FHI-aims User and Developer Workshop 2023, Hamburg, Germany

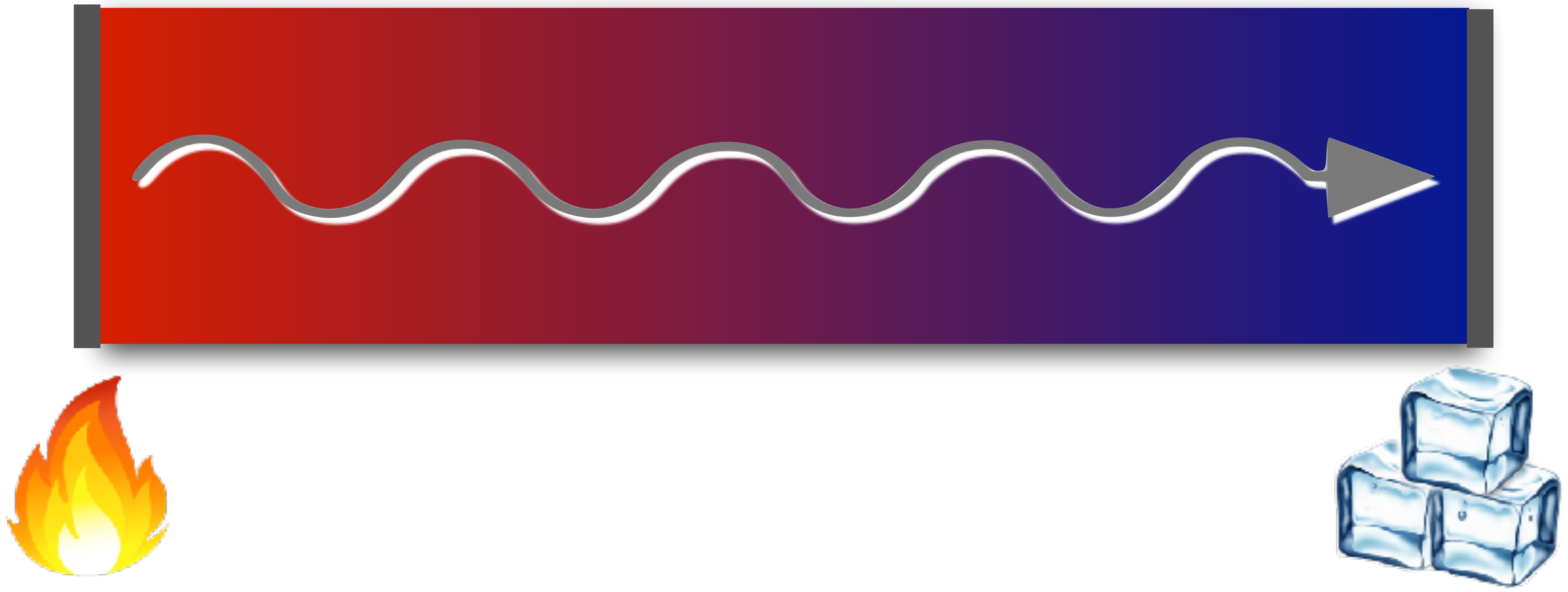
Lessons learned in **Heat and Charge Transport** *over the last couple of years*

Christian Carbogno

FRITZ-HABER-INSTITUT
MAX-PLANCK-GESELLSCHAFT

Heat & Charge Transport in Solids

Heat Flux: Photons, Electrons, and Nuclei



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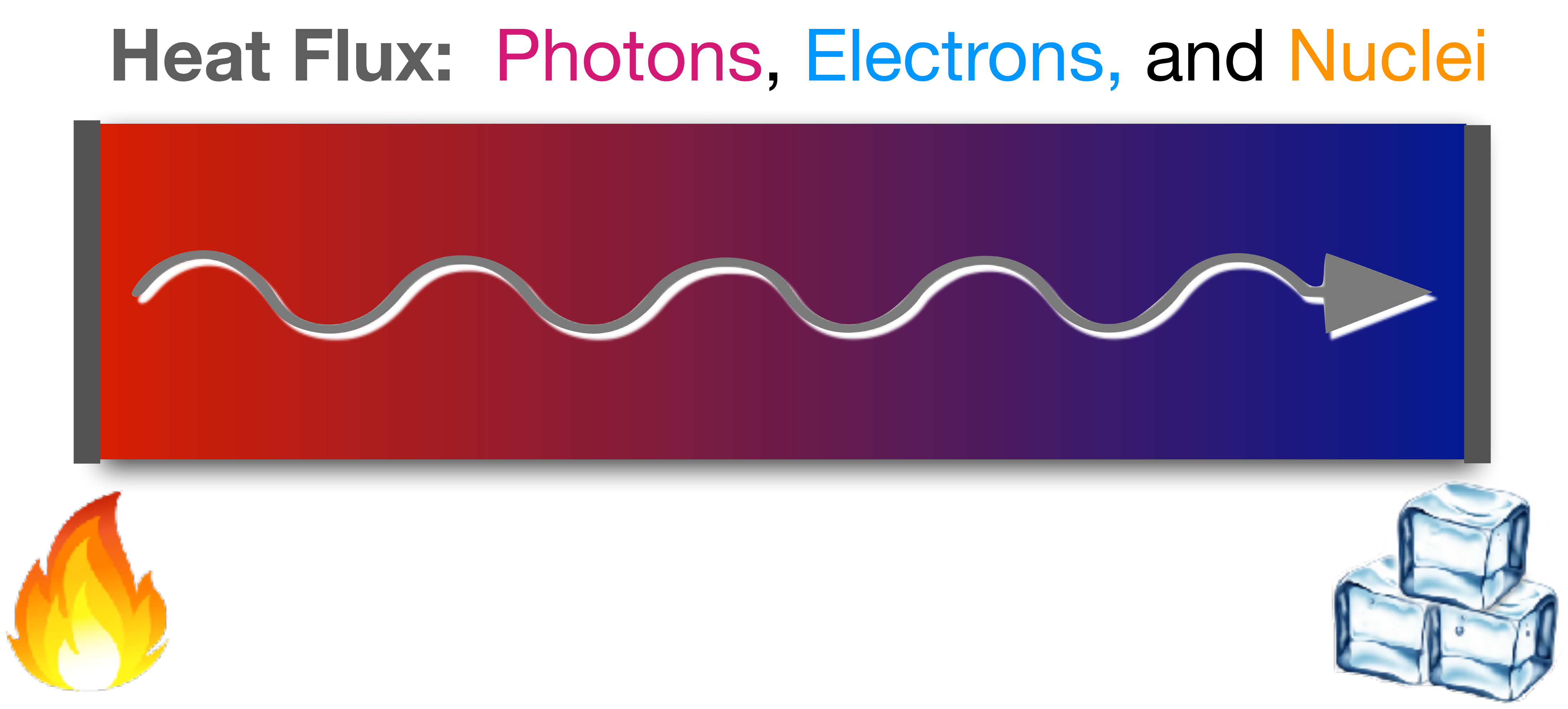

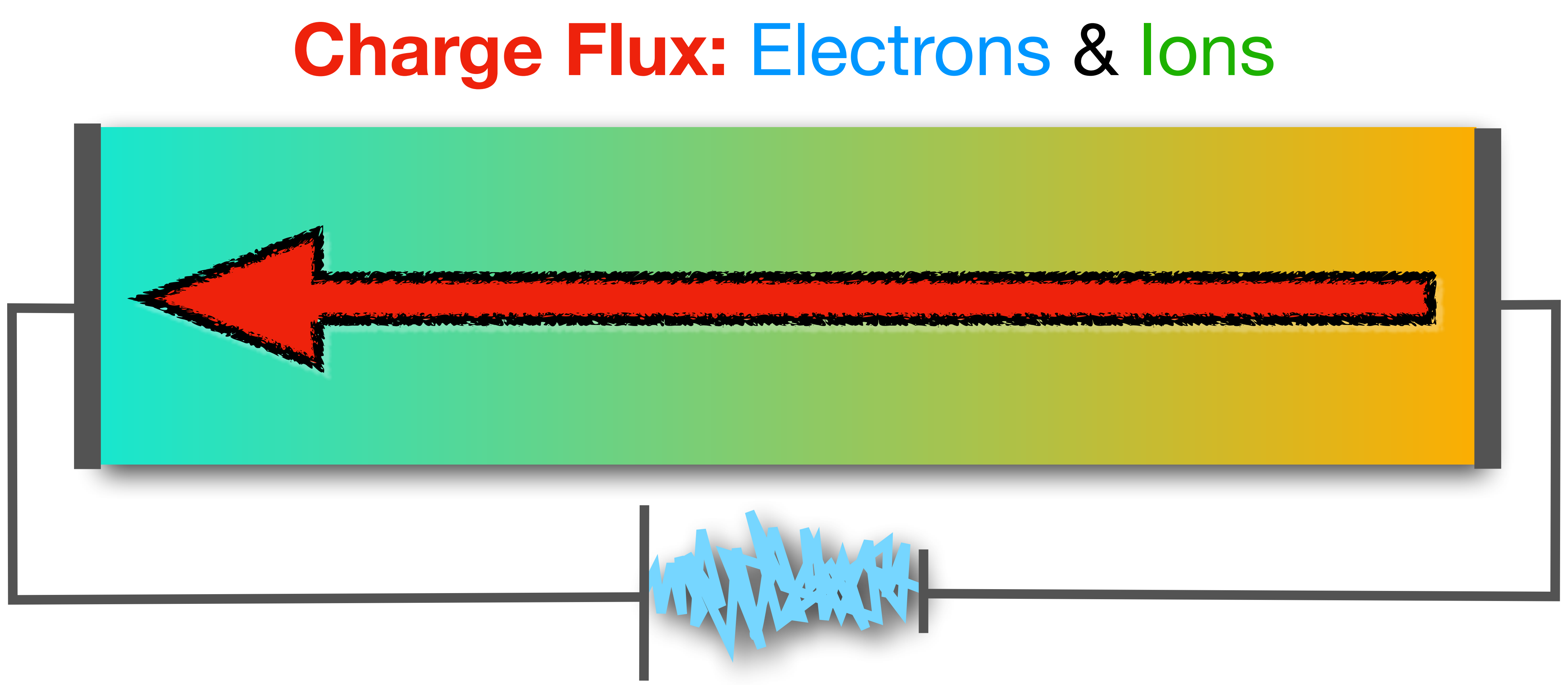

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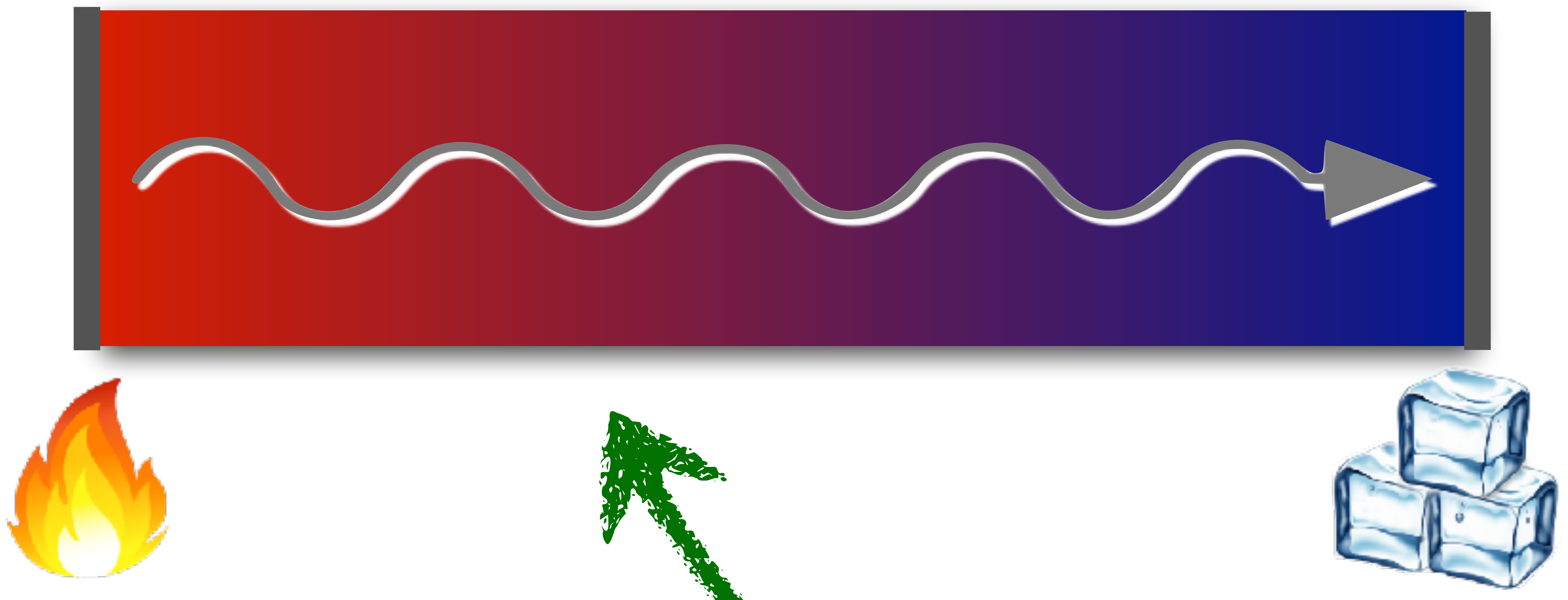
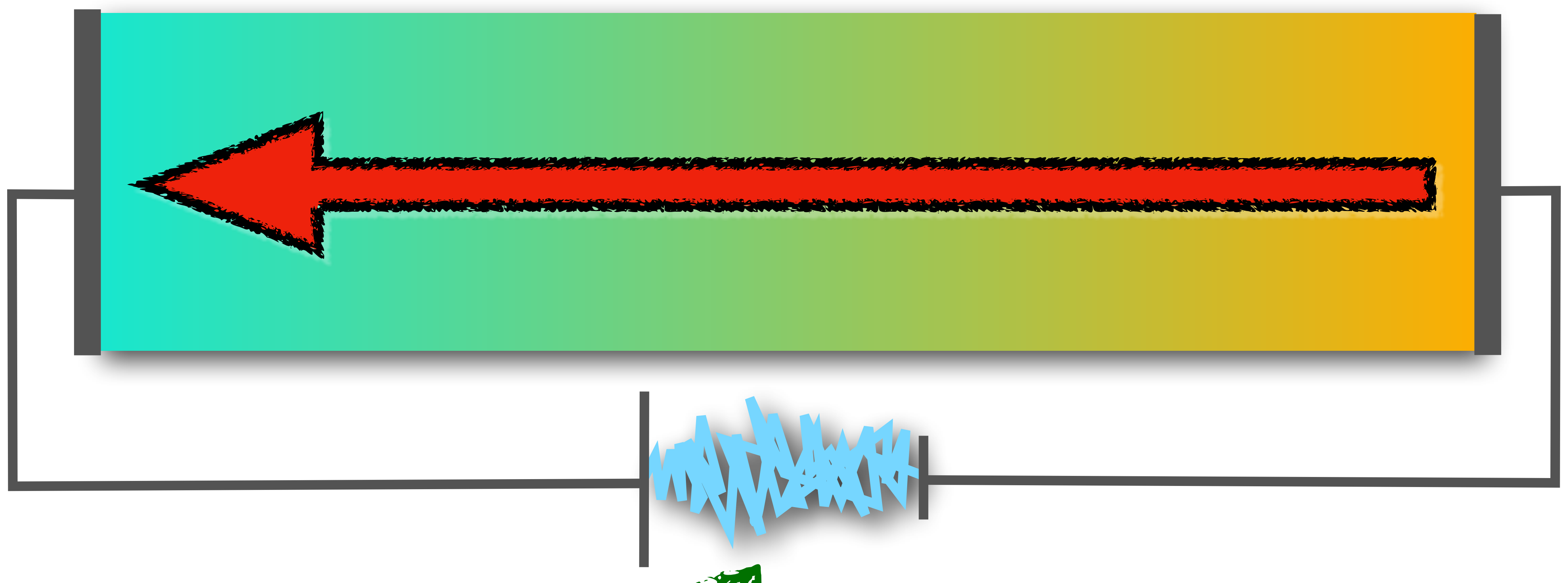


Charge Flux: Electrons & Ions

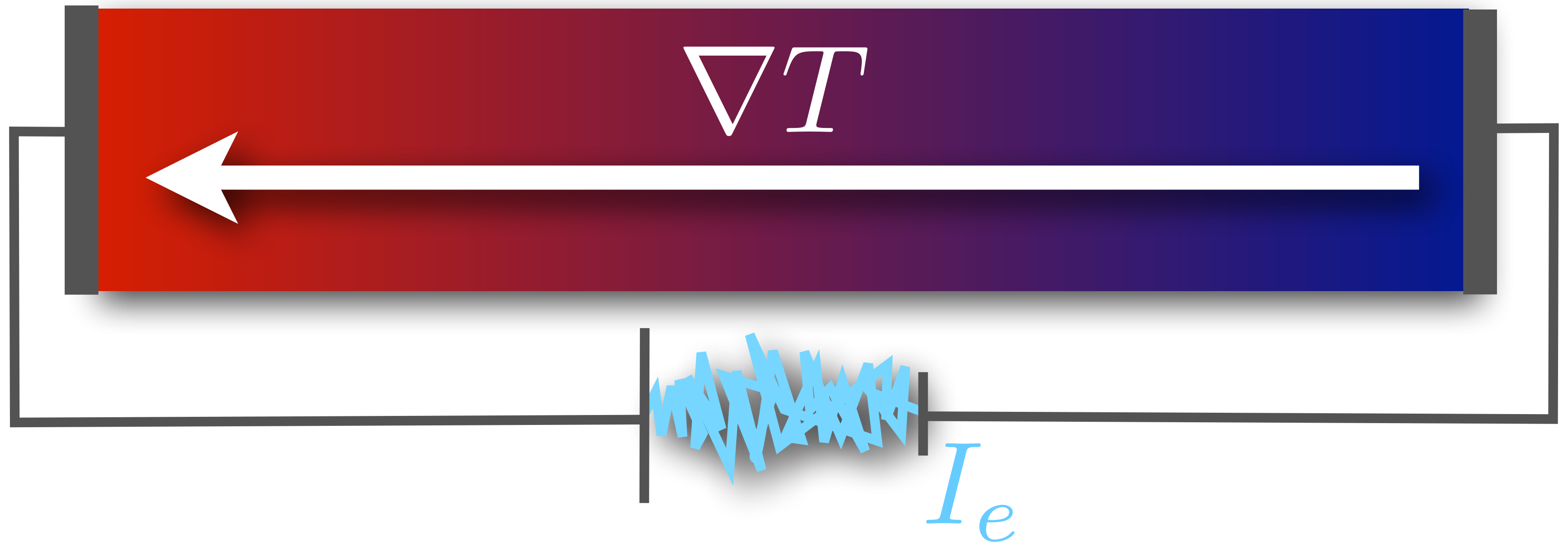


Charge and Heat Flux can couple!

Thermoelectric Materials:

Seebeck Effect: Heat flux induces a Potential Gradient
Peltier Effect: Charge Flux induces a Temperature Gradient

Thermoelectric Materials



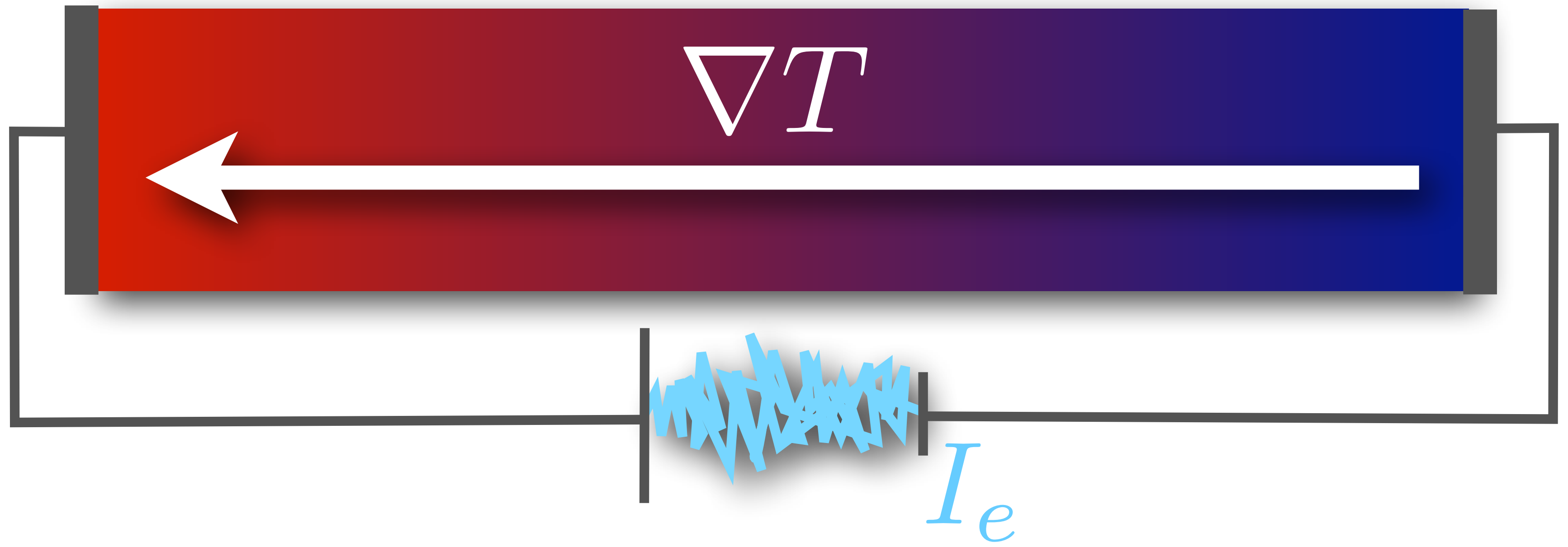
Thermoelectric materials are able to convert **waste-heat** into useful **voltage**.

=> Substantial energy efficiency gains.

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

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

Thermoelectric Materials



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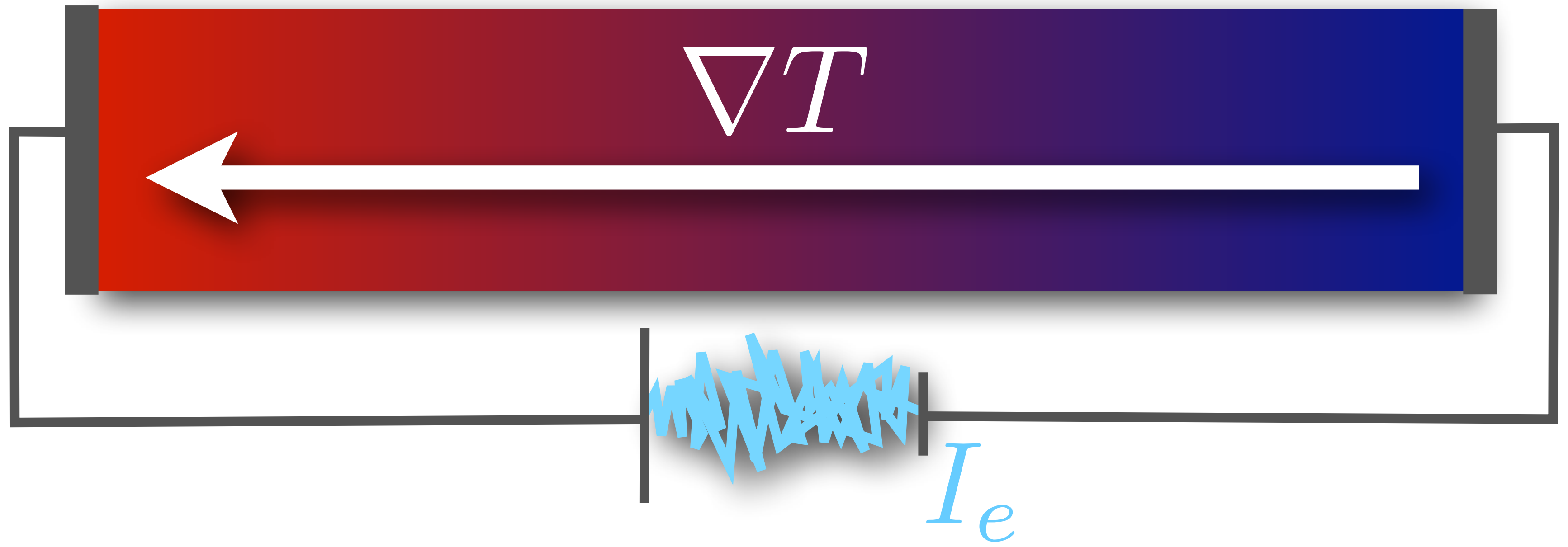

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More **efficient** ***thermoelectric materials*** can **enable** these applications!

Minimize *vibrational* **heat** transport!

Maximize *charge* transport!

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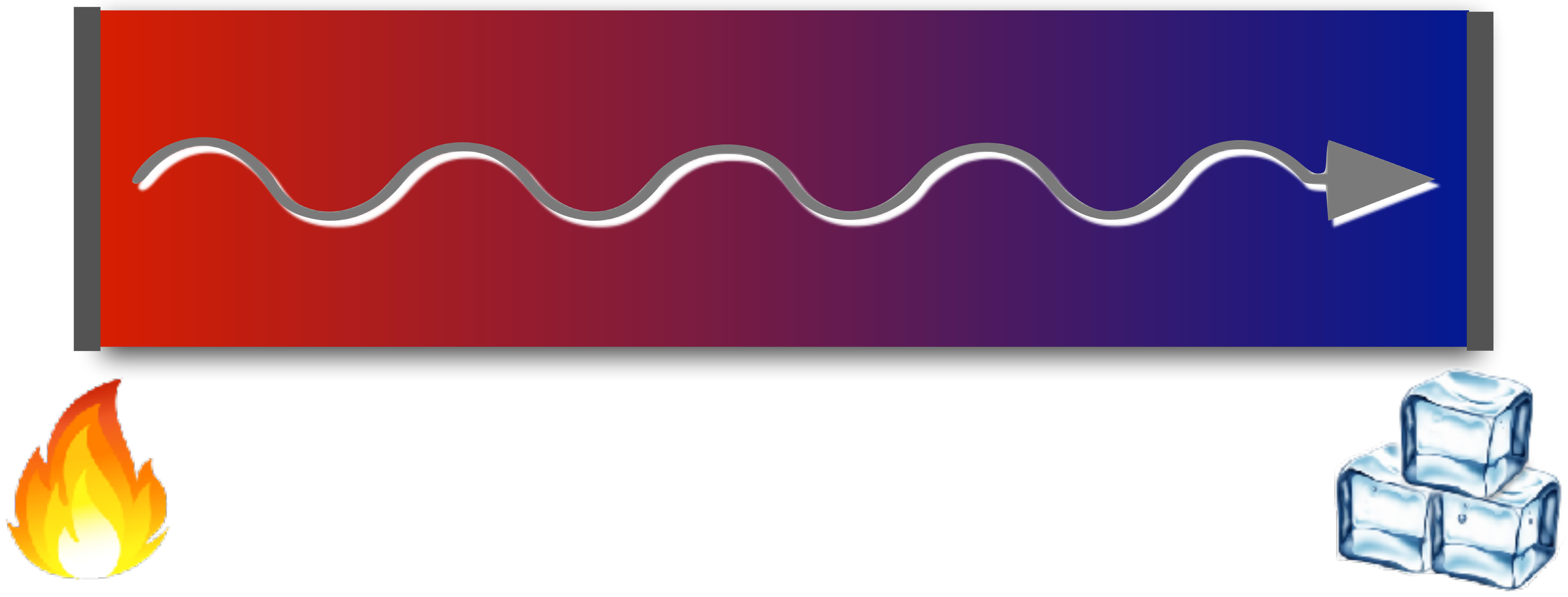

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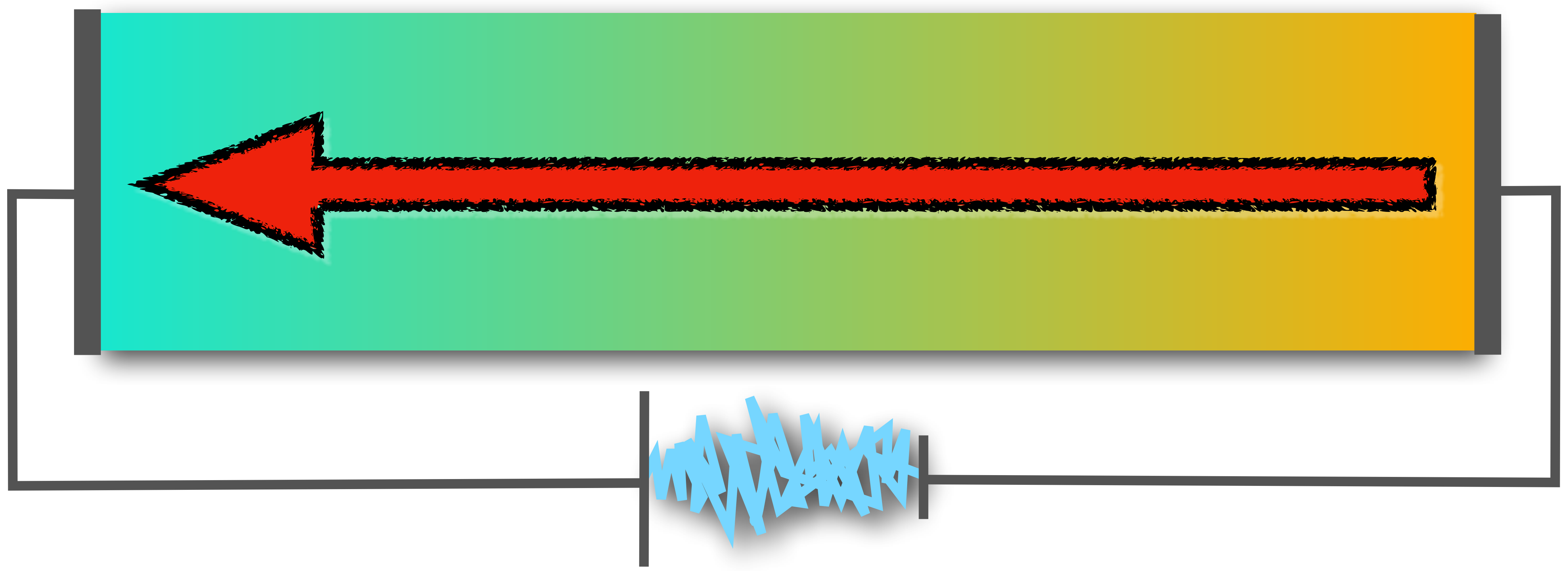
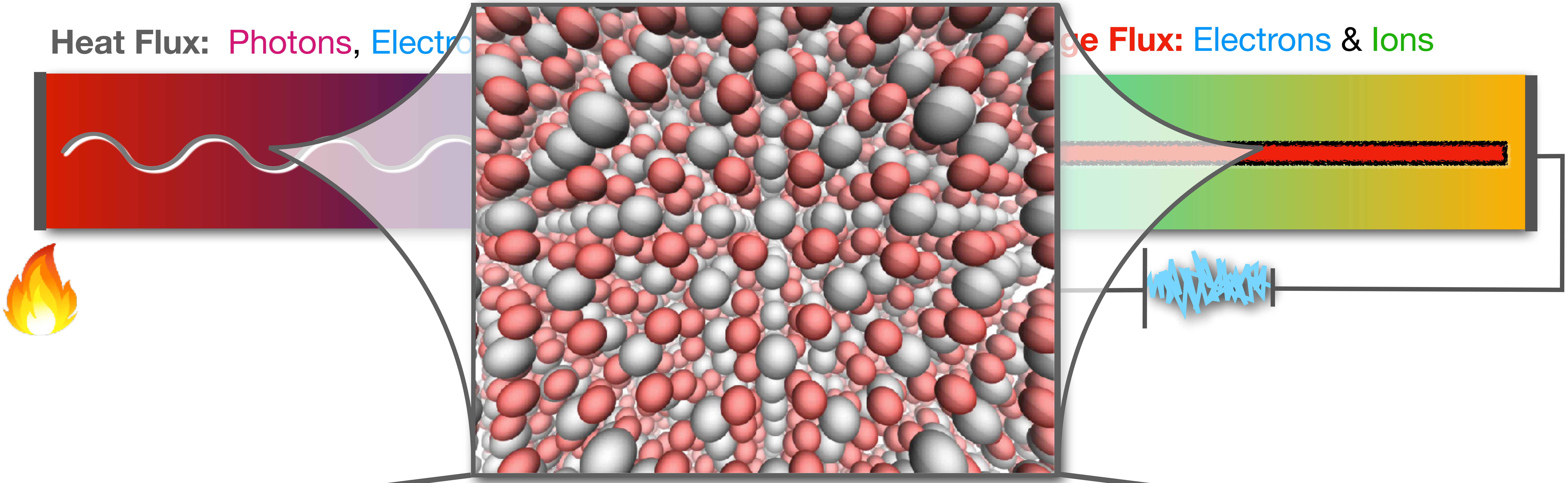


Heat & Charge Transport in Solids



Nuclear Motion causes Dissipation!

Fourier's Law:

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

This Talk:

How can we *accurately* and *predictively* compute, understand, and tailor κ and σ?

