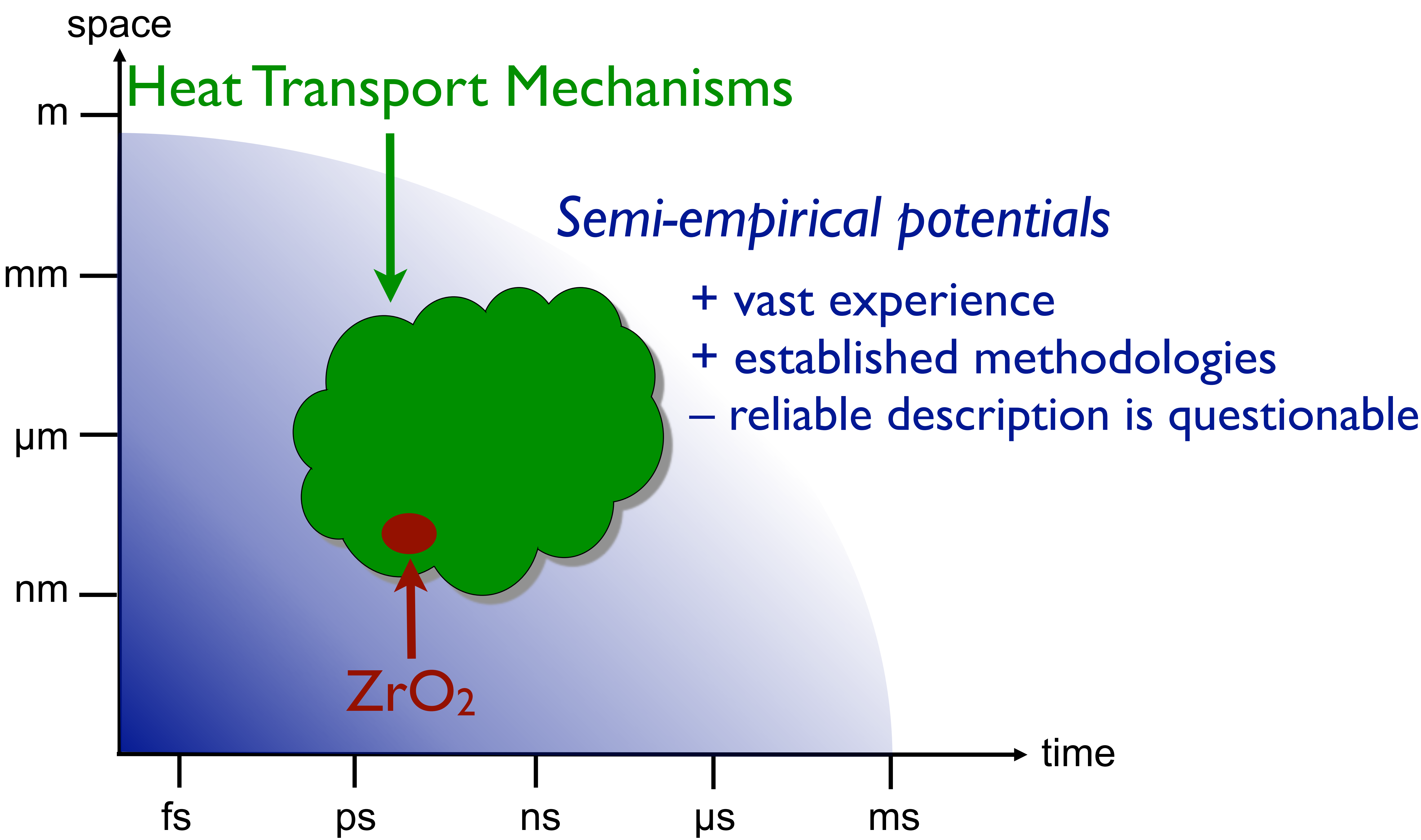
Ferroelastic Switches between these configurations occur quite **frequently**.

⇓

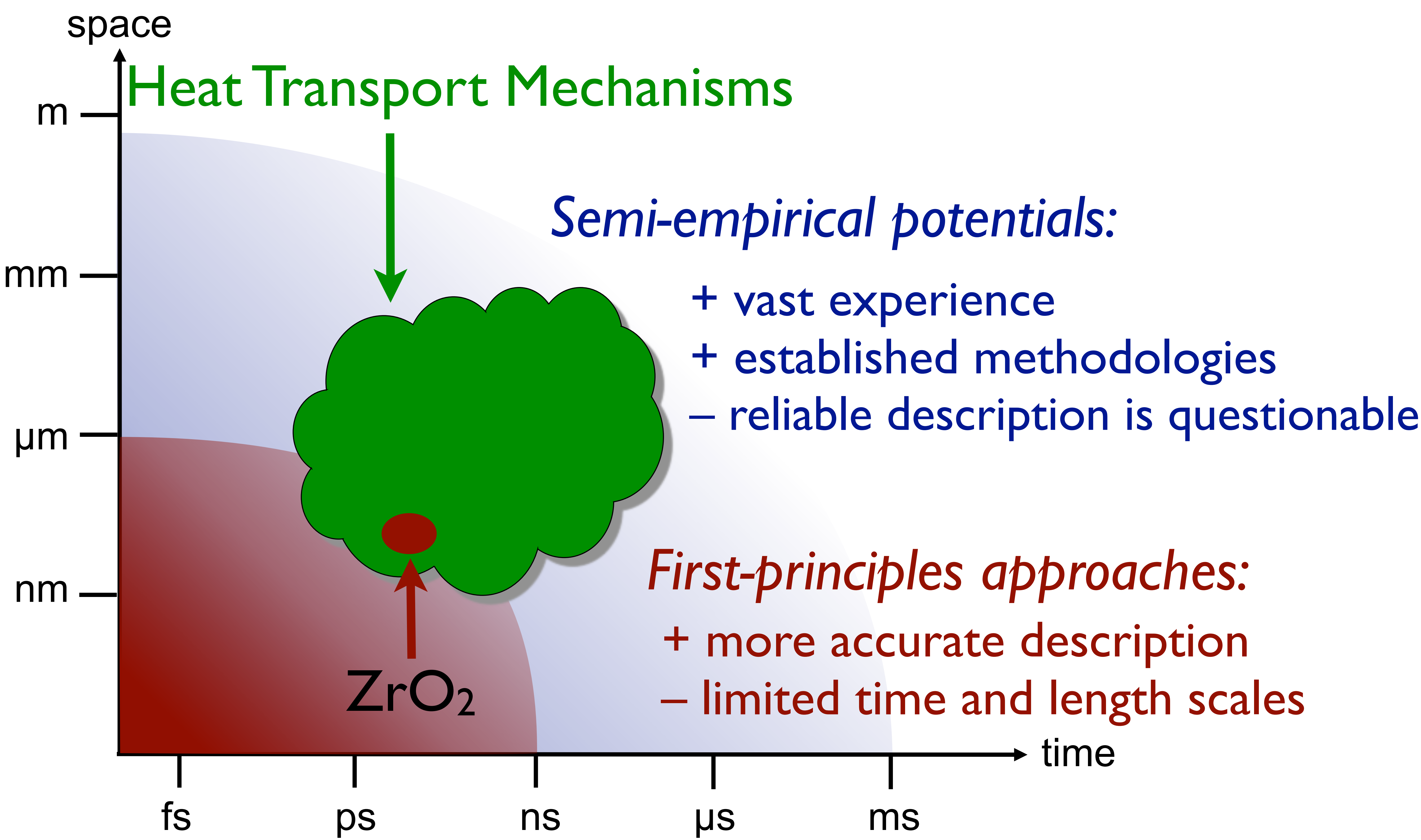
Severe violation of the harmonic approximation.

