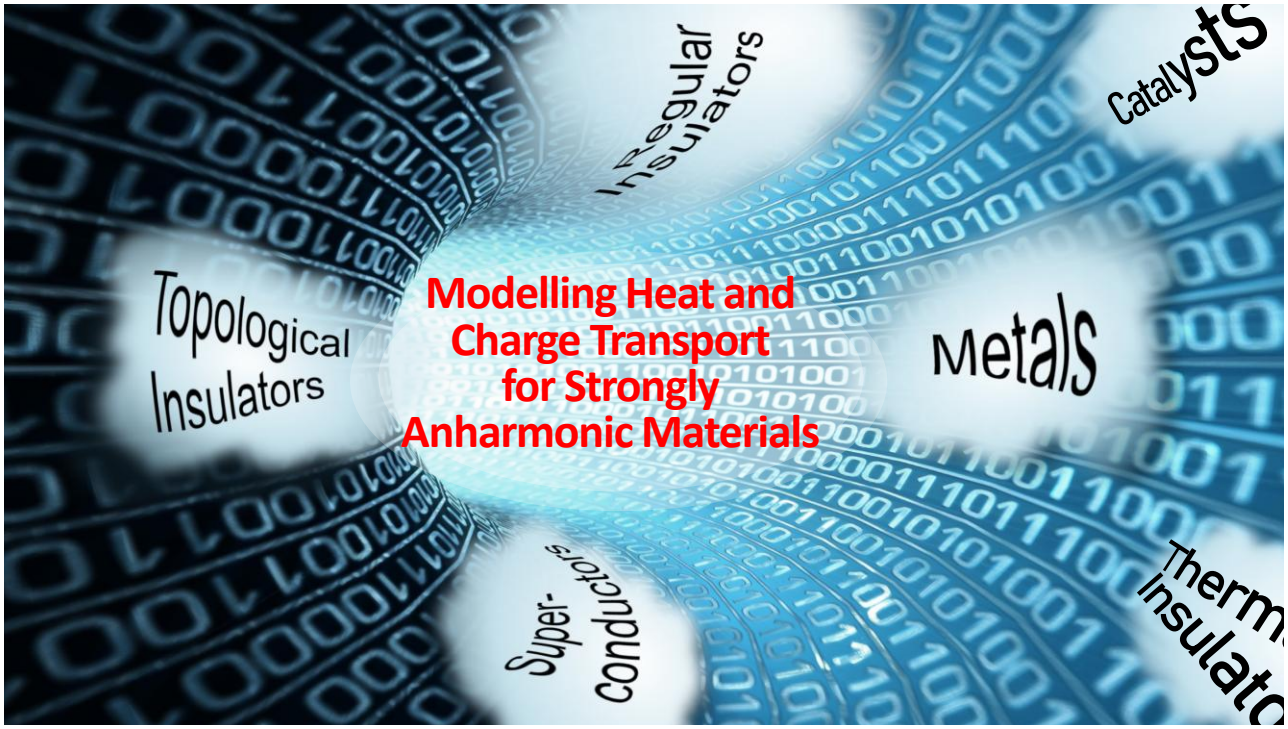
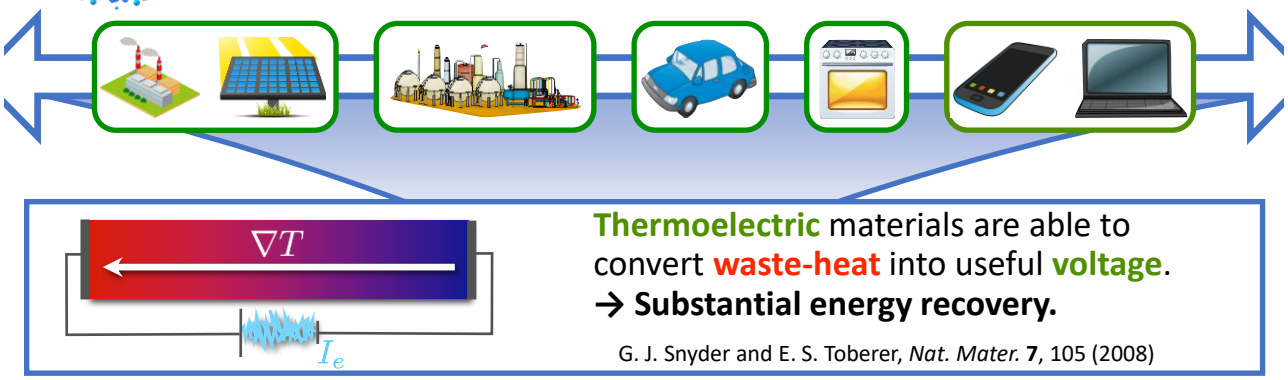


Thermoelectric Materials



Thermoelectric materials are able to convert **waste-heat** into useful **voltage**.
→ **Substantial energy recovery.**

G. J. Snyder and E. S. Toberer, *Nat. Mater.* **7**, 105 (2008)

Efficient *thermoelectric materials* are not known, so far.

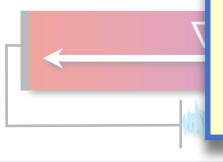
Minimize *vibrational* **heat** transport!

Maximize *electronic* **charge** transport!

2

Thermoelectric Materials

Developing a first-principles methodology to describe & understand heat transport for thermal insulators.



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ful **voltage**.
ery.

G. J. Snyder and E. S. Toberer, *Nat. Mater.* **7**, 105 (2008)

Efficient *thermoelectric materials* are not known, so far.

Part I

Minimize *vibrational* **heat** transport!

Maximize *electronic* **charge** transport!

3

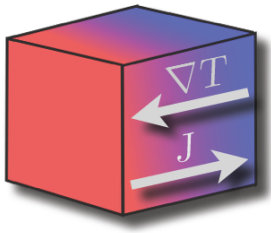
Lattice Thermal Conductivity

NOVEL MATERIALS DISCOVERY

2. Law of Thermodynamics:

Heat flows spontaneously from hot to cold.

Macroscopic Effect:



4

Lattice Thermal Conductivity

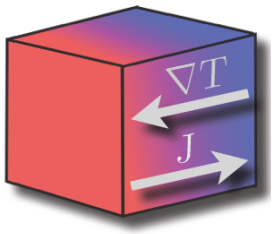
2. Law of Thermodynamics:

Heat flows spontaneously from hot to cold.

How do we define "hot" and "cold"?

This is the direction in which the heat flows.

Macroscopic Effect:

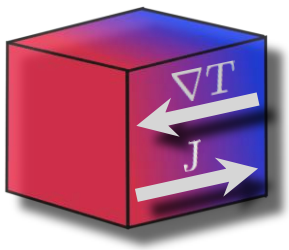


5

Lattice Thermal Conductivity

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

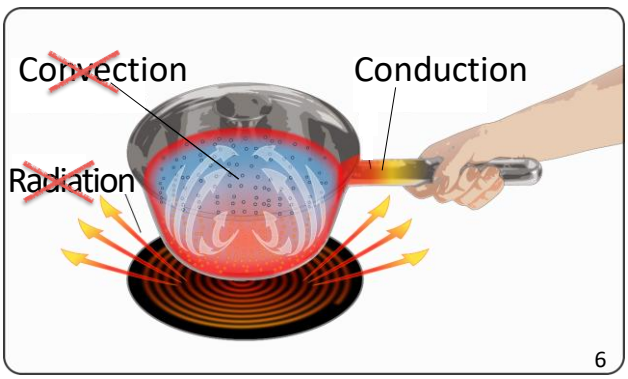
Macroscopic Effect:



Fourier's Law:

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

κ = thermal-conductivity tensor

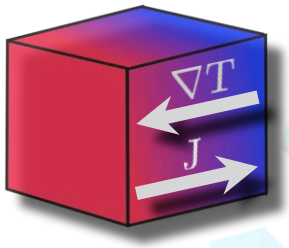


6

Lattice Thermal Conductivity

NOVEL MATERIALS DISCOVERY

Macroscopic Effect:



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

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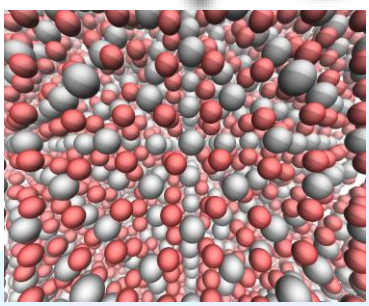
$\kappa = \kappa_{\text{photon}} + \kappa_{\text{elec.}} + \kappa_{\text{nucl.}}$



Zr
O

1s ≙ 0.1ps
xc = PBEsol

tetragonal ZrO_2@ $T = 1800$ K

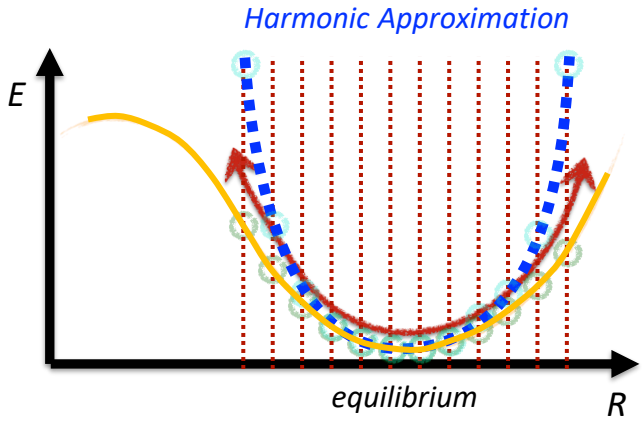
7

For a harmonic crystal,
the lattice thermal conductivity is infinite

8

Anharmonicity Quantification

F. Knoop, T. A. R. Purcell, M. Scheffler, and C. Carbogno, *Phys. Rev. Mater.* **4**, 083809 (2020).



1) Run *ab initio* Molecular Dynamics (MD) simulations to obtain trajectories $\boldsymbol{R}_I^{DFT}(t)$.