Ohm's Law:

$$\mathbf{J}^{\mathrm{c}} = -\sigma \, \nabla U$$

Heat & Charge Transport in Solids

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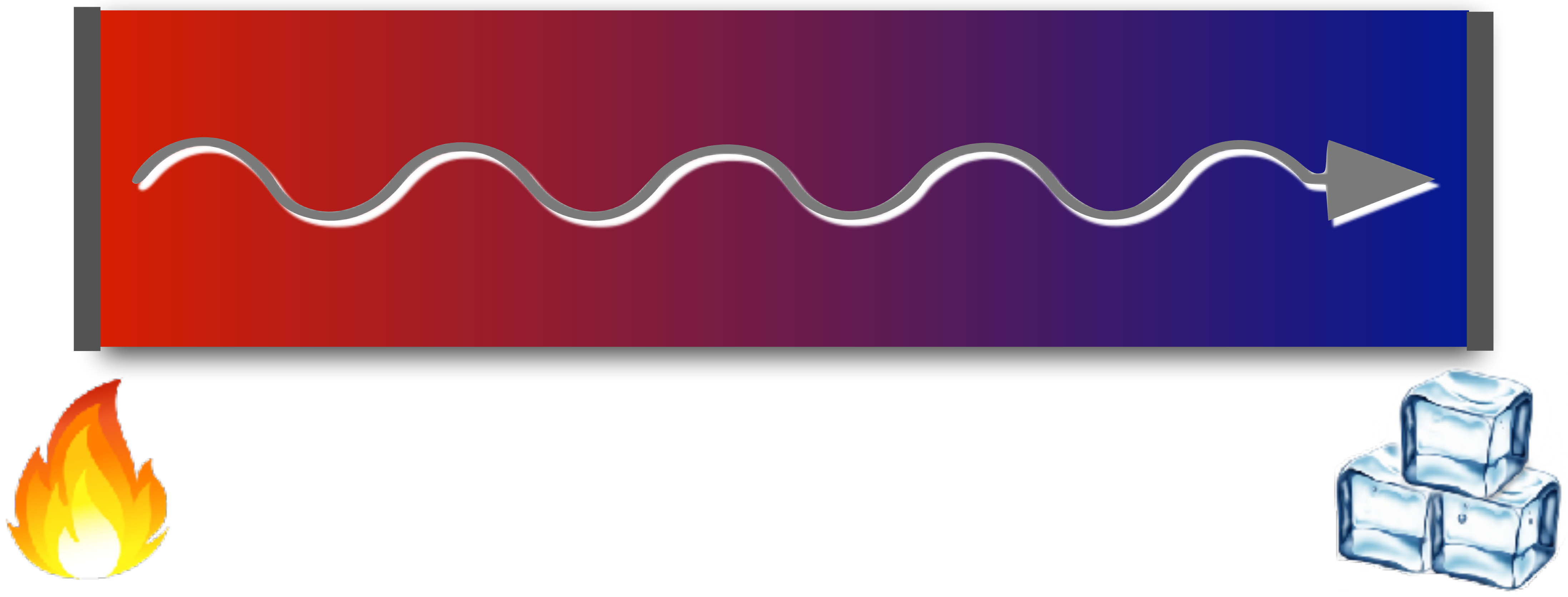

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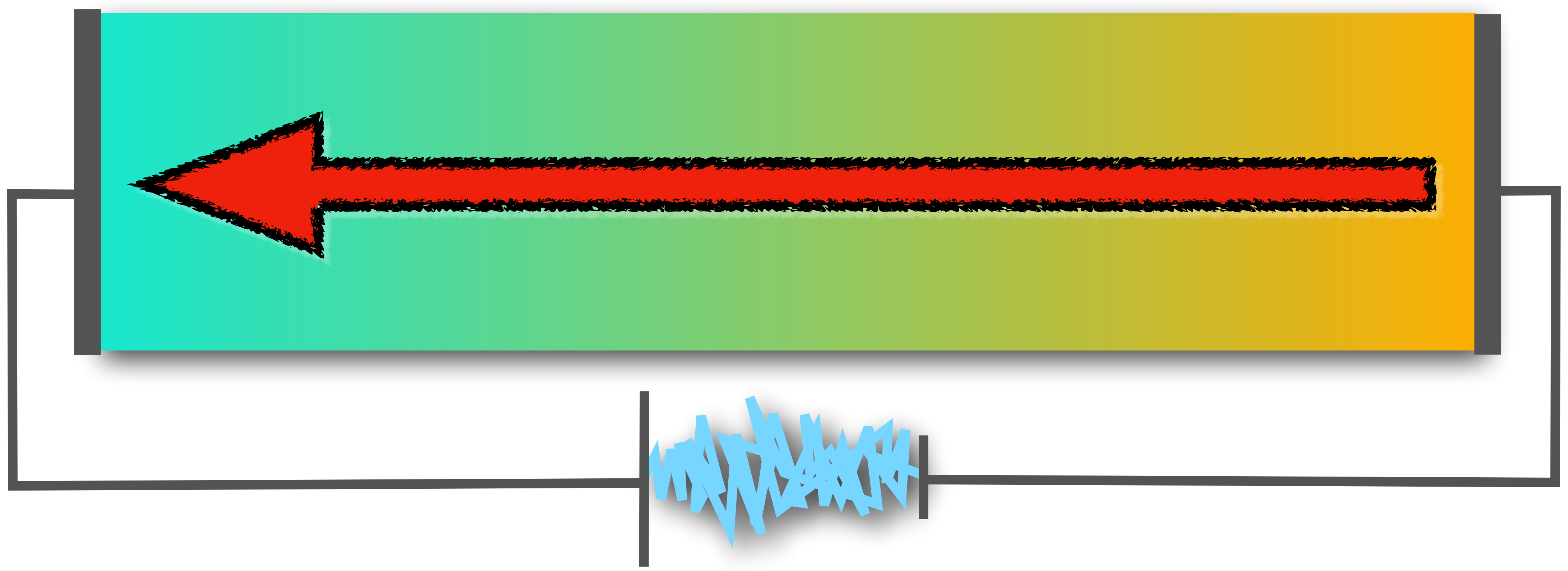

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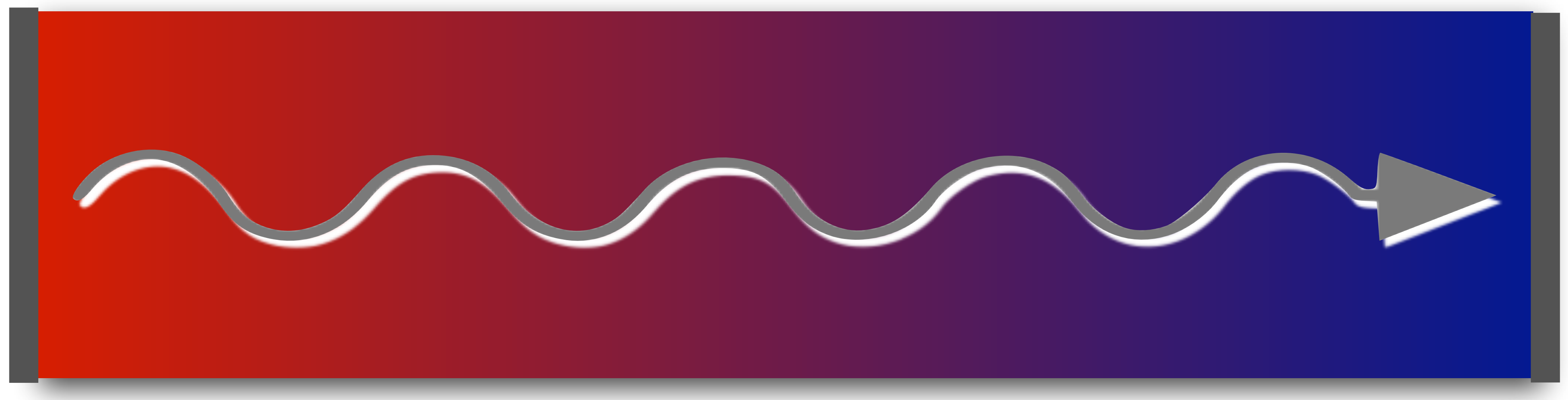

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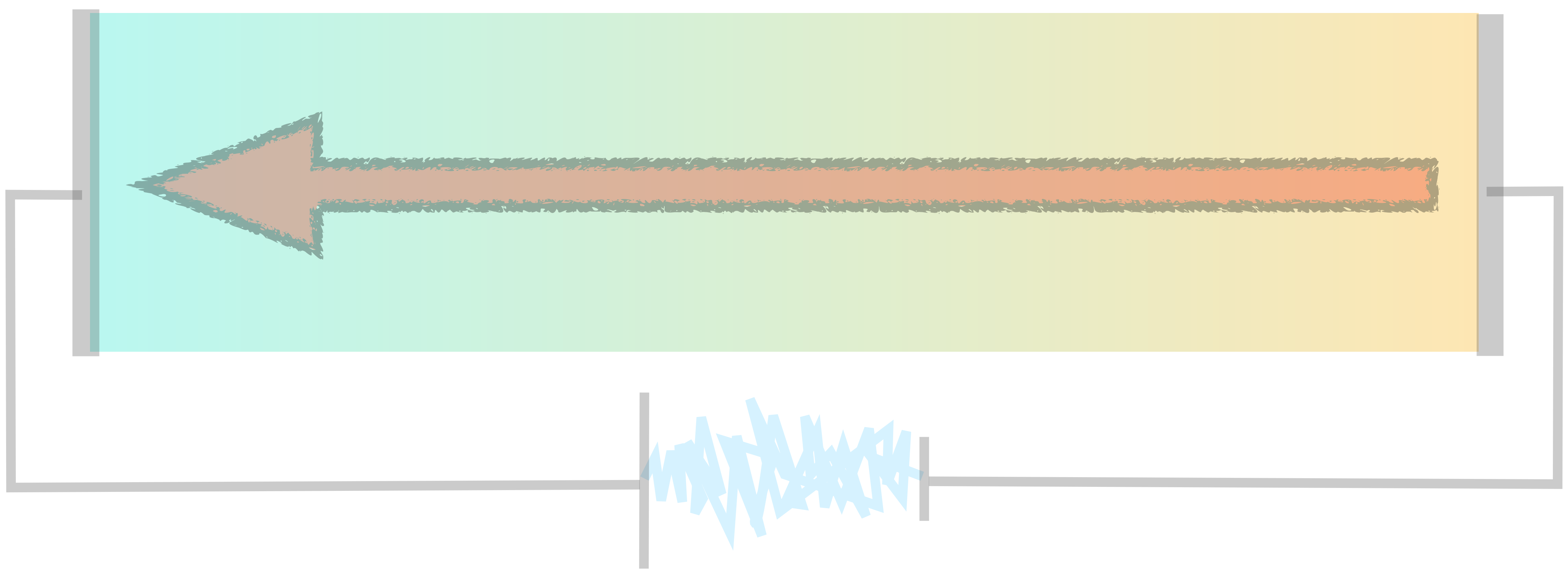
Charge Flux: Electrons & Ions



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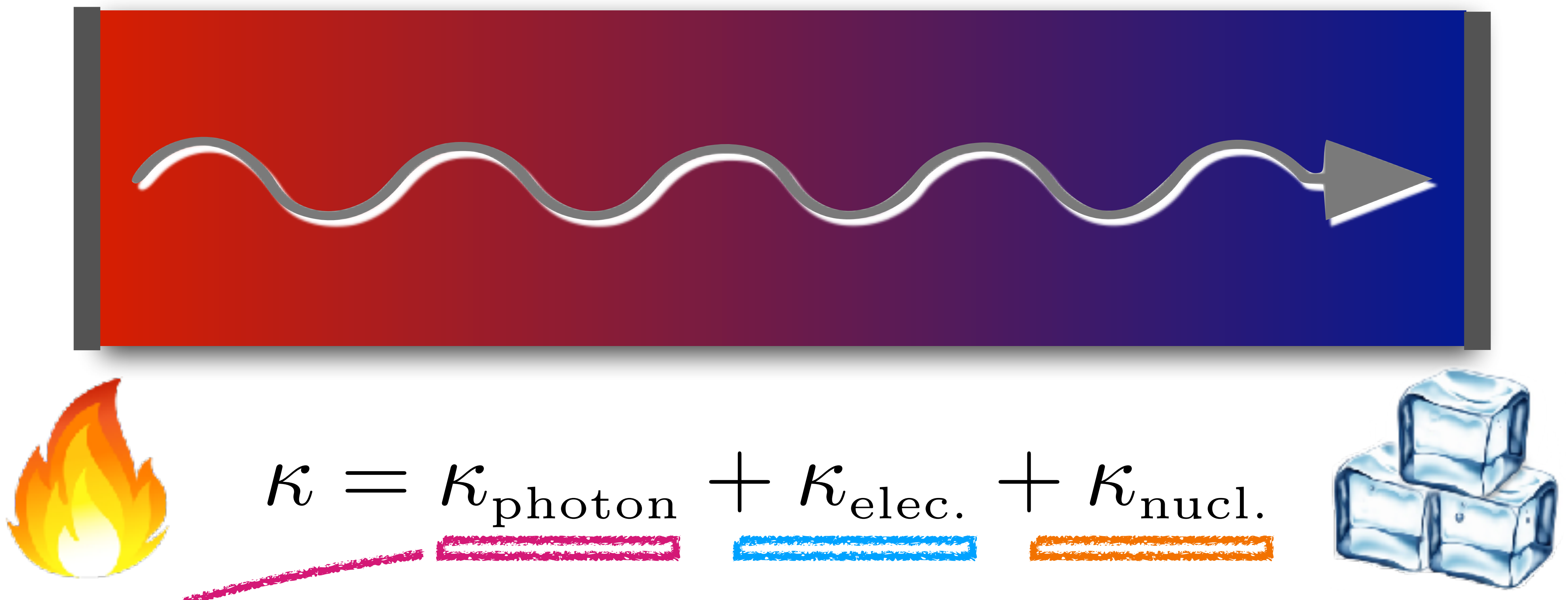

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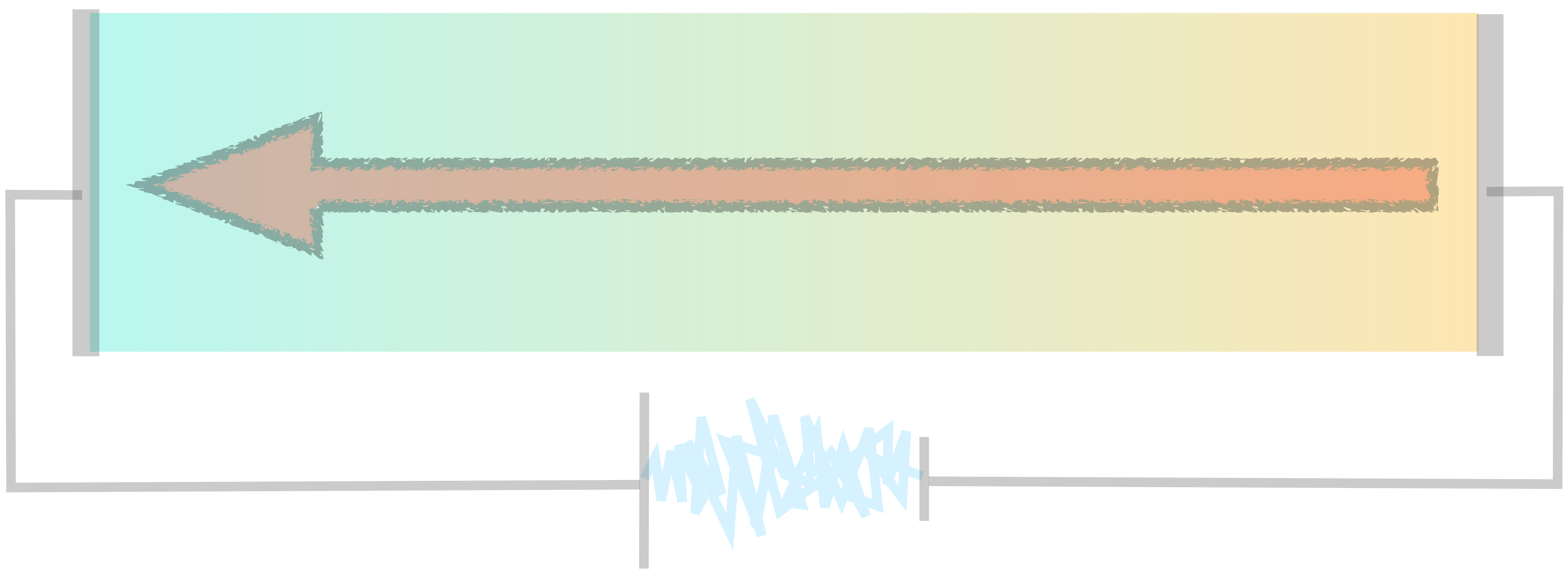
Relevant in **transparent, incandescent** materials!

Charge Flux: Electrons & Ions



Heat & Charge Transport in Solids

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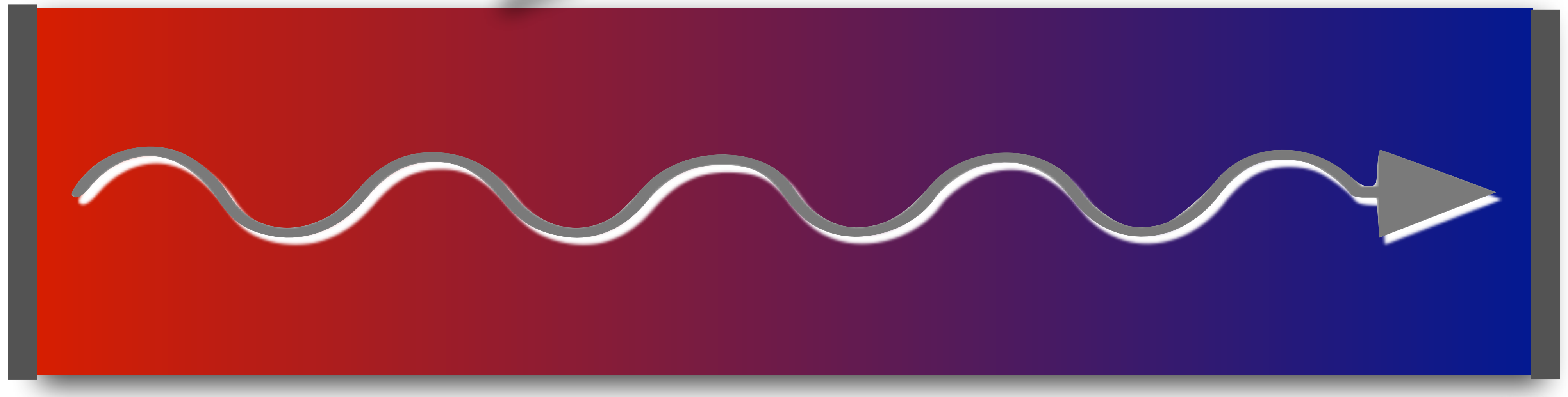

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Relevant in **metals** and **degenerate semiconductors.**

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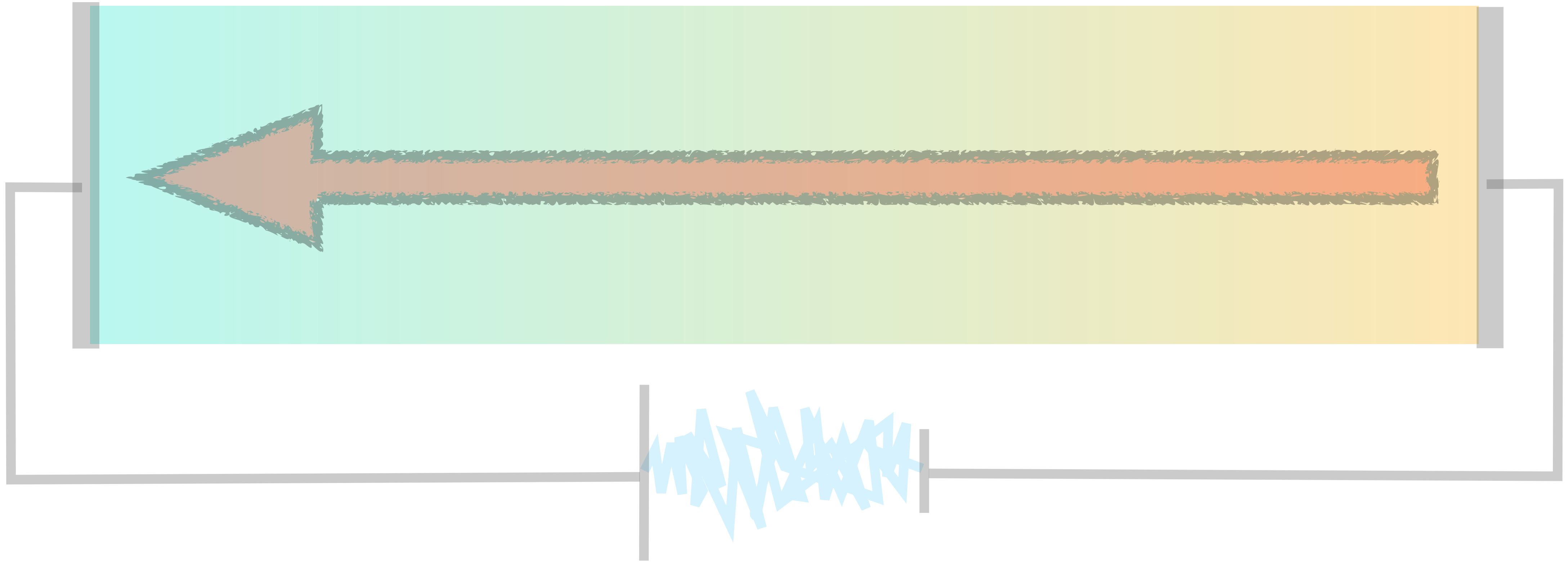

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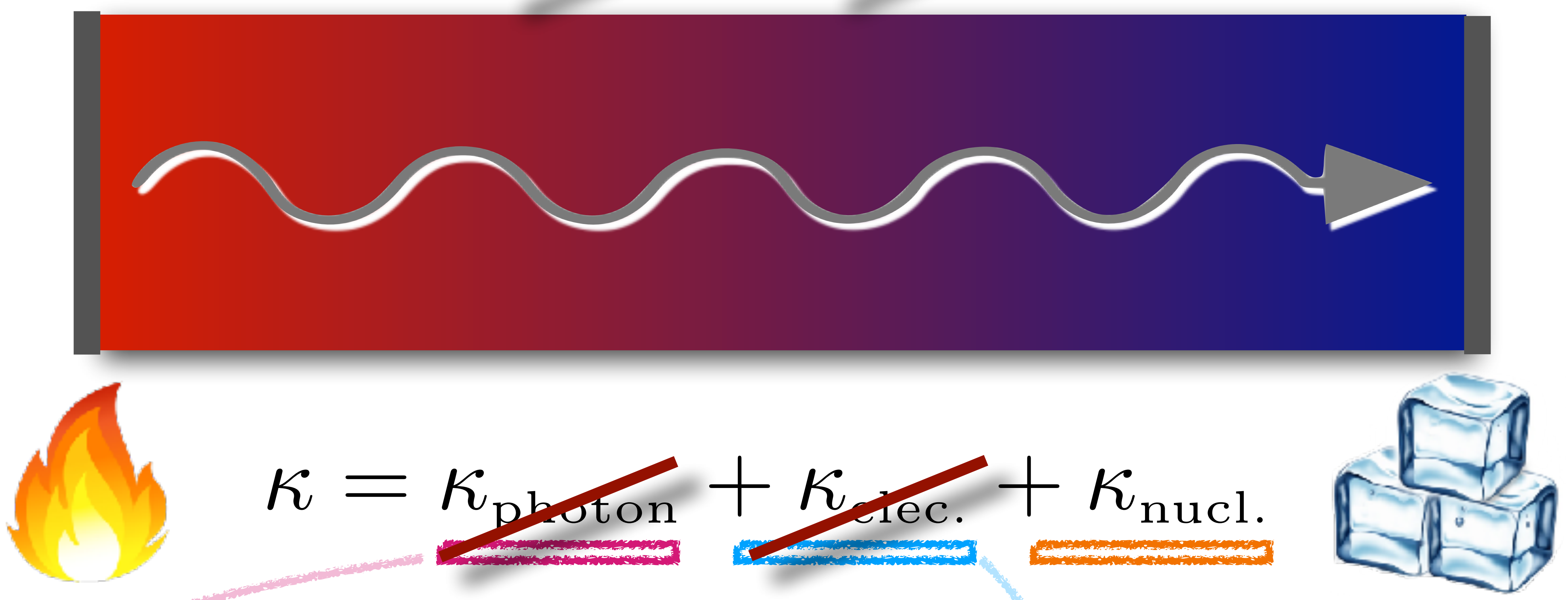

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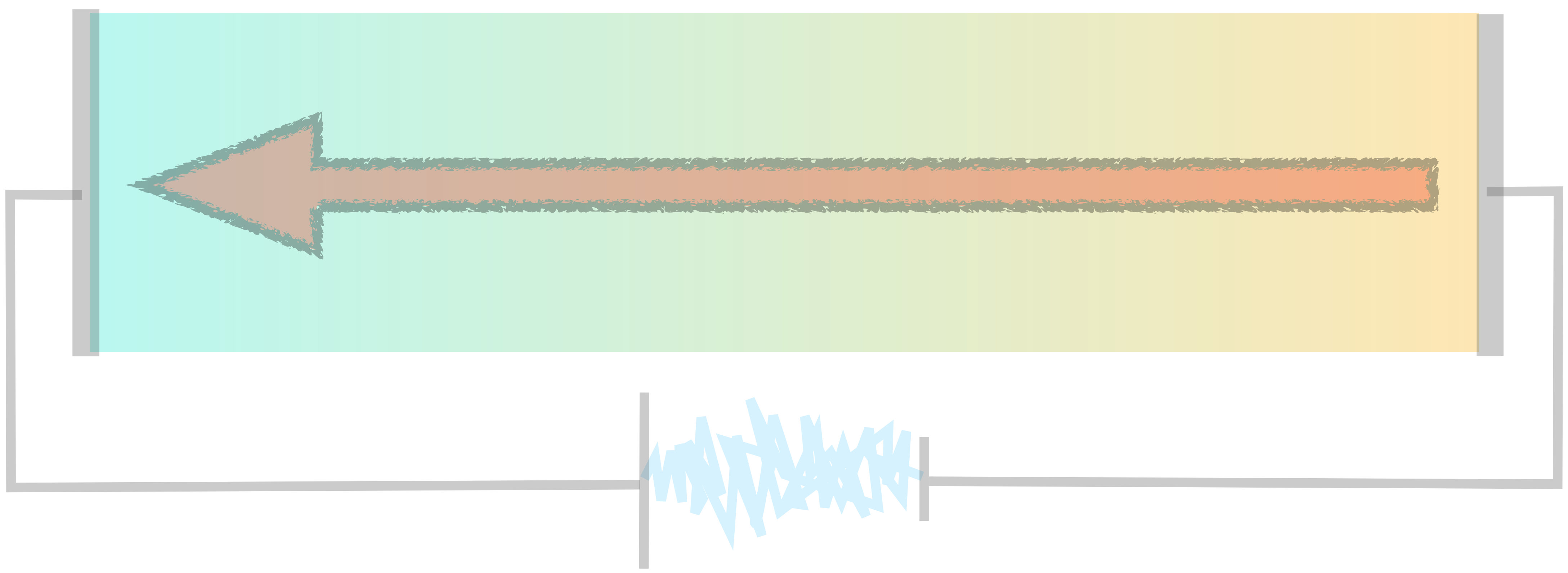

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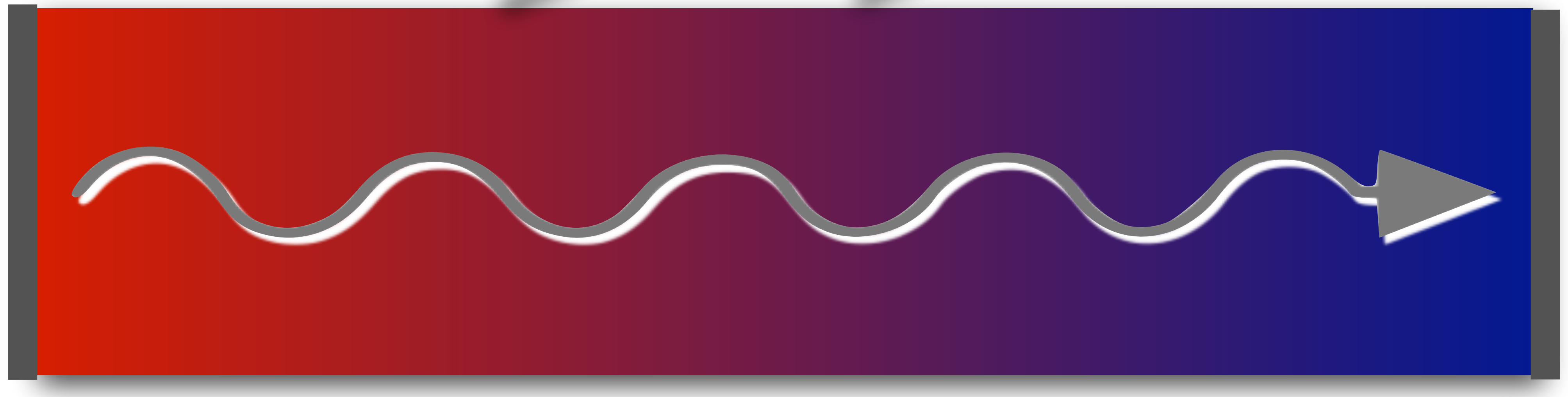

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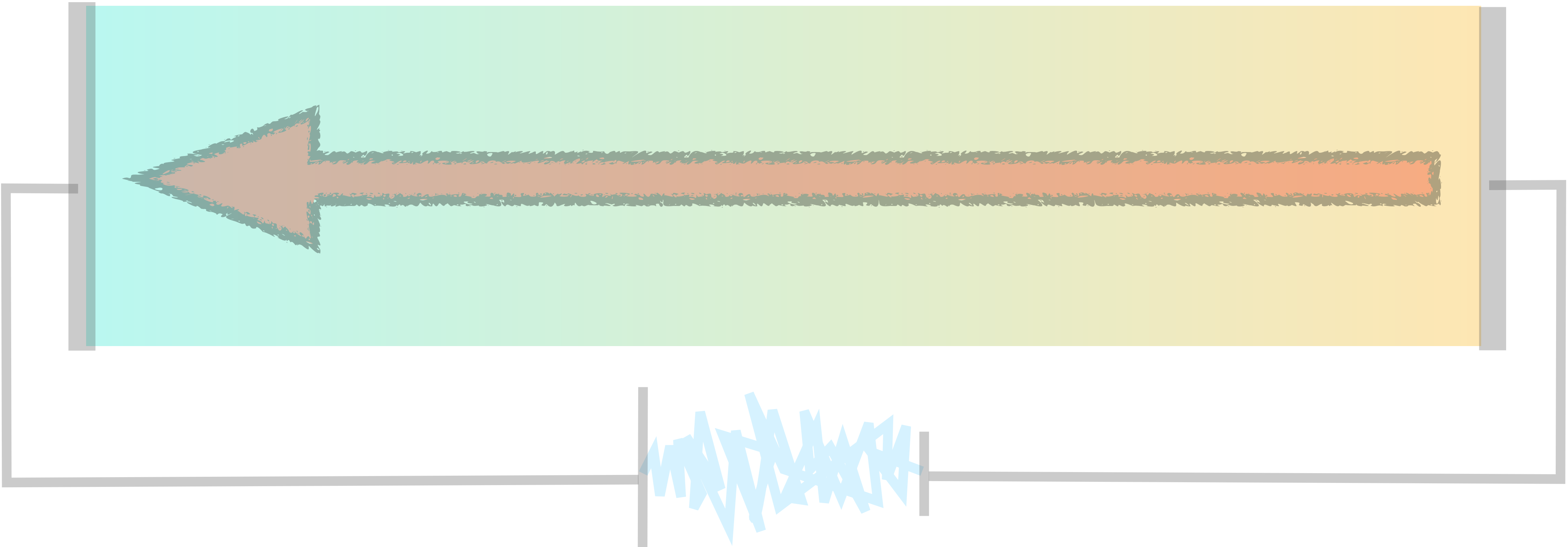
Relevant in **transparent, incandescent** materials!

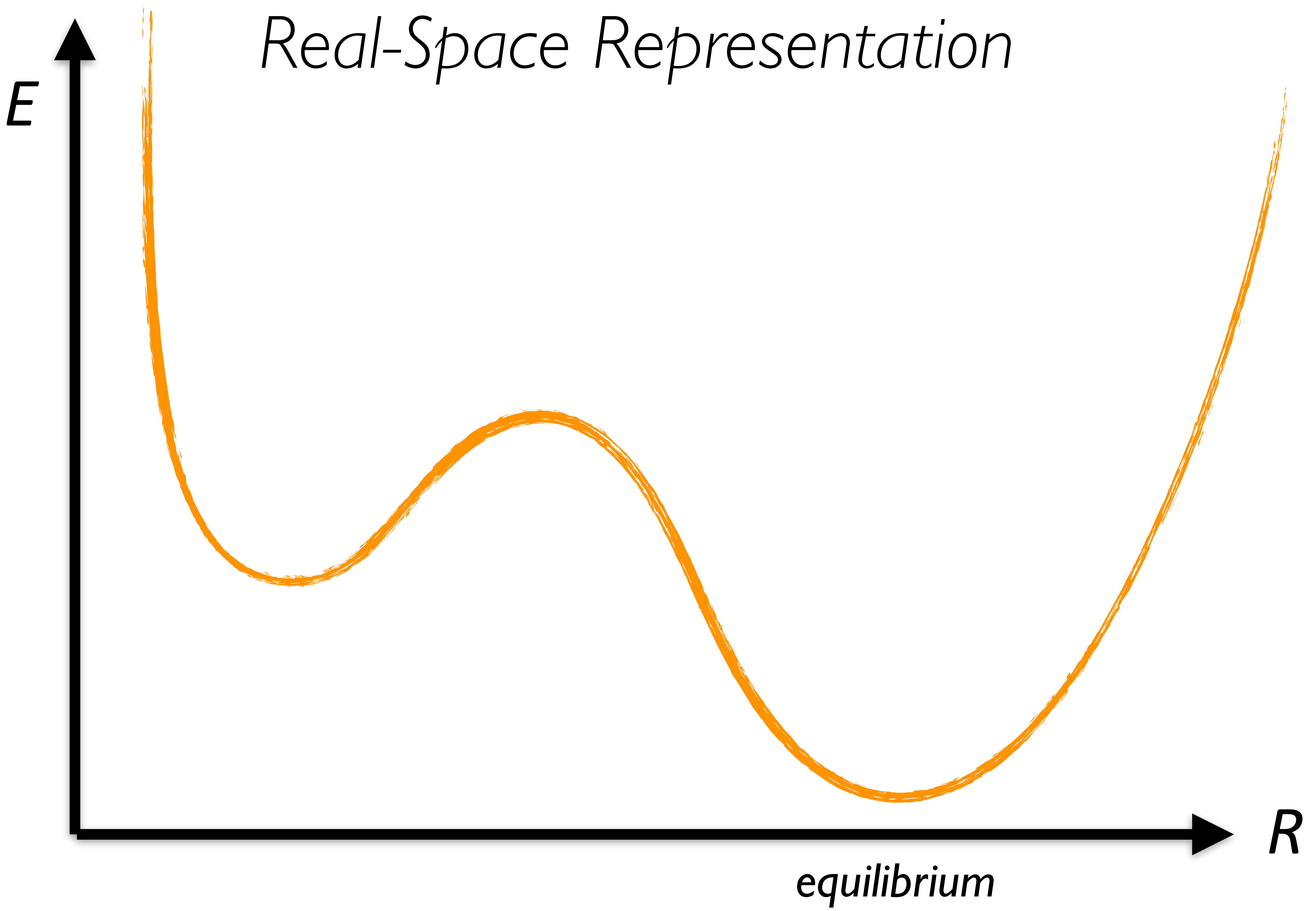
Relevant in **metals** and **degenerate semiconductors**.

The **dominant** contribution in **insulators** and **non-degenerate semiconductors**.