Theory

TIME AND LENGTH SCALES

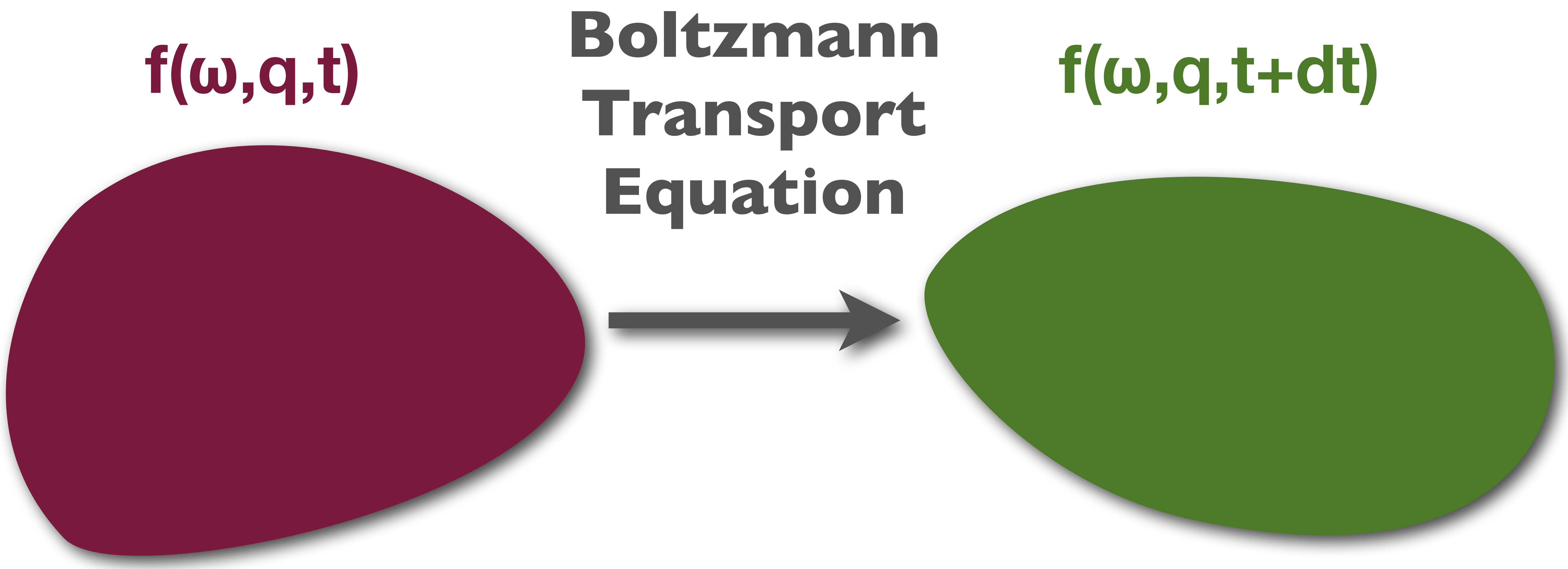


TIME AND LENGTH SCALES



BOLTZMANN TRANSPORT EQUATION

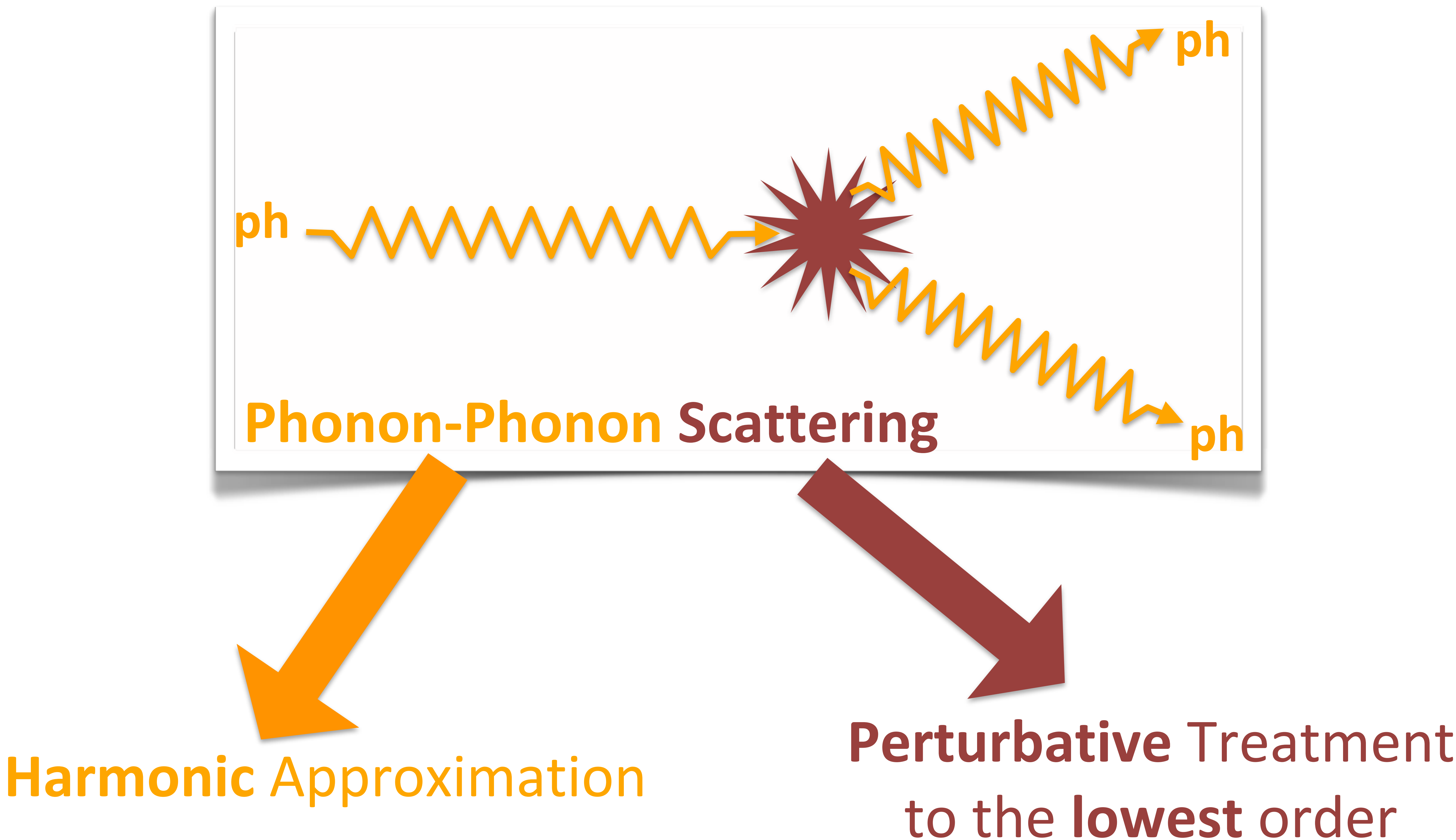
R. Peierls, *Ann. Phys.* **395**, 1055 (1929).
D. A. Broido *et al.*, *Appl. Phys. Lett.* **91**, 231922 (2007).



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

BOLTZMANN TRANSPORT EQUATION

R. Peierls, *Ann. Phys.* **395**,1055 (1929).
D. A. Broido *et al.*, *Appl. Phys. Lett.* **91**, 231922 (2007).



Phonon Lifetimes from First Principles

- from **Density Functional Perturbation Theory**

  D. A. Broido *et al.*, *Appl. Phys. Lett.* **91**, 231922 (2007).
  J. Garg *et al.*, *Phys. Rev. Lett.* **106**, 045901 (2011).

- from **fitting** the **forces** in ***ab initio MD***

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

- from **fitting** the **phonon line width** determined via ***ab initio MD***

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

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

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

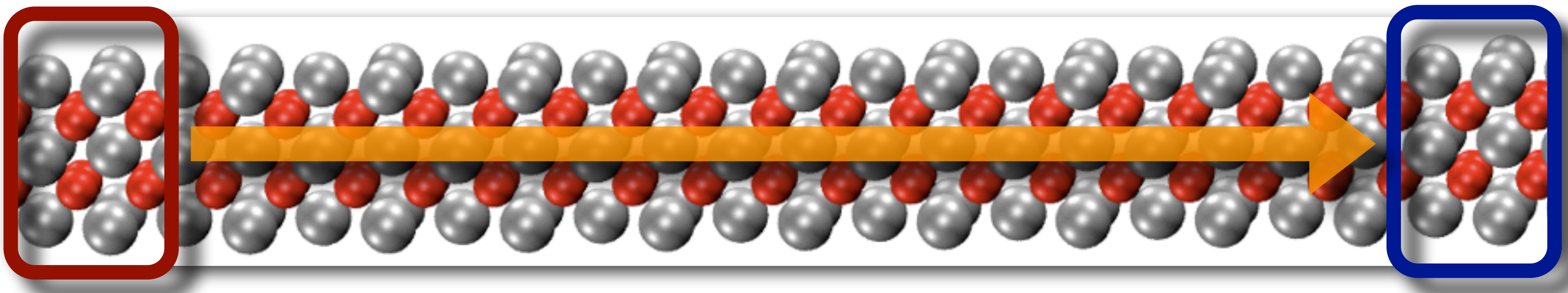
FIRST-PRINCIPLES APPROACHES

	Order of interaction	Validity & Applicability	Finite Size Effects	Disorder
Boltzmann-Transport Eq.	$\sim\square(r^3)$	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**

$\Downarrow$

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

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

FIRST-PRINCIPLES APPROACHES

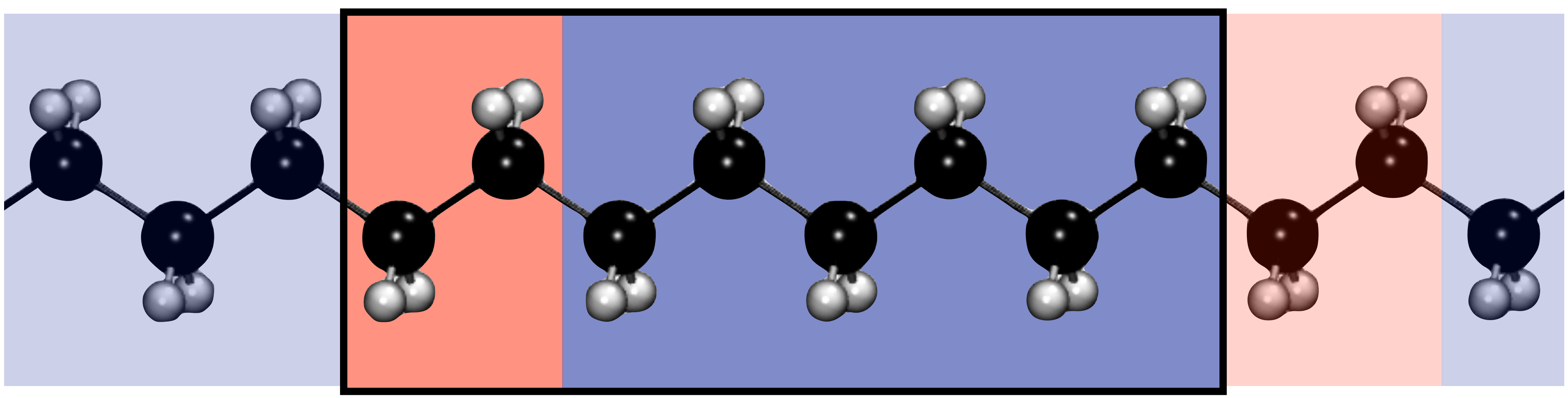
	Order of interaction	Validity & Applicability	Finite Size Effects	Disorder
Boltzmann-Transport Eq.	$\sim\square(r^3)$	low T	Minute	Parameter
Non-Equilib. MD	Full	all T	Huge	as in supercell
Laser-flash MD				
Green-Kubo MD				

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

„LASER FLASH" SIMULATIONS

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

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

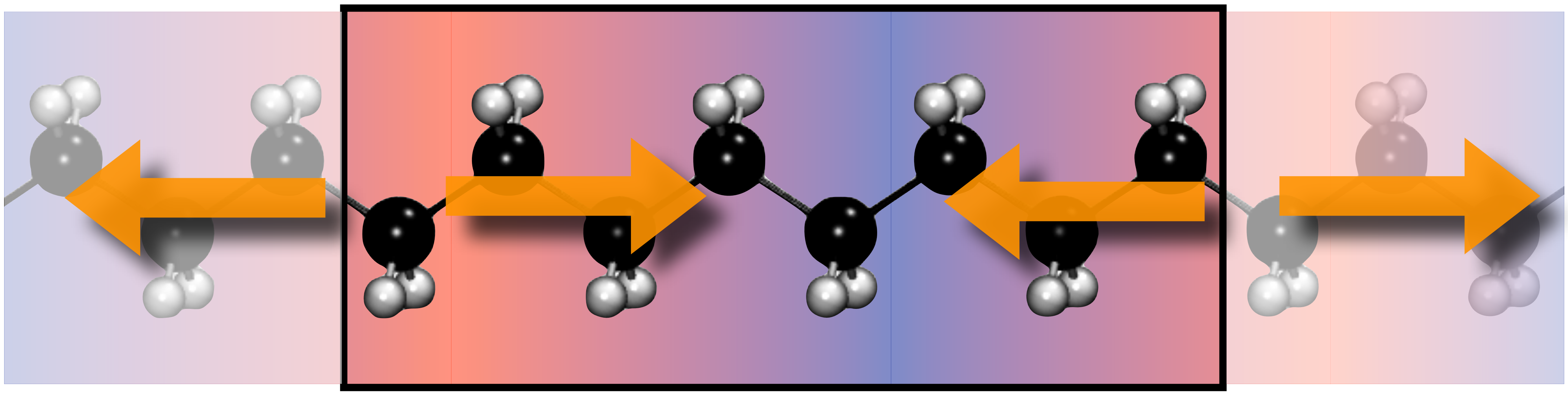


(A) Prepare two supercells: a small hot one and a large cold one.

„LASER FLASH" SIMULATIONS

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

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)**.