2) Store the potential energies $E^{DFT}(t)$ observed along $\boldsymbol{R}_I^{DFT}(t)$.

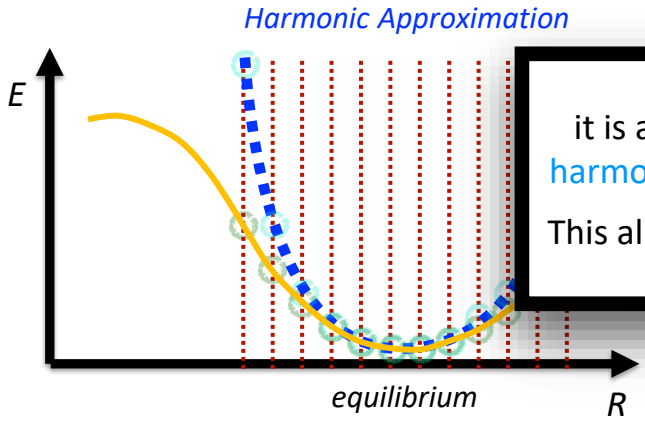
3) Evaluate which potential energies the *harmonic approximation* would predict along $\boldsymbol{R}_I^{DFT}(t)$: $E^{harm}(t)$.

4) The difference $E^{harm}(t)$ - $E^{DFT}(t)$ quantifies the strength of anharmonic effects.

9

Anharmonicity Quantification

F. Knoop, T. A. R. Purcell, M. Scheffler, and C. Carbogno, *Phys. Rev. Mater.* **4**, 083809 (2020).



1) Run *ab initio* Molecular Dynamics (MD)

In practice,
it is advantageous to work with forces:
harmonic $\mathbf{F}_I^{harm}(t)$ and anharmonic $\mathbf{F}_I^{DFT}(t)$.

This allows for an atom-specific resolution of anharmonic effects.

along $\boldsymbol{R}_I^{DFT}(t)$: $E^{harm}(t)$.

4) The difference $E^{harm}(t)$ - $E^{DFT}(t)$ quantifies the strength of anharmonic effects.

10

How To Quantify Anharmonicity? What is σ^{A} and Why Is It A Useful Concept?

$$\sigma^{A}(t) = \sigma^{A}(\boldsymbol{R}(t)) = \sqrt{\frac{\sum_{I,\alpha}(F^{A}_{I,\alpha})^2}{\sum_{I,\alpha}(F_{I,\alpha})^2}}$$

$F_{I,\alpha}$ = force acting on atom I,
$\alpha = x, y, z$;

$F^{A}_{I,\alpha}$ = anharmonic part of the force

F. Knoop, T.A.R. Purcell, M. Scheffler, and Ch. Carbogno, PR Mat **4**, 083809 (2020)

11

How To Quantify Anharmonicity? What is σ^{A} and Why Is It A Useful Concept?

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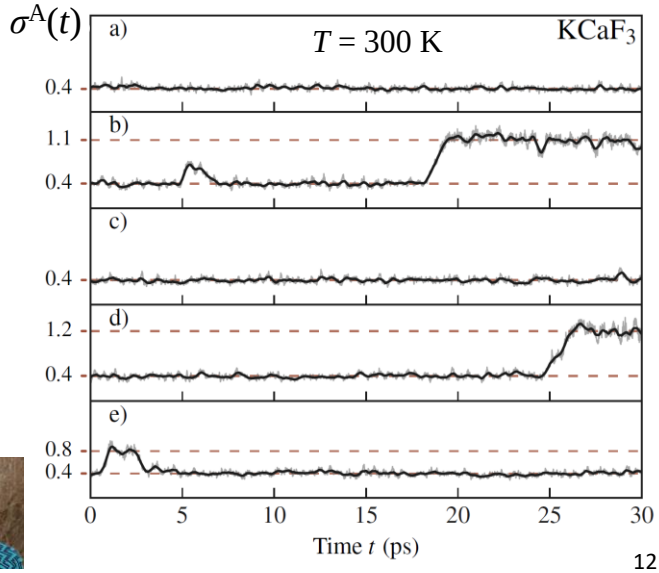
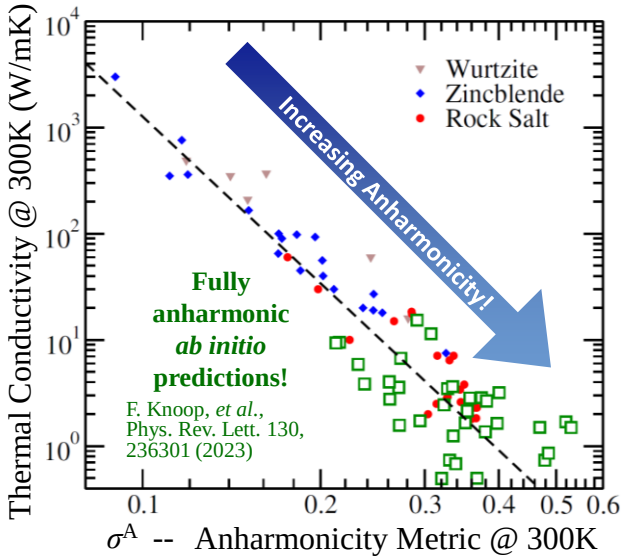
F. Knoop, T.A.R. Purcell, M. Scheffler, and Ch. Carbogno, PR Mat **4**, 083809 (2020)



12

Good Thermal Insulators Are Strongly Anhamonic

F. Knoop, T.A.R. Purcell, M. Scheffler, and Ch. Carbogno, PR Mat **4**, 083809 (2020)



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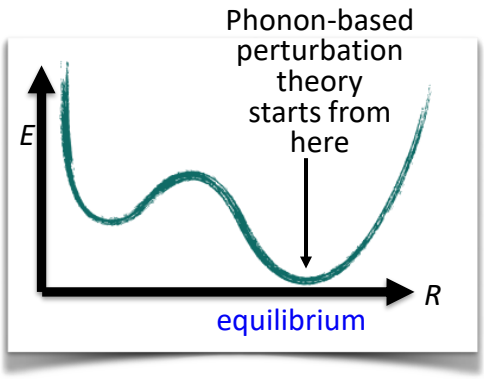
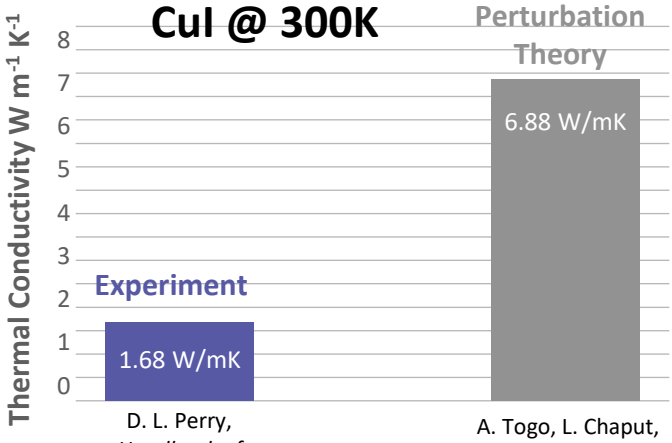


F. Knoop, T. A. R. Purcell, M. Scheffler, and C. Carbogno, *Phys. Rev. Lett.* **130**, 236301 (2023)
F. Knoop, M. Scheffler, and C. Carbogno, *Phys. Rev. B* **107**, 224304 (2023)



D. L. Perry, *Handbook of Inorganic Compounds,* CRC Press, (2016).

A. Togo, L. Chaput, and I. Tanaka, *Phys. Rev. B* ***91****, 094306 (2015).*

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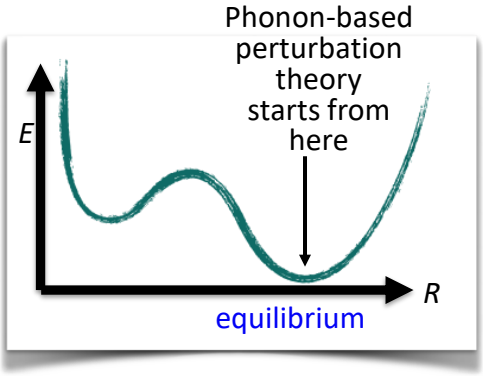