Charge Flux: Electrons & Ions



Heat Transport Theory 101



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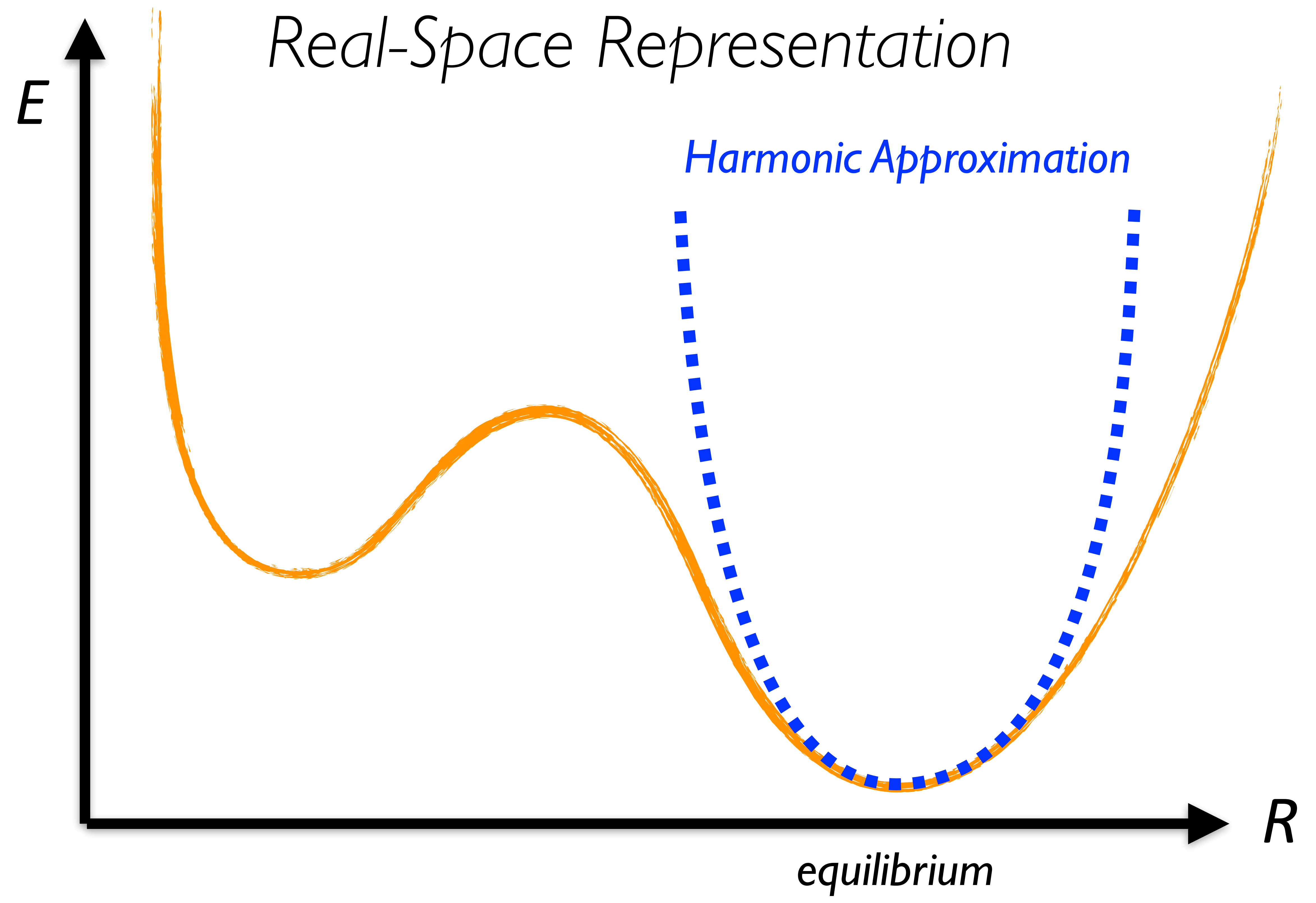

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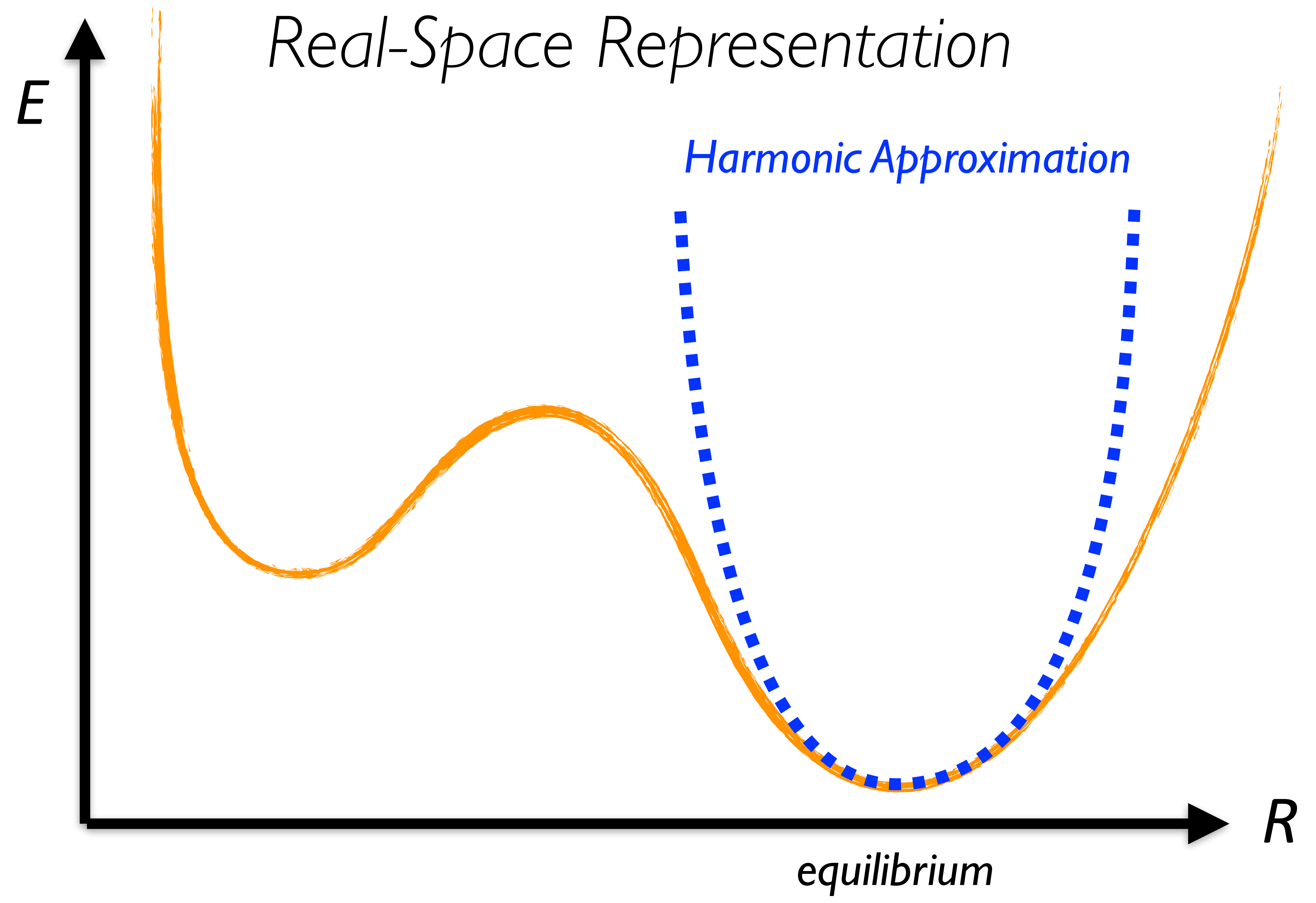

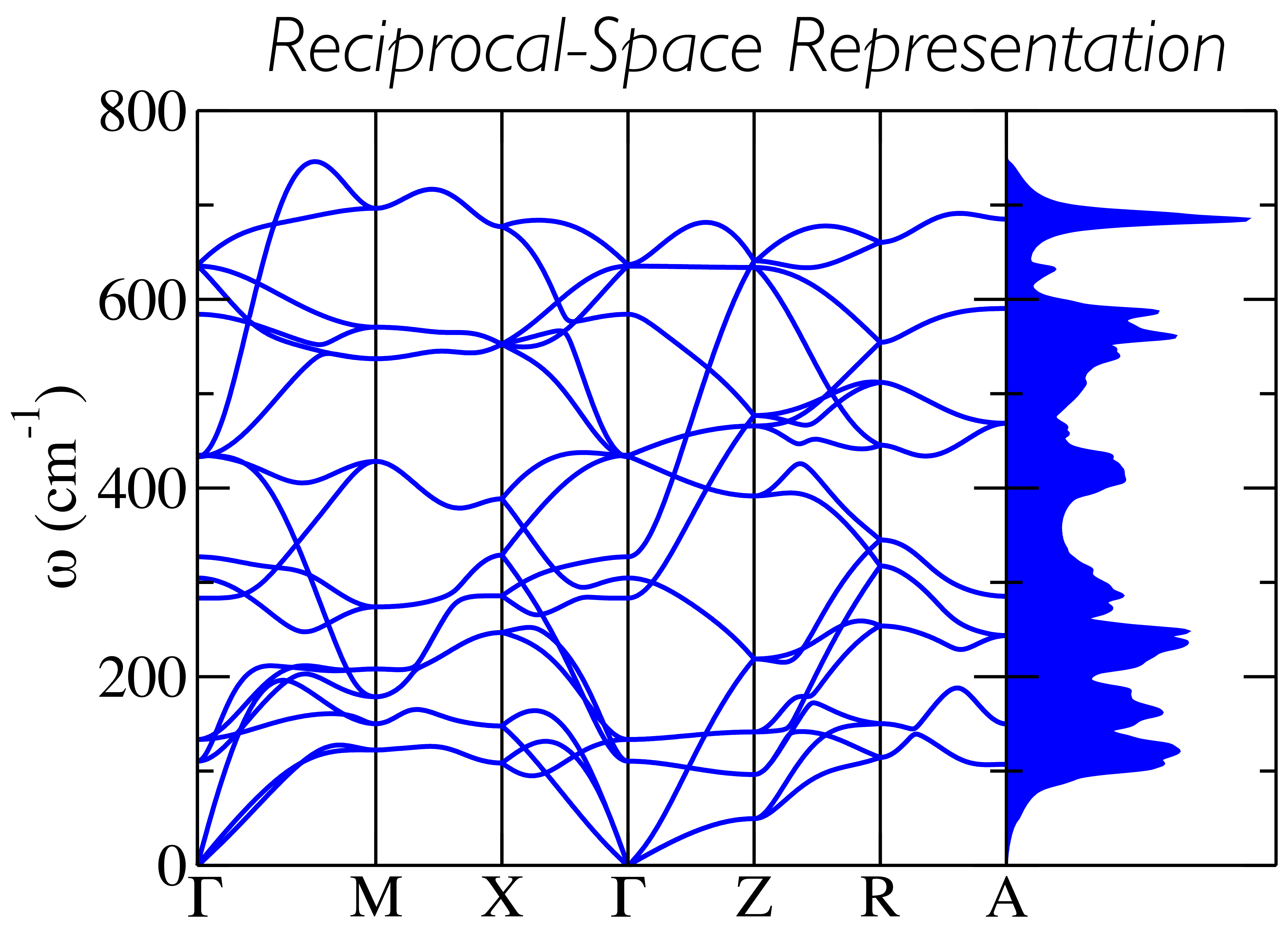

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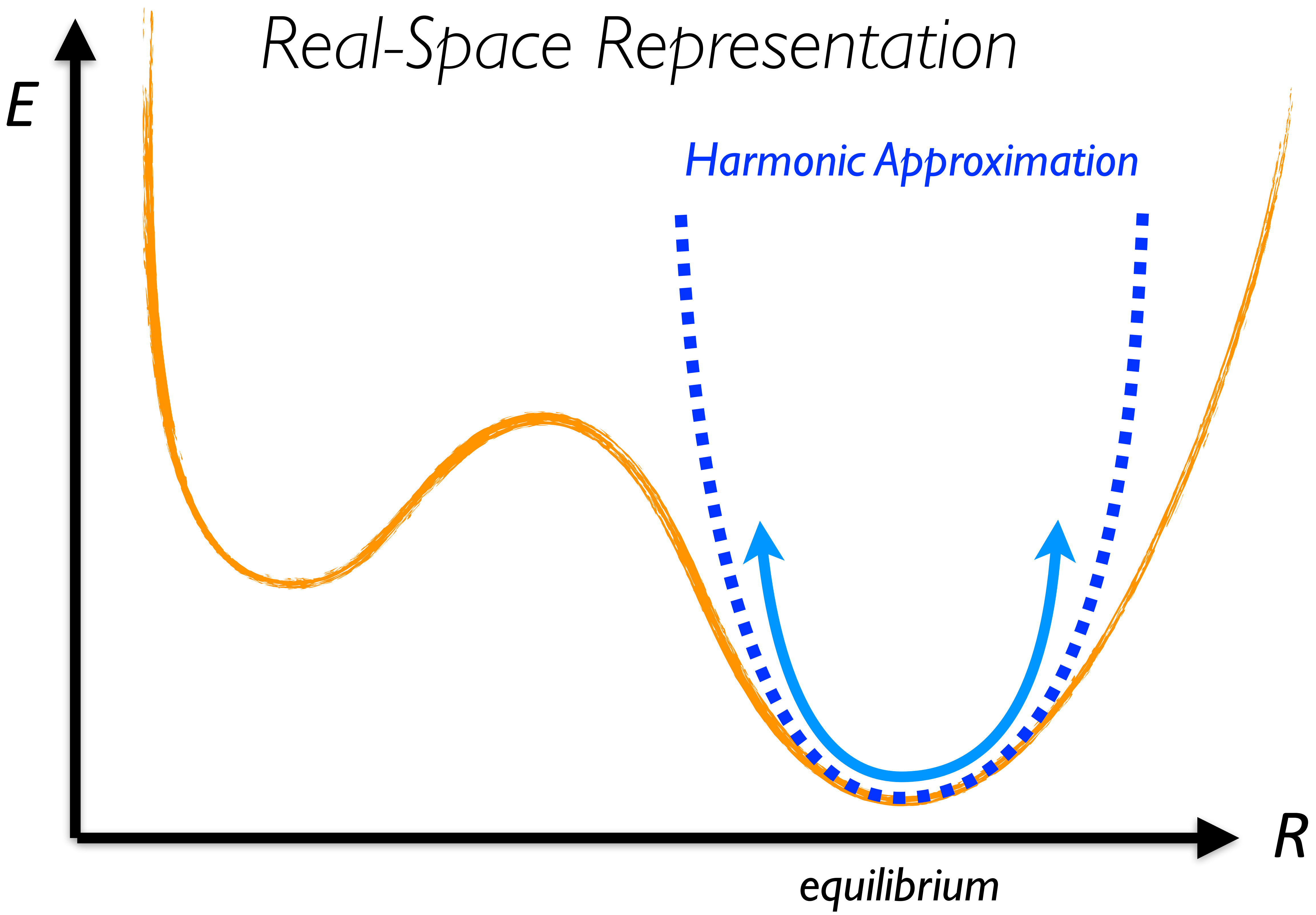
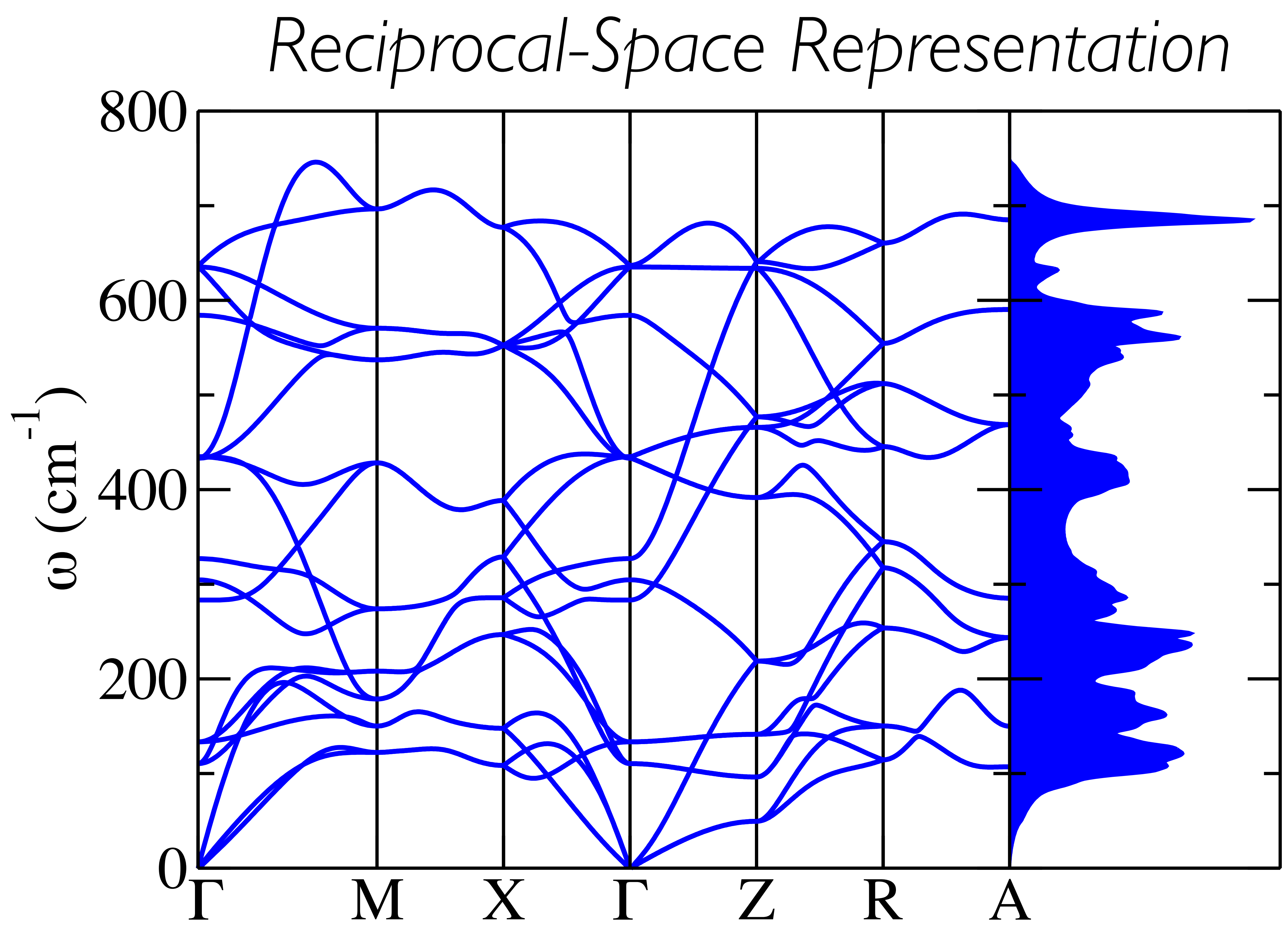


Decoupled Modes



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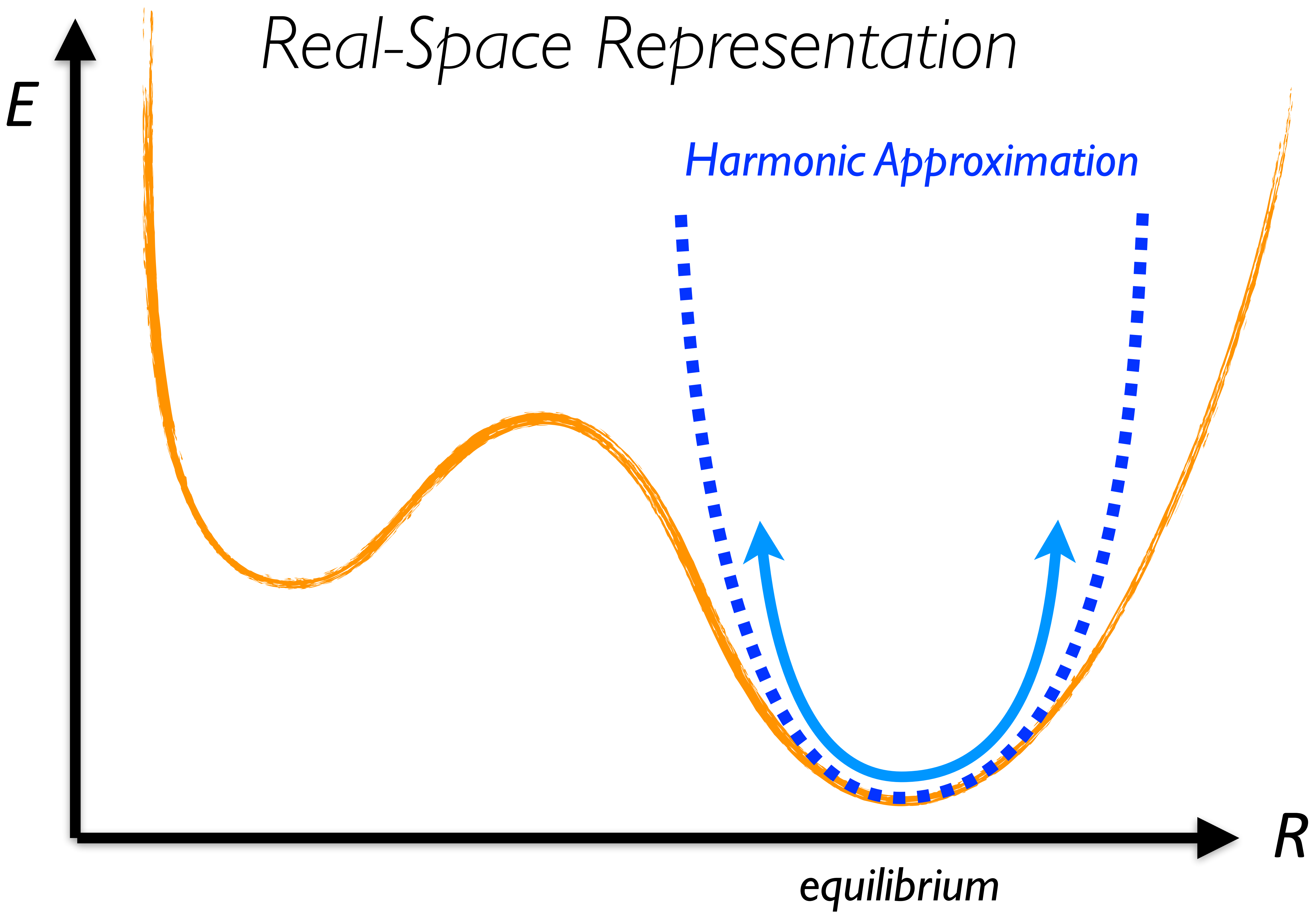
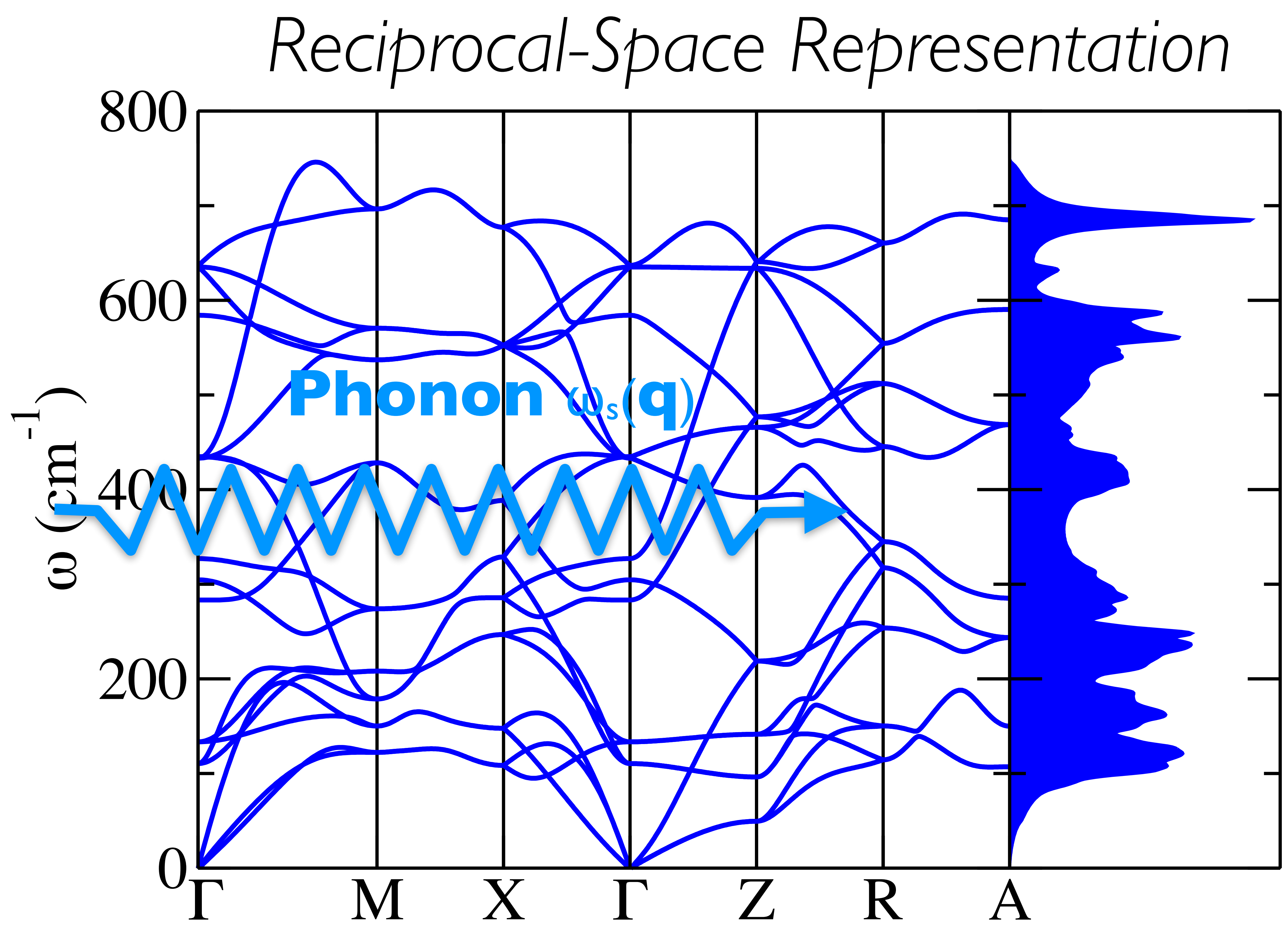
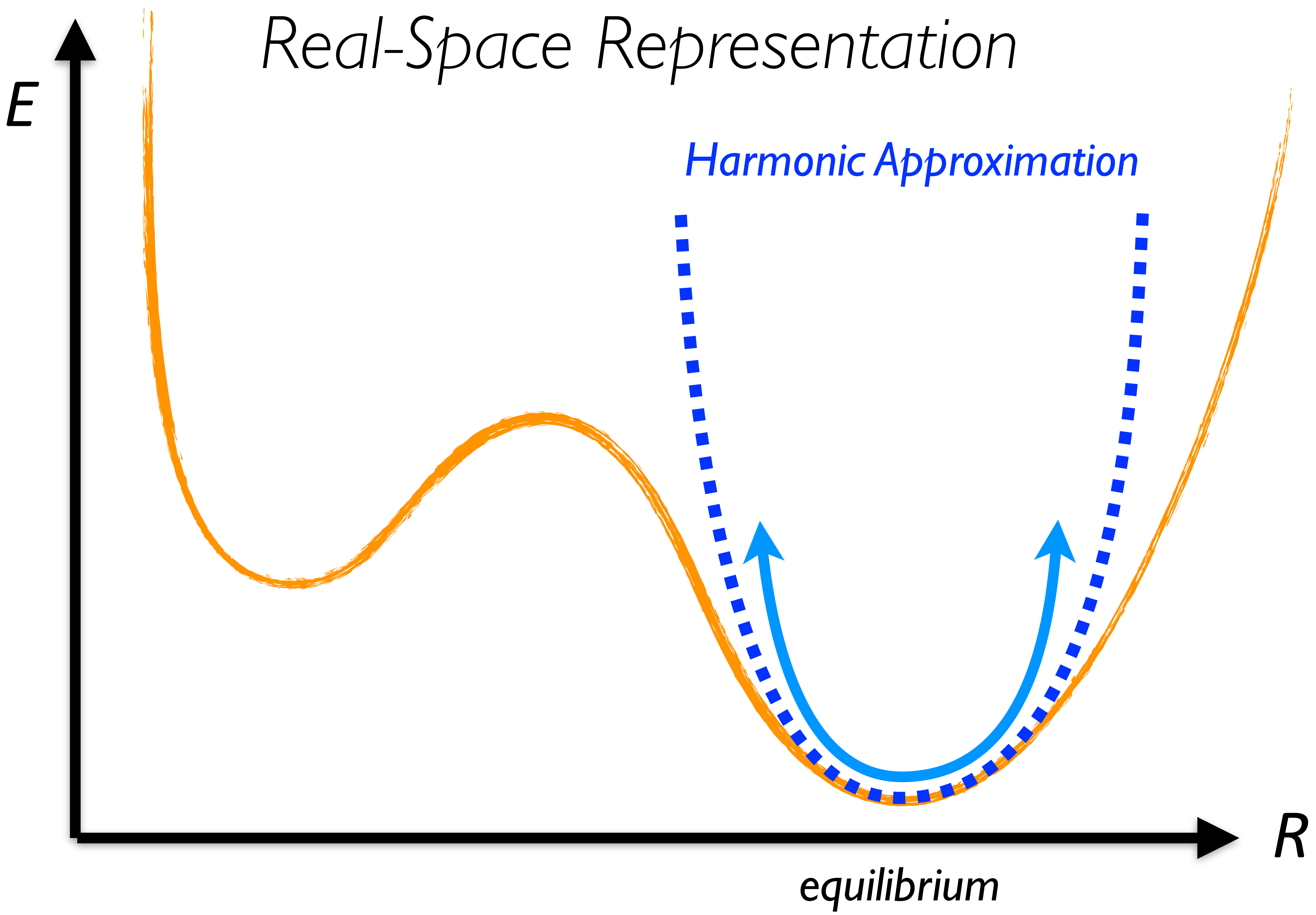