FIRST-PRINCIPLES APPROACHES

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

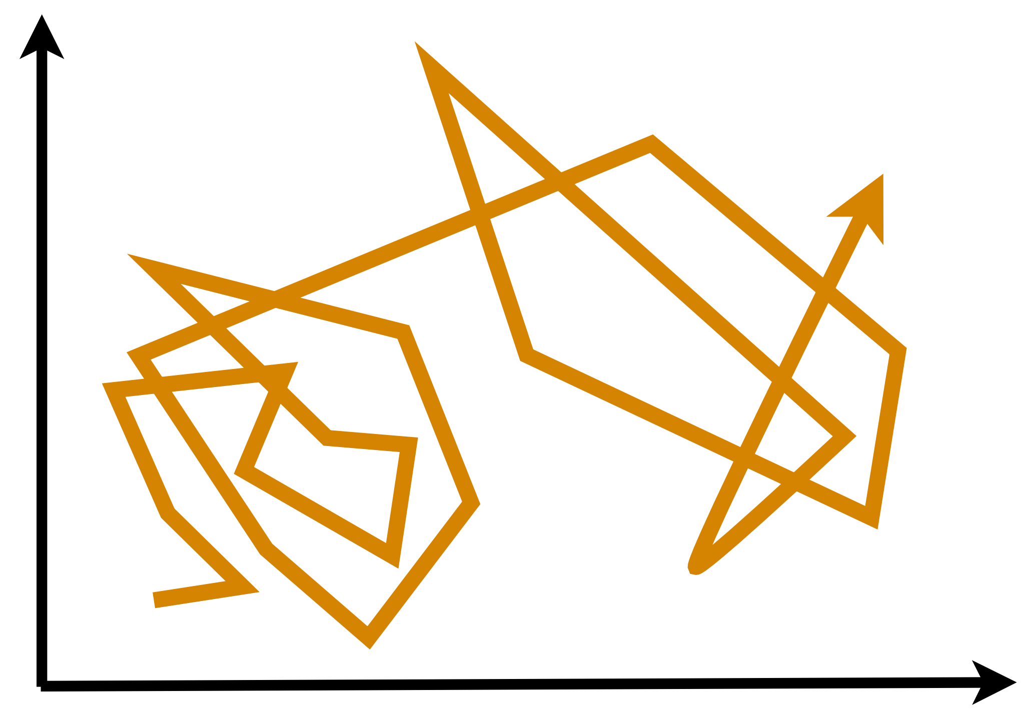
Laser-flash MD yields **accurate qualitative results** at **low temperatures** within **moderate computational costs**. **Quantitative** predictions require **finite size corrections**, though.

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

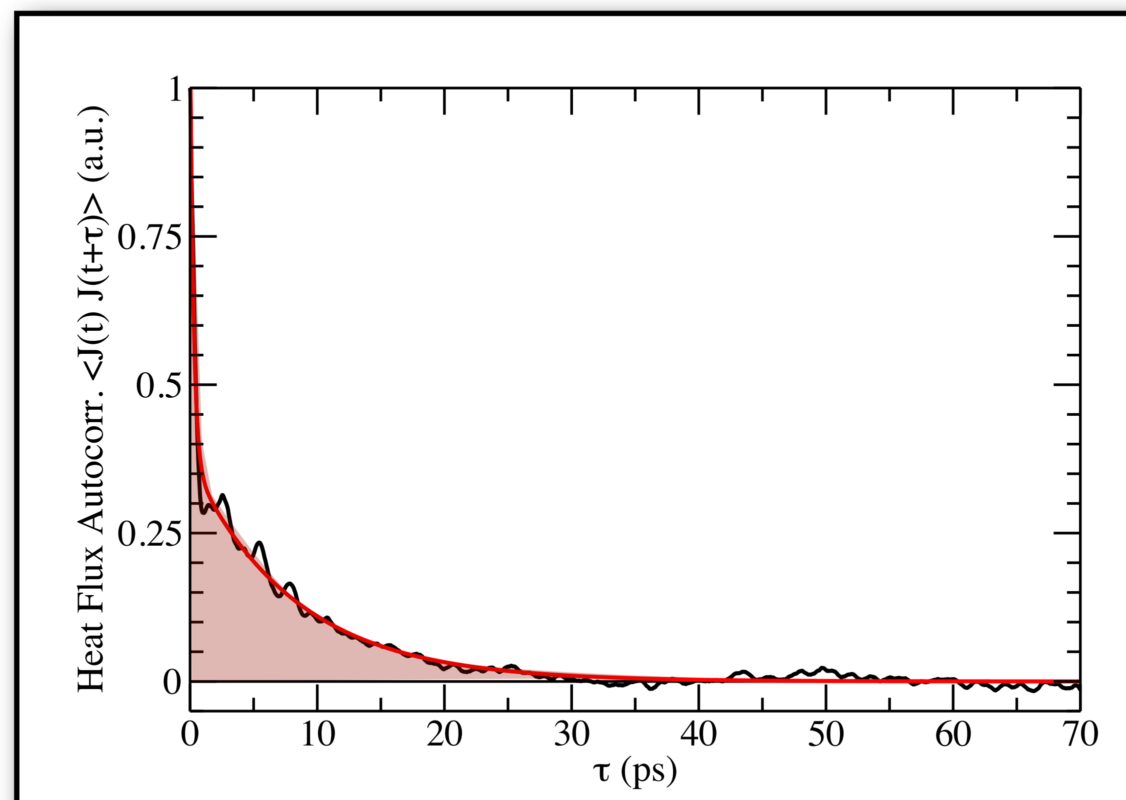
Simulations of the **thermodynamic equilibrium**

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

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).

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

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

$\boxed{\varepsilon_i \quad \cdots \quad \text{Energy of atom } i}$

Energy contribution ε_i of the individual atoms required!

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

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:

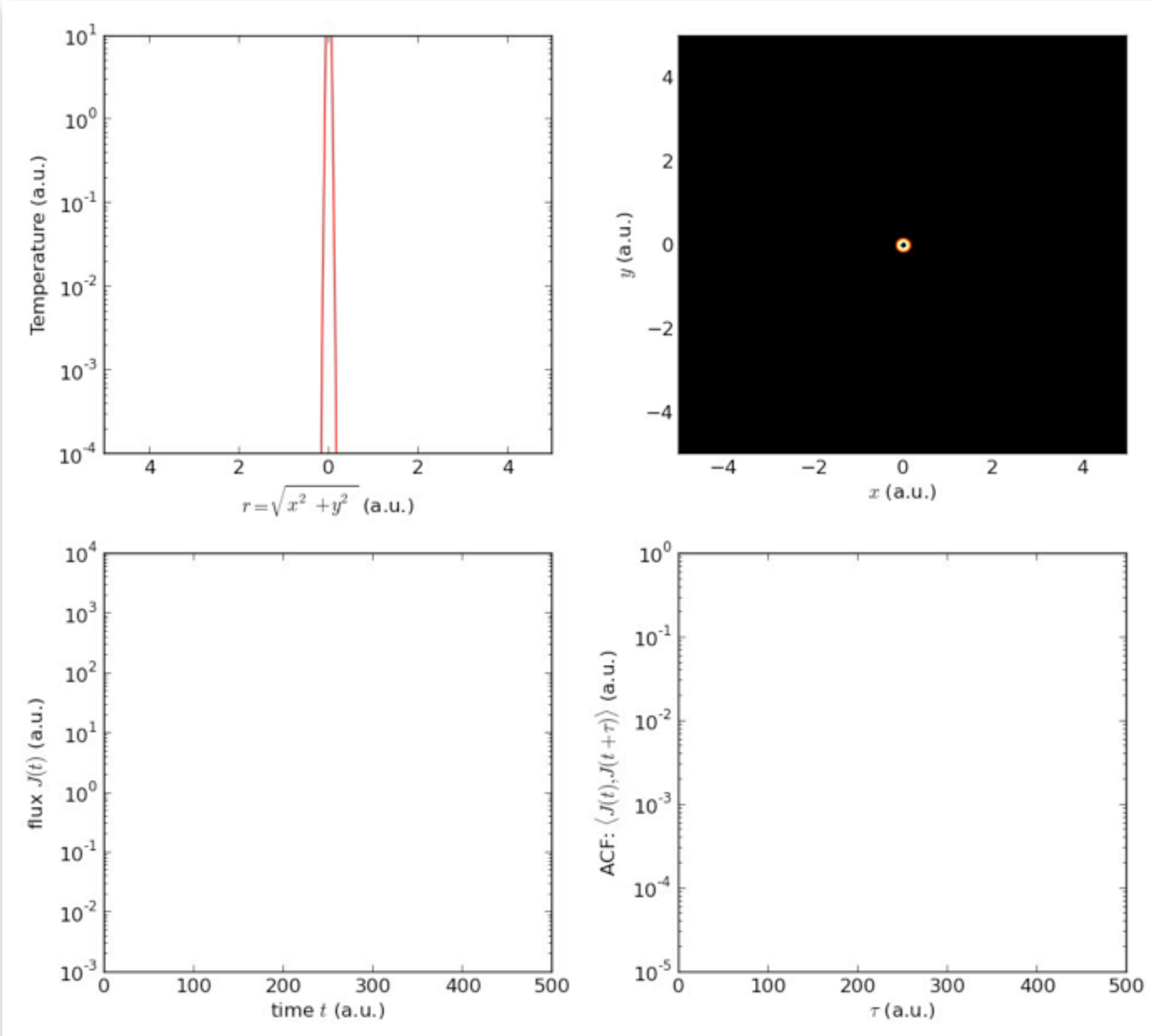
$$\mathbf{j} \quad = \quad -\lambda \, \nabla \rho$$