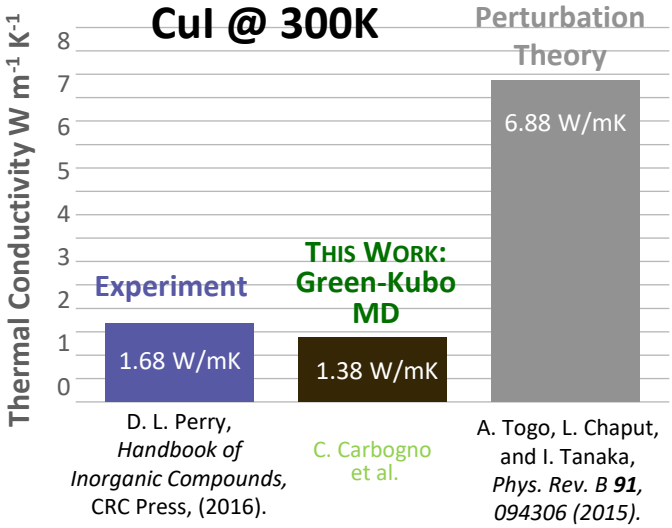

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15

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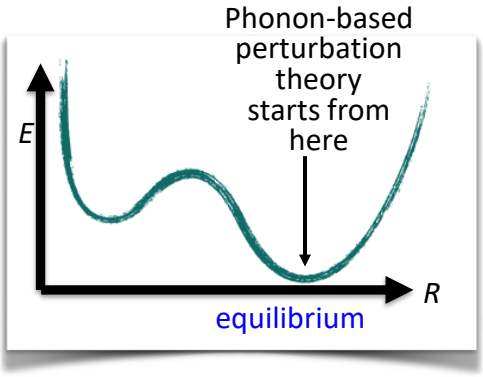

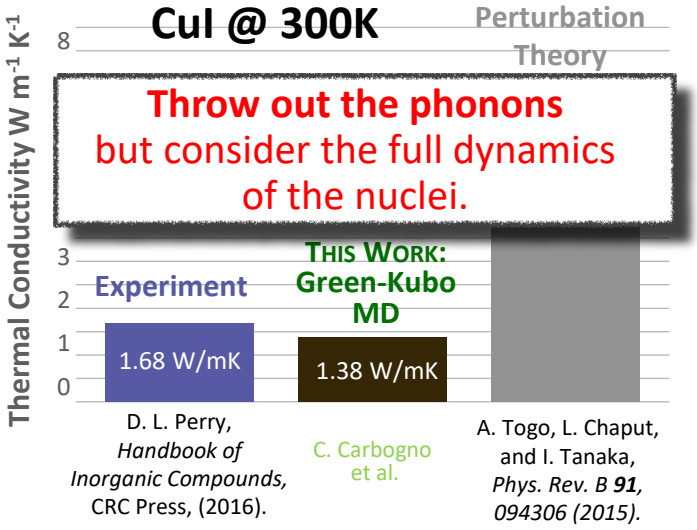

F. Knoop, T. A. R. Purcell, M. Scheffler, and C. Carbogno, *Phys. Rev. Lett.* **130**, 236301 (2023)
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C. Carbogno et al.

A. Togo, L. Chaput, and I. Tanaka, *Phys. Rev. B* ***91****, 094306 (2015).*

16

Green-Kubo Molecular Dynamics:

Non-Perturbative *ab initio* Theory of Thermal Transport

Considering Anharmonic Effects to All Orders

17

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

$$\boldsymbol{\kappa} = \frac{1}{3Vk_{\mathrm{B}}T^2}\int_0^{\infty}\langle \boldsymbol{J}(0)\cdot\boldsymbol{J}(t)\rangle\, dt$$

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

18

Green-Kubo Method

R. Kubo, M. Yokota, and S. Nakajima, J. Phys. Soc. Japan 12,1203 (1957)

Fluctuation-Dissipation Theorem

Green-Kubo method...

...works in thermal equilibrium (linear response)

...accounts for anharmonic effects to all orders

$$\boldsymbol{\kappa} = \frac{1}{3Vk_{\mathrm{B}}T^2}\int_0^{\infty}\langle \boldsymbol{J}(0)\cdot\boldsymbol{J}(t)\rangle\, dt$$

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

19

THE ATOMISTIC HEAT FLUX

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

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

Energy decomposition $\qquad$ *Heat flux*

$$E(\mathbf{r}) = \sum_I E_I\,\delta(\mathbf{r}-\mathbf{R}_I) \quad \Rightarrow\!\!\Rightarrow \quad \mathbf{J}(t) = \frac{d}{dt}\left(\sum_I \mathbf{R}_I E_I\right)$$

Heat flux definition requires a **decomposition** of the **energy**, which **is not unique**.

20

THE VIRIAL HEAT FLUX

R. J. HARDY, *PHYS. REV.* **132**,168 (1963)

Helfands' Heat Flux | **Hardys' Heat Flux**

$$\mathbf{J}(t) = \frac{d}{dt}\left(\sum_I \mathbf{R}_I E_I\right) = \sum_I \mathbf{v}_I E_I + \sum_I \mathbf{R}_I \dot{E}_I$$

~~Convective Heat Flux~~

Liquids & Gases:

⇒ use energy density

A. Marcolongo, P. Umari, and S. Baroni, *Nat. Phys.* **12**, 80 (2016).

Virial Heat Flux:

- Unique: Does not depend on partitioning
- Describes vibrational heat transport
- Well-defined for classical potentials
- Well-defined in ***first-principles*** frameworks

21

Numerical Challenge:
Time and Size Convergence

FHI-aims The ab initio materials simulation package

Numerical/statistical convergence requires at least 10 MD runs in a 1024-atom cell, each run 12 ns long.

Extrapolation method (2017): Split off the harmonic contribution to the heat flux, transform this to q-space, and converge there:

Ch. Carbogno, R. Ramprasad, and M. Scheffler, Phys. Rev. Lett. **118**, 175901 (2017).

Extrapolation method (2023+): Use the *ab initio* MD results and train a NN. Then do long time-scale calculations with larger super cells:

M. F. Langer, F. Knoop, Ch. Carbogno, M. Scheffler, and M. Rupp, Phys. Rev. B 108, L100302 (2023);
K. Kang, T. A. R. Purcell, C. Carbogno, and M. Scheffler, Phys. Rev. Materials 9, 063801 (2025);
S. Zhao. K. Kang, and M. Scheffler, in preparation.

22

Take-Home Messages (Part I)

1) The strength of **anharmonic** effects can be quantified using *ab initio* molecular dynamics: **anharmonicity metric,** σ^{A}.
F. Knoop, T. A. R. Purcell, M. Scheffler, and C. Carbogno, *Phys. Rev. Mater.* **4**, 083809 (2020).

2) Ab initio Green-Kubo method **quantitatively** describes the **lattice thermal conductivity** both for **very harmonic** and for **strongly anharmonic** systems.
C. Carbogno, R. Ramprasad, and M. Scheffler, *Phys. Rev. Lett.* **118**, 175901 (2017).

3) Local and/or **temporary** distortions can lead to a **breakdown of the phonon picture** (breaking the Ioffe-Regel limit).
F. Knoop, T. A. R. Purcell, M. Scheffler, and C. Carbogno, *Phys. Rev. Lett.* **130**, 236301 (2023).

23

Searching for Statistically Exceptional Heat Insulators

Green-Kubo approach is expensive. Only use it when necessary, i.e. for strongly anharmonic materials. Link it with Artificial Intelligence (AI).

See the AI talk by Lucas Foppa tomorrow (for a general discussion).

Create ***a map of thermal conductivity of material*** by SISSO, as demonstrated by T.A.R. Purcell, M. Scheffler, L.M. Ghiringhelli, and C. Carbogno, npj Comput. Mater. 9, 112 (2023)

24

Thermoelectric Materials

Developing a first-principles methodology to describe & understand charge-carrier transport in strongly anharmonic materials.

e able to
ful voltage.
ency gains.

G. J. Snyder and E. S. Toberer, *Nat. Mater.* **7**, 105 (2008).

More **efficient** ***thermoelectric materials*** can **enable** these applications!

Minimize *vibrational* **heat** transport!

Maximize *electronic* **charge** transport!

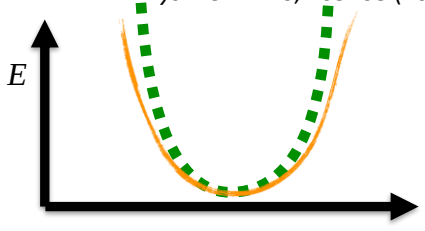
Part II

25

Vibronic Coupling 101

Traditional Perturbation Theory

P. B. Allen and V. Heine, *J. Phys. C* **9**, 2305 (1976).
F. Giustino, M. L. Cohen, and S. G. Louie, *Phys. Rev. B* **76**, 165108 (2007).