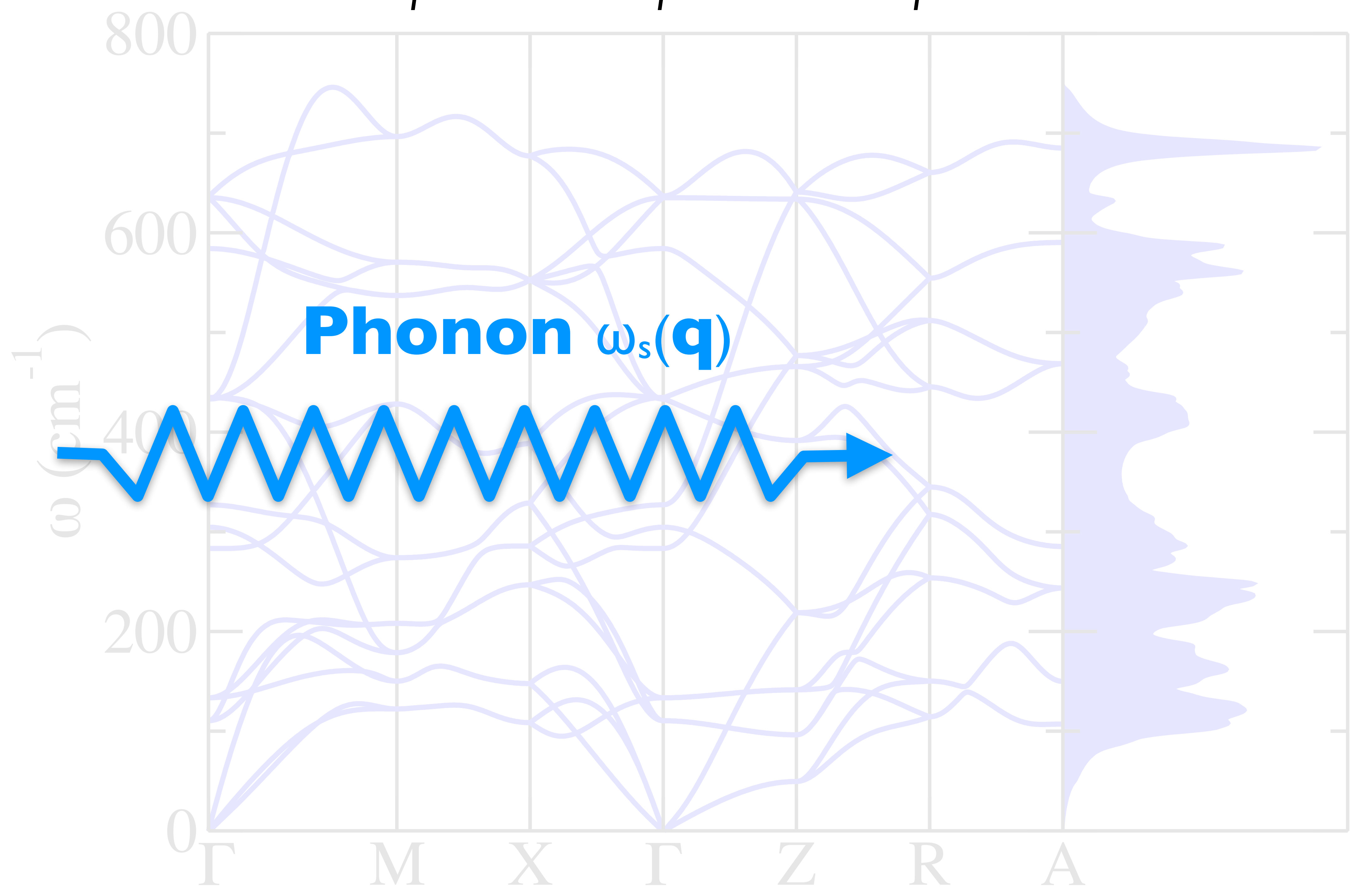


Decoupled Modes

Infinite Lifetimes

Heat Transport Theory 101



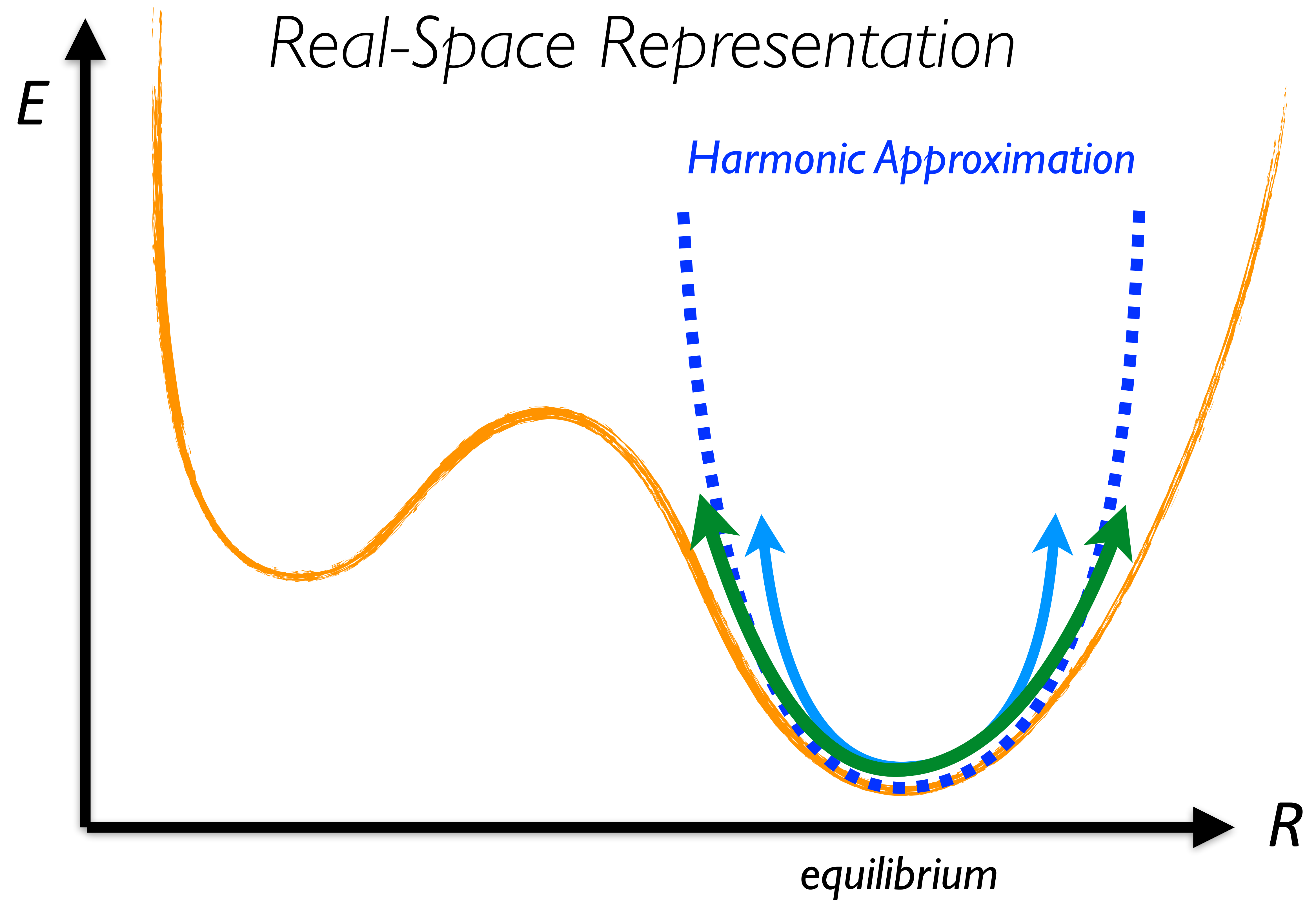


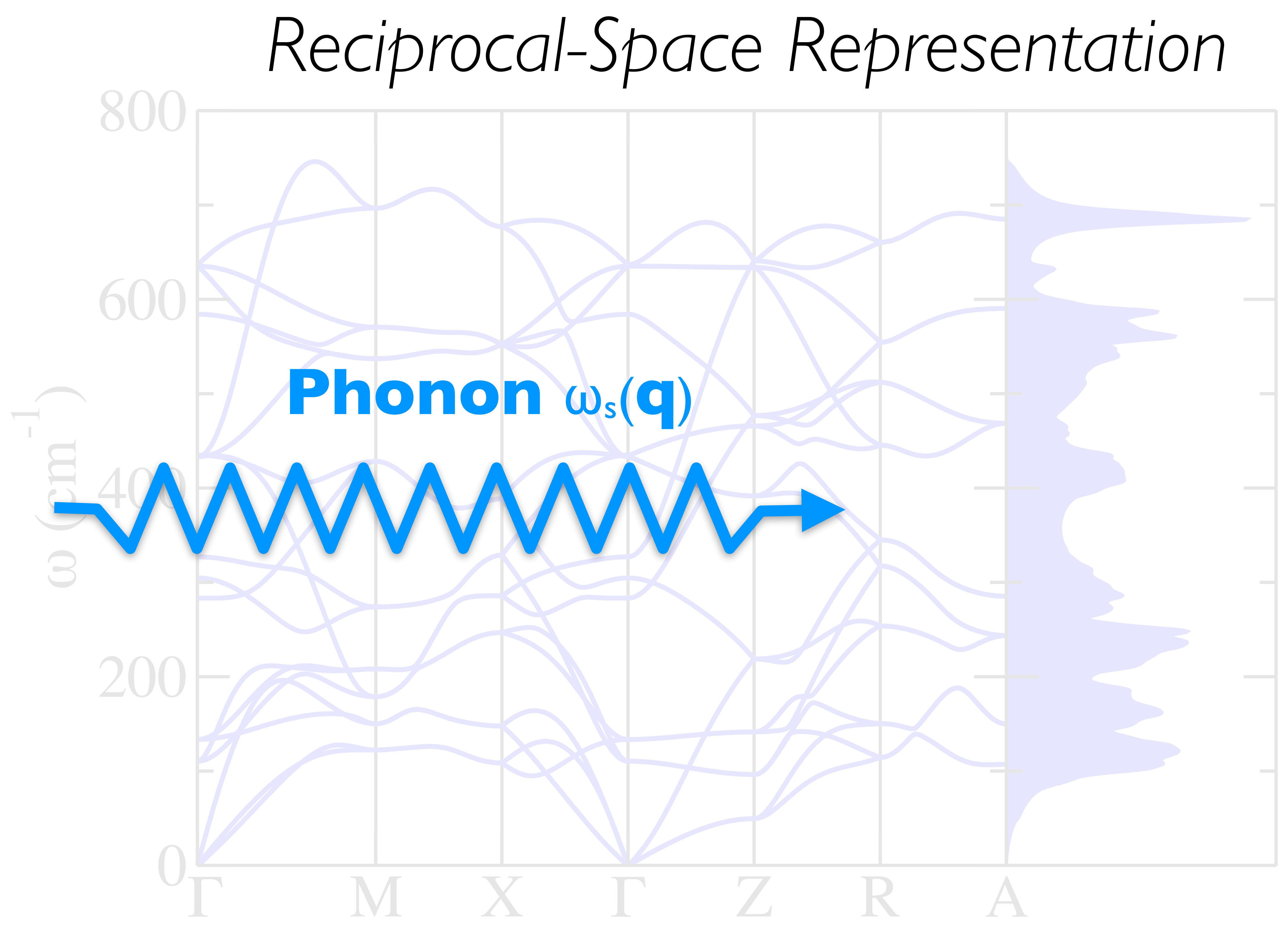
Decoupled Modes

Infinite Lifetimes

Infinite Thermal Conductivity

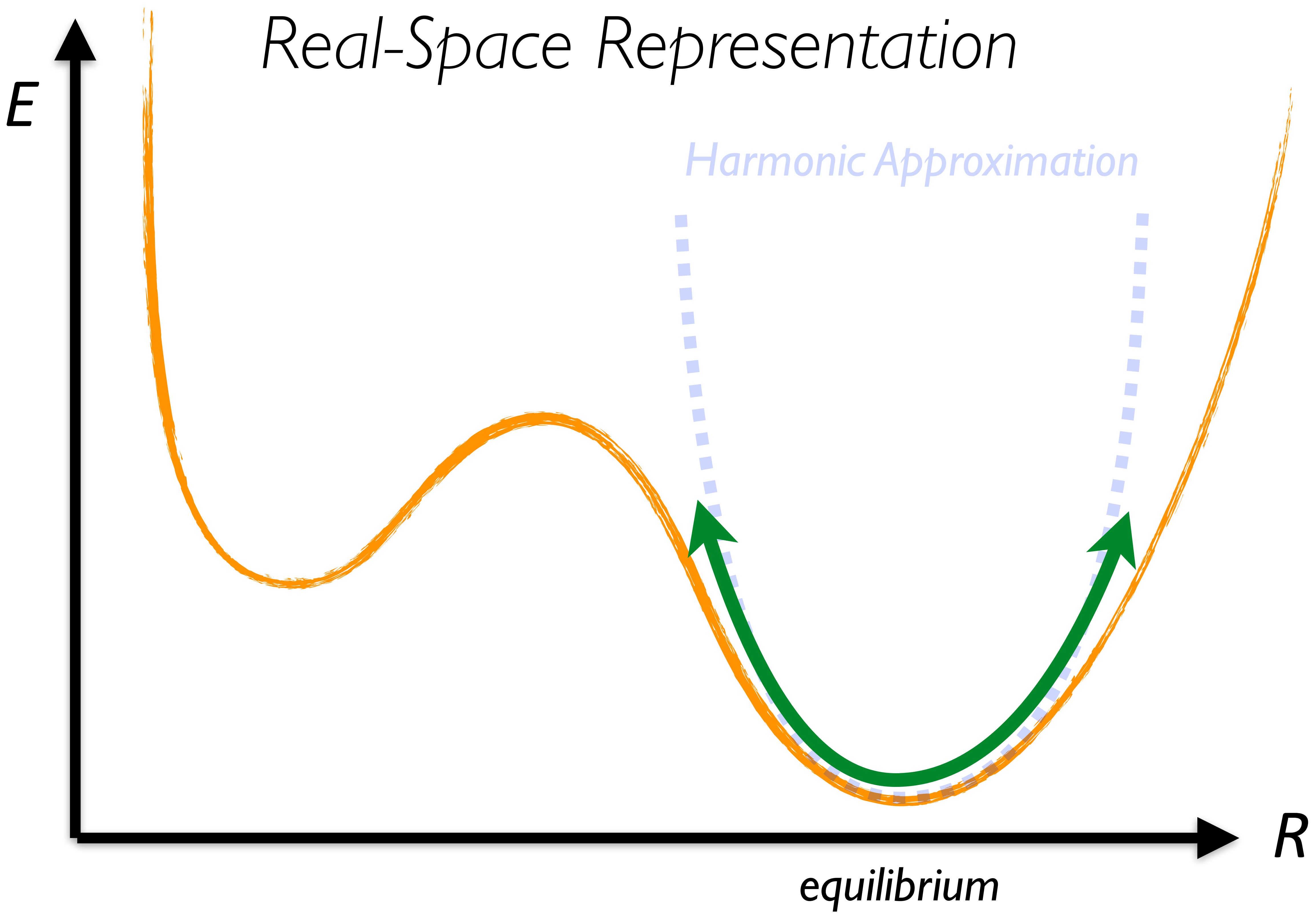
Heat Transport Theory 101

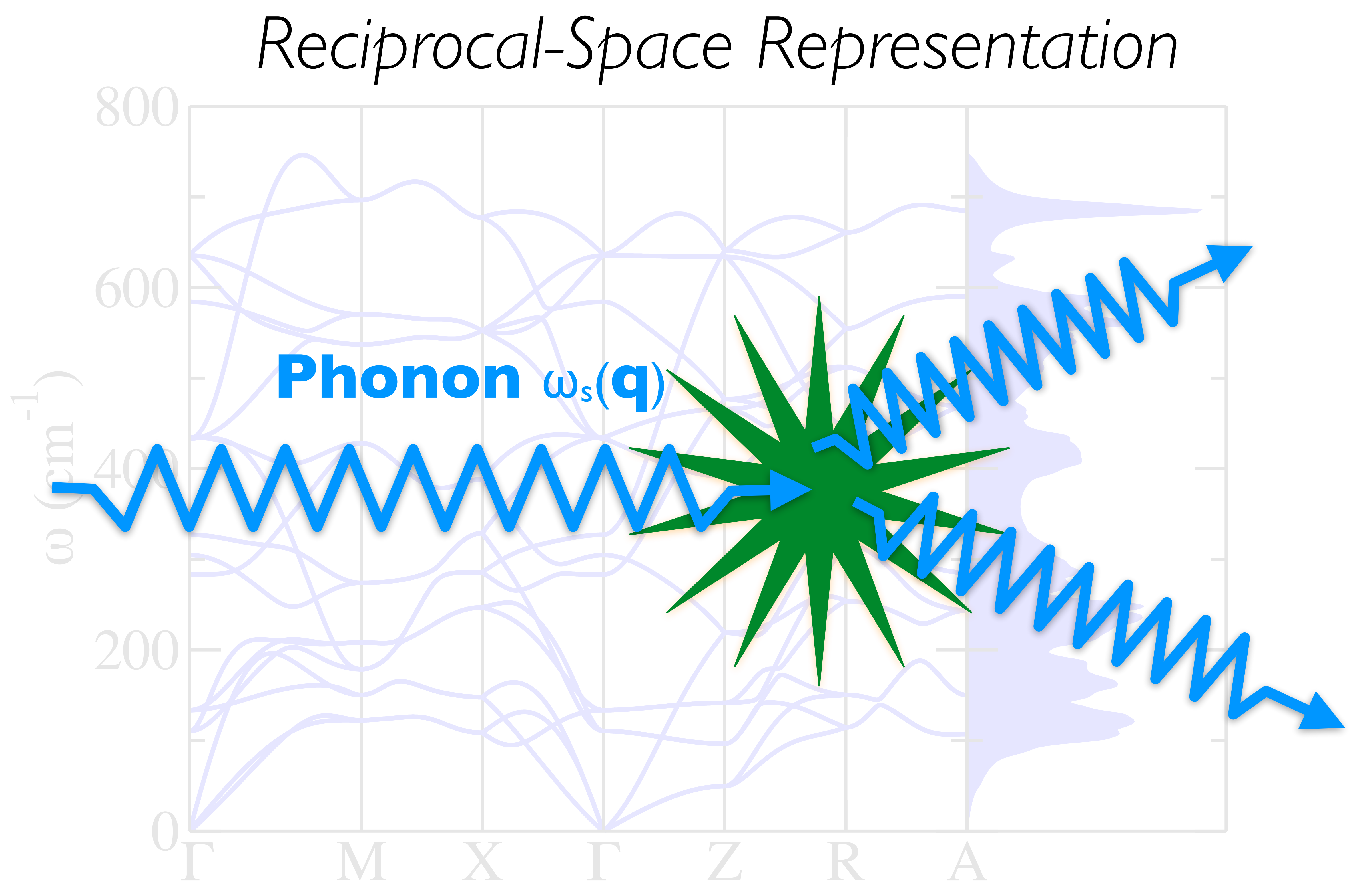




Anharmonic Dynamics

Heat Transport Theory 101





Anharmonic Dynamics

Phonon **Scattering**

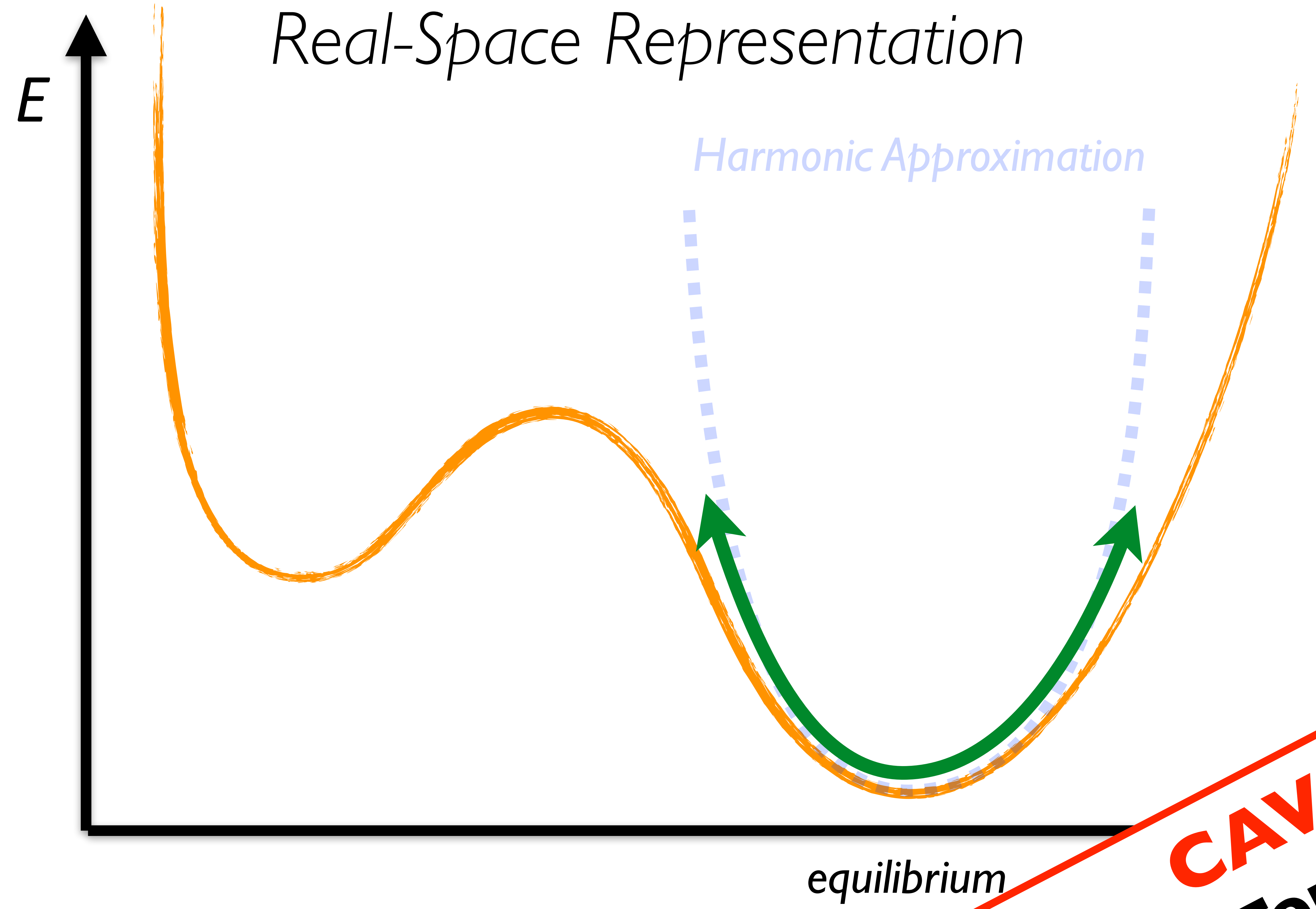
Perturbation Theory:

Scattering Cross Sections + *Transport Equation*

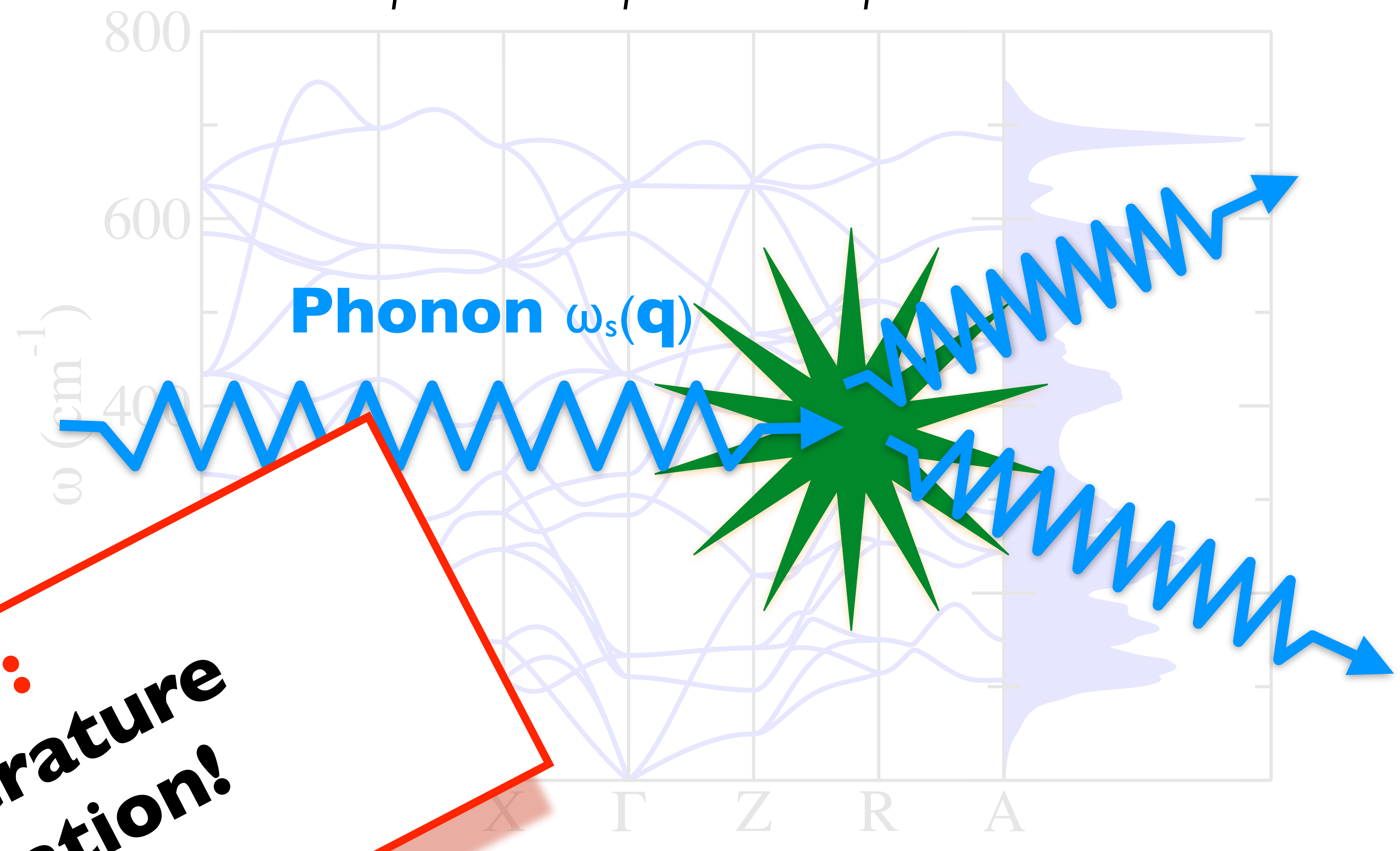
D. A. Broido *et al.*, *Appl. Phys. Lett.* **91**, 231922 (2007).

Heat Transport Theory 101

Real-Space Representation



Reciprocal-Space Representation



Anharmonic D

Phonon **Scattering**

CAVEAT:

Low Temperature Approximation!

$E_{harm} \gg E_{anha}$!

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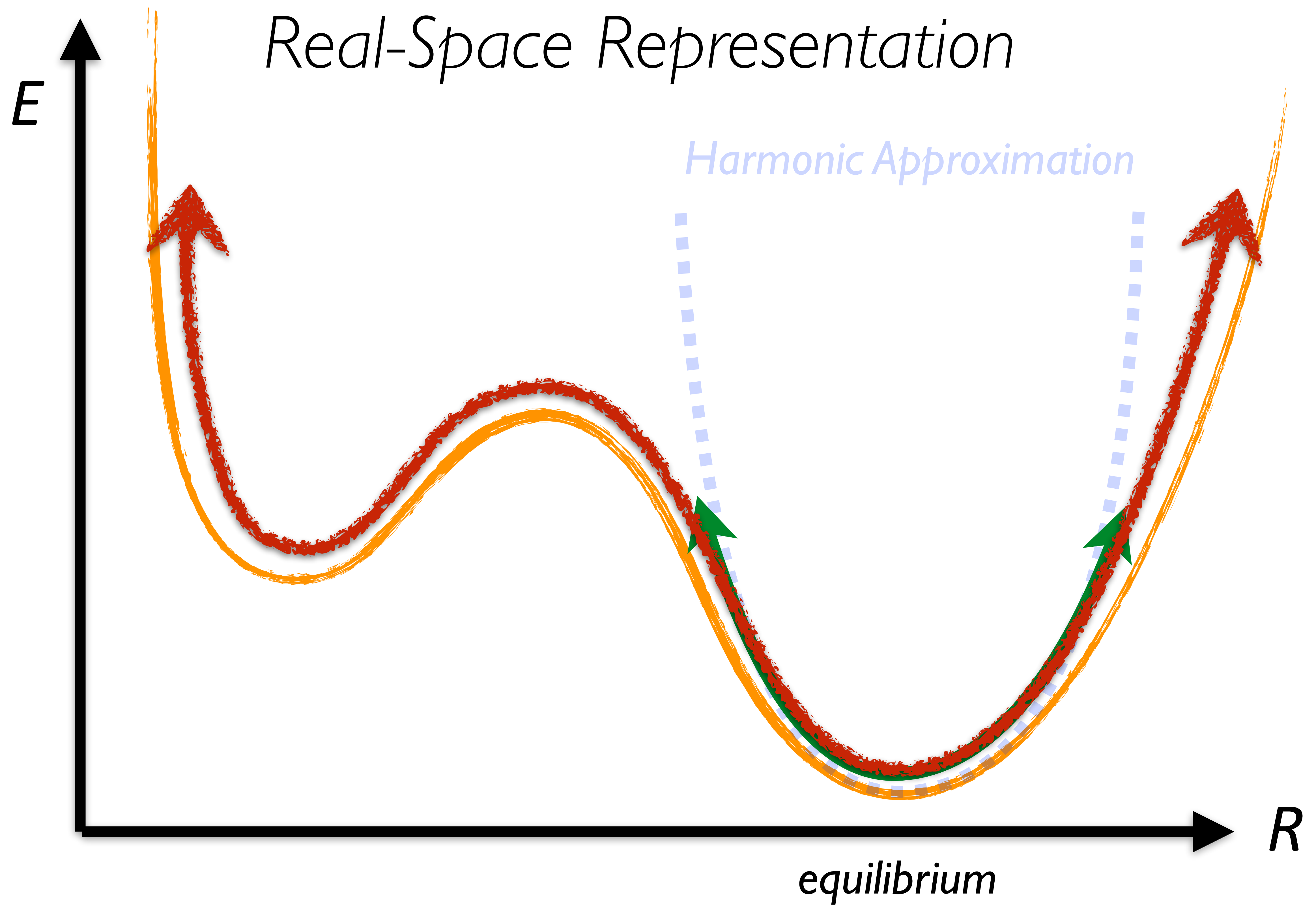

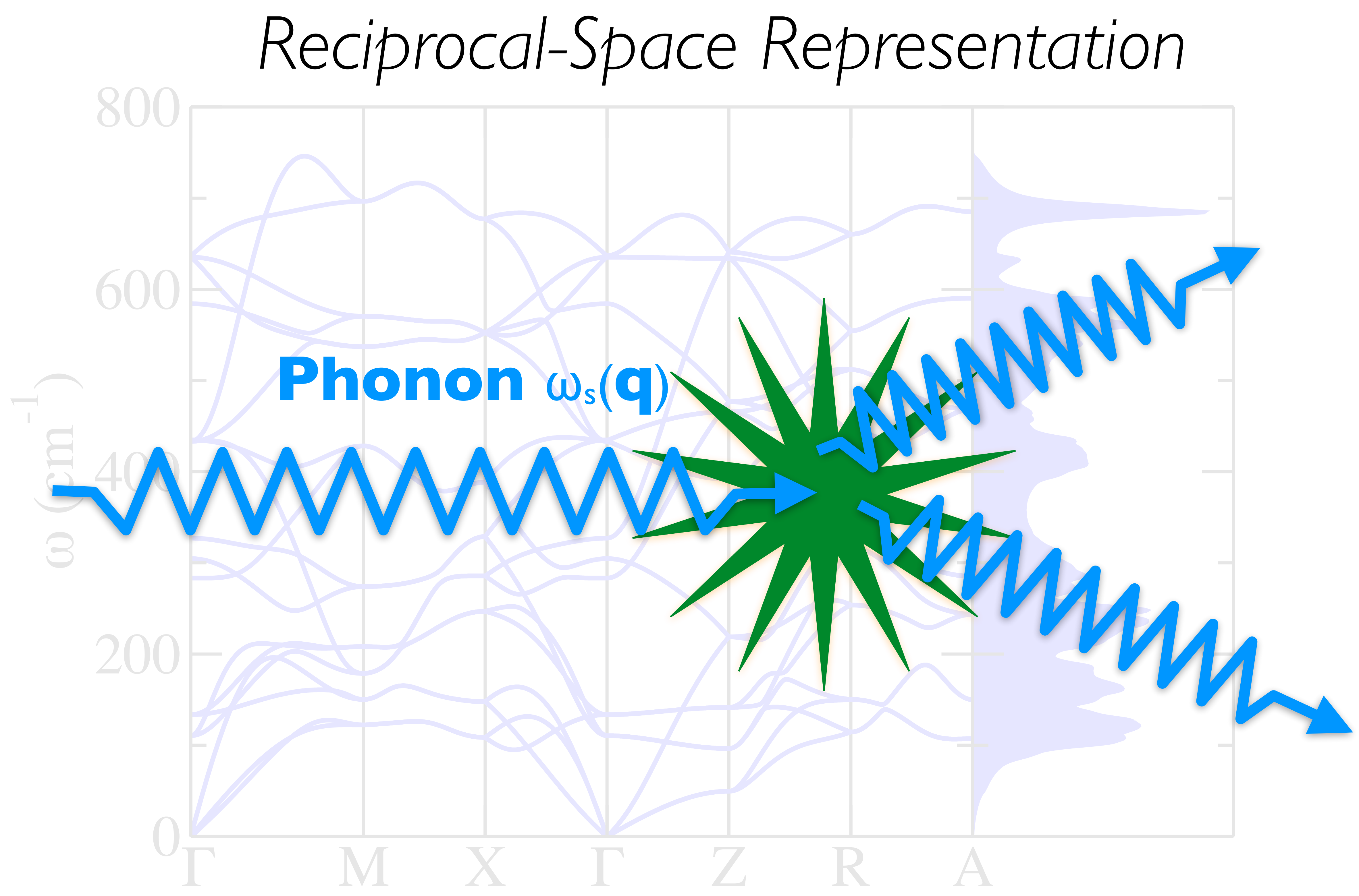

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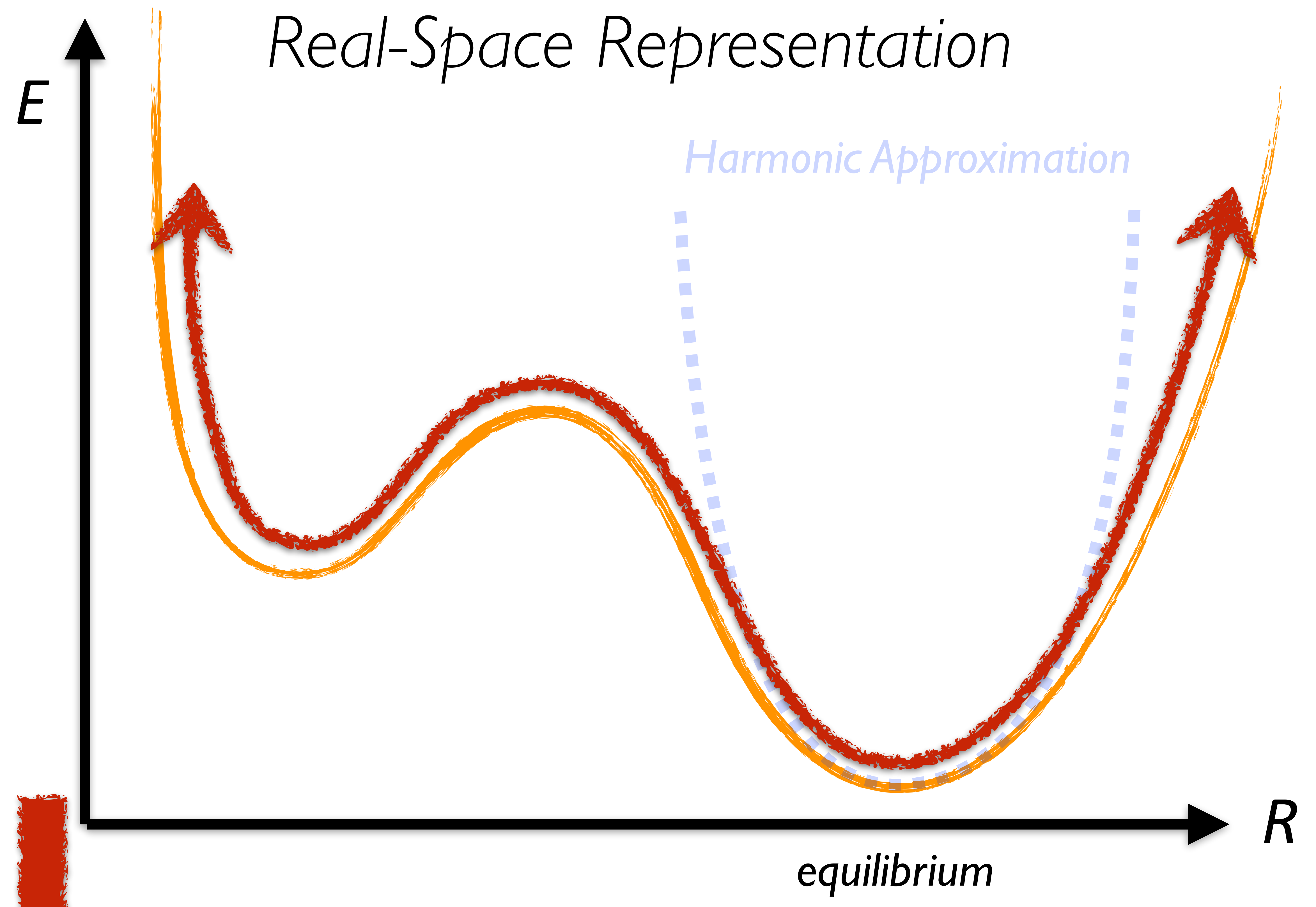

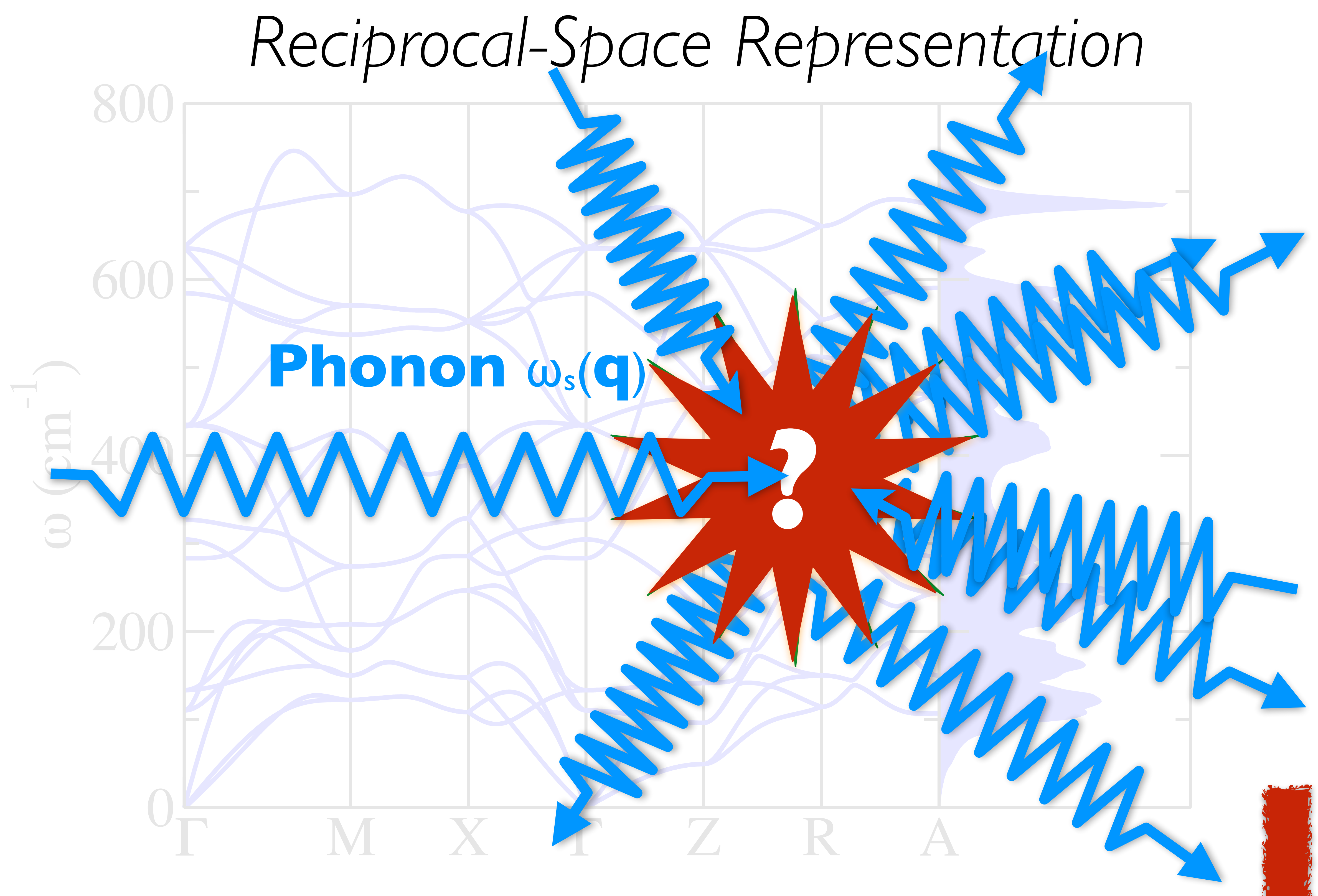

Anharmonic Dynamics

Phonon **Scattering**

Strong Anharmonic Effects beyond the Realm of Perturbation Theory:

$E_{harm} \ll E_{anha}$ **!**

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**.

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Green-Kubo method...

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...accounts for **anharmonic** effects **to all orders**

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FHI-aims
The ab initio materials simulation package

Green-Kubo simulations in *FHI-aims:*

- Conductive **heat flux** evaluation using ***virials***.