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

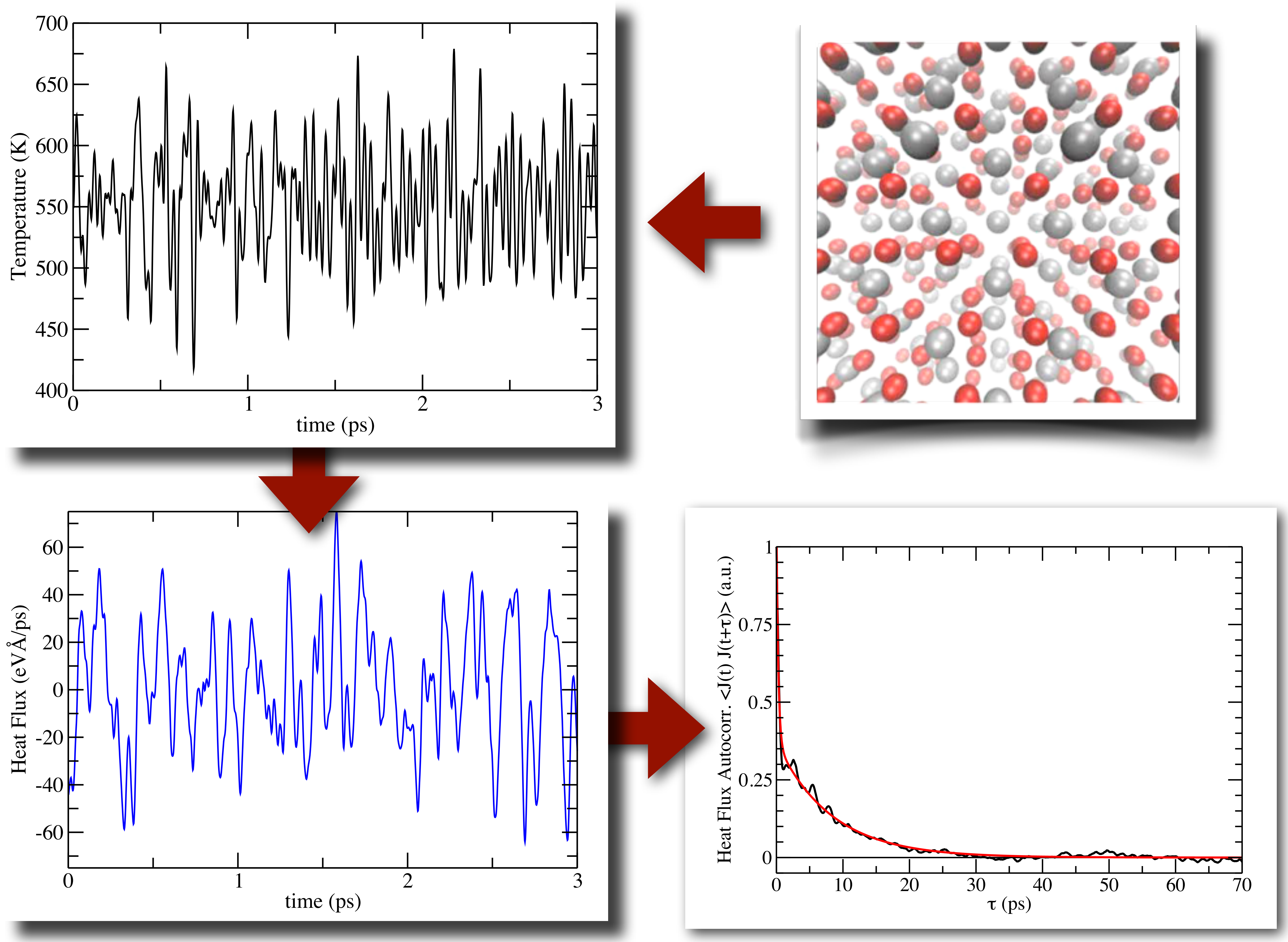
$$\frac{\partial \rho(\mathbf{r}, t)}{\partial t} = \lambda \nabla^2 \rho(\mathbf{r}, t)$$

Analytic Solution:

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



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



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

BASICS OF MACROSCOPIC TRANSPORT

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

The Continuity Equation:

$$\frac{\partial E(\mathbf{r})}{\partial t} + \nabla \cdot \mathbf{j}(\mathbf{r}) = 0$$

$$E = \sum_i \varepsilon_i \delta(\mathbf{r} - \mathbf{r}_i)$$

$$\mathbf{J} = \frac{1}{V} \int \mathbf{j}(\mathbf{r}, \mathbf{t}) \, d\mathbf{r}$$

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

Heat transport: $E \longrightarrow T \quad \Longrightarrow \quad \varepsilon_i \longrightarrow \varepsilon_i - \langle \varepsilon_i \rangle$

THE *AB INITIO* HEAT FLUX

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

Energy Density in Density Functional Theory:

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

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

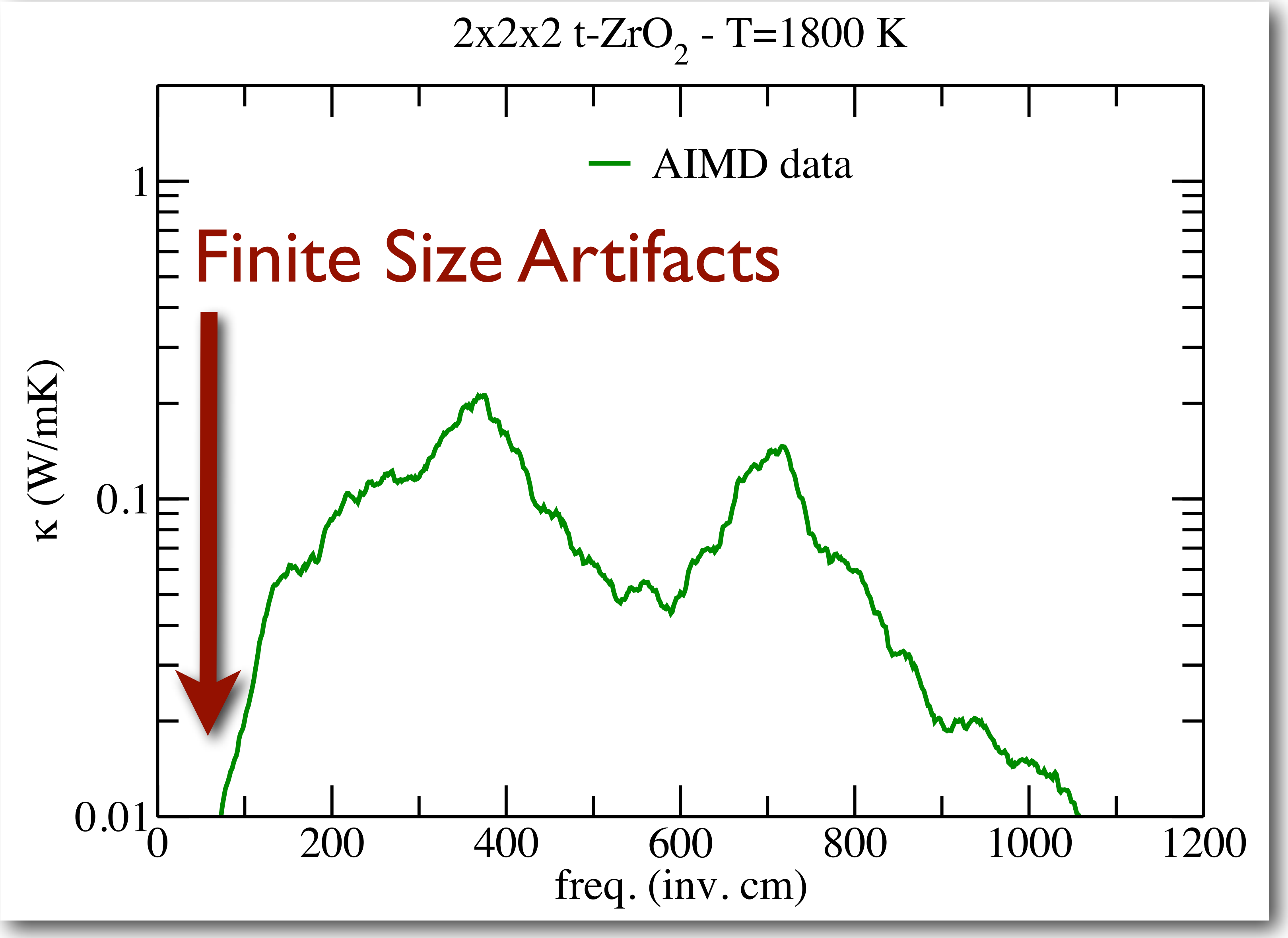
$$\begin{aligned}\varepsilon(\mathbf{r},\{\mathbf{R}\}) \quad = \quad & \sum_i T_i + \sum_l \varepsilon_l f_l^{occ} |\Psi_l(\mathbf{r})|^2 - n(\mathbf{r}) v_{xc}\left[n(\mathbf{r})\right] \\ & + E_{xc}\left[n(\mathbf{r})\right] - \frac{1}{2} n(\mathbf{r}) v_{es}(\mathbf{r}) + \frac{1}{2}\sum_{ij} \frac{Z_i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

ASSESSING THE THERMAL CONDUCTIVITY

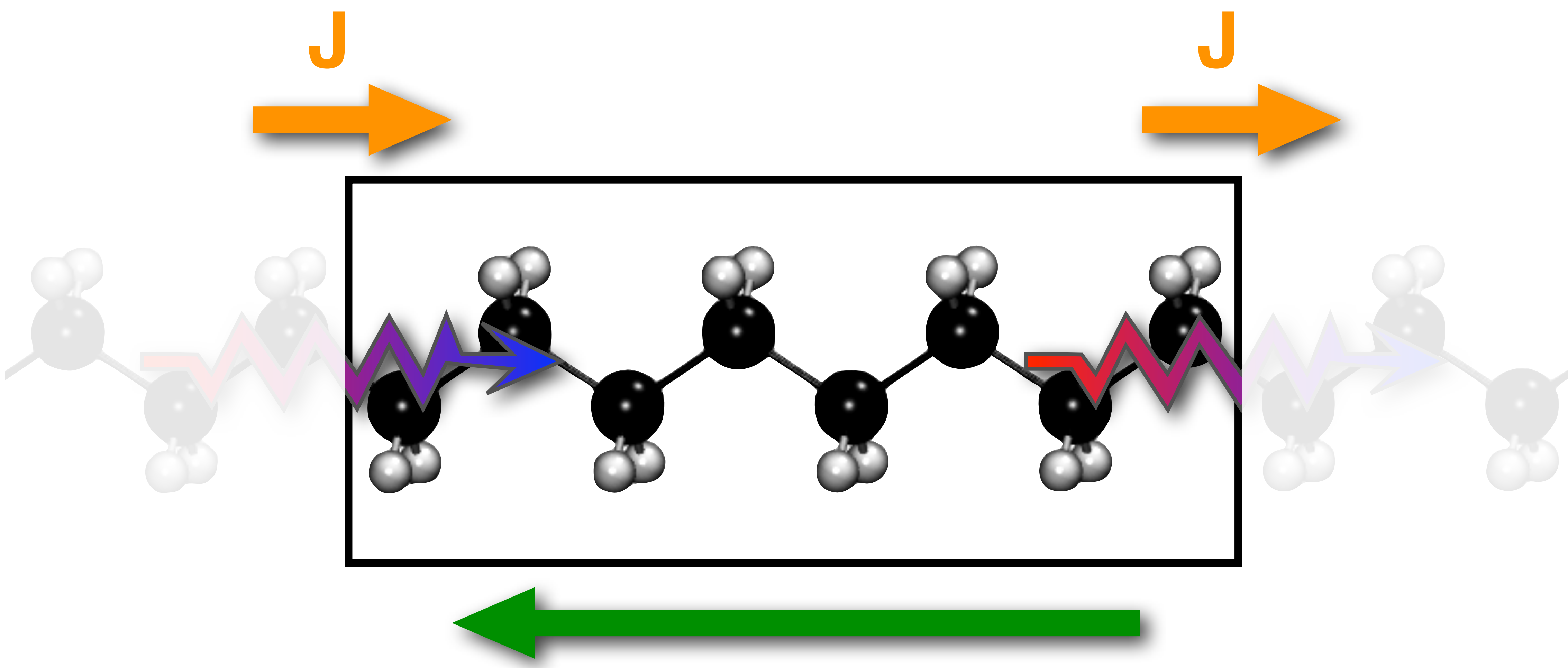
$$\kappa = \frac{V}{3k_B T^2} \int_0^\infty d\tau \, \langle \, \mathbf{J}(0) \, \mathbf{J}(\tau) \rangle_{eq} \xrightarrow{\text{Fourier Trans.}} \kappa = \frac{V}{3k_B T^2} \lim_{\omega \to 0} |\mathbf{J}(\omega)|^2$$