Harmonic Approximation for the PES

26

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F. Giustino, M. L. Cohen, and S. G. Louie,
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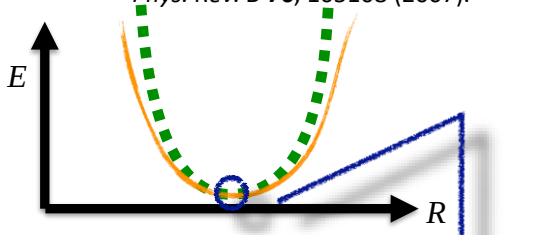

***Harmonic* Approximation for the PES**

Equilibrium wavefunction $\Psi_{n\mathbf{k}}^{\mathrm{eq}}(\mathbf{R}^{\mathrm{eq}})$

27

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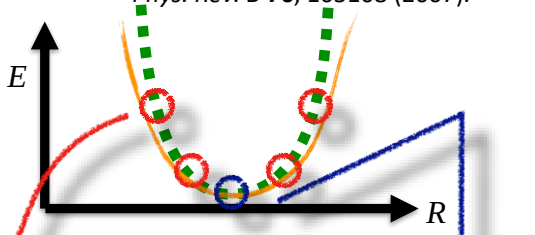

***Harmonic* Approximation for the PES**

Equilibrium wavefunction $\Psi_{n\mathbf{k}}^{\mathrm{eq}}(\mathbf{R}^{\mathrm{eq}})$

Perturbation Theory

$$\Psi_{n\mathbf{k}}(\mathbf{R}) \approx \Psi_{n\mathbf{k}}^{\mathrm{pt}}(\Delta\mathbf{R}) = \Psi_{n\mathbf{k}}^{\mathrm{eq}} + \sum_{l,\mathbf{k}'} \Delta\mathbf{R}\, C_{nl}^{\mathbf{k}\mathbf{k}'}\Big|_{\mathbf{R}^{\mathrm{eq}}} \cdot \Psi_{l\mathbf{k}'}^{\mathrm{eq}}$$

How to overcome this approximation?

28

Vibronic Coupling 101

Traditional Perturbation Theory

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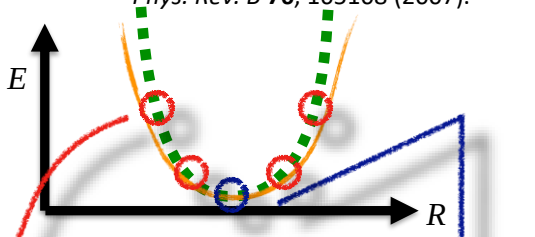


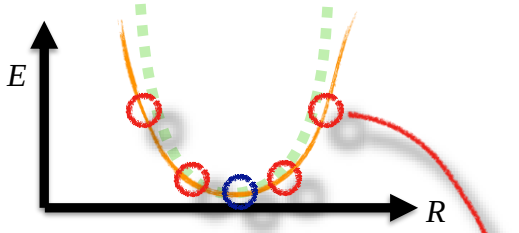
Harmonic Approximation for the PES

Equilibrium wavefunction $\Psi^{\mathrm{eq}}_{n\mathbf{k}}(\mathbf{R}^{\mathrm{eq}})$

Perturbation Theory

$$\Psi_{n\mathbf{k}}(\mathbf{R}) \approx \Psi^{\mathrm{pt}}_{n\mathbf{k}}(\Delta\mathbf{R}) = \Psi^{\mathrm{eq}}_{n\mathbf{k}} + \sum_{l,\mathbf{k}'} \Delta\mathbf{R}\, C^{\mathbf{k}\mathbf{k}'}_{nl}\Big|_{\mathbf{R}^{\mathrm{eq}}} \cdot \Psi^{\mathrm{eq}}_{l\mathbf{k}'}$$

This Work:
Non-Perturbative Theory

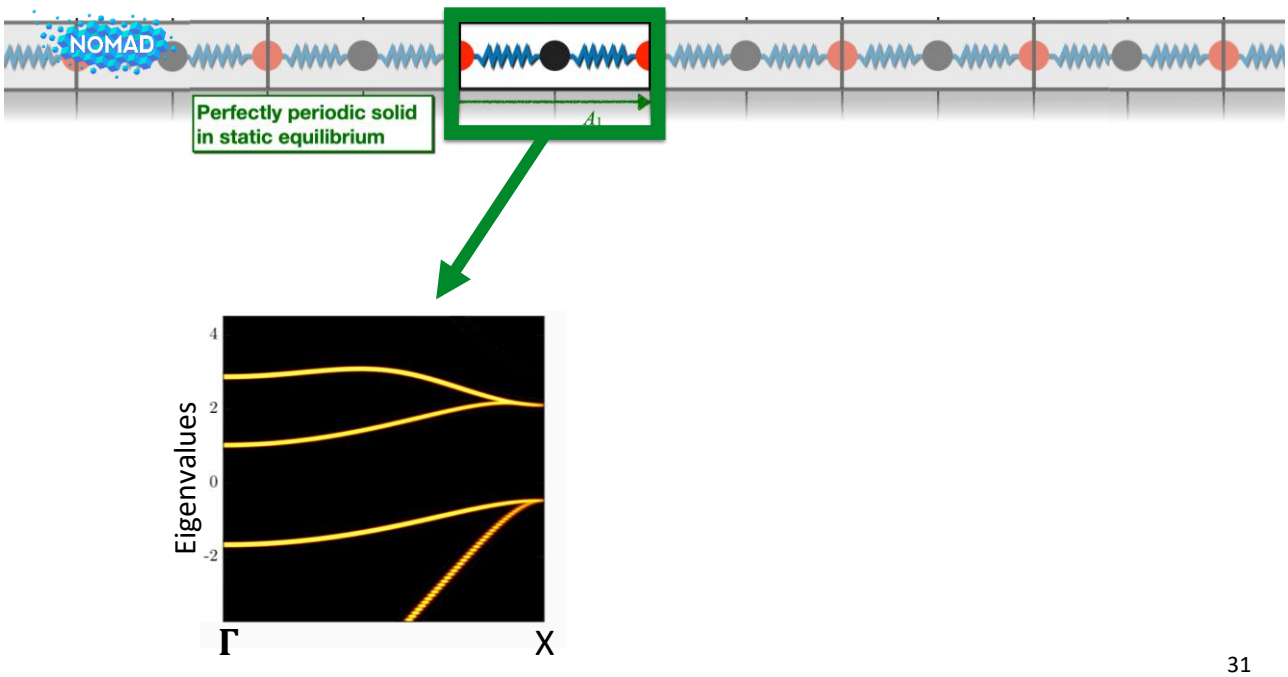


Fully anharmonic PES by ab initio Molecular Dynamics

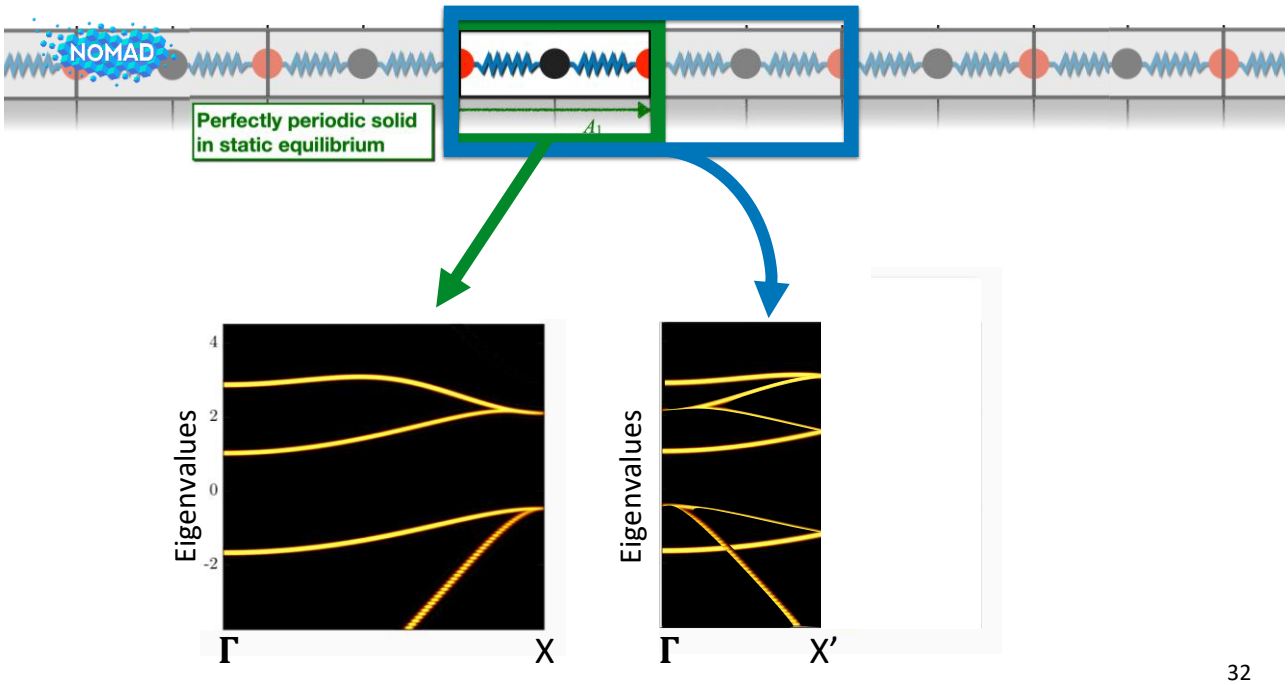
Self-Consistent Wavefunctions:

$$\Psi_{n\mathbf{k}}(\mathbf{R}) = \Psi_{n\mathbf{k}}(\mathbf{R}) = \sum_{l,\mathbf{k}'} \alpha^{\mathbf{k}\mathbf{k}'}_{nl}(\mathbf{R})\, \Psi^{\mathrm{eq}}_{l\mathbf{k}'}$$