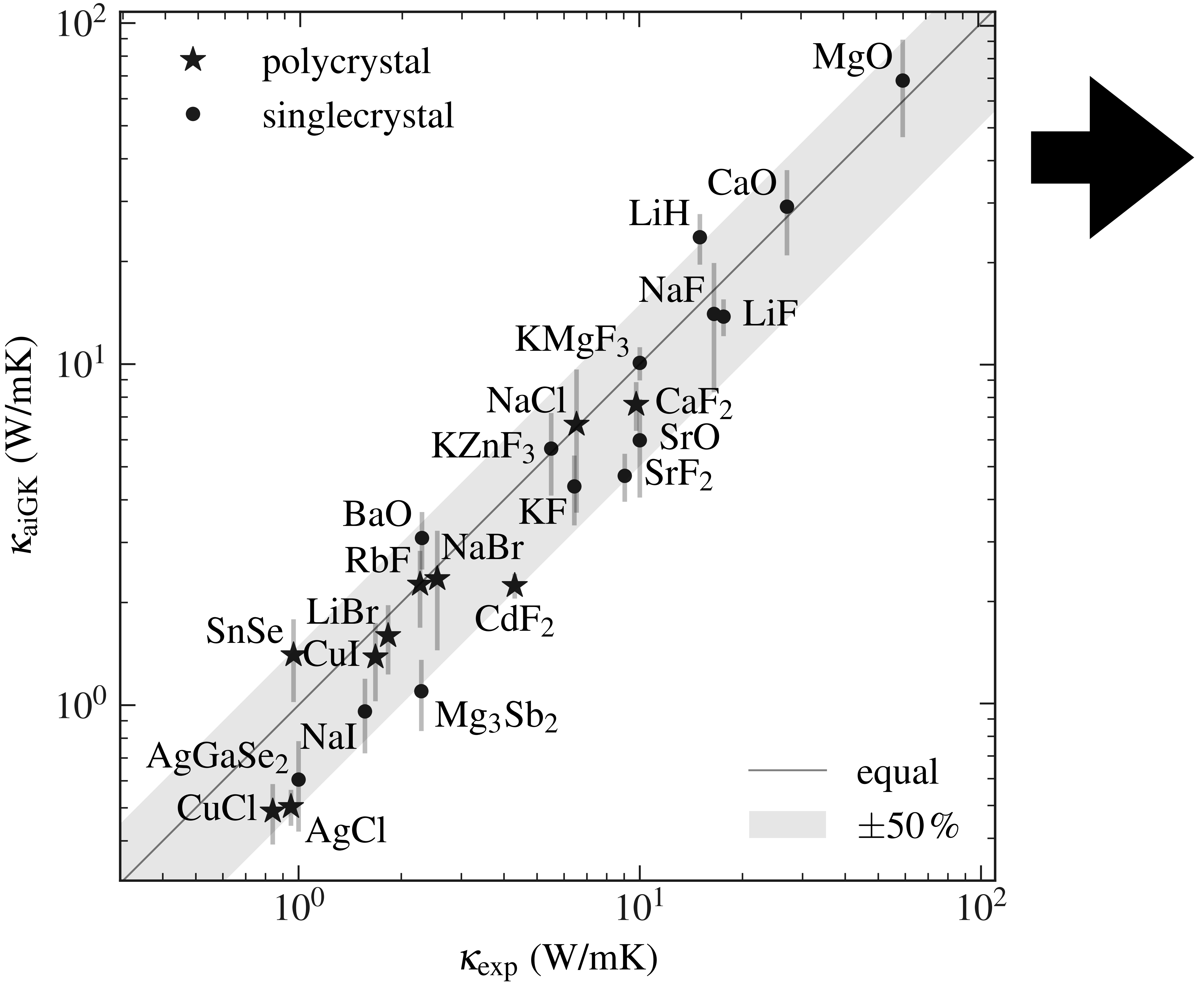
  C. Carbogno, R. Ramprasad, and M. Scheffler, *Phys. Rev. Lett.* **118**, 175901 (2017).

- Numerical **post-processing** via *FHI-vibes*

  F. Knoop, M. Scheffler, and C. Carbogno, Phys. Rev. B 107, 224304 (2023).

Ab initio Green-Kubo Validation

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



Mean Absolute Percentage Error
MAPE ~ 25%

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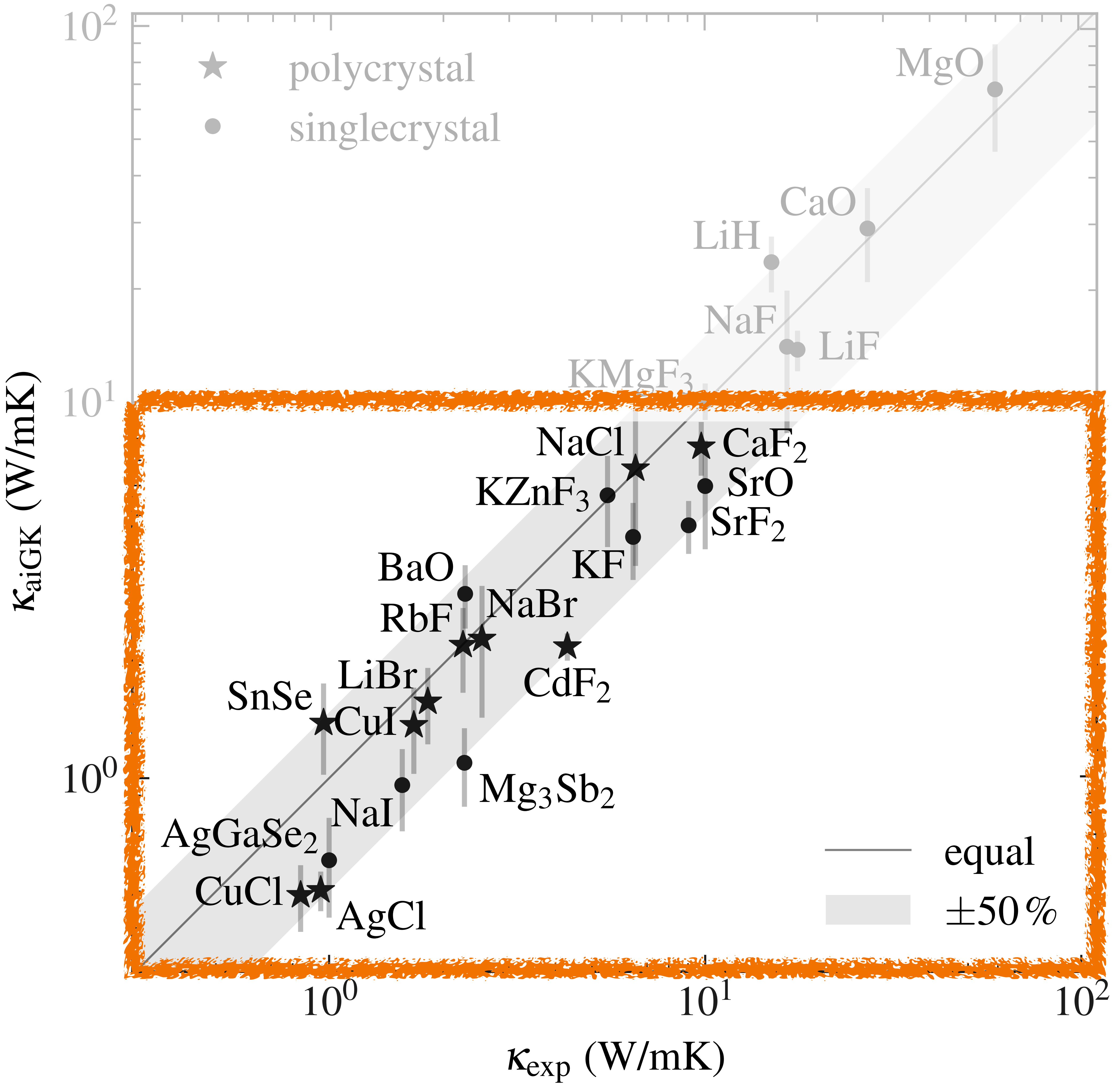

Mean Absolute Percentage Error
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Mean Absolute Error
MAE ~ 1 W/mK

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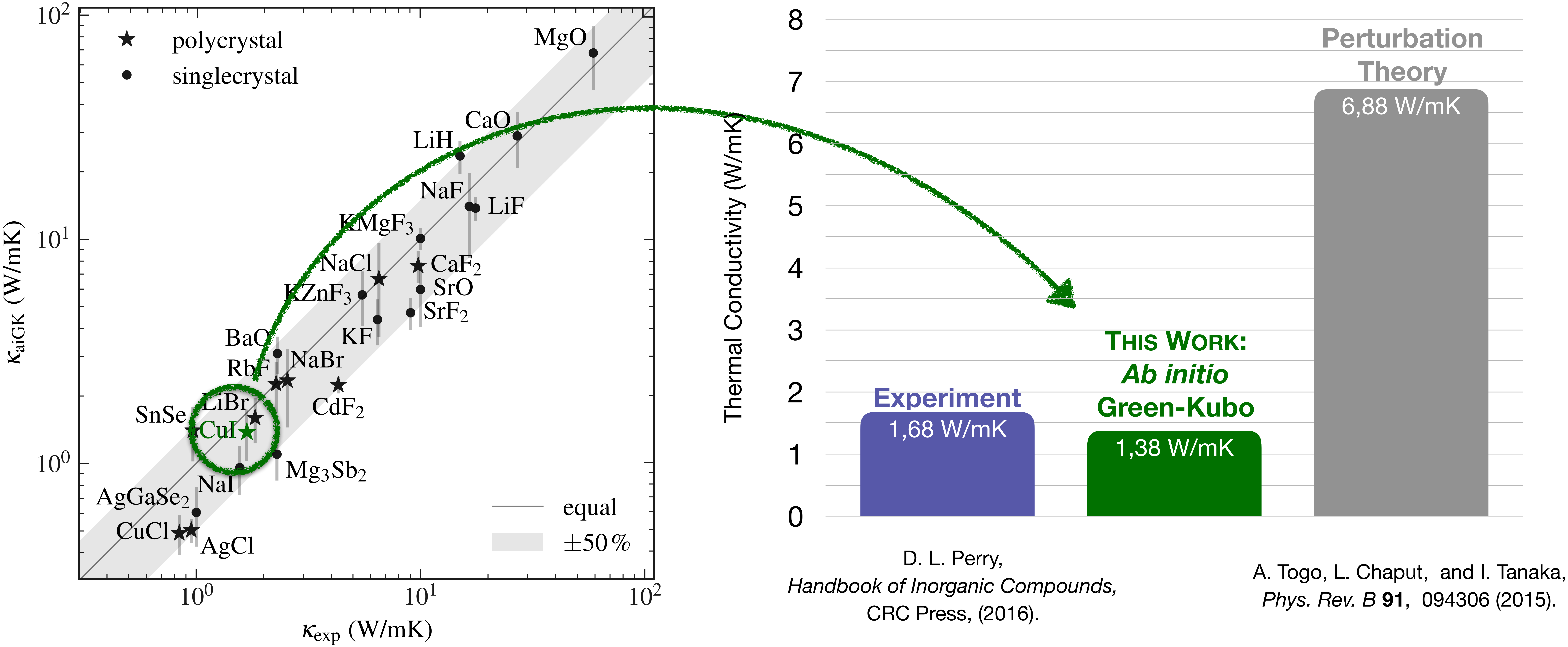
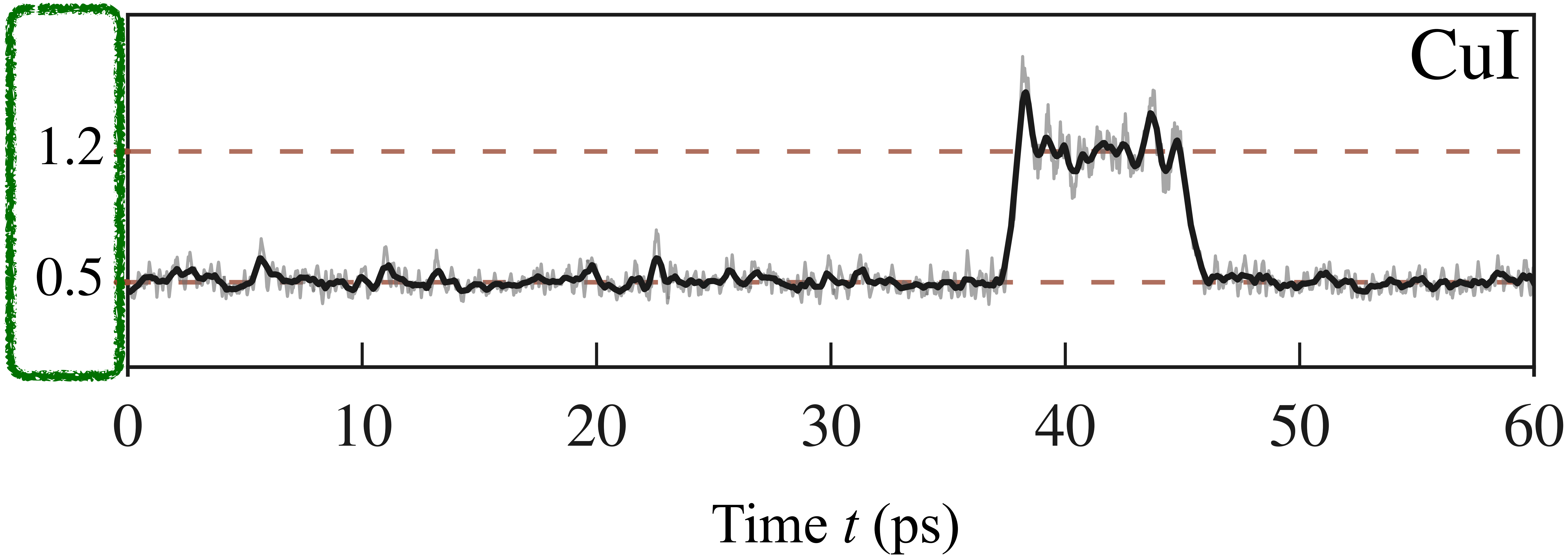


Anharmonicity in Copper Iodide

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

Anharmonicity Metric σ^A

F. Knoop *et al.*, *Phys. Rev. Mater.* **4**, 083809 (2020).



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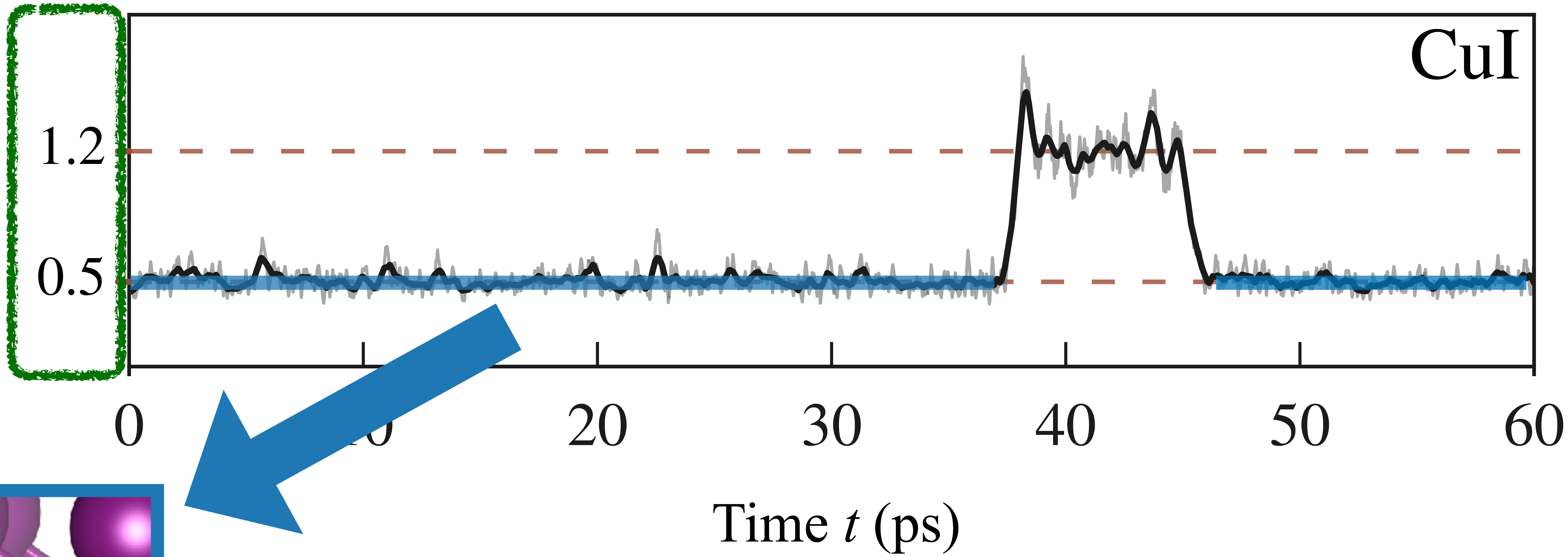

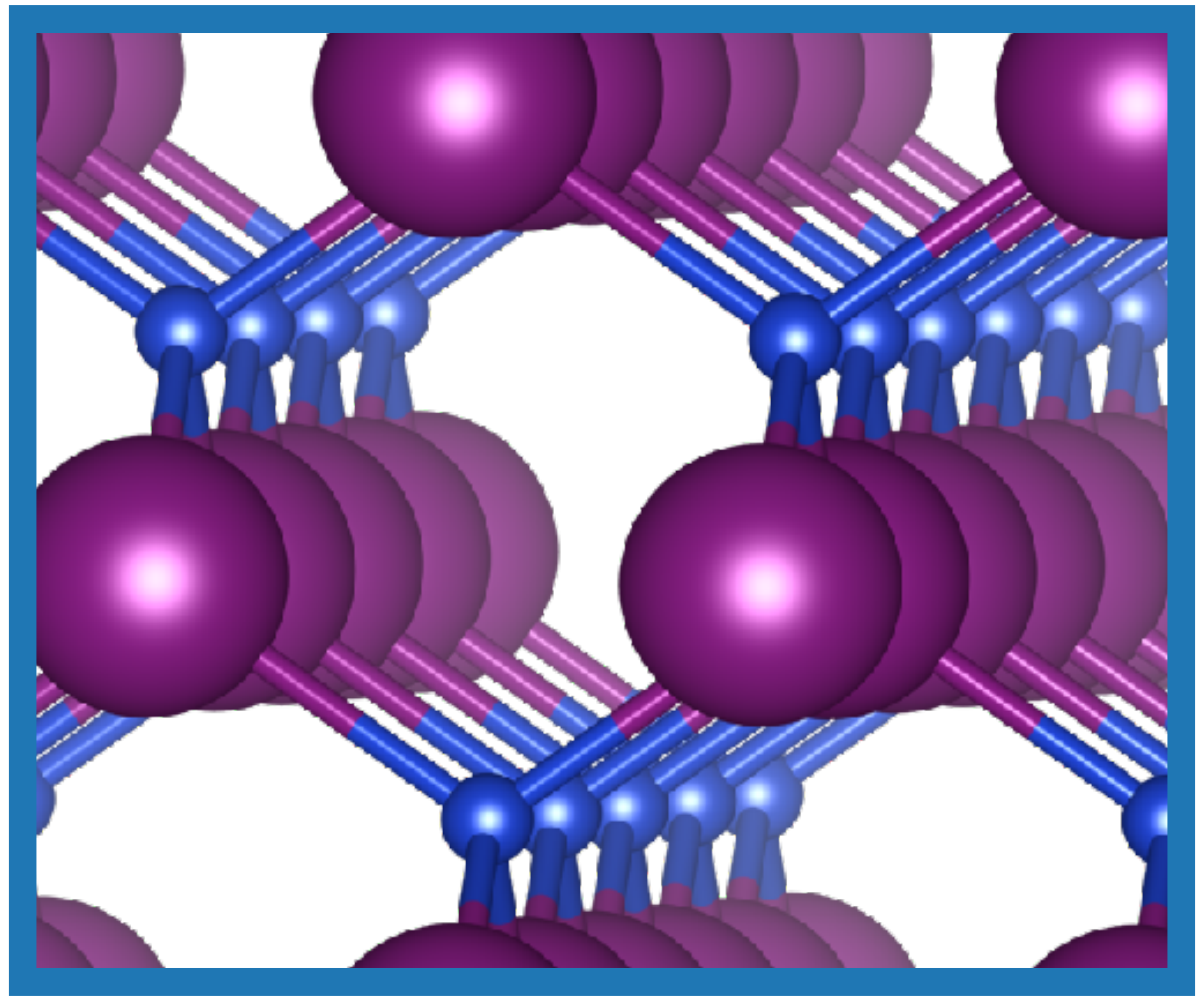

Time-averaged Structure:
Pristine *Zincblende*
Structure of Copper Iodide

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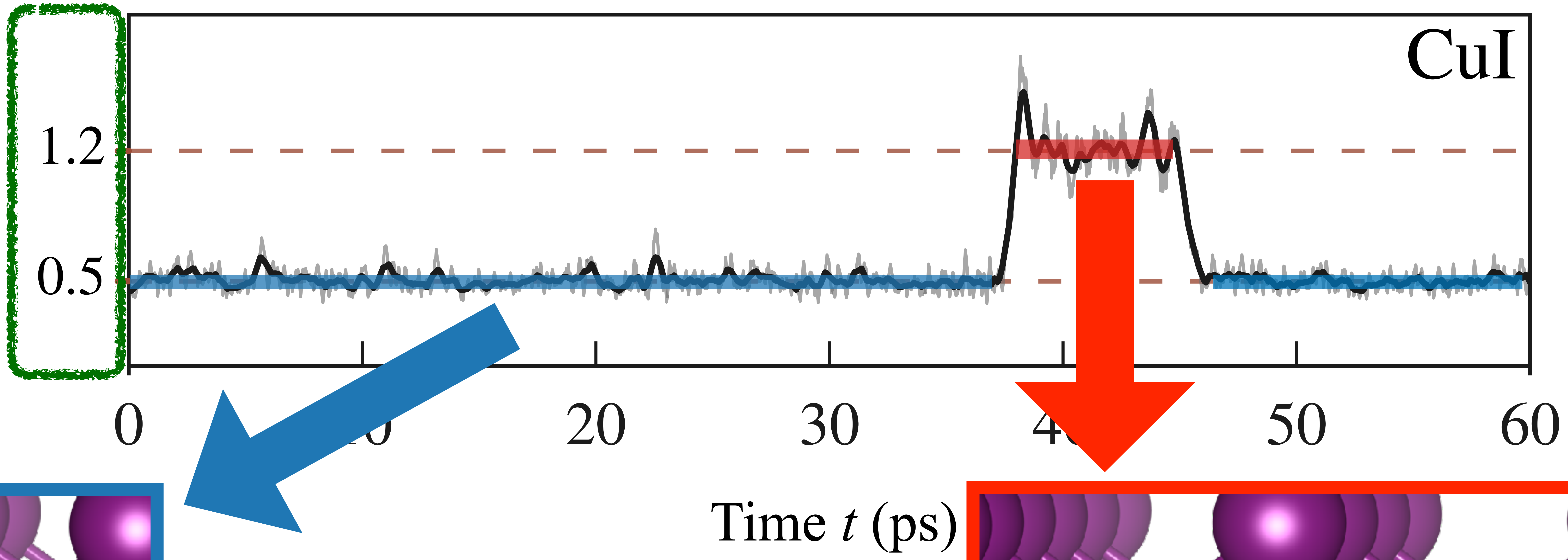

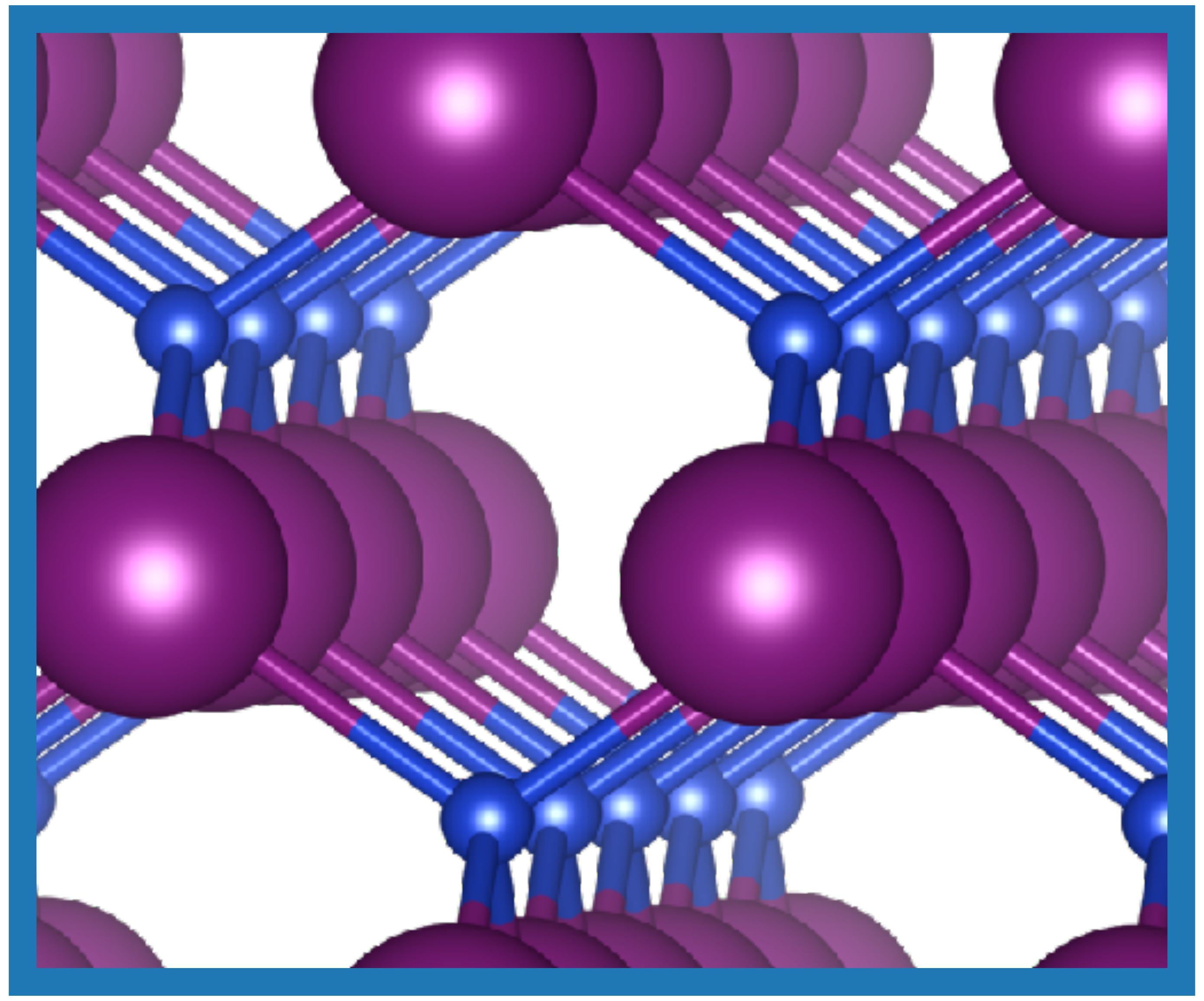

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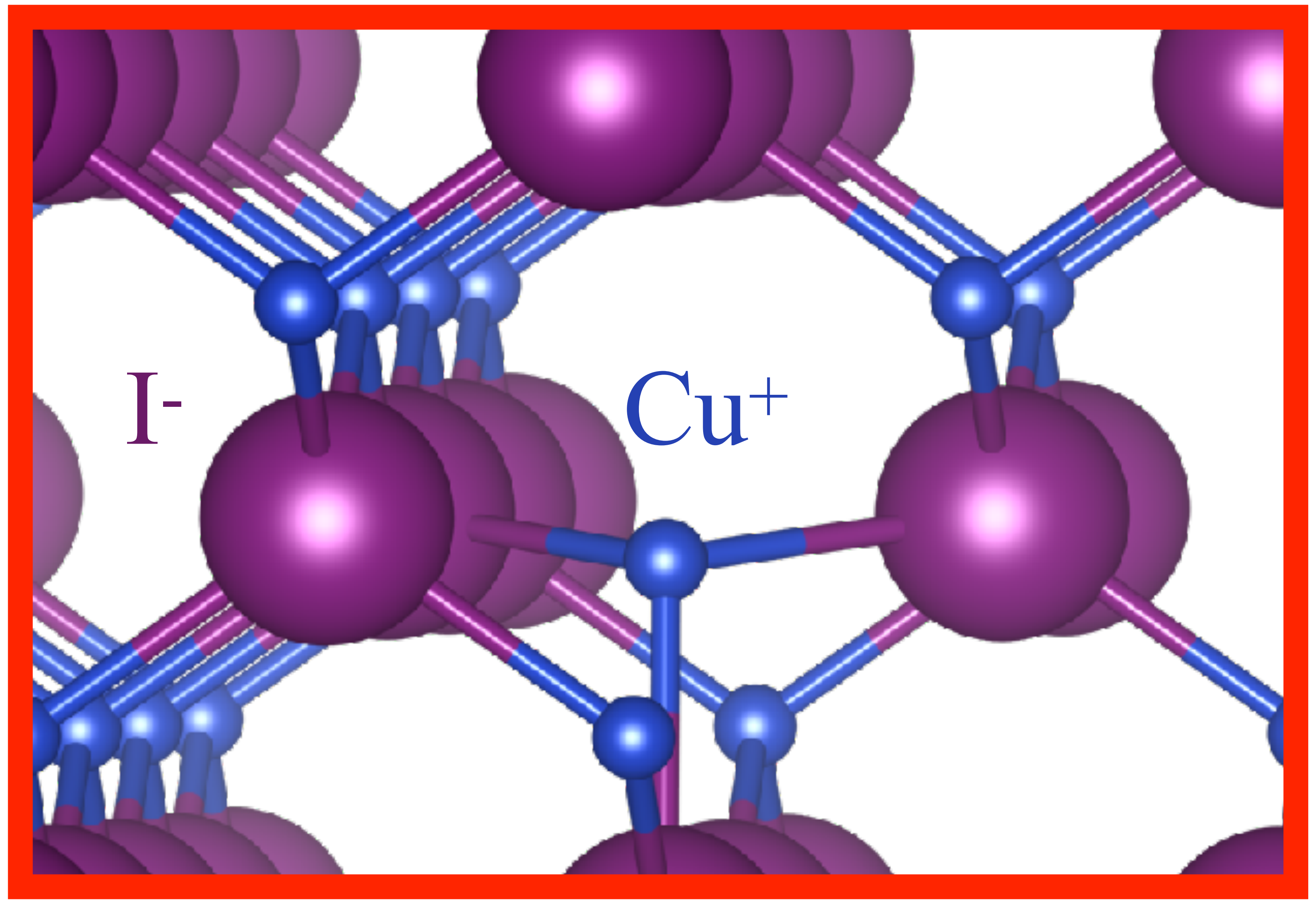

Time-averaged Structure:
A *metastable* Copper
Self-Interstitial has formed!


Anharmonicity in Copper Iodide
F. Knoop
236301 (2023).
Anharmonicity Metric σ^A
F. Knoop et al., Phys. Rev. Mater. 4, 083809 (2020).
CuI
50
60
Harmonic Approximation
E
R
equilibrium
Time-averaged Structure:
Pristine Zincblende Structure of Copper Iodide
Time-averaged Structure:
A metastable Copper Self-Interstitial has formed!
I-
Cu+

Anharmonicity in Copper Iodide

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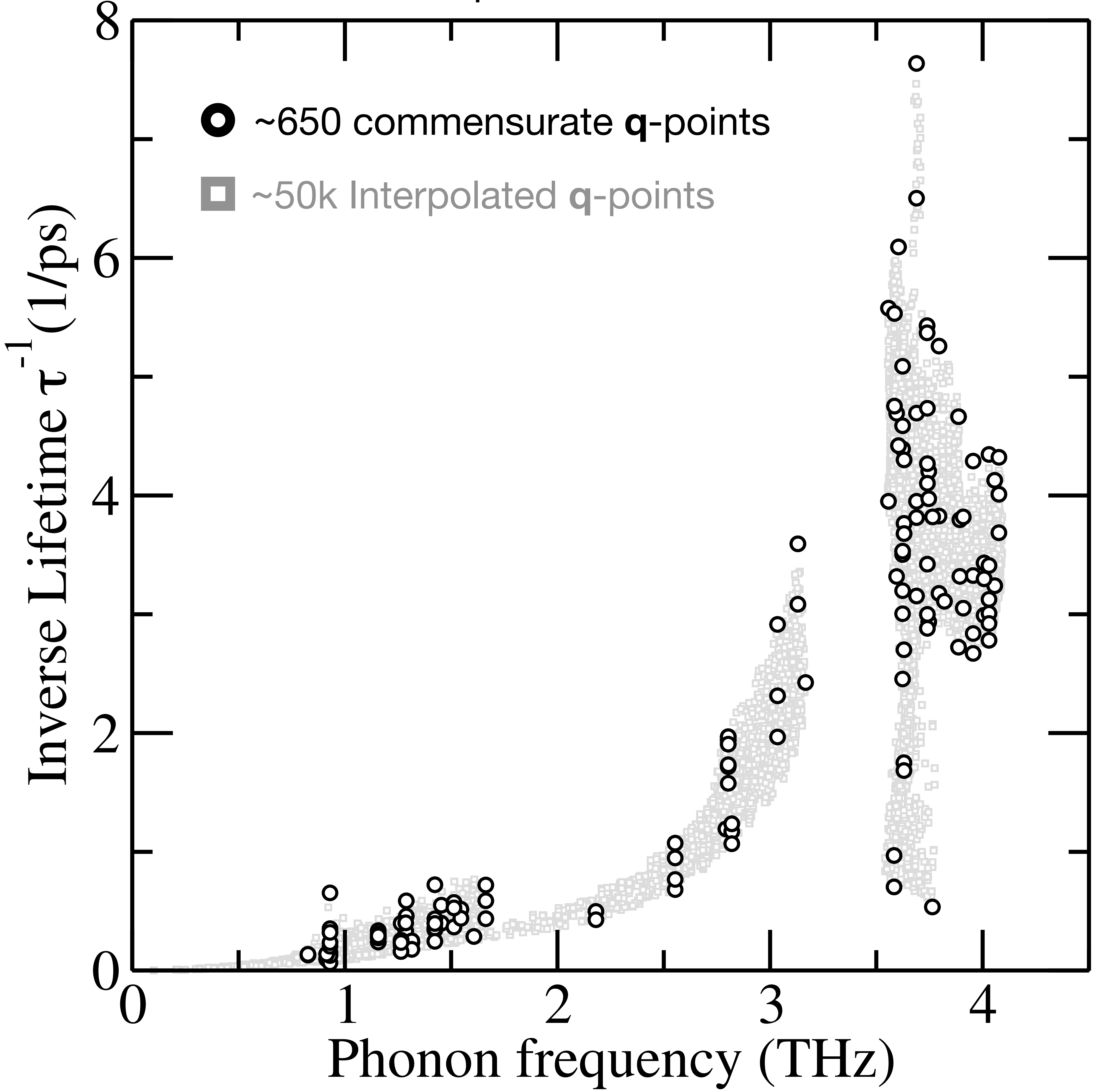

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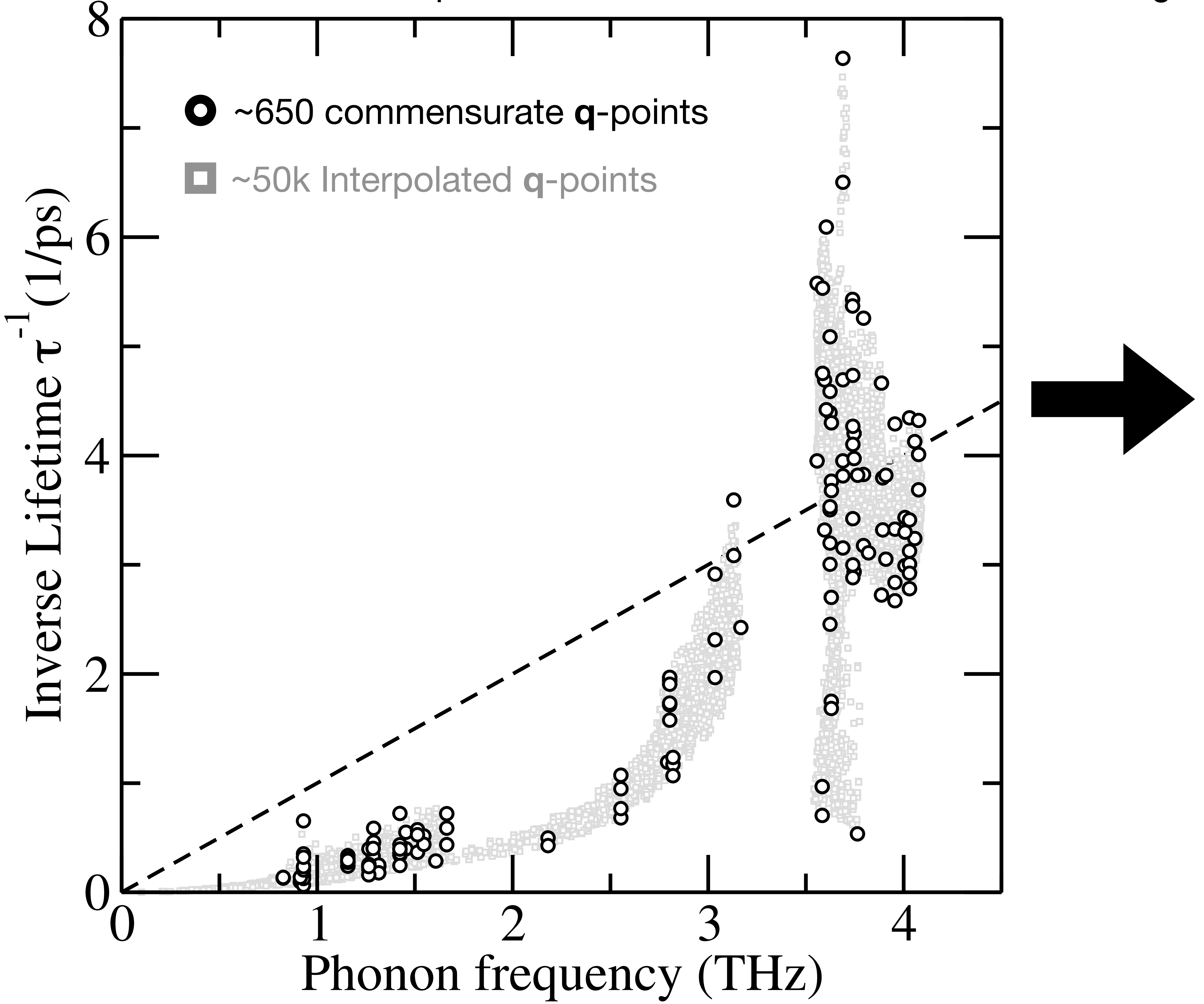