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



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

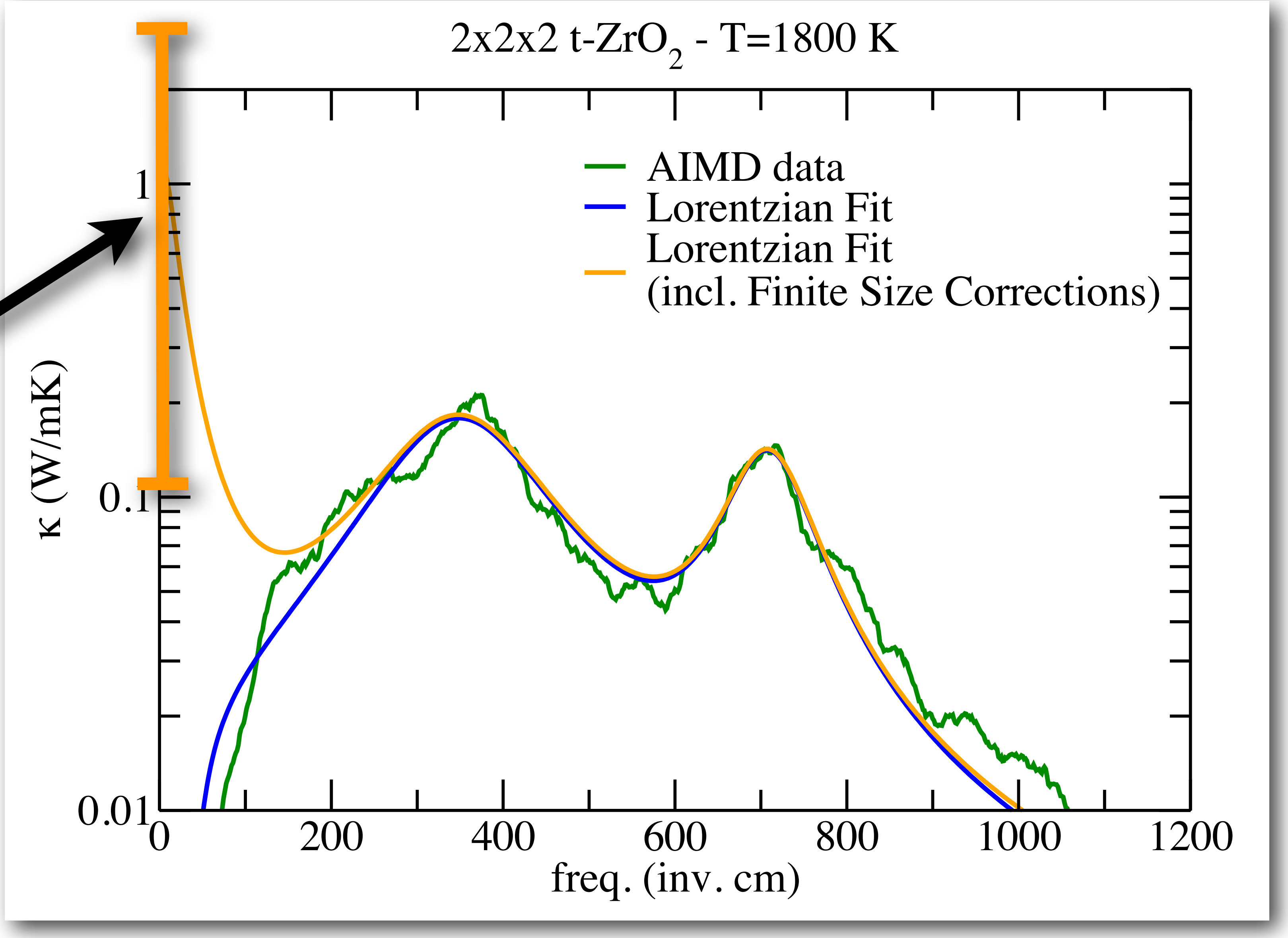
Small heat flux through boundaries
leads to **huge change in energy barycenter.**

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 corrections however exhibit unacceptable "fitting uncertainty".



THE *AB INITIO* HEAT FLUX

$$\mathbf{J}(t) = \boxed{\frac{d}{dt}\sum_i \mathbf{r}_i(\varepsilon_i(t) - \langle\varepsilon_i\rangle)} = \boxed{\sum_i \mathbf{v}_i(\varepsilon_i(t) - \langle\varepsilon_i\rangle) + \sum_i \mathbf{r}_i \frac{\partial \varepsilon_i(t)}{\partial t}}$$

Convective Heat Flux

Virial Heat Flux

$$\mathbf{J}_v = \sum_i \mathbf{r}_i \frac{\partial \varepsilon_i(t)}{\partial t} = \sum_i \mathbf{r}_i \sum_j \frac{\partial \varepsilon_i(t)}{\partial \mathbf{r}_j} \cdot \frac{\partial \mathbf{r}_j}{\partial t} = \sum_j \sigma_j \cdot \mathbf{v}_j$$

σ... Stress contribution

THE *AB INITIO* HEAT FLUX

$\mathbf{J}(t) =$

$\frac{\partial \varepsilon_i(t)}{\partial t}$

$\sigma_j \cdot \mathbf{v}_j$

Formulas for analytical stress

F. Knuth, FHI

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

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

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

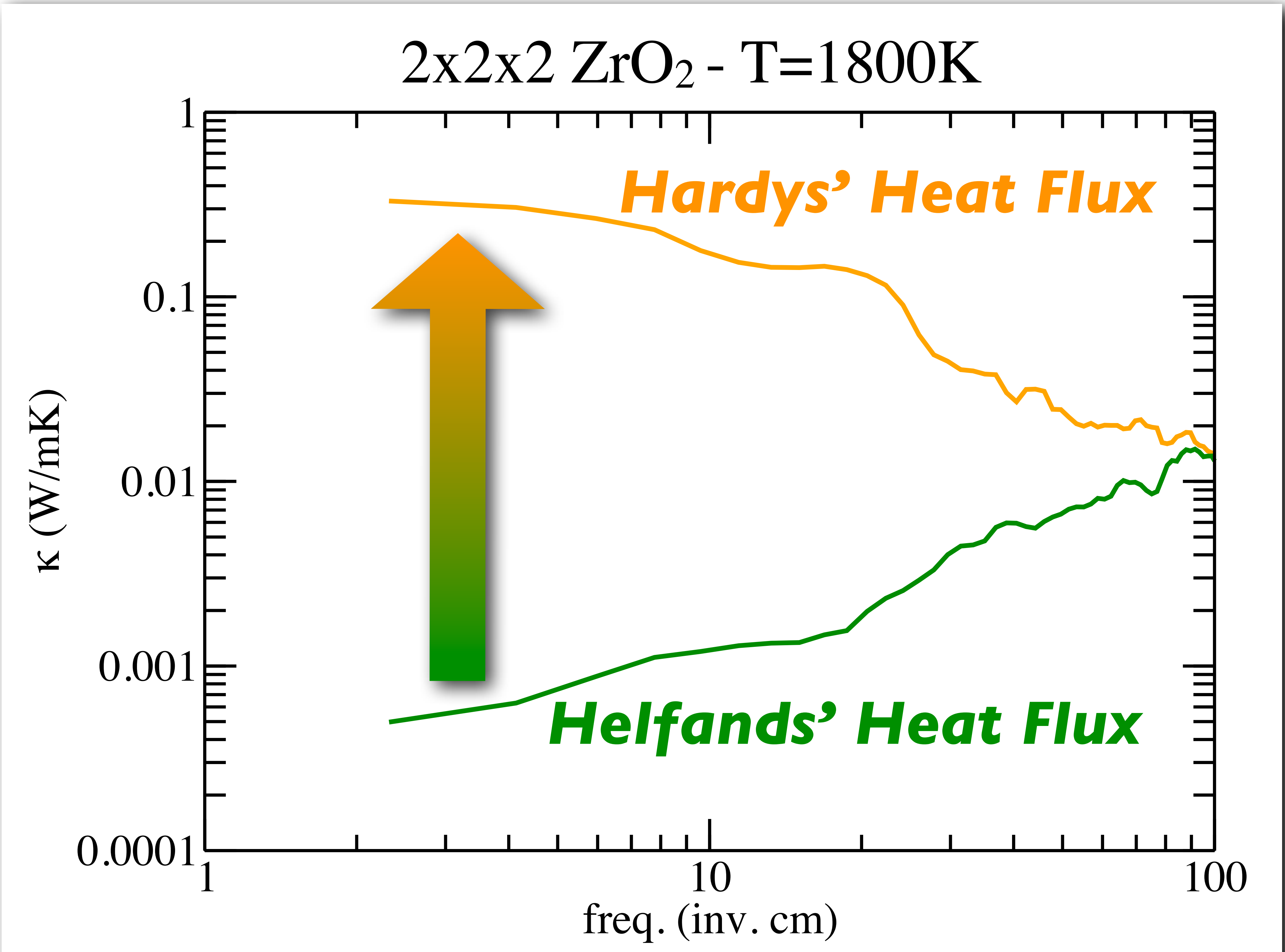
$$\sigma_{ij}^{\mathrm{Pulay}} = \frac{2}{V} \sum_{k} \sum_{\alpha,l(\alpha)} \sum_{\beta,m(\beta)} f_k c_{kl} c_{km} \int_{\mathrm{UC}} d\mathbf{r} \frac{\partial \varphi_l(\mathbf{r} - \mathbf{R}_\alpha)}{\partial r_i} (\mathbf{r} - \mathbf{R}_\alpha)_j \left[\hat{h}_{\mathrm{KS}} - \varepsilon_k \right]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