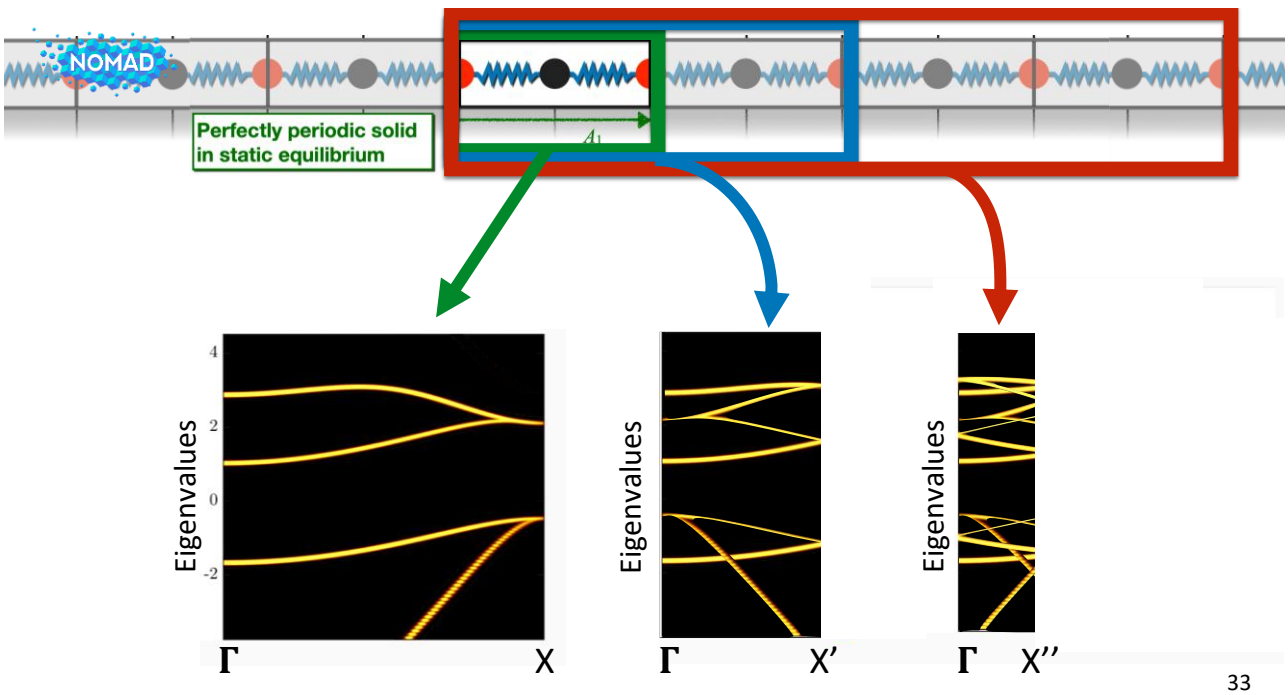
30



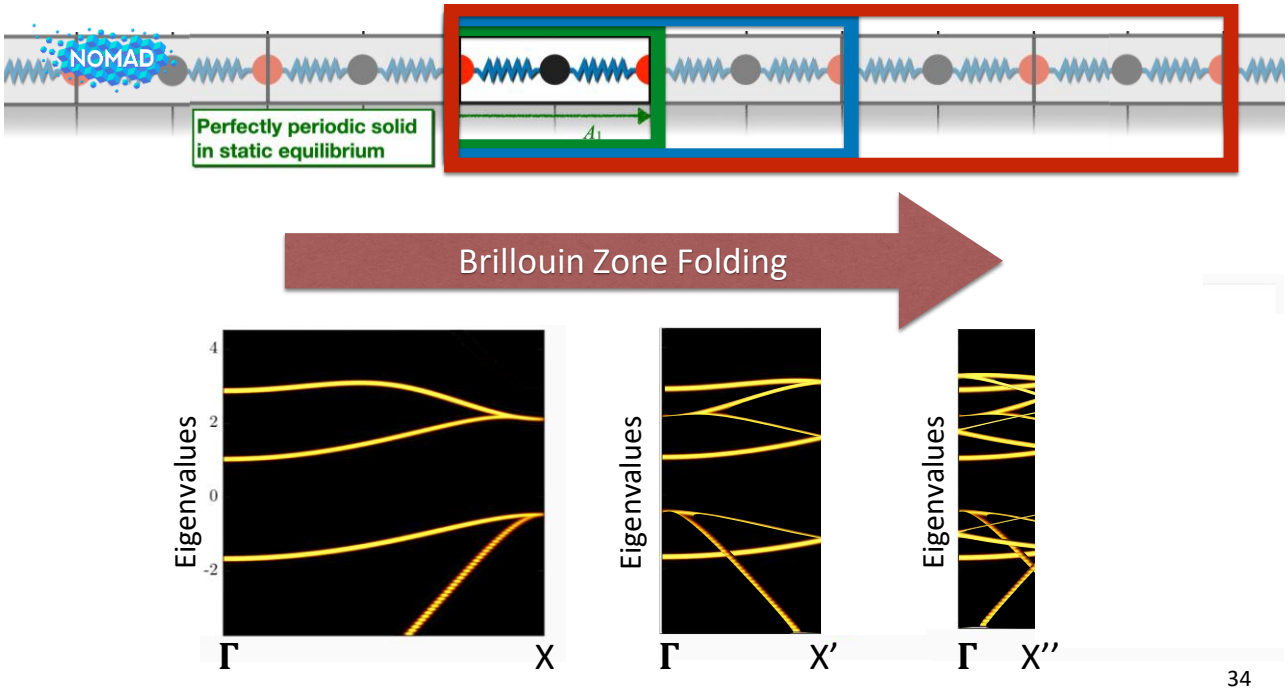
31


NOMAD
Perfectly periodic solid in static equilibrium
A_1
Eigenvalues
4
2
0
-2
Γ
X
Eigenvalues
Γ
X'

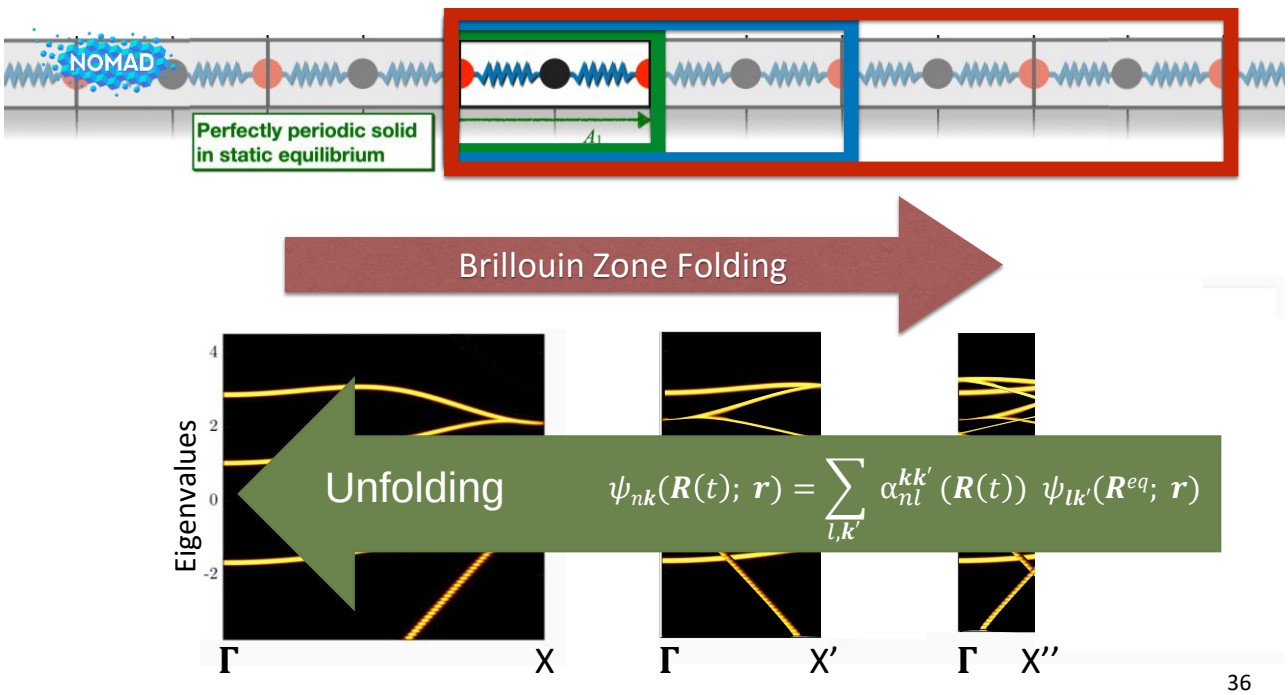
32


NOMAD
Perfectly periodic solid in static equilibrium
A_1
Eigenvalues
4
2
0
-2
Γ
X
Eigenvalues
Γ
X'
Eigenvalues
Γ
X''