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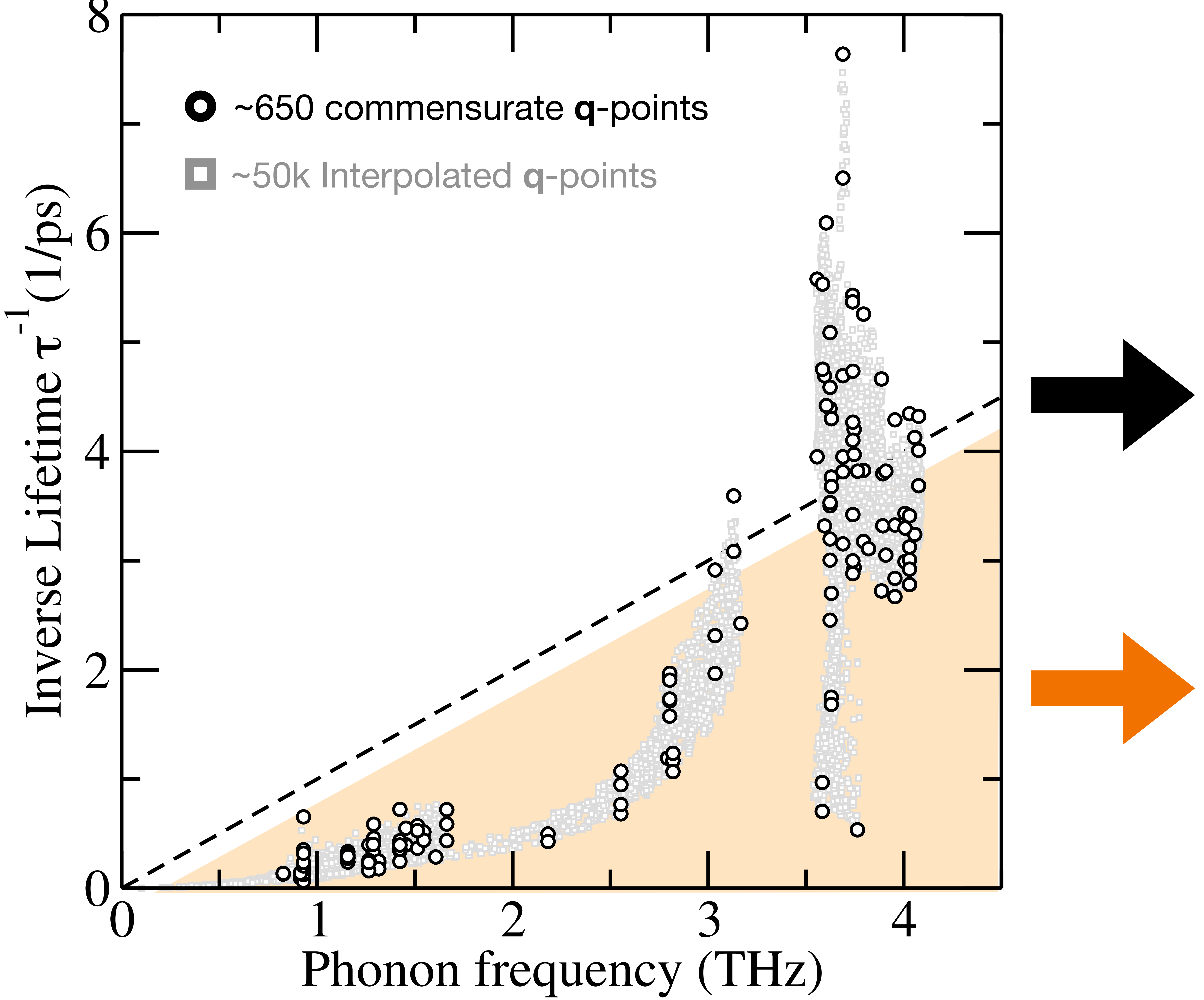

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Phonon Picture

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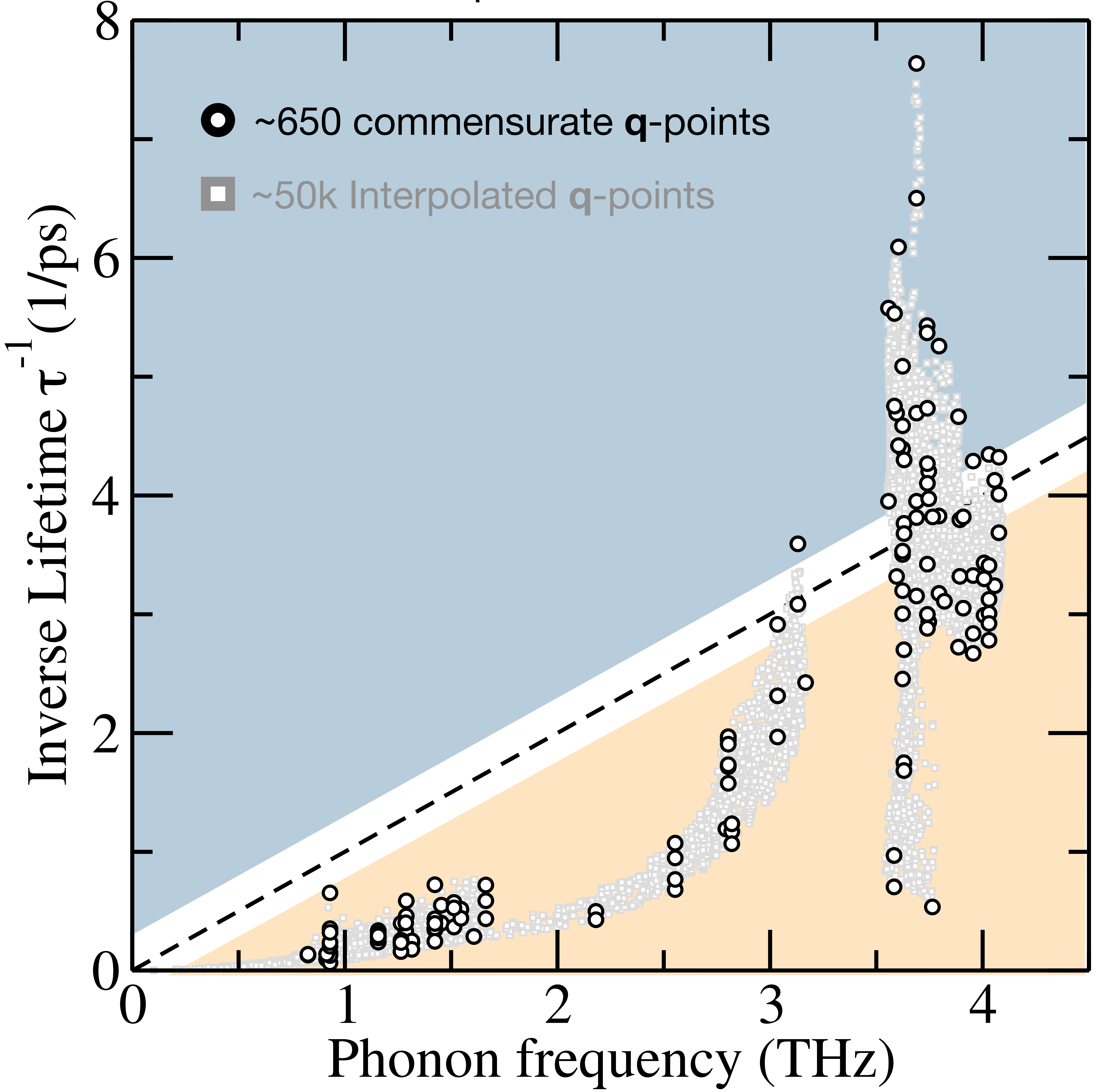

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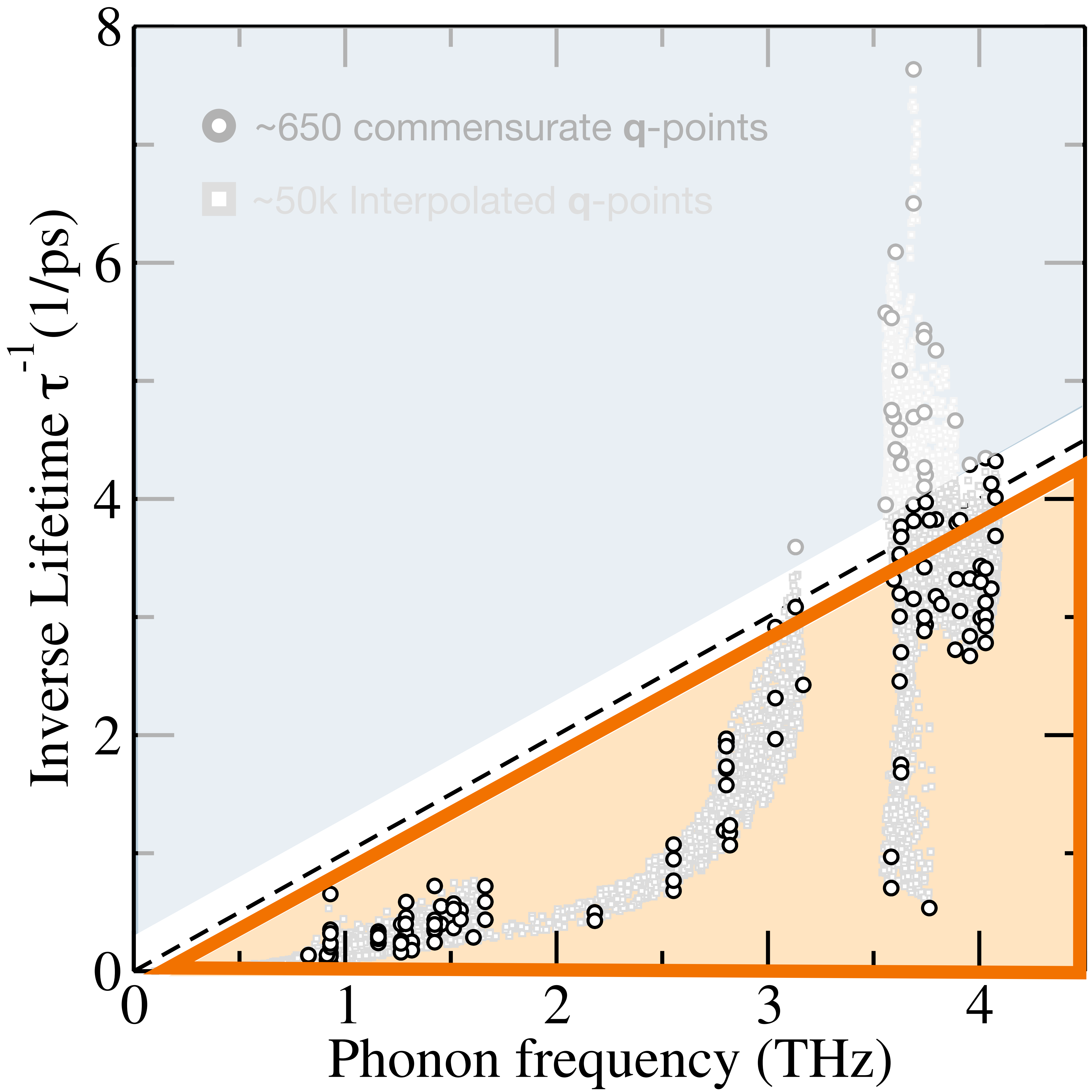

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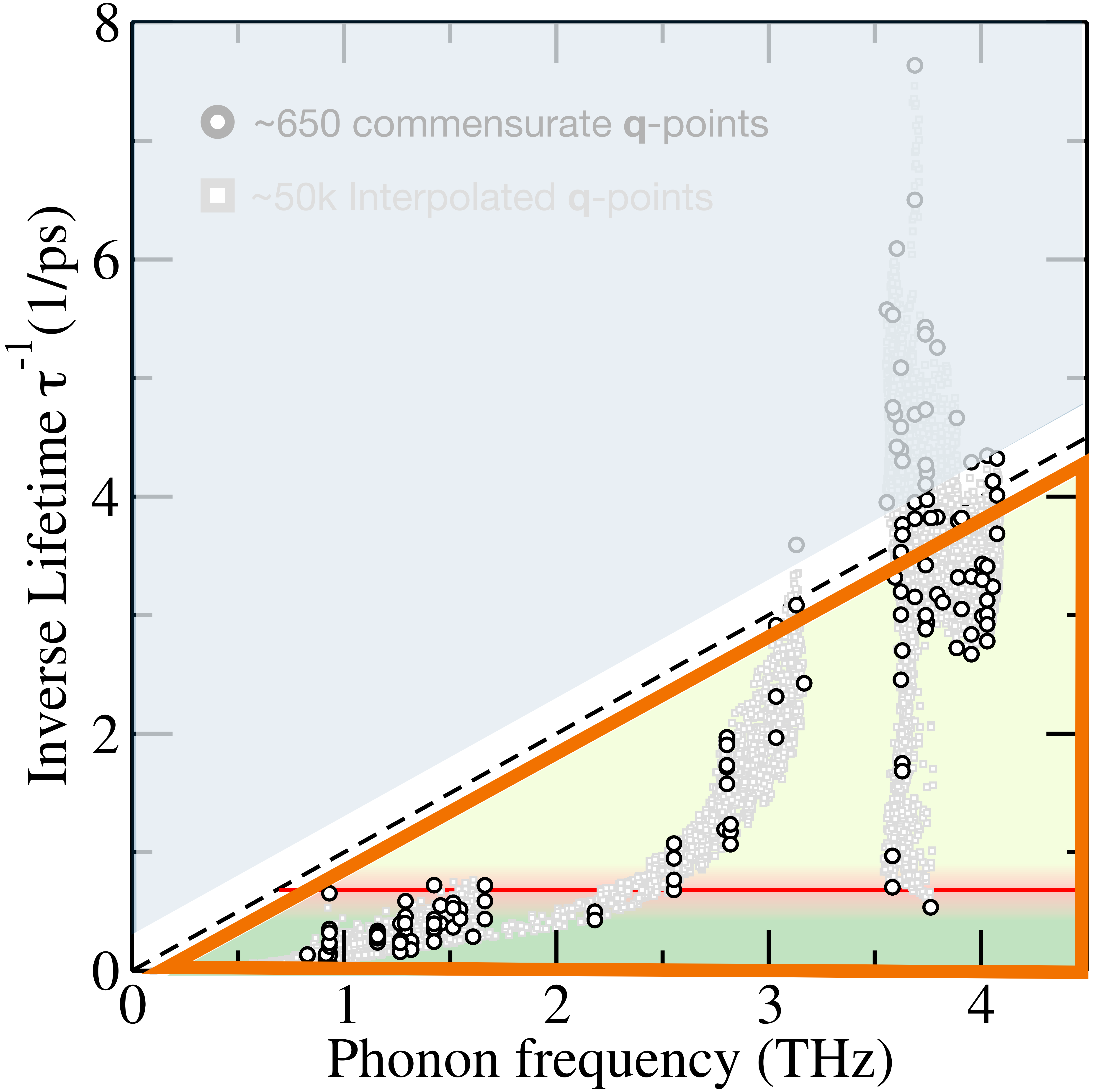

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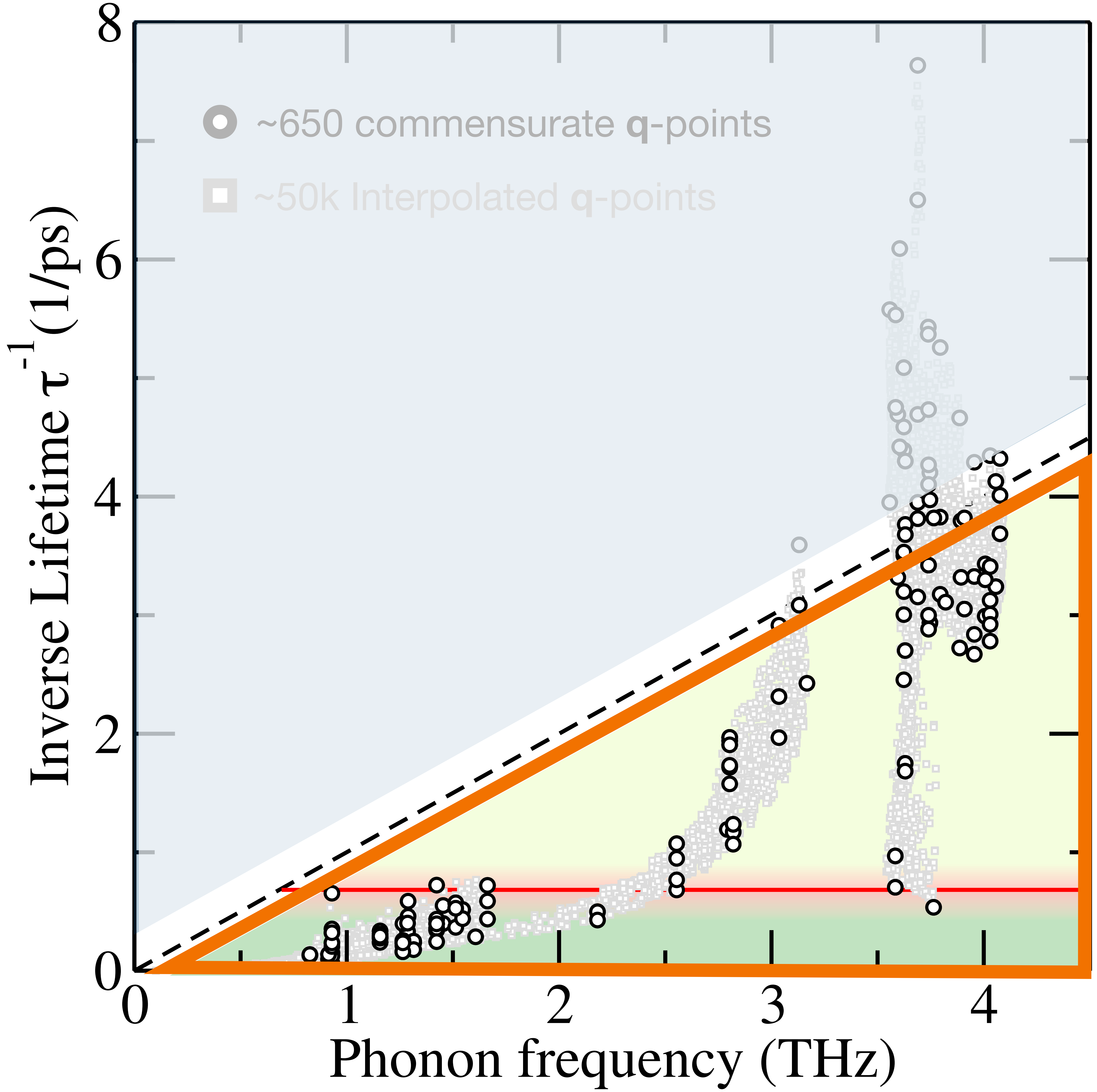

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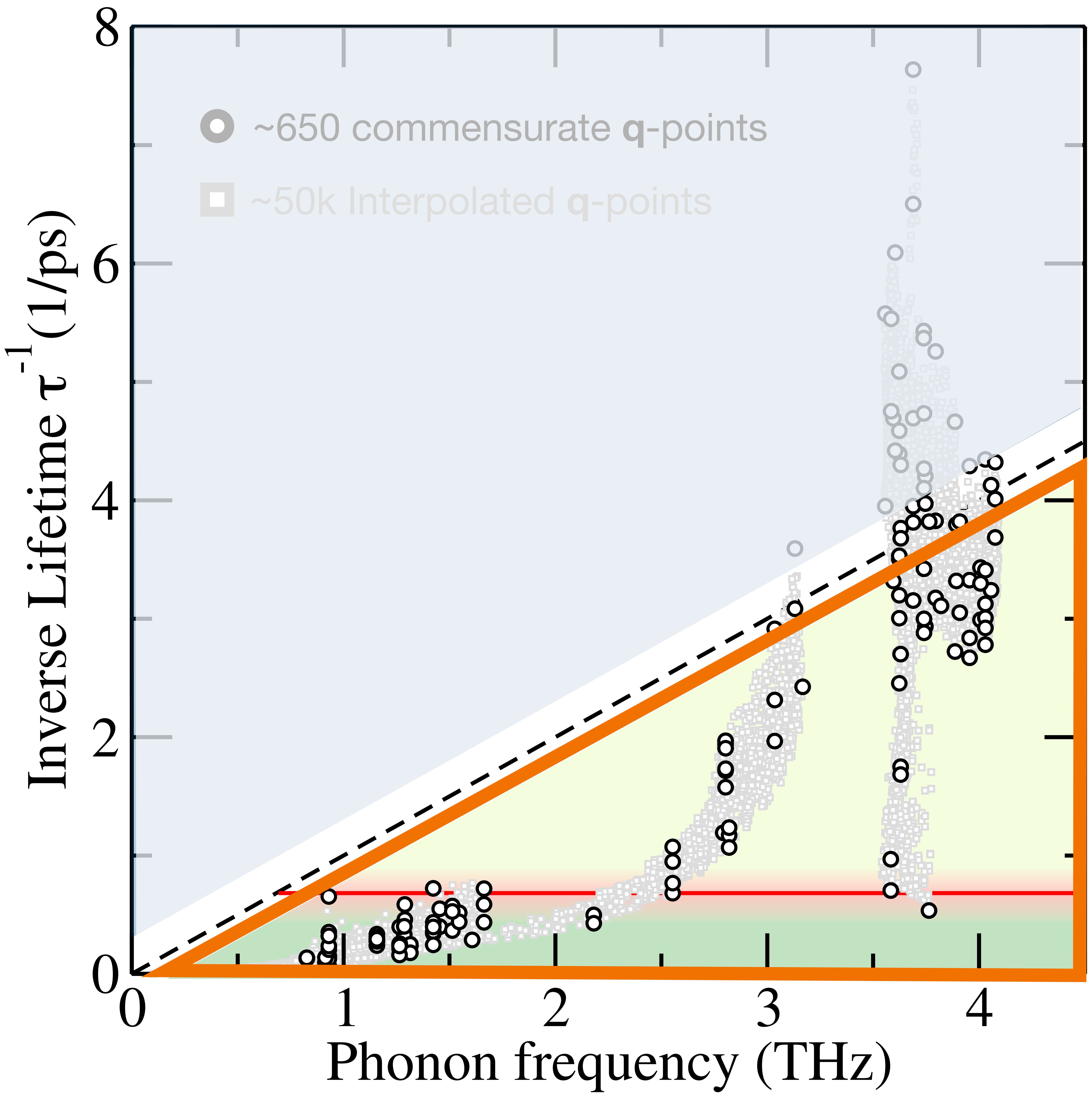

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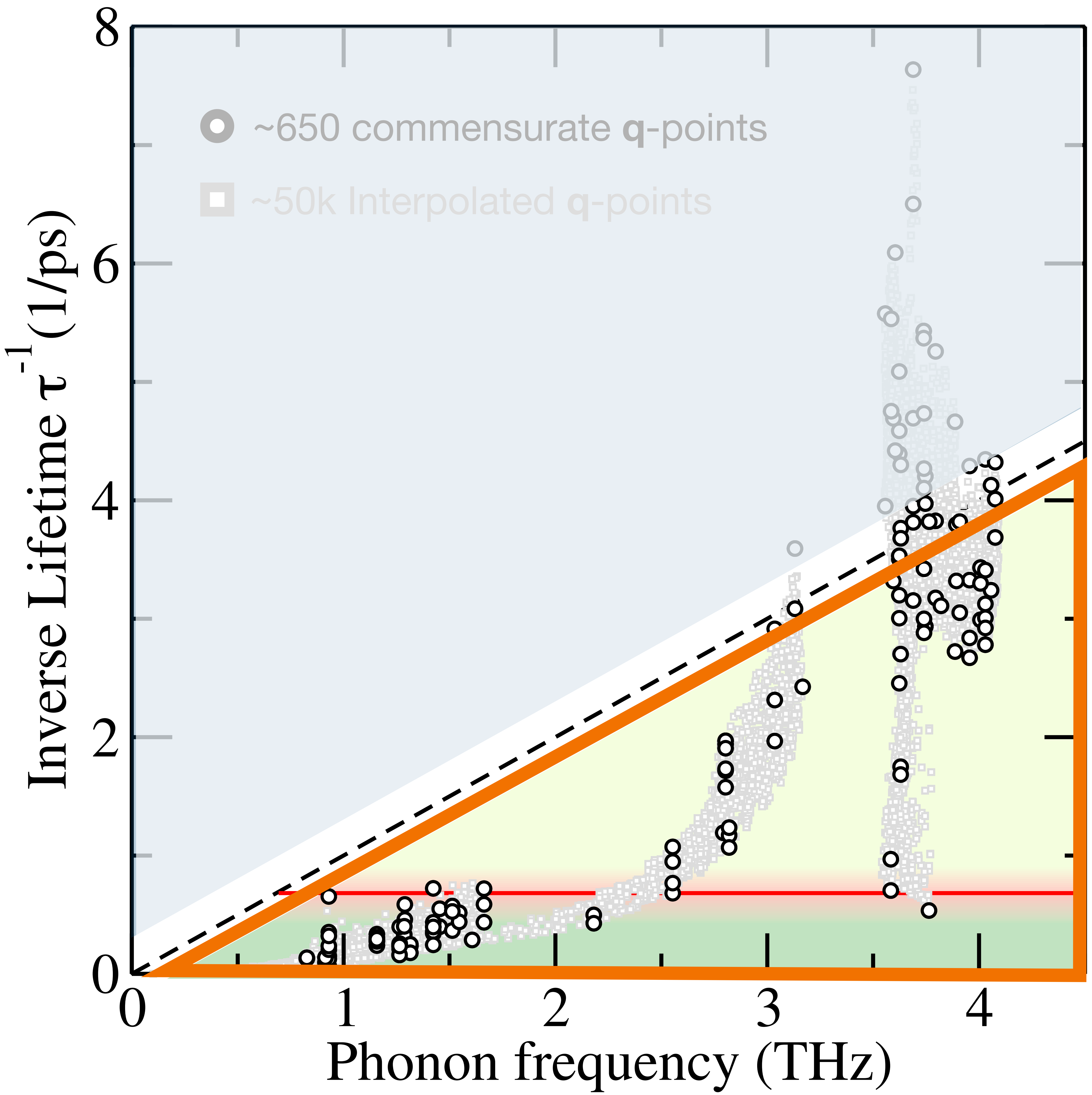

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Average interband spacing

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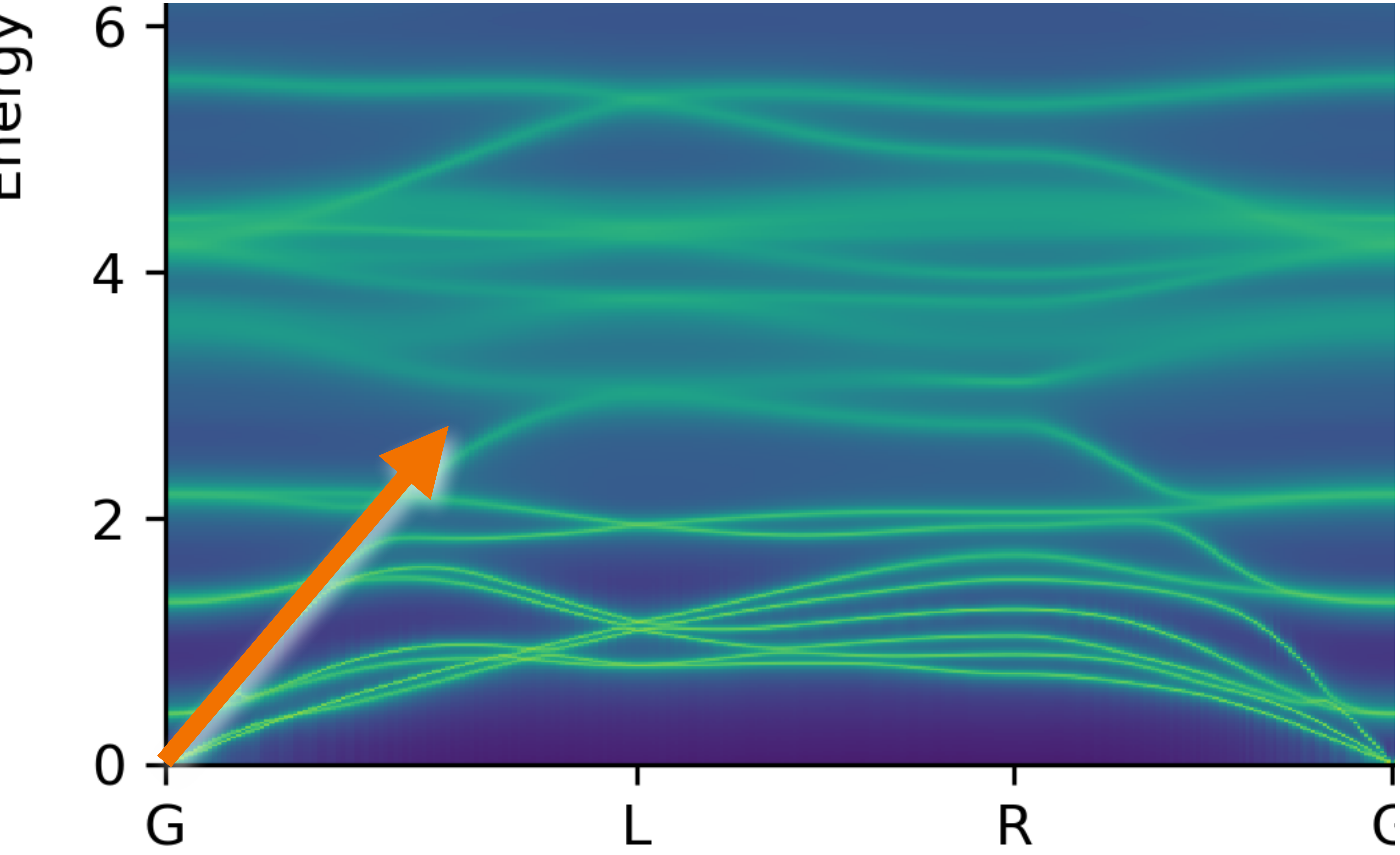
Wigner vs. Boltzmann Transport

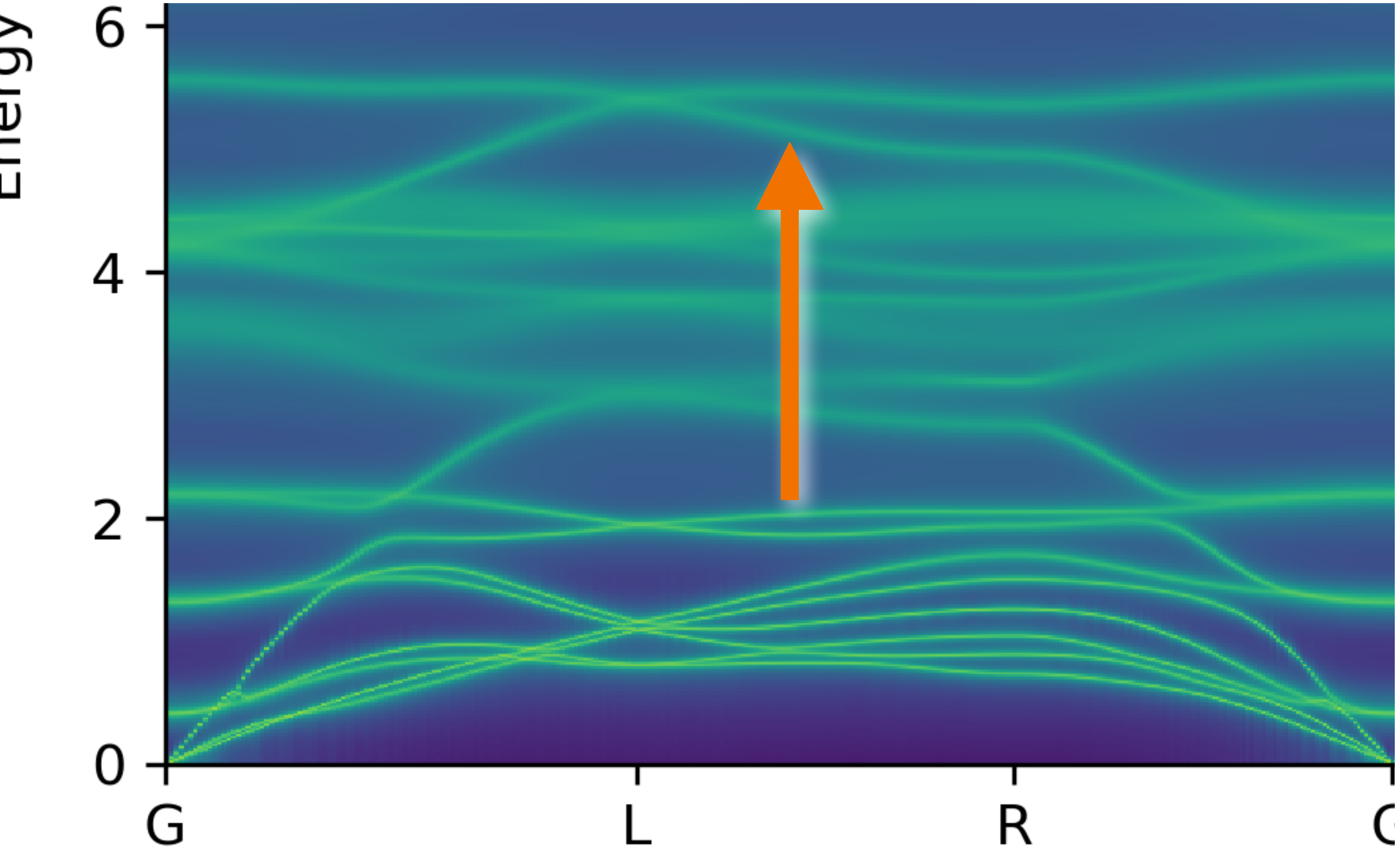


Spectral function of $AgGaGeS_2$; F.Knoop, Ph.D. Thesis

Boltzmann Transport:

Transport determined by **group** velocity, i.e., the diagonal of the **momentum matrix:** $\mathbf{v}_g = < s | \mathbf{v} | s >$

Wigner vs. Boltzmann Transport



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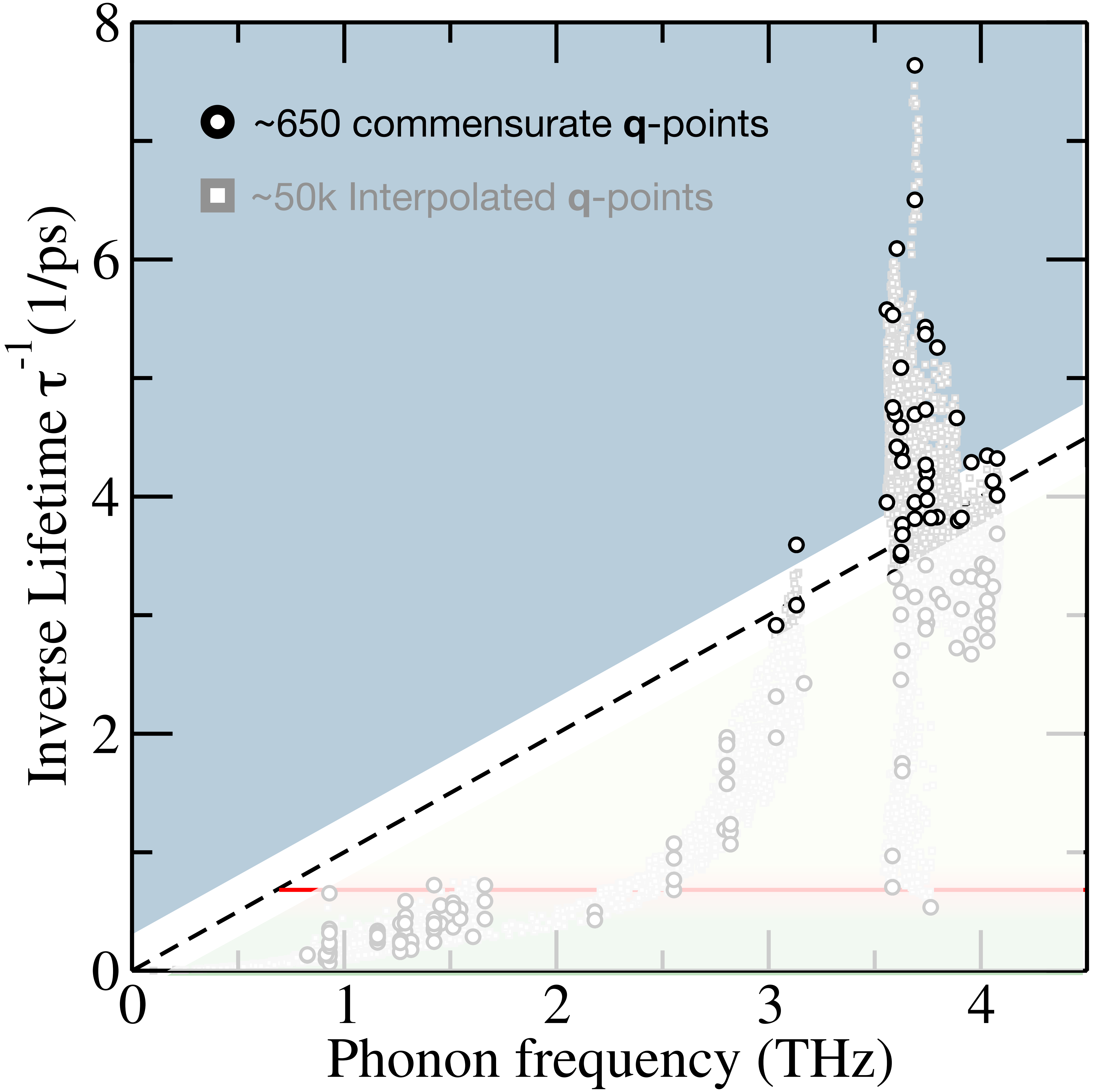
Boltzmann Transport:

Transport determined by **group** velocity, i.e., the diagonal of the **momentum matrix:** $\mathbf{v}_g = < s \,|\, \mathbf{v} \,|\, s >$

Wigner Transport:

Transport determined by **direct transition**, i.e., the off-diagonal of the **momentum matrix:** $< s \,|\, \mathbf{v} \,|\, s' >$

Validity of Phonon-based Theories



Strongly Anharmonic Regime

What happens with **electronic transport** in this regime?