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

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

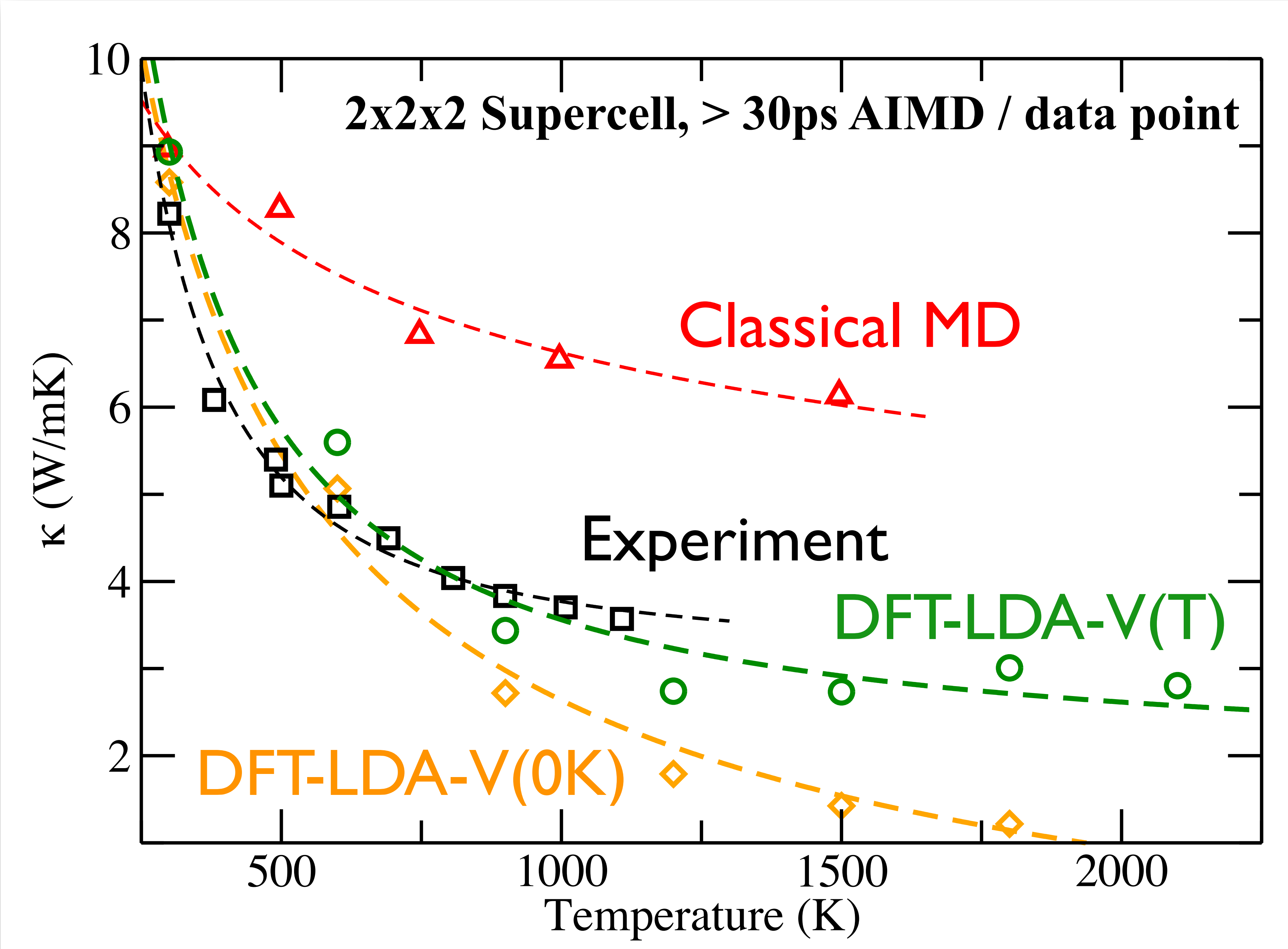
ELIMINATING THE FINITE SIZE ARTIFACTS

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



FINITE SIZE ARTIFACTS ELIMINATED!

APPLICATION TO ZIRCONIA



Experiment:

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

Classical MD:

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

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 $T > T_D$	Small	as in supercell

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

Outlook & Discussion

...for the mathematicians...

The Harmonic Approximation

0th order

2nd order

≥ 3rd order

$$E \approx E\left(\{\mathbf{R}_0\}\right) + \frac{1}{2}\sum_{i,j} \frac{\partial^2 E}{\partial \mathbf{R}_i \partial \mathbf{R}_j}\bigg|_{\mathbf{R}_0} \Delta\mathbf{R}_i \Delta\mathbf{R}_j + \boxed{\frac{1}{6}\sum_{i,j,k} \frac{\partial^3 E}{\partial \mathbf{R}_i \partial \mathbf{R}_j \partial \mathbf{R}_k}\bigg|_{\mathbf{R}_0} \Delta\mathbf{R}_i \Delta\mathbf{R}_j \Delta\mathbf{R}_k + \cdots}$$

Static Equilibrium Energy

Phonons

Terms that determine the thermal conductivity

Is a *Taylor Expansion* the best possible approach for this problem?

Wish list:

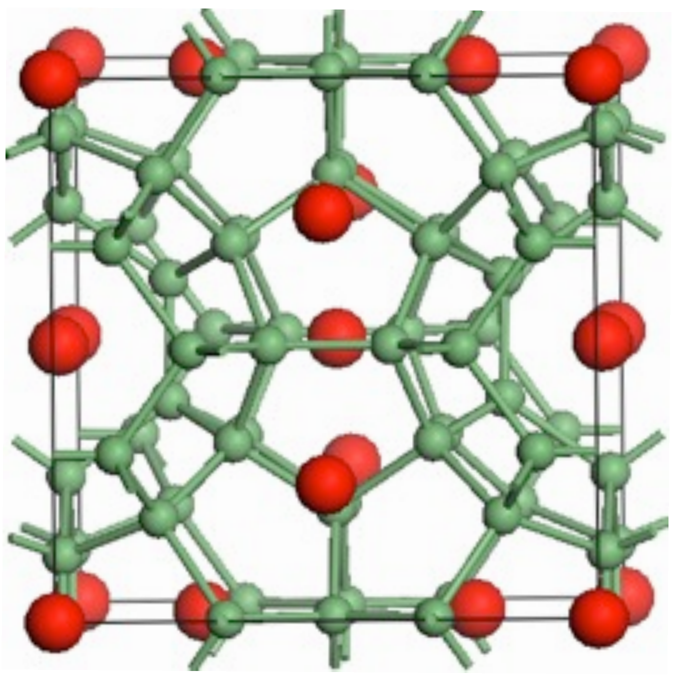
- **Global** Approximation Theory ⇒ No ***R₀*** dependence!
- **Multi-dimensional** Theory ⇒ (Truncated) **interactions** matter!
- **Accurate** description of "**anharmonicity**"! ⇒ **Predictive**!
- Numerically **rapid** both in **generation** and **evaluation**!

Outlook & Discussion

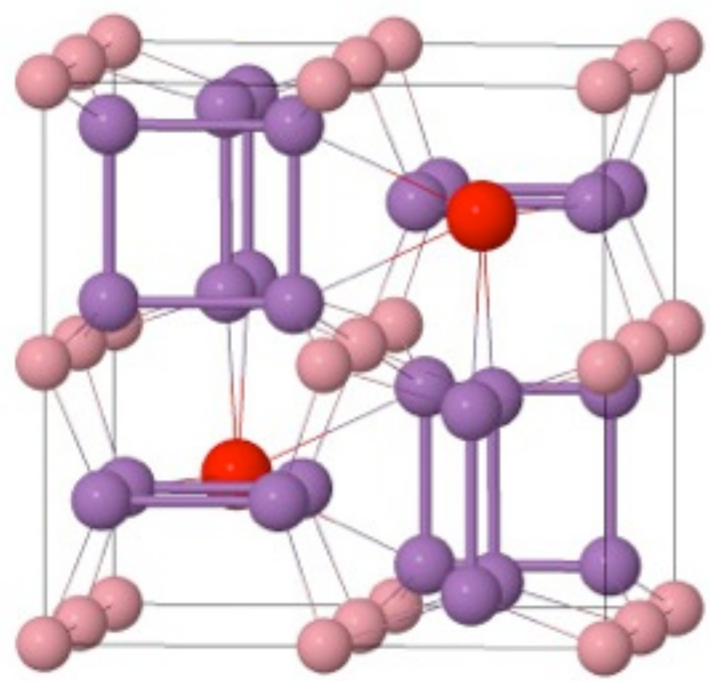
...for the rest of us...

Promising Thermoelectric Materials

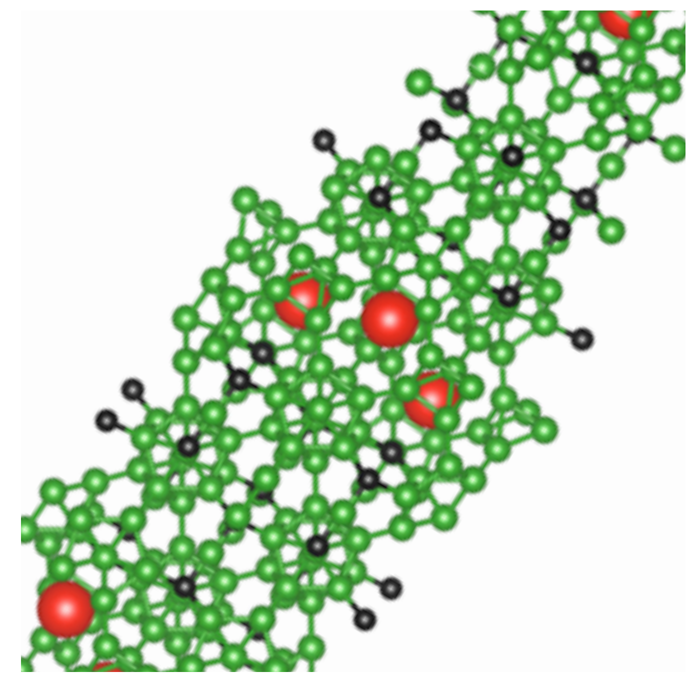
Many *novel* thermoelectric materials feature **cavities**, that can be filled with **guest atoms**.



Clathrates



Skutterudites

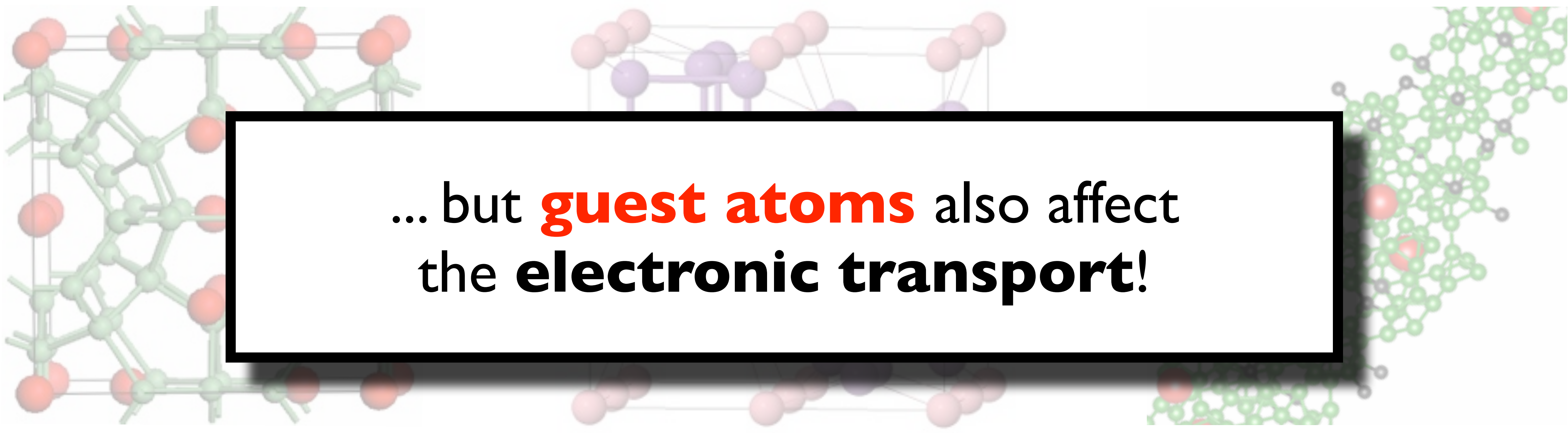


Borcarbides

- **Quasi-free guest atoms** give rise to strong anharmonic effects that can be captured with the *Green-Kubo method*.
- Varying the *species* and the *concentration* of **guest atoms** gives **ample opportunities for optimization**.