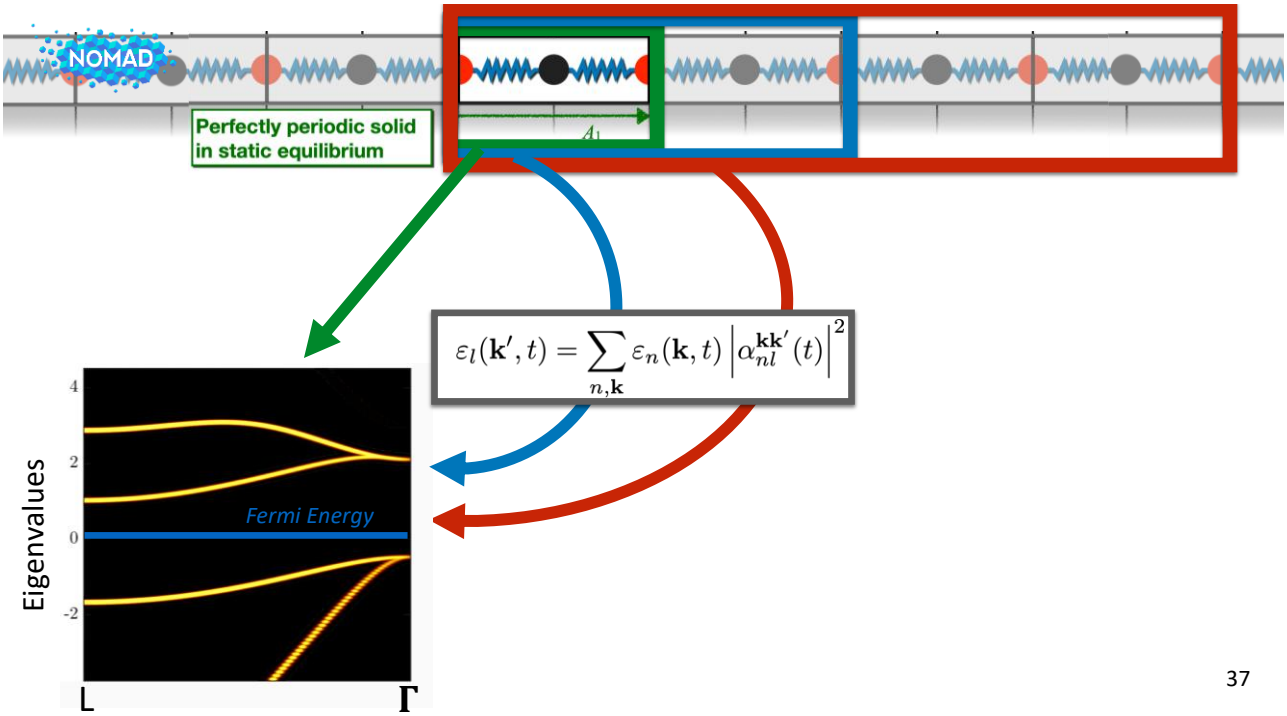
33


NOMAD
Perfectly periodic solid in static equilibrium
A_1
Brillouin Zone Folding
Eigenvalues
4
2
0
-2
Γ
X
Eigenvalues
Γ
X'
Eigenvalues
Γ
X''

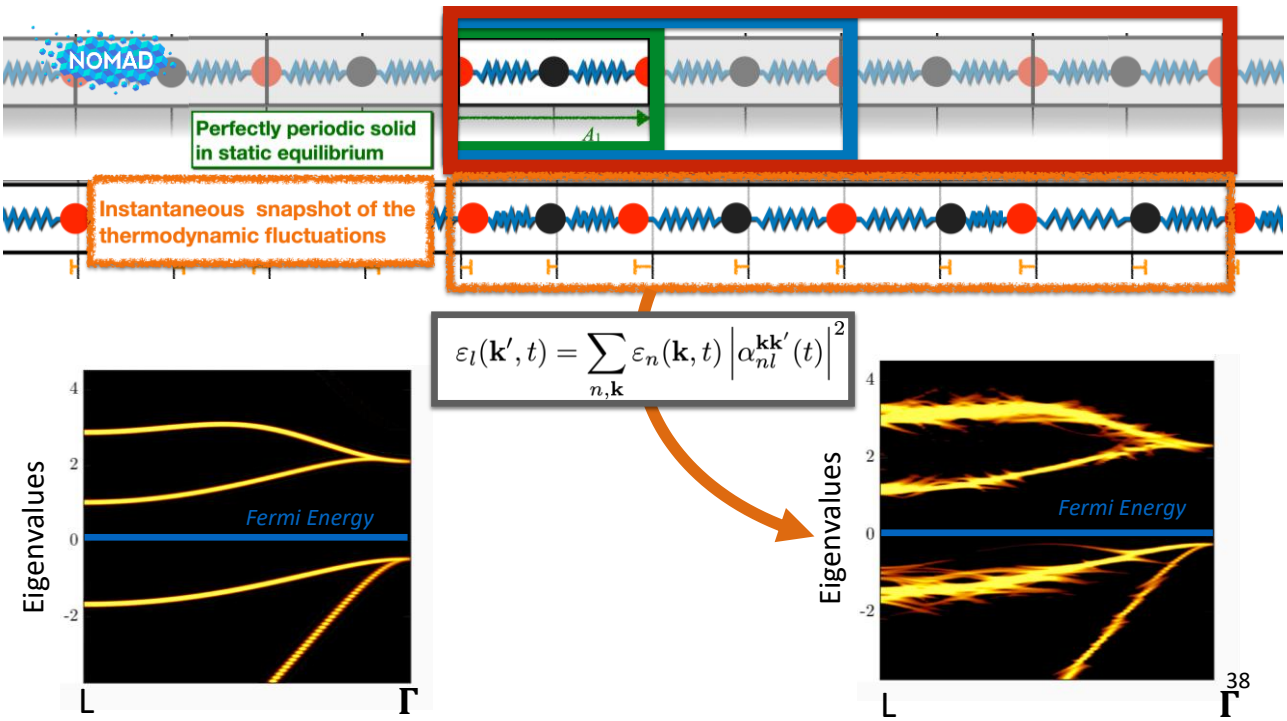
34


NOMAD
Perfectly periodic solid in static equilibrium
A_1
Brillouin Zone Folding
Eigenvalues
4
2
0
-2
Γ
X
Γ
X'
Γ
X''
Unfolding
$\psi_{nk}(\boldsymbol{R}(t);\, \boldsymbol{r}) = \sum_{l,k'} \alpha_{nl}^{kk'}\,(\boldsymbol{R}(t))\;\psi_{lk'}(\boldsymbol{R}^{eq};\, \boldsymbol{r})$

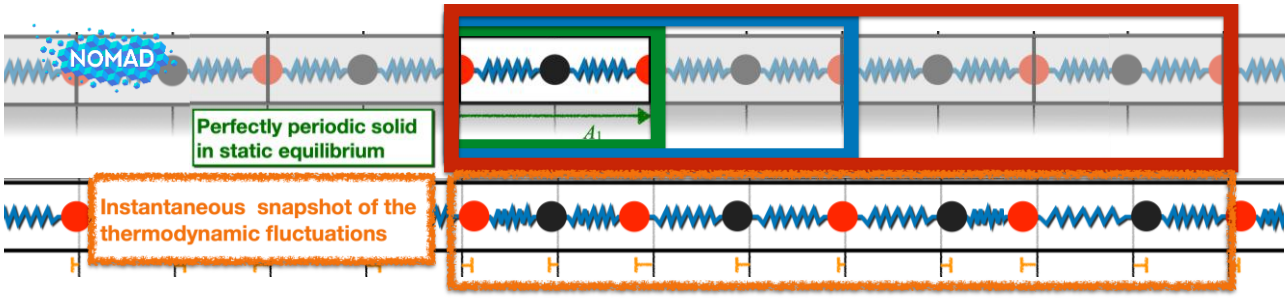
36


NOMAD
Perfectly periodic solid in static equilibrium
A_1
$\varepsilon_l(\mathbf{k}',t) = \sum_{n,\mathbf{k}} \varepsilon_n(\mathbf{k},t) \left|\alpha_{nl}^{\mathbf{k}\mathbf{k}'}(t)\right|^2$
Eigenvalues
4
2
0
-2
Fermi Energy
L
Γ