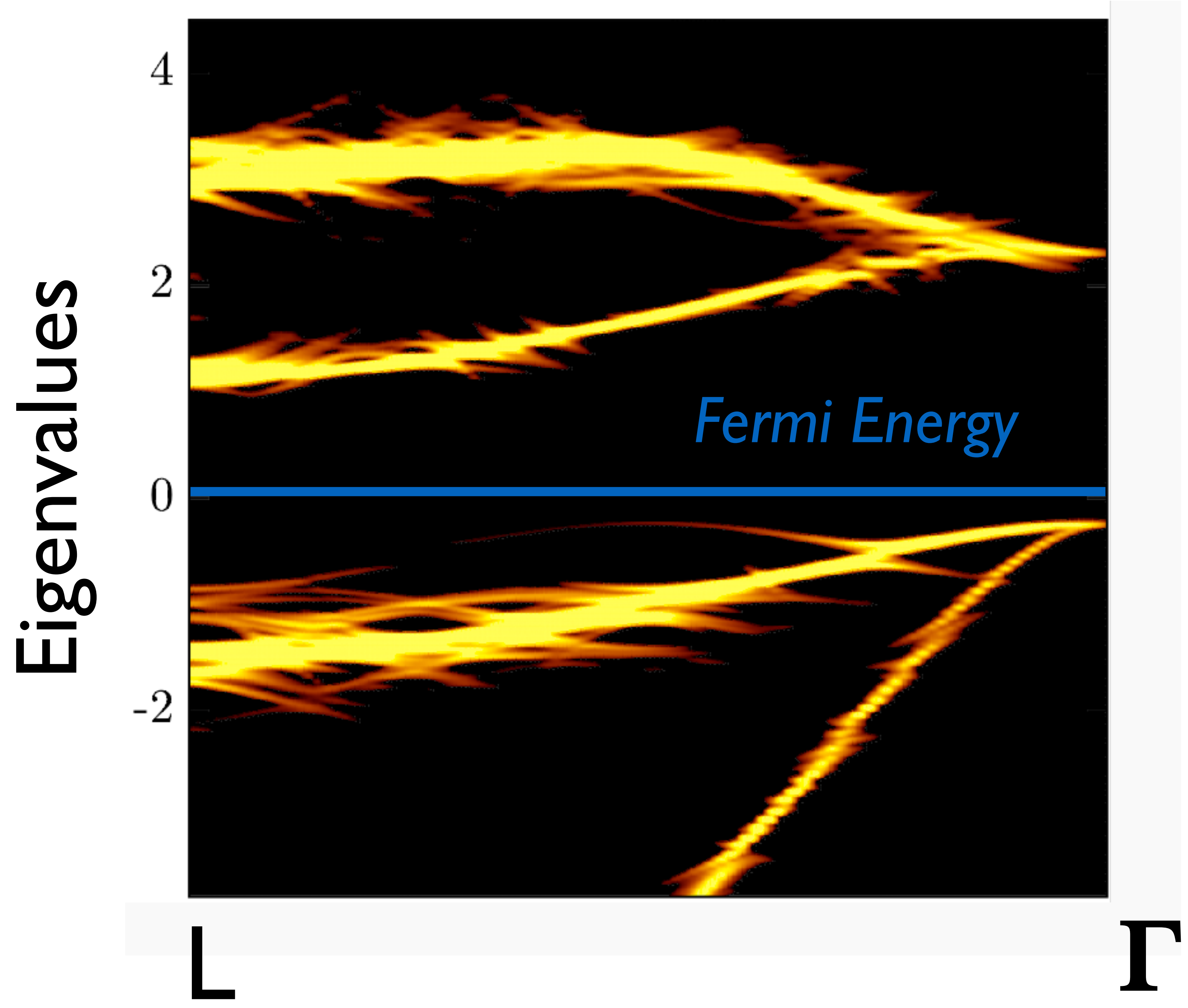
Anharmonic Effects in Electronic Transport

Ab initio MD

Band Structure Unfolding

Fully Anharmonic, non-perturbative assessment of vibronically renormalized electronic band structures.

M. Zacharias, M. Scheffler, and C. Carbogno,
Phys. Rev. B **102**, 045126 (2020).



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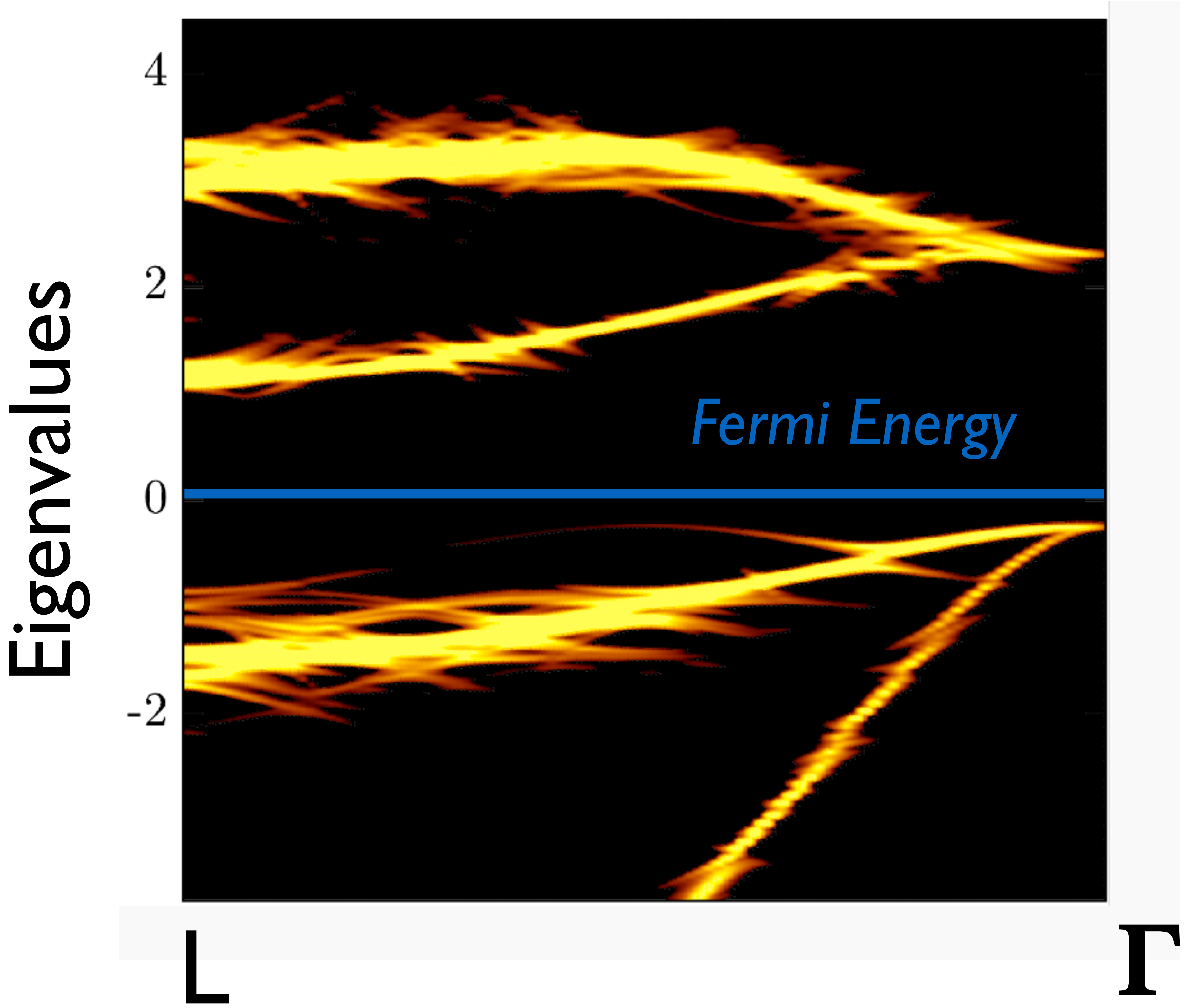
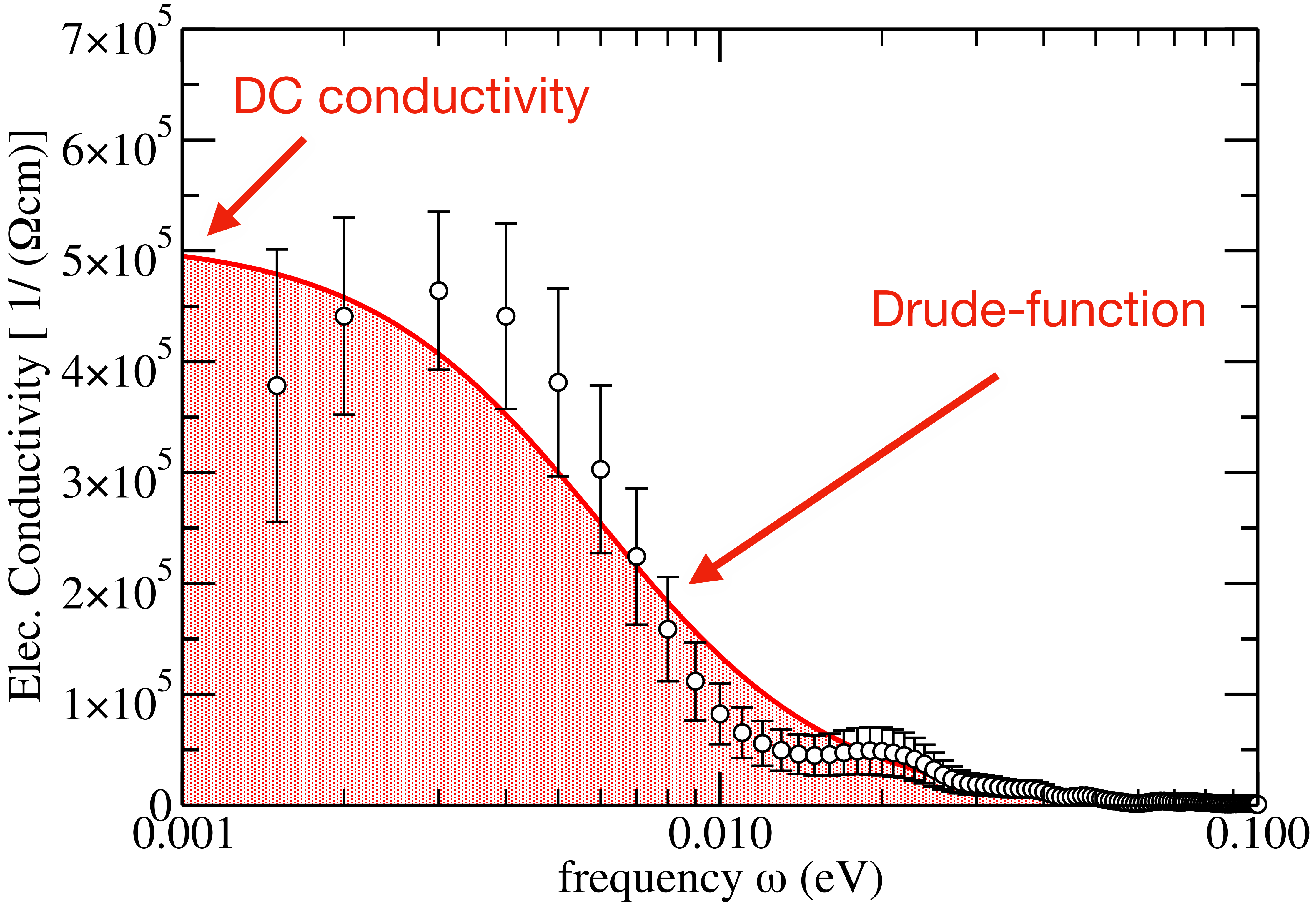


Ab initio MD

Kubo-Greenwood Formalism

Fully Anharmonic, non-perturbative assessment of electronic transport coefficients.

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



GREENWOOD-KUBO FORMALISM

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

Kubo's Linear Response:

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

Independent Particle Picture:

$$\mathbf{j}_c = -\frac{e}{\hbar} \frac{\partial \varepsilon_n(\mathbf{k})}{\partial \mathbf{k}} \quad \xrightarrow{\text{Heisenberg picture}} \quad \mathbf{j}_c(t)$$

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

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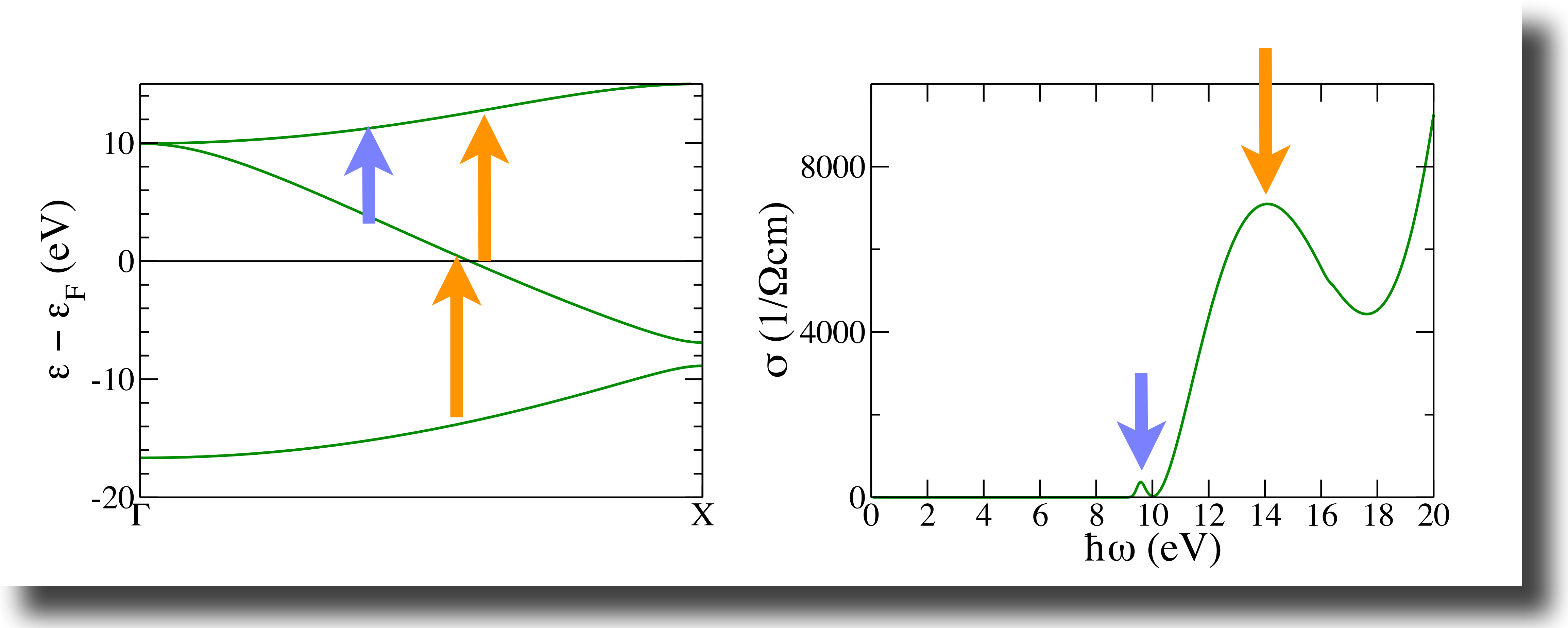

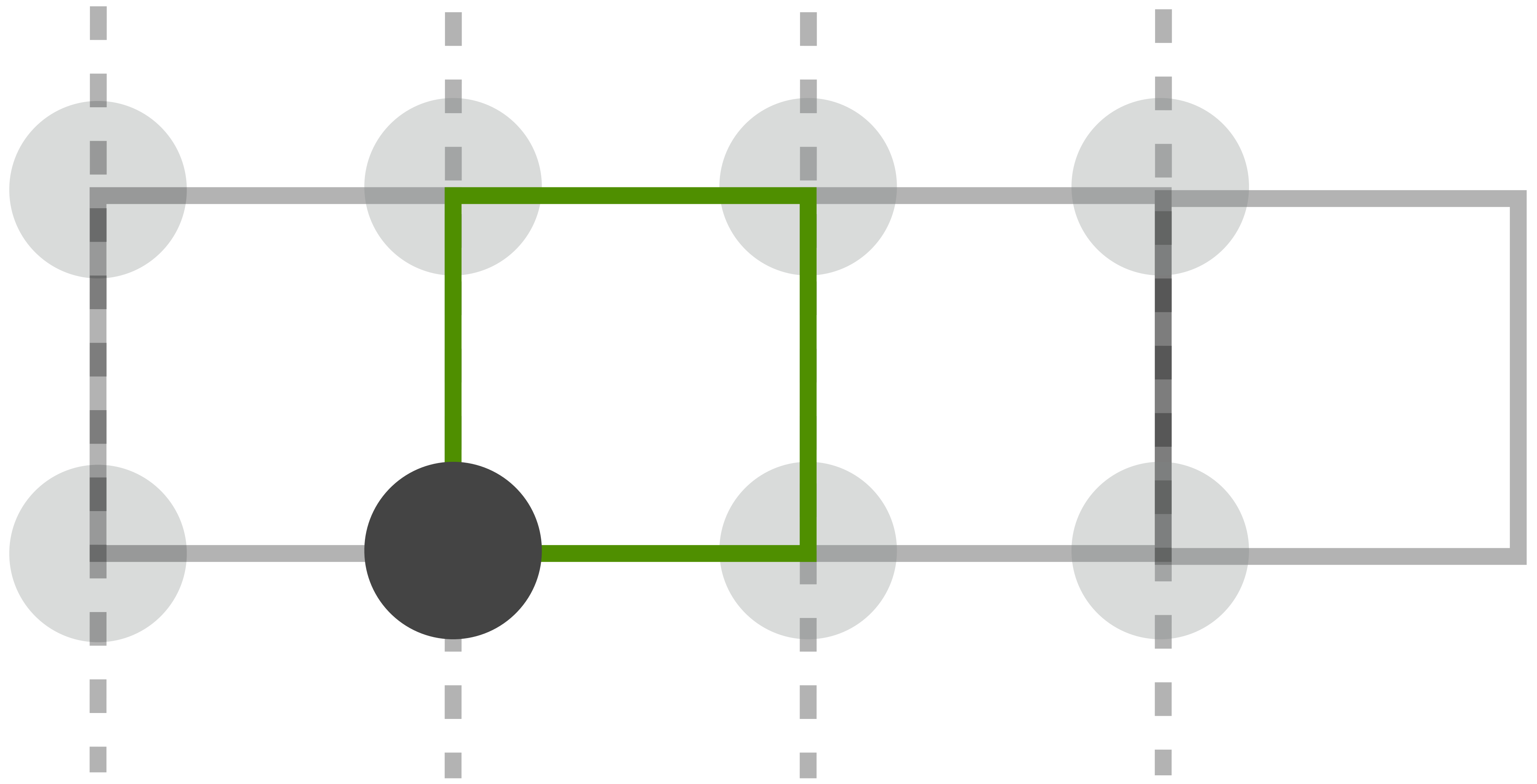

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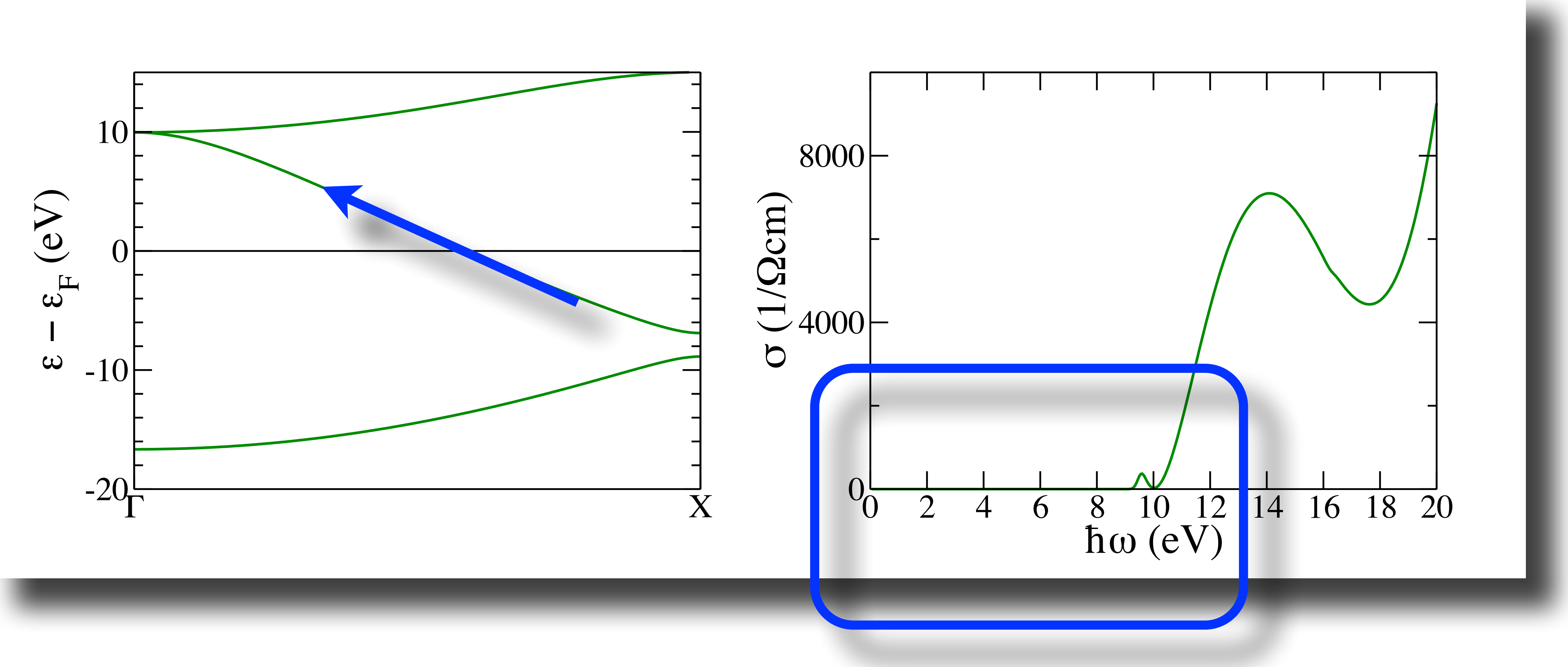

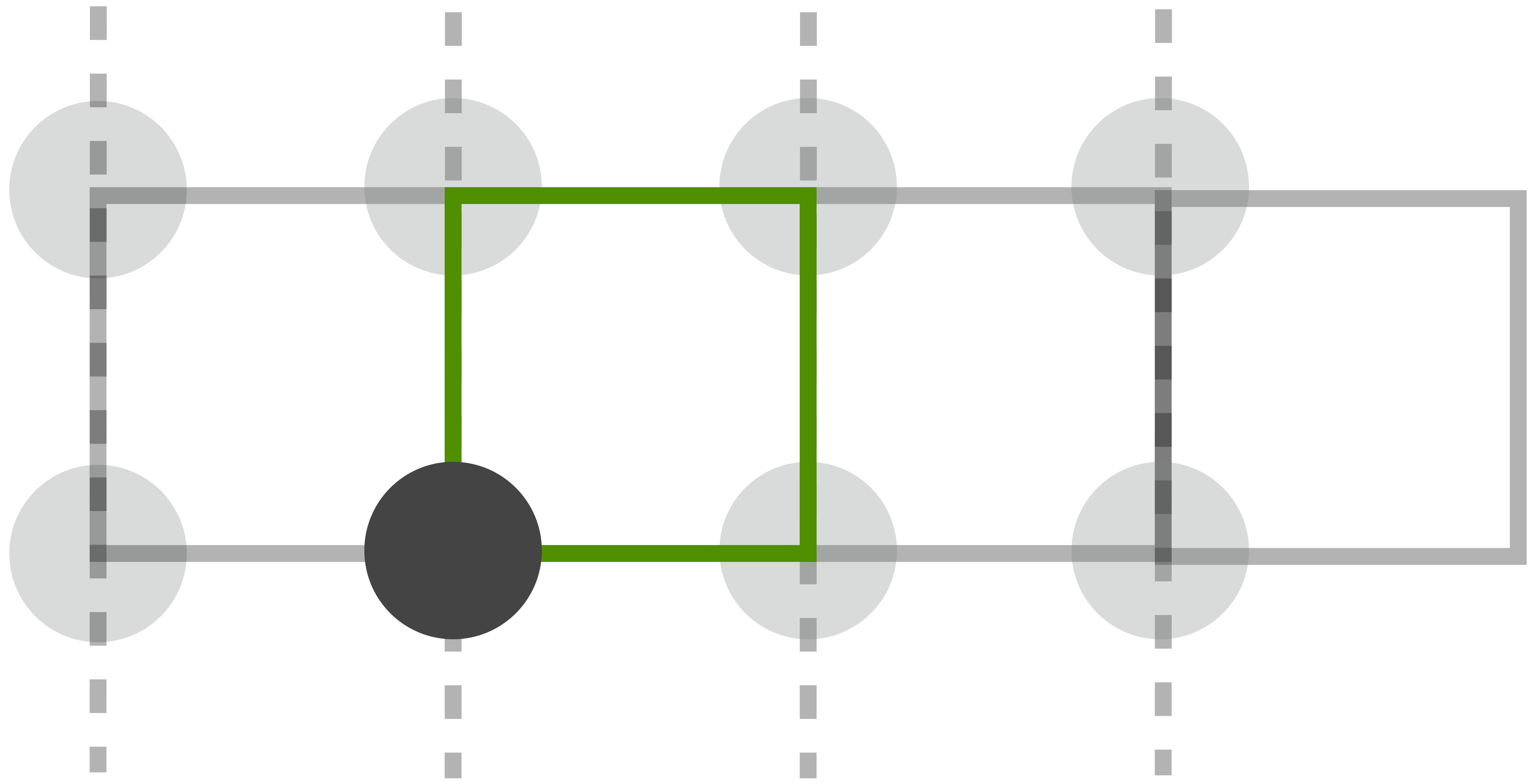

Crystal Momentum Conservation:
Non-vertical transitions require **phonons**

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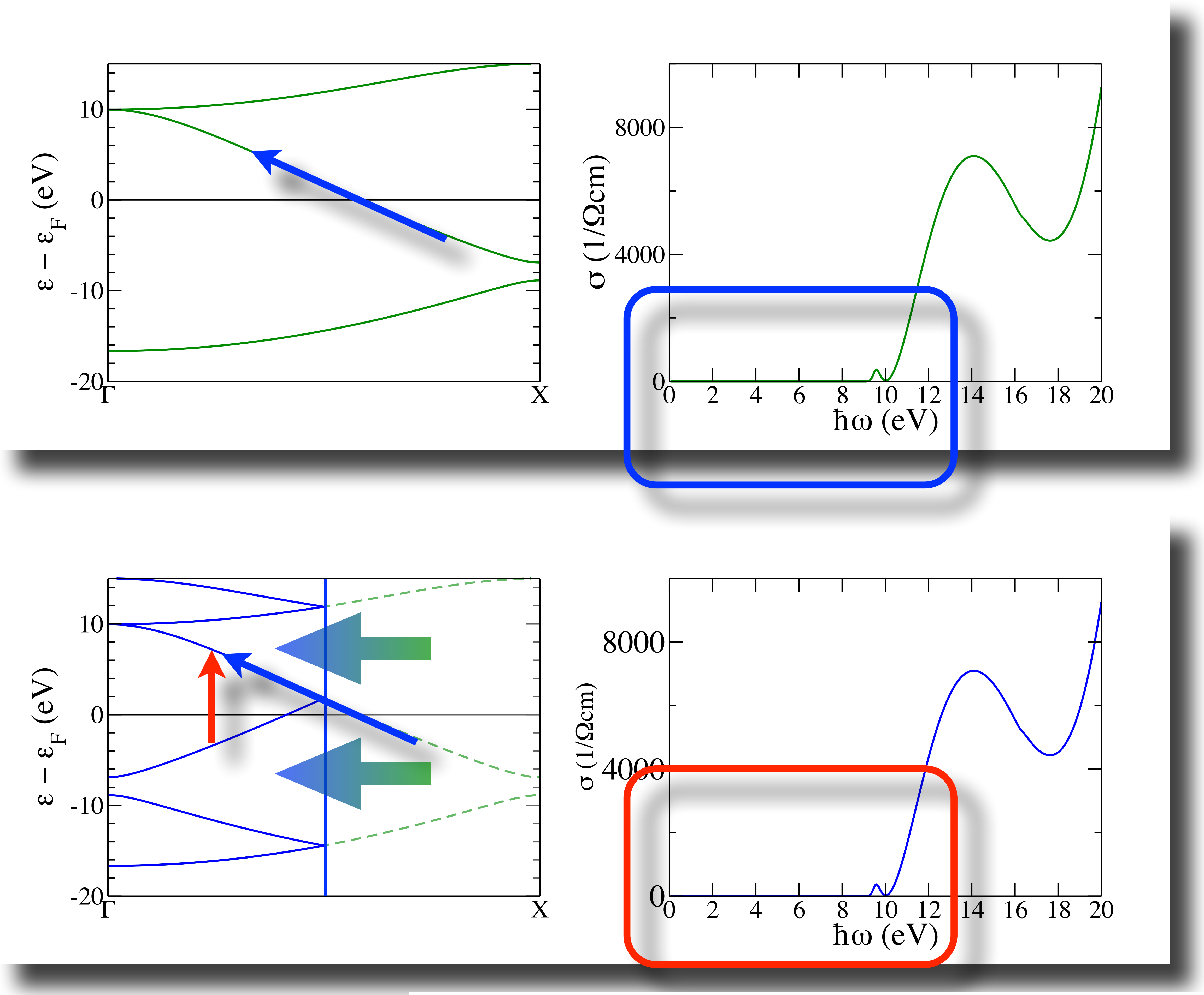

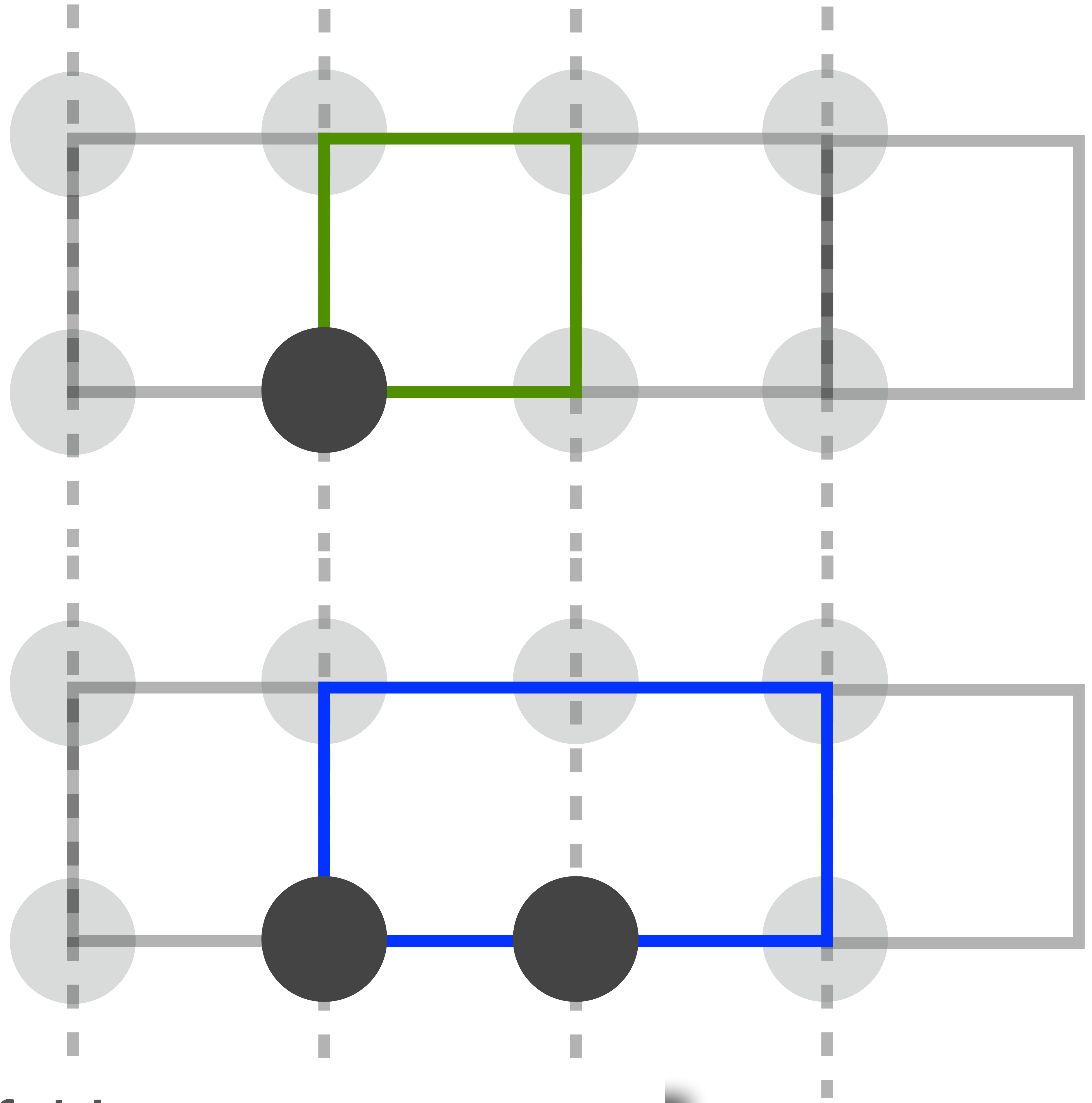

Brillouin zone folding:
Larger supercells allow for **direct transitions**
that are however suppressed by **symmetry**.