Promising Thermoelectric Materials

Many *novel* thermoelectric materials feature **cavities**, that can be filled with **guest atoms**.



... but **guest atoms** also affect the **electronic transport**!

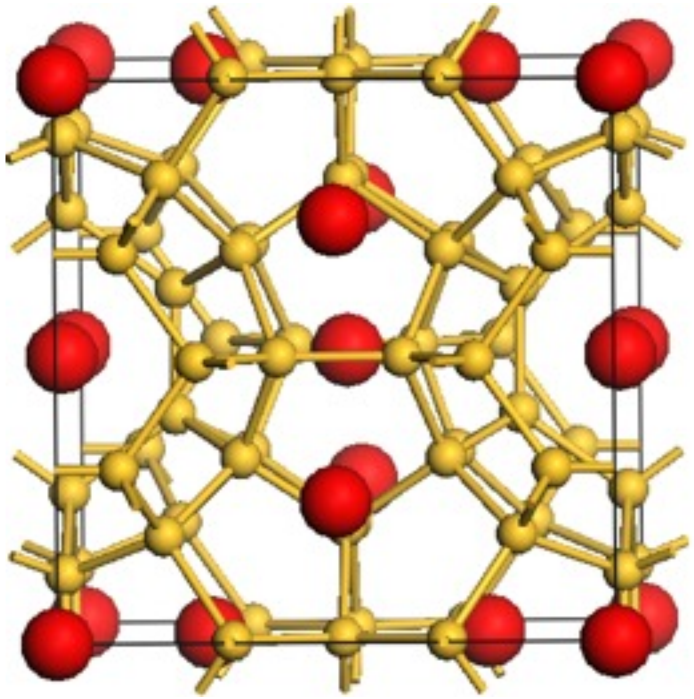
Clathrates *Skutterudites* *Borcarbides*

- **Quasi-free guest atoms** give rise to strong anharmonic effects that can be captured with the *Green-Kubo method*.
- Varying the *species* and the *concentration* of **guest atoms** gives **ample opportunities for optimization**.

Clathrates filled with K

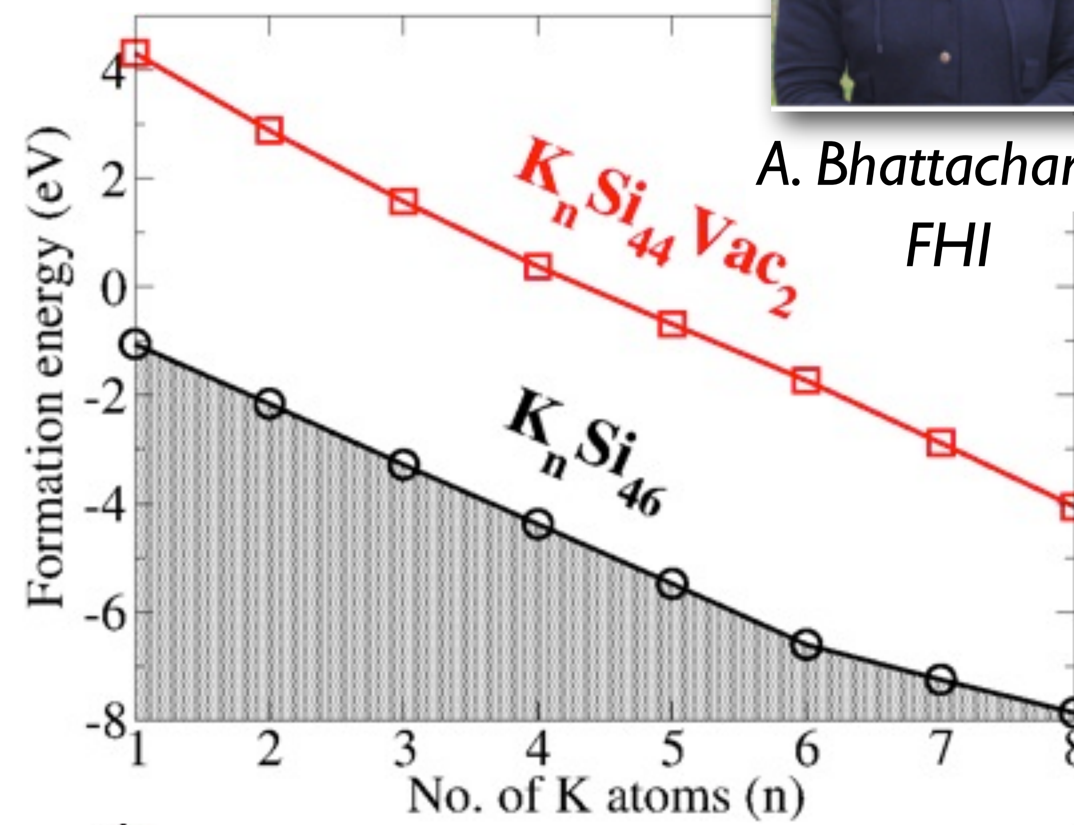
in collaboration with Juri Grin, MPG CPfS Dresden