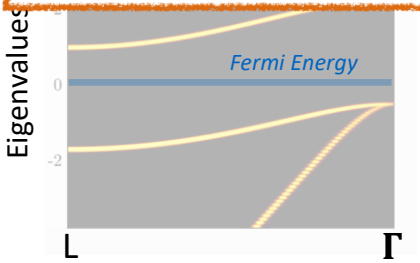
37

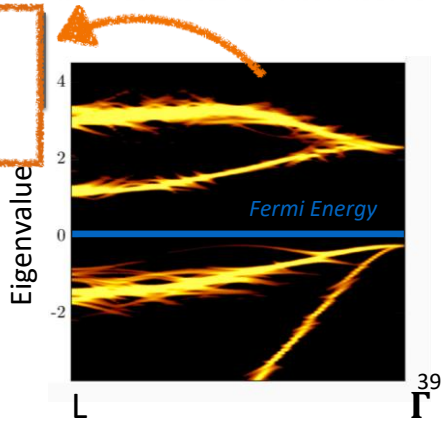

NOMAD
Perfectly periodic solid in static equilibrium
A_1
Instantaneous snapshot of the thermodynamic fluctuations
$\varepsilon_l(\mathbf{k}',t) = \sum_{n,\mathbf{k}} \varepsilon_n(\mathbf{k},t) \left|\alpha_{nl}^{\mathbf{k}\mathbf{k}'}(t)\right|^2$
Eigenvalues
4
2
0
-2
Fermi Energy
L
Γ
Eigenvalues
4
2
0
-2
Fermi Energy
L
Γ

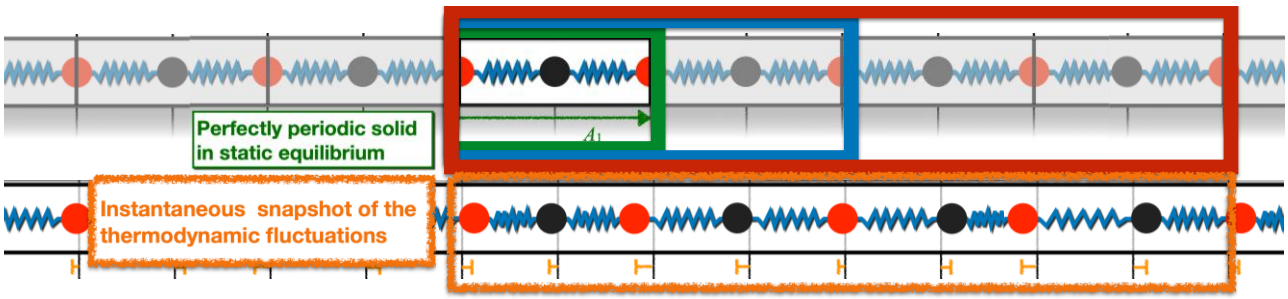
38



This is the ***electronic self-energy*** *renormalised by* ***vibronic coupling*** *for* ***one configuration****!*



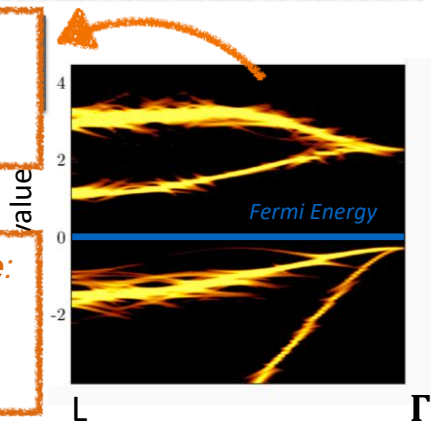




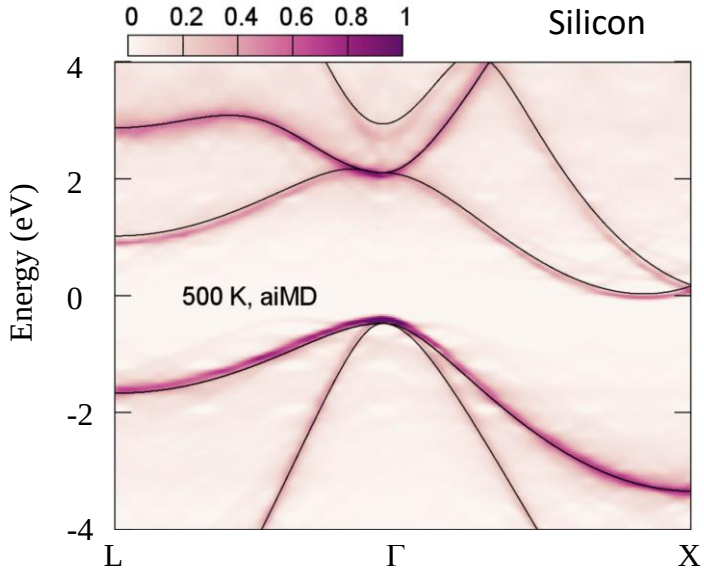
This is the ***electronic self-energy*** *renormalised by* ***vibronic coupling*** *for* ***one configuration****!*

Thermodynamic *average gives* ***expectation value****:*

$$\langle \varepsilon_l(\mathbf{k}') \rangle_T^{\mathrm{MD}} = \frac{1}{t_0} \int_0^{t_0} \varepsilon_l(\mathbf{k}', t)\, dt \ .$$



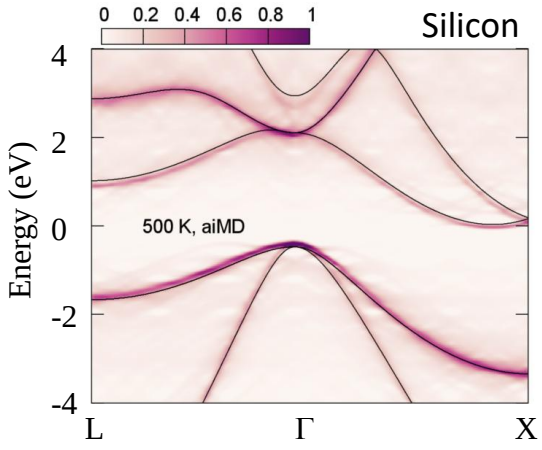
A Real Example: Si

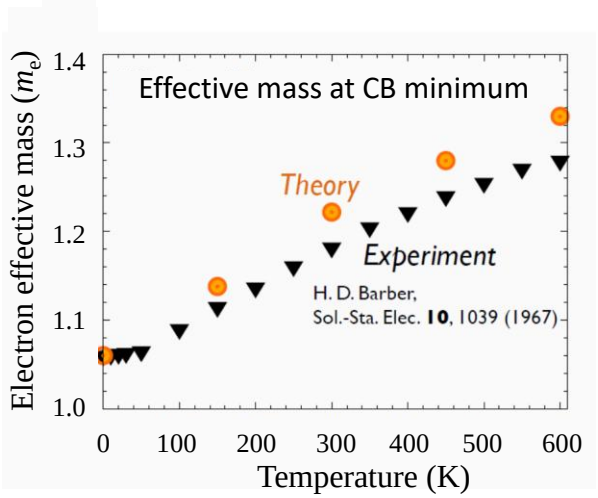


Changes of

- band gap
- effective masses
- width of the levels (life-time; e-vib component)

Lattice Vibrations And The Electronic Band Structure





KUBO-GREENWOOD FORMALISM

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

Kubo's Linear Response:

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

We are interested in the $\omega \to 0$ limit!

Independent Particle Picture:

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

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

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

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KUBO-GREENWOOD FORMALISM

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

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

Challenges:

J. Quan, C. Carbogno, and M. Scheffler, *Phys. Rev. B 110, 235202 (2024).*

— **Extremely dense k-grids needed to resolve $\omega \to 0$ limit**

$\Longrightarrow$ solved via *Fourier* Interpolation

— **Large supercell needed to resolve anharmonic vibrations**

$\Longrightarrow$ requires *extrapolation* to **bulk limit**

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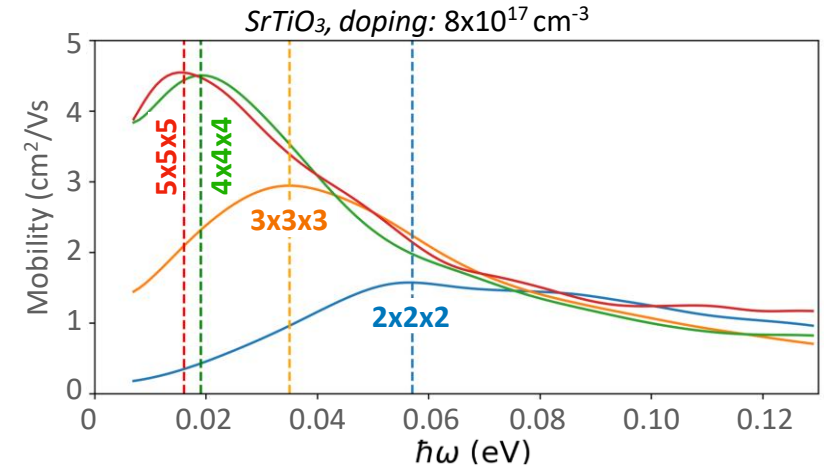
SUPERCELL CONVERGENCE