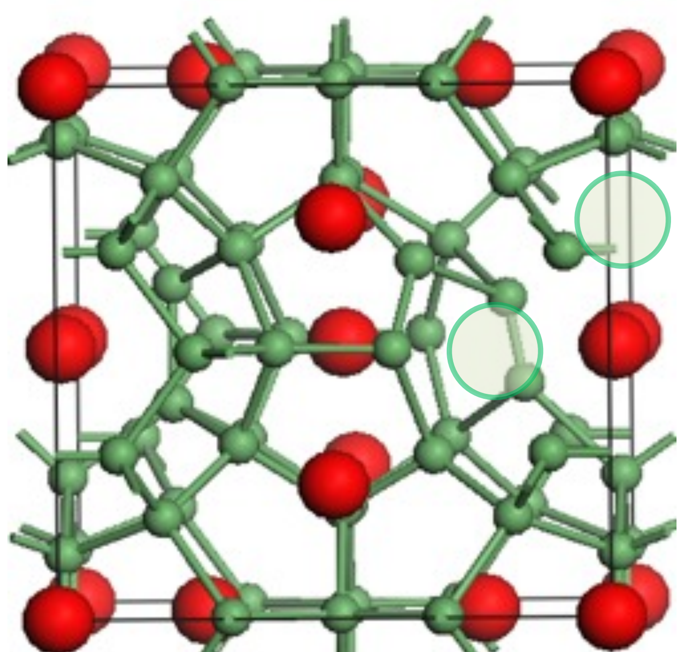
A. Bhattacharya
FHI



K_8Si_{46}

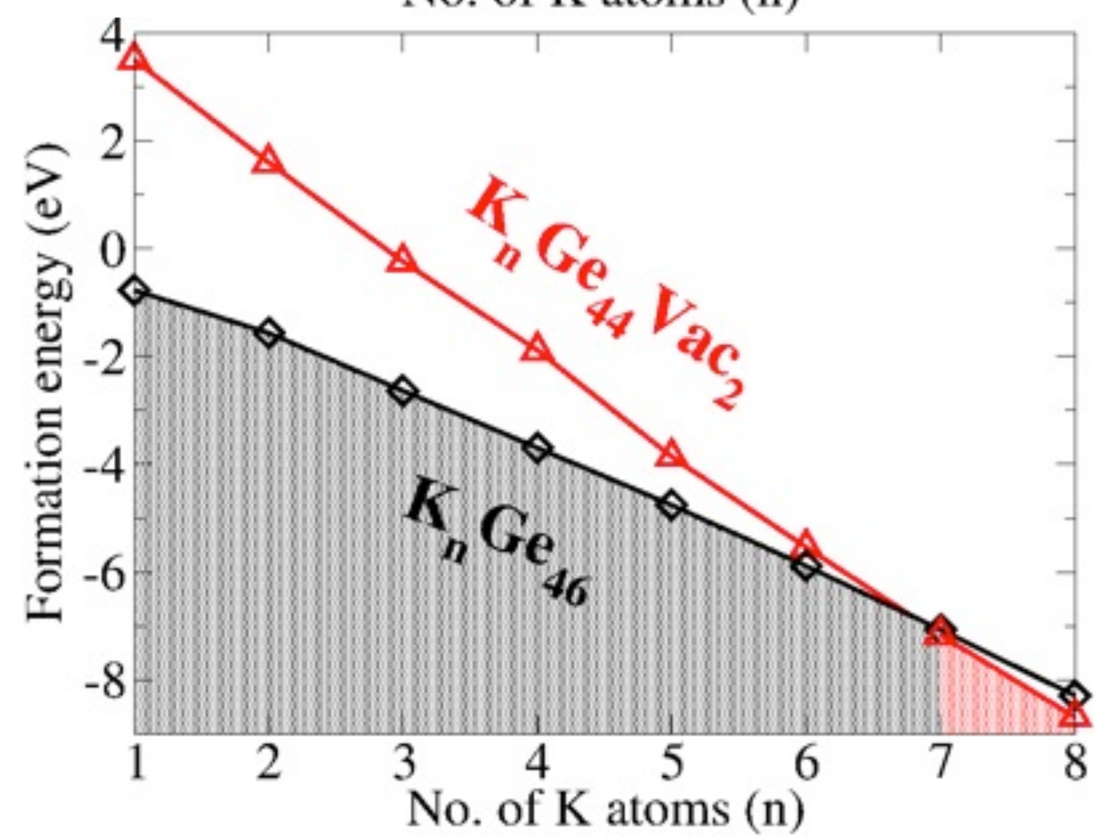
metallic





$K_8Ge_{44}\square_2$

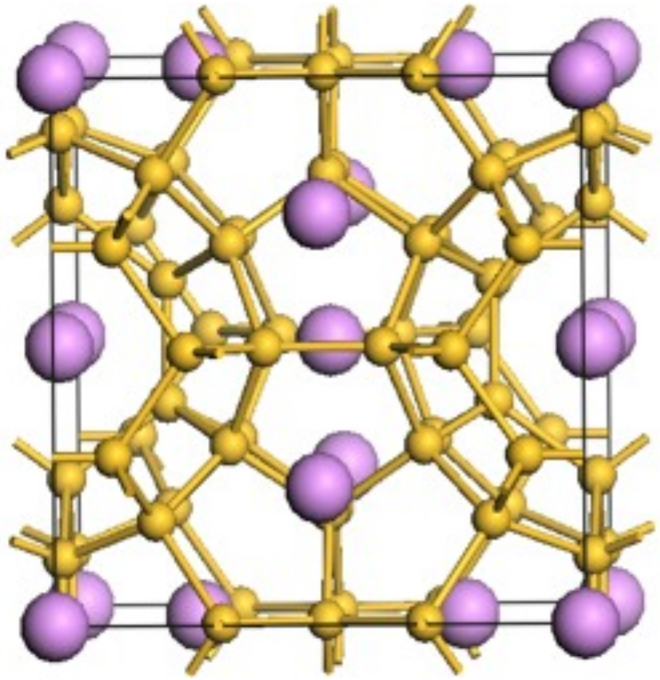
semiconducting



Clathrates filled with Ba

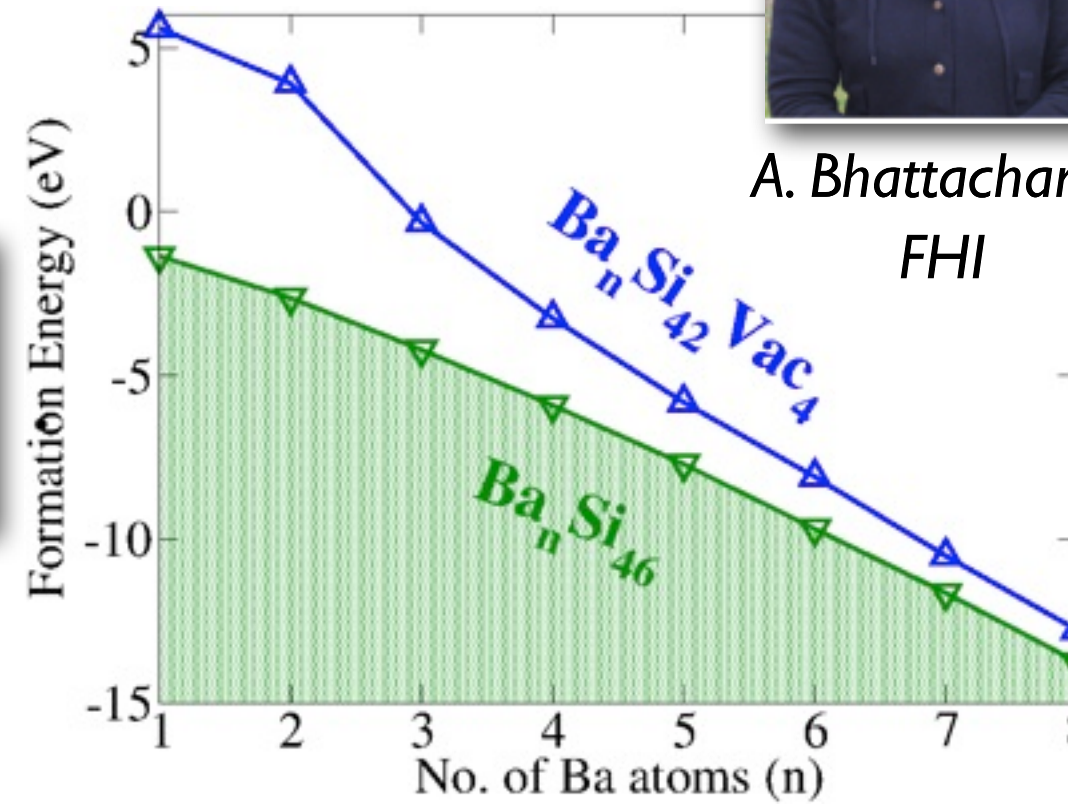
in collaboration with Juri Grin, MPG CPfS Dresden

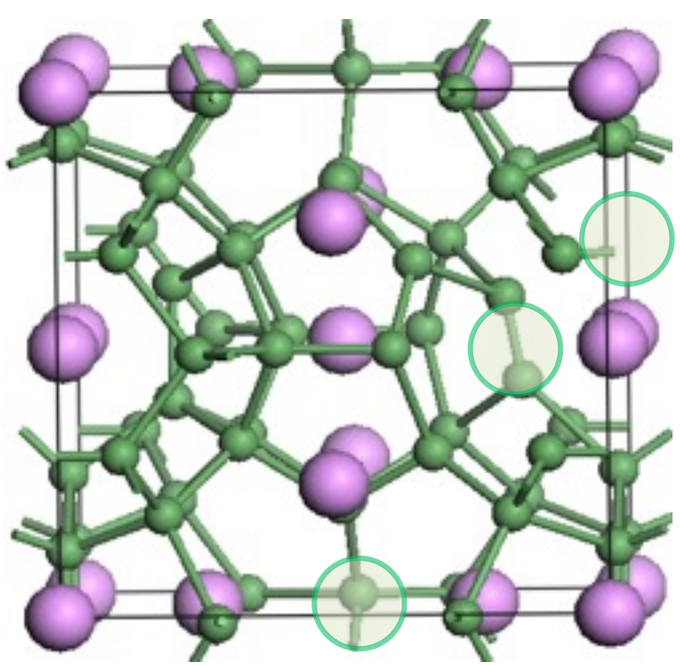
A. Bhattacharya
FHI



Ba_8Si_{46}

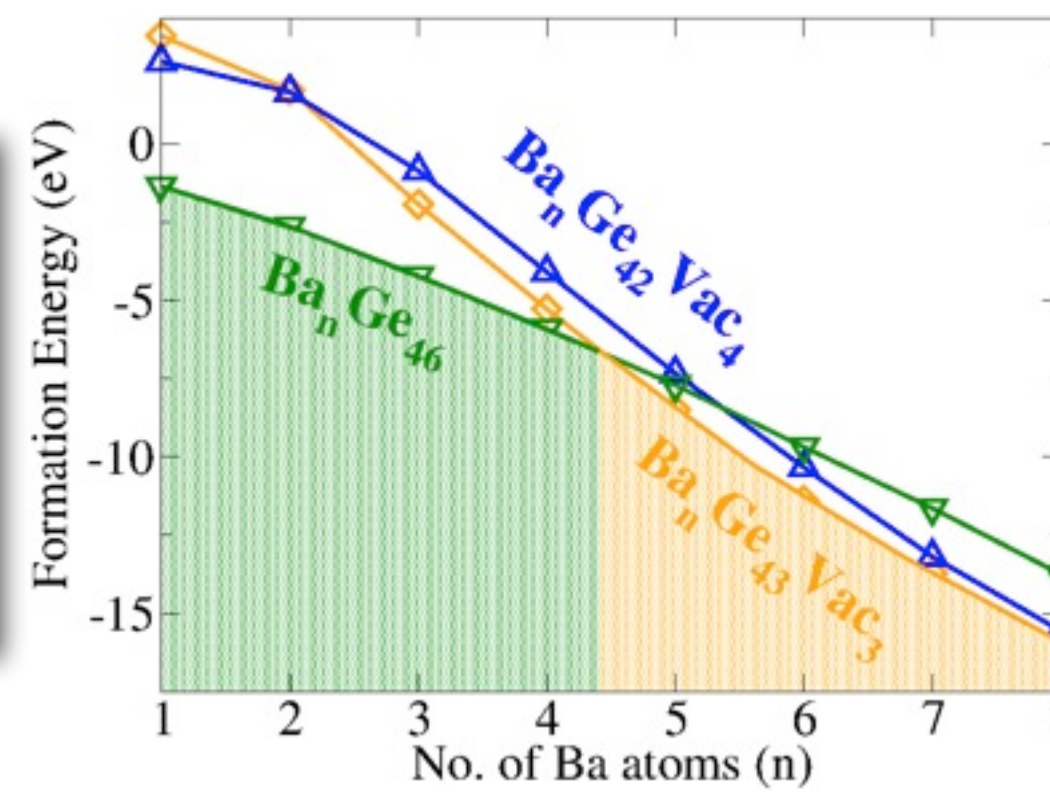
metallic





$Ba_8Ge_{43}\square_3$

metal-semiconductor-transition at 280 K



Conclusion

Higher-order anharmonic effects can play a decisive role for the **thermal conductivity.**

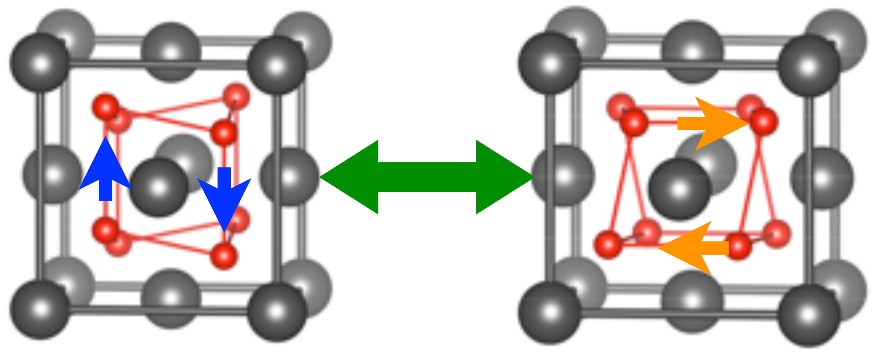
- ***Ab initio* MD in thermal equilibrium**
- **Includes all orders of interactions**

⇓ ⇓ ⇓

Ab initio Green-Kubo approach allows the **accurate** and **predictive** computation of thermal conductivities κ for **highly anharmonic systems** & at **arbitrarily high temperatures**!

ACKNOWLEDGEMENTS

ZrO_2 / YSZ Dynamics



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Chris G. Van de Walle

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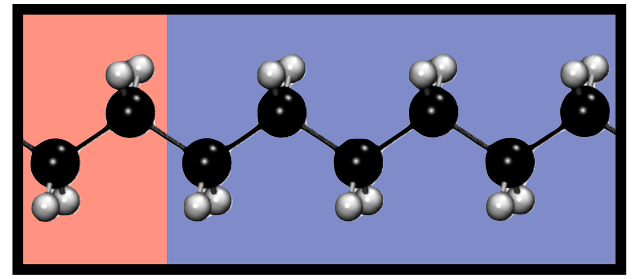
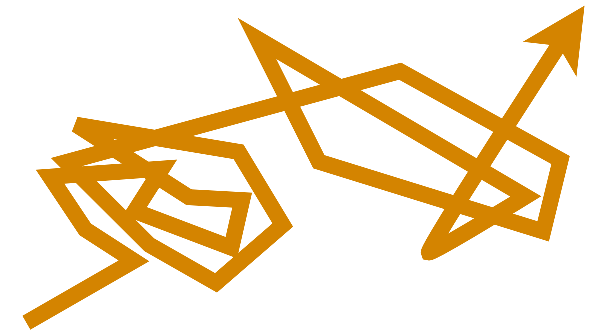
"Laser-flash" MD



Stefan Estreicher

Texas Tech

Green-Kubo MD



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MATERIALS UC Santa Barbara

NSF

DFG