J. Quan, C. Carbogno, and M. Scheffler, Phys. Rev. B 110, 235202 (2024)

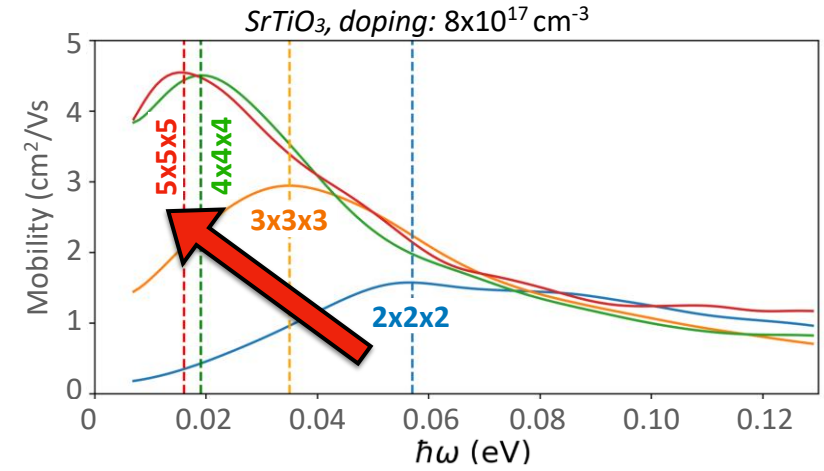


$$\mu = \frac{\sigma}{nq}$$

45

SUPERCELL CONVERGENCE

J. Quan, C. Carbogno, and M. Scheffler, Phys. Rev. B 110, 235202 (2024)

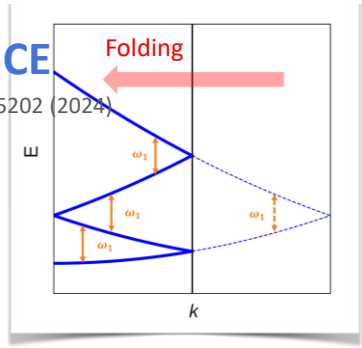


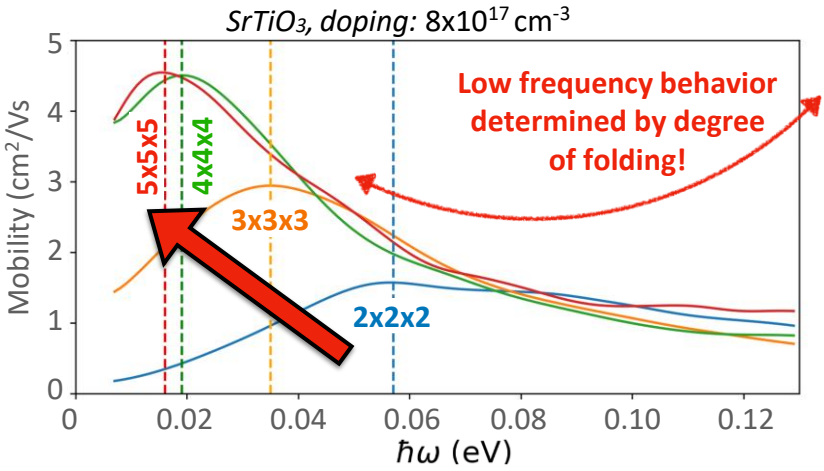
$$\mu = \frac{\sigma}{nq}$$

46

SUPERCELL CONVERGENCE

J. Quan, C. Carbogno, and M. Scheffler, Phys. Rev. B 110, 235202 (2024)



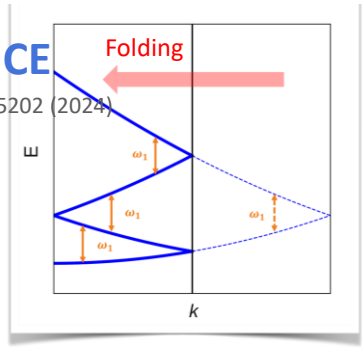


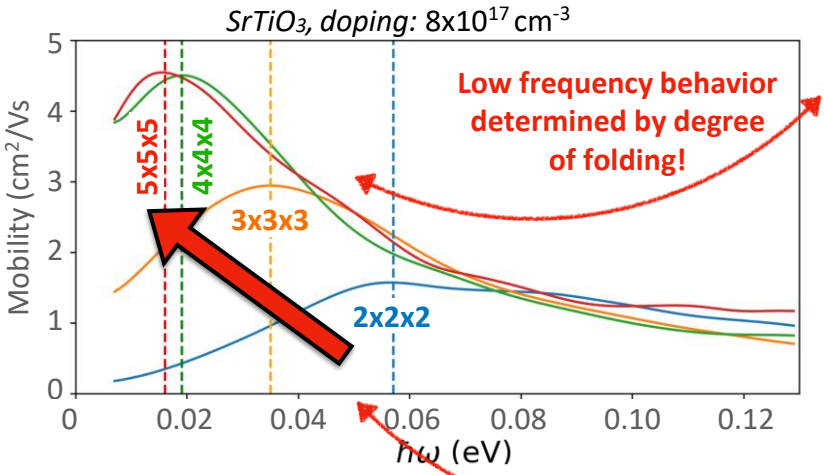
$$\mu = \frac{\sigma}{nq}$$

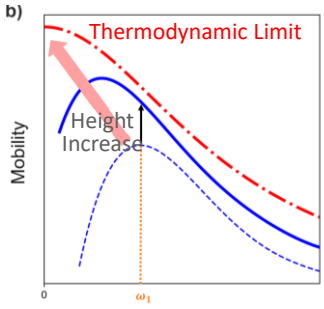
47

SUPERCELL CONVERGENCE

J. Quan, C. Carbogno, and M. Scheffler, Phys. Rev. B 110, 235202 (2024)







$$\mu = \frac{\sigma}{nq}$$

Extrapolation to bulk limit by *Drude function* fit!

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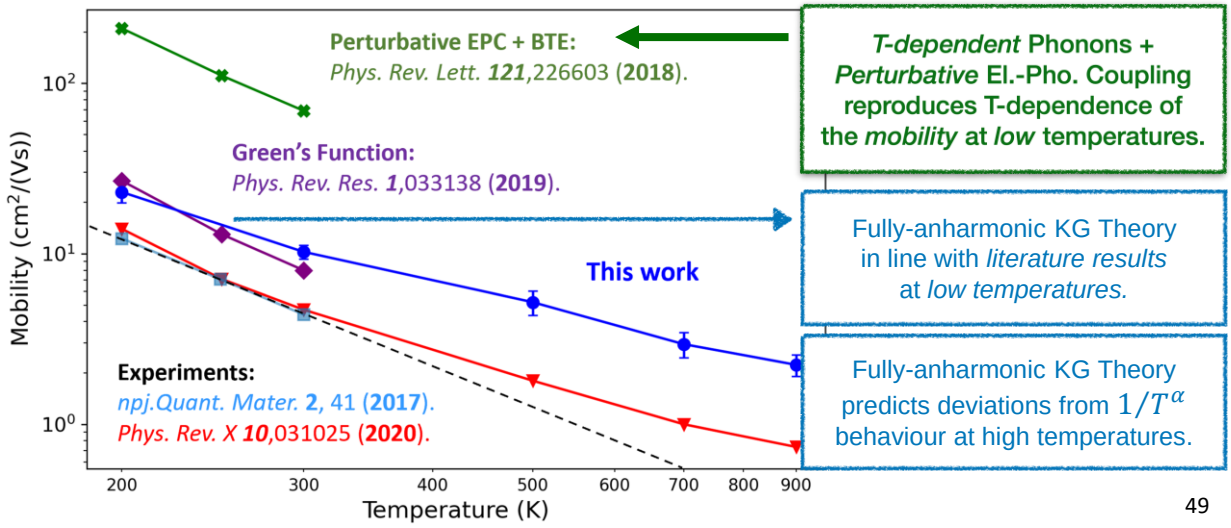
Mobility in Highly Anharmonic $SrTiO_3$

Doping: 8×10^{17} cm^{-3}

J. Quan, C. Carbogno, and M. Scheffler, Phys. Rev. B 110, 235202 (2024)



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Summary … Strongly Anharmonic Materials

- **Green-Kubo** calculations of the ***thermal conductivity*** with efficient extrapolation to the needed time and length scales (*i)* in q-space or *ii)* via neural network machine-learned interatomic potenials (MLIPs).
- Creating ***maps of thermal conductivity***, identify regions of interest, and efficiently zoom in via sensitivity analysis and active learning.
- Identification of materials with ***ultra-low thermal conductivity*** (< 1 W/mK).
- Band-structure based electrical conductivity by the ***Kubo-Greenwood*** equation. Computationally very demanding, so far. Speed ups are under development (DeepH by Jong Yu et al.).

THANKS!
Q&A