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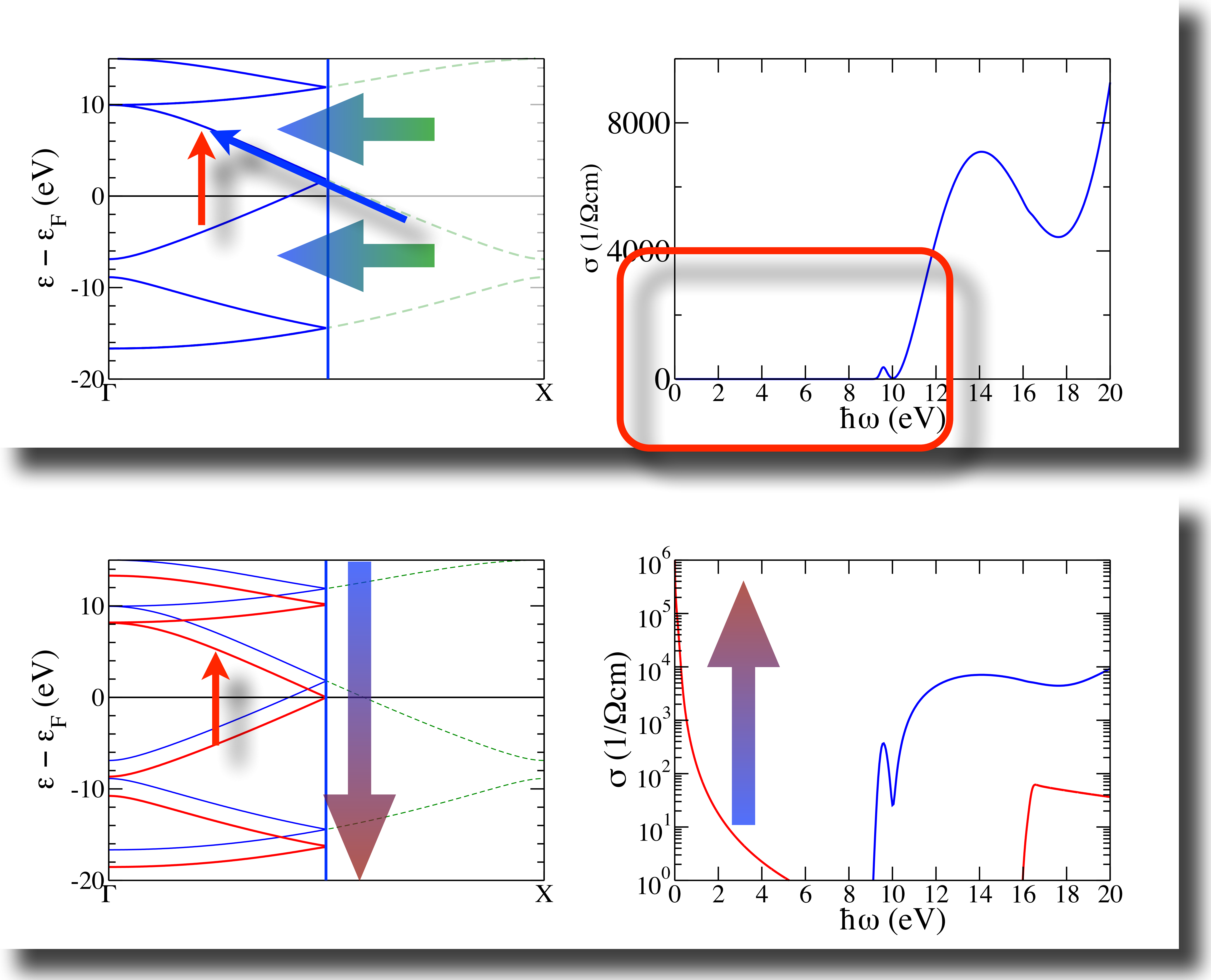

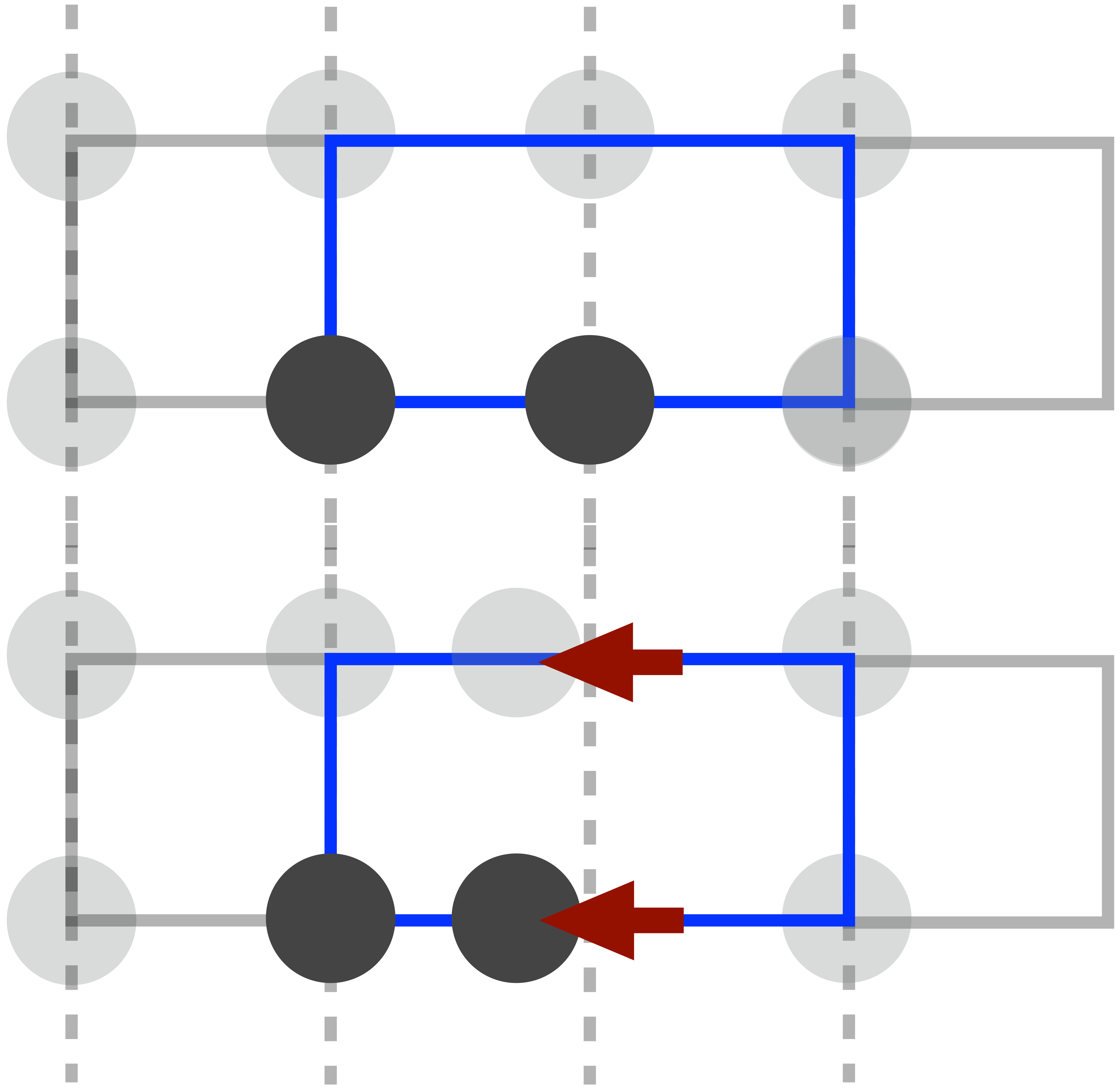

Thermal Motion of the nuclei:

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

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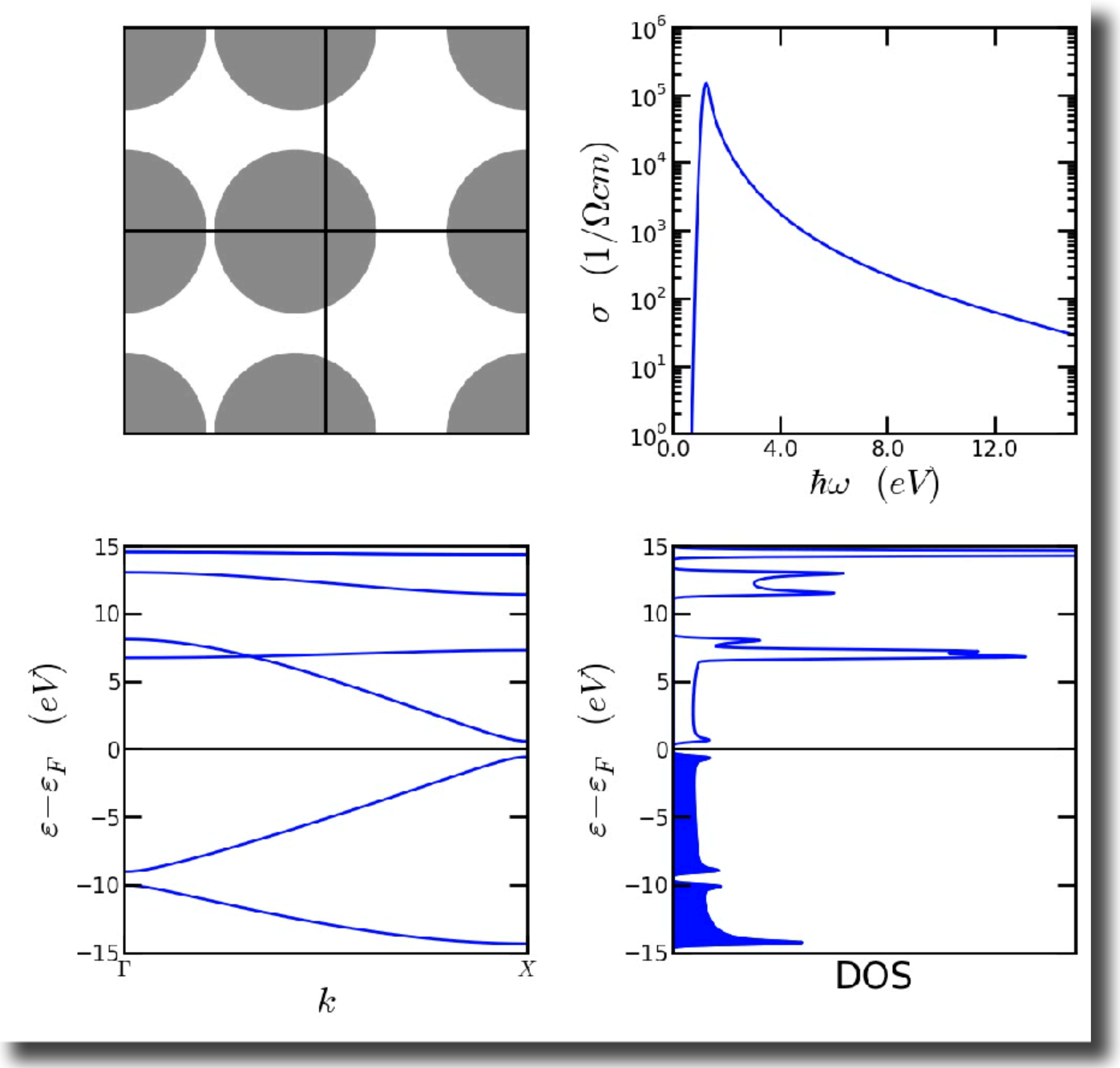

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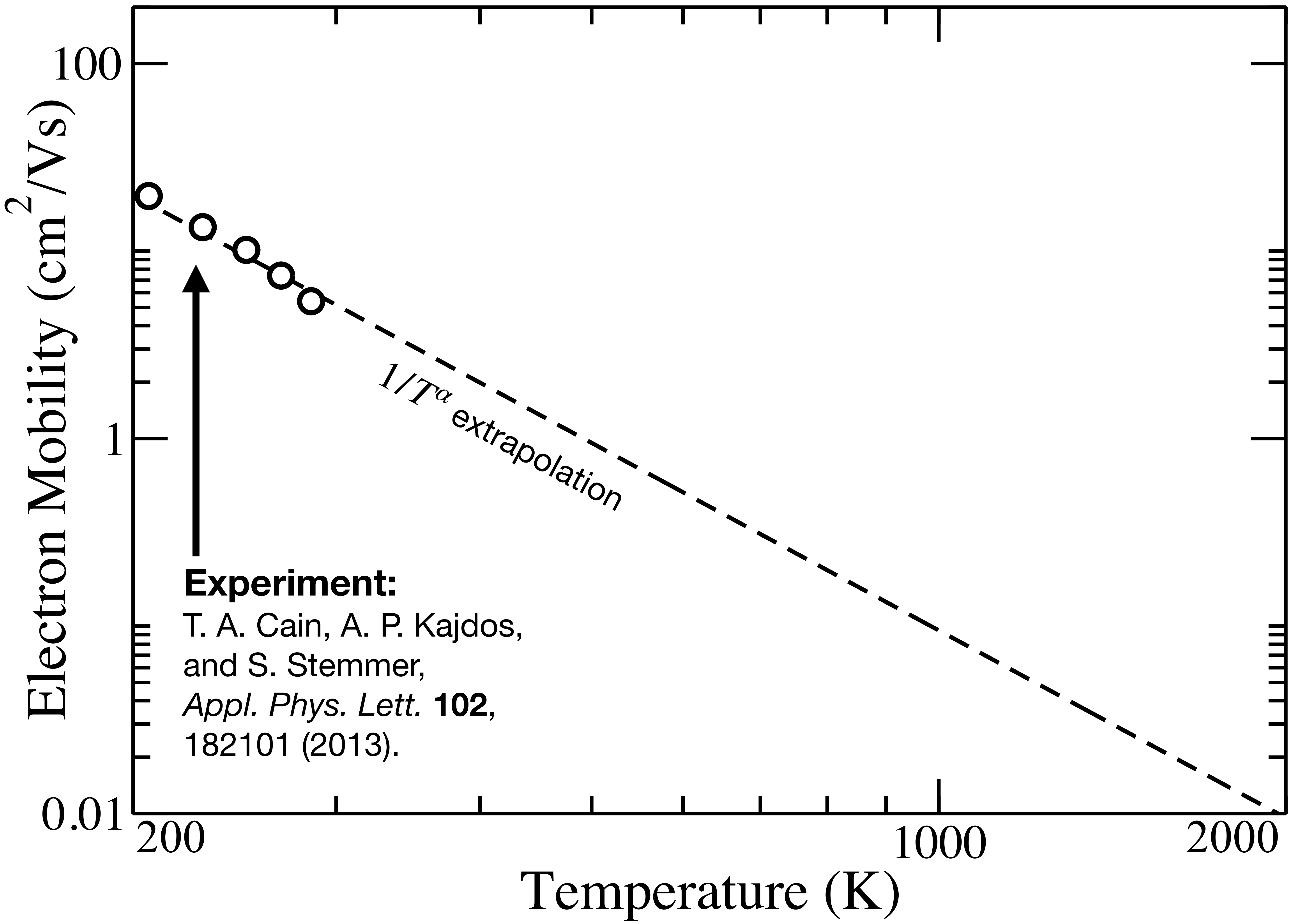
Challenges:

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

– **Large supercell needed to resolve phonon dispersion**

Mobility in Highly Anharmonic $SrTiO_3$

Doping: $8x10^{17}$ cm^{-3}



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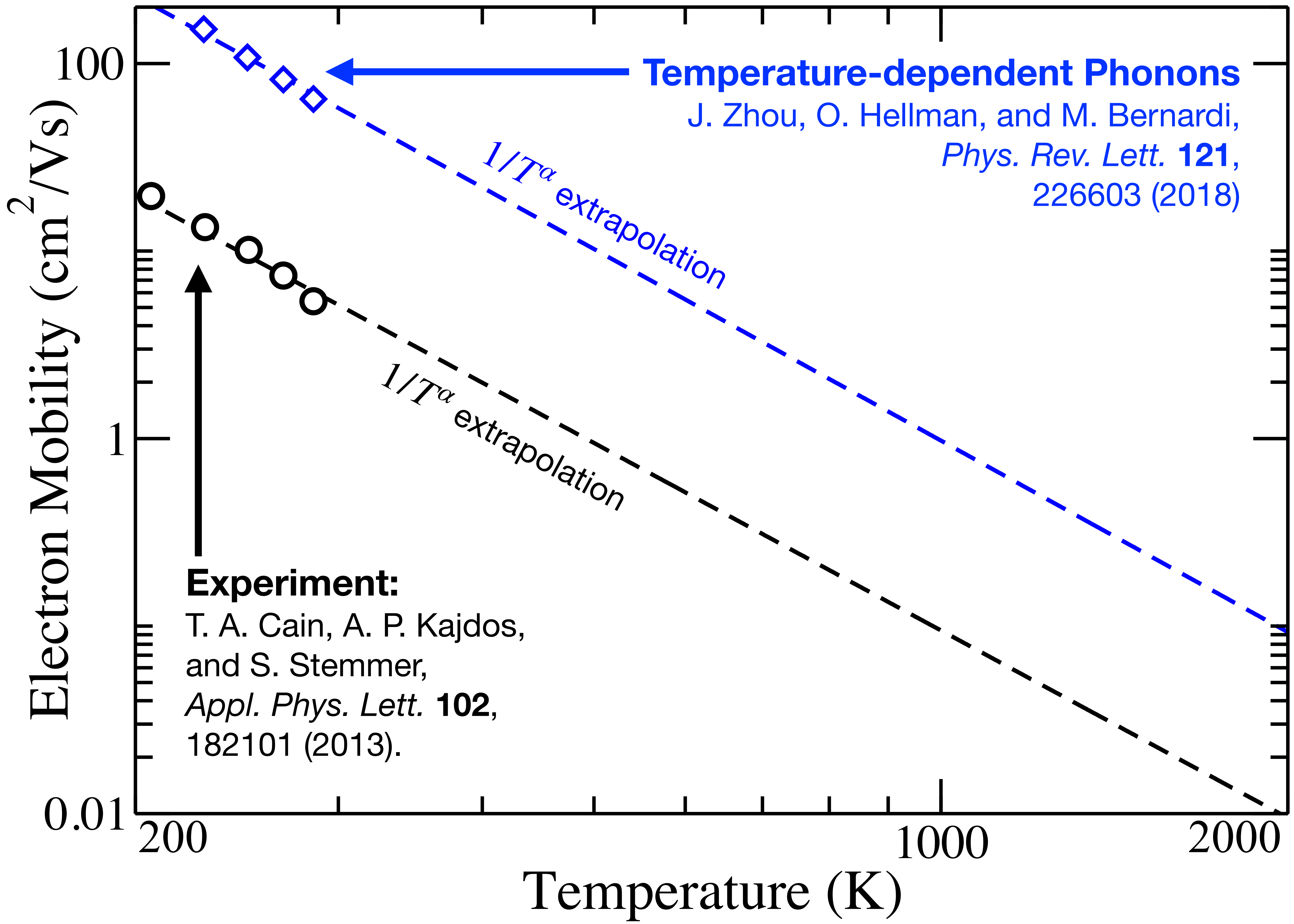

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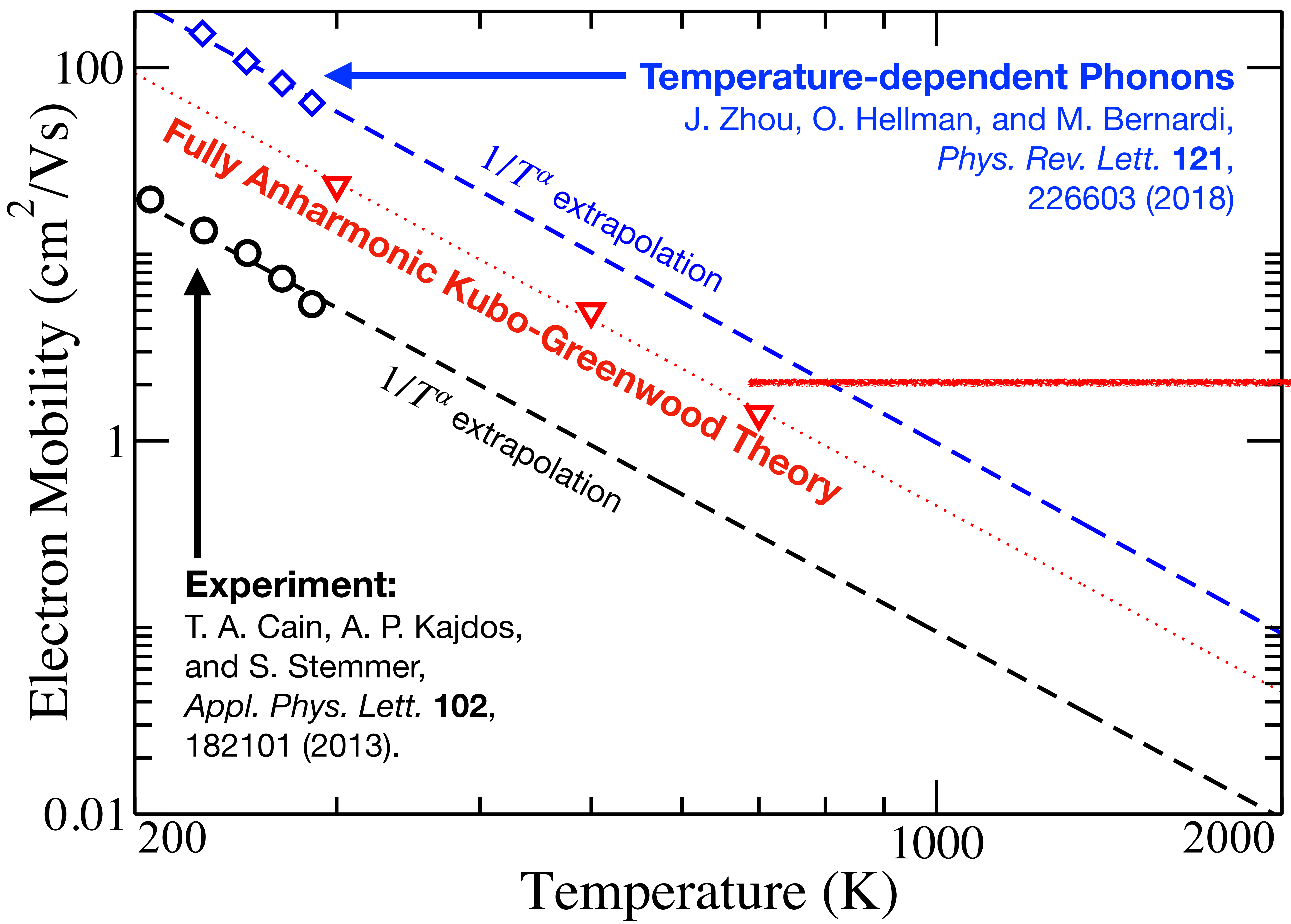

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Fully-anharmonic KG Theory
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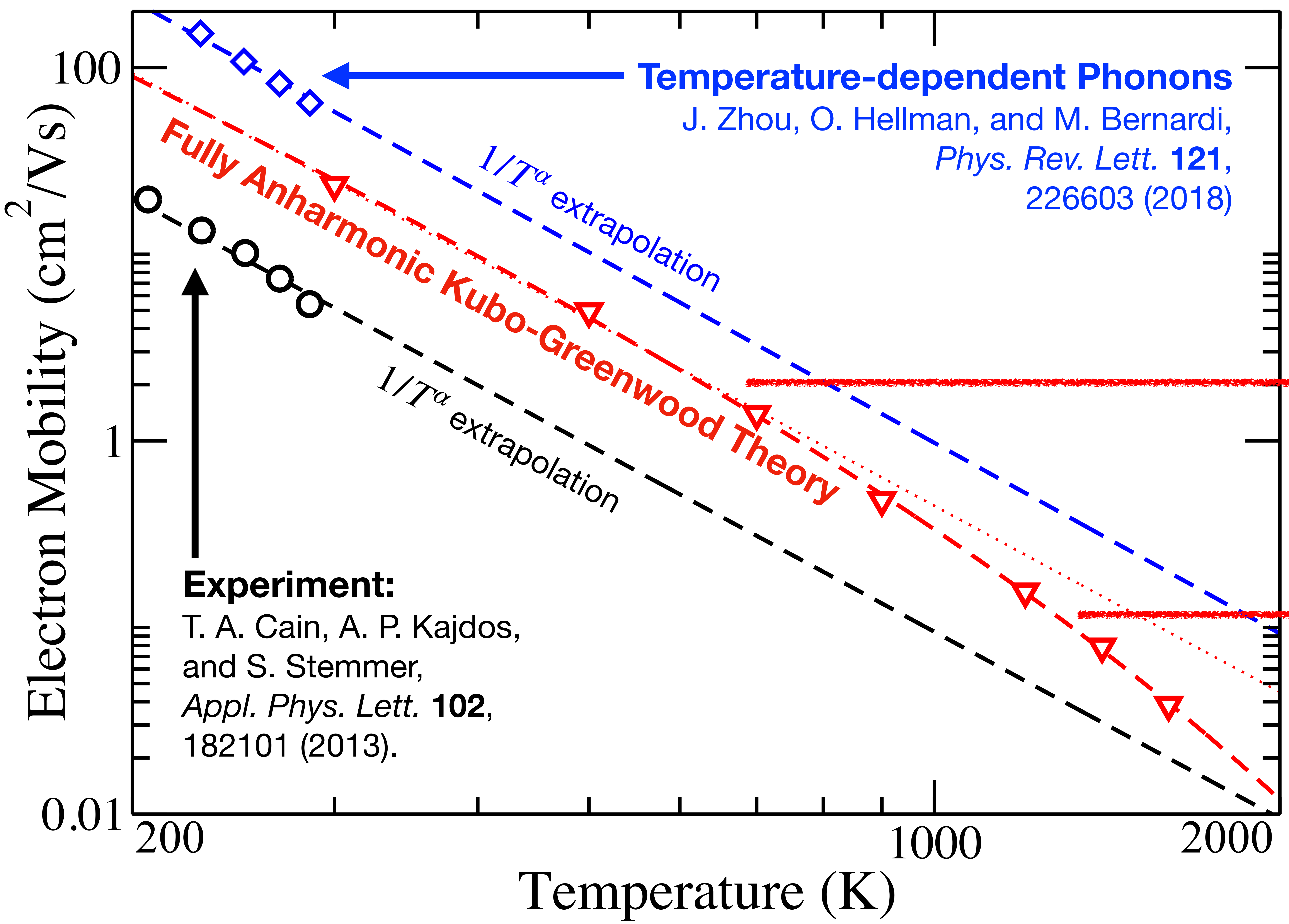

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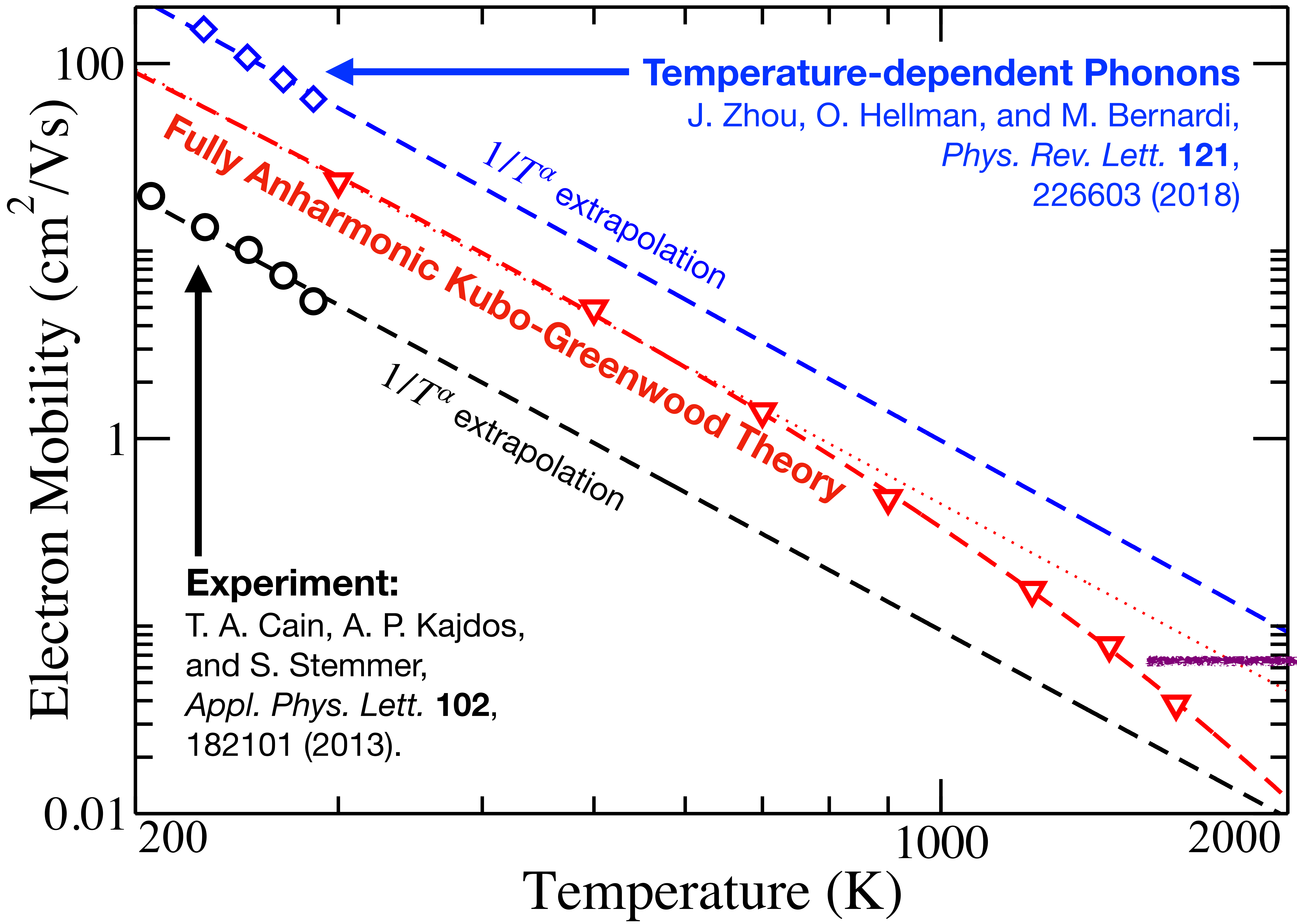
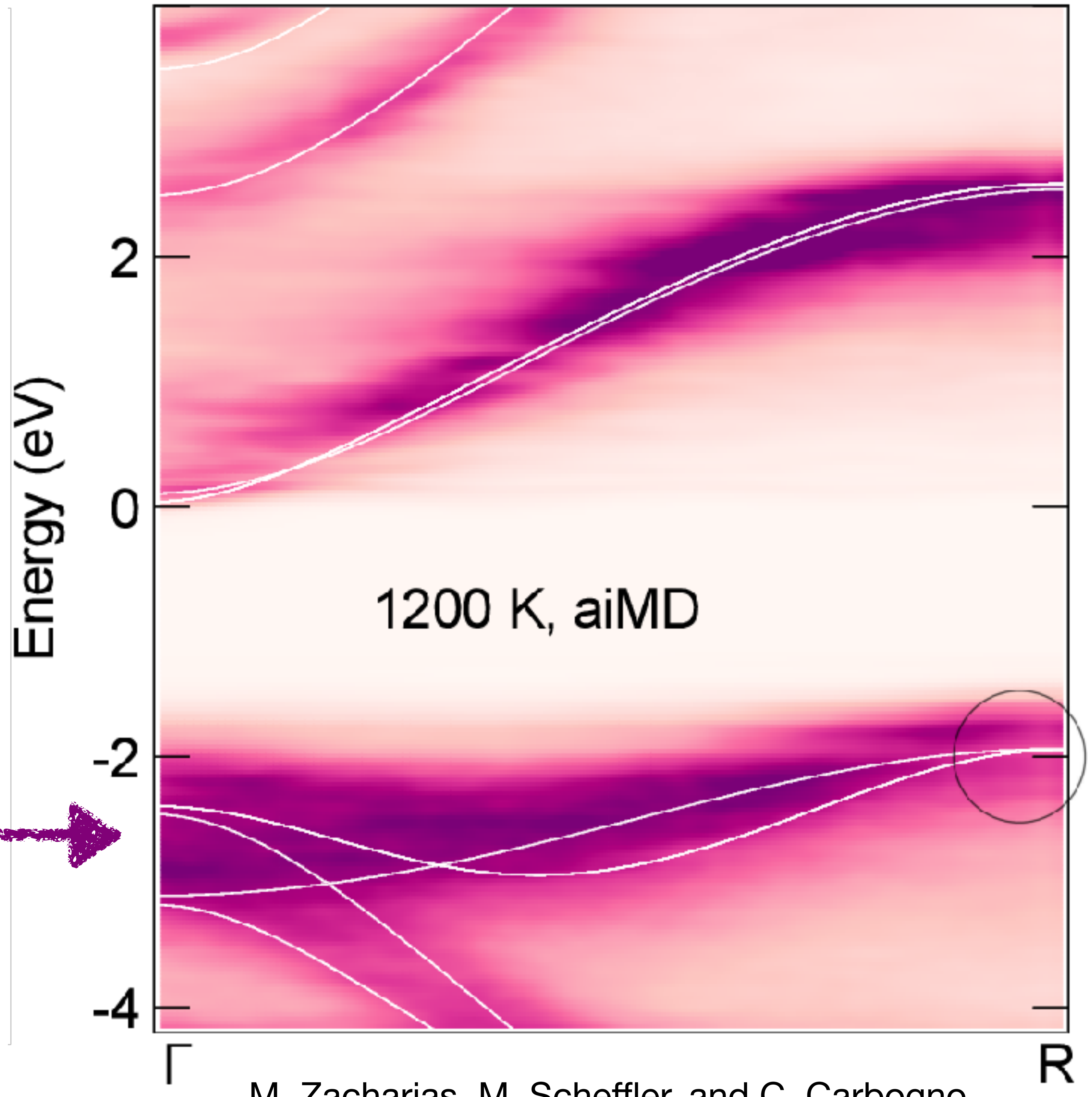


Fully Anharmonic Spectral Function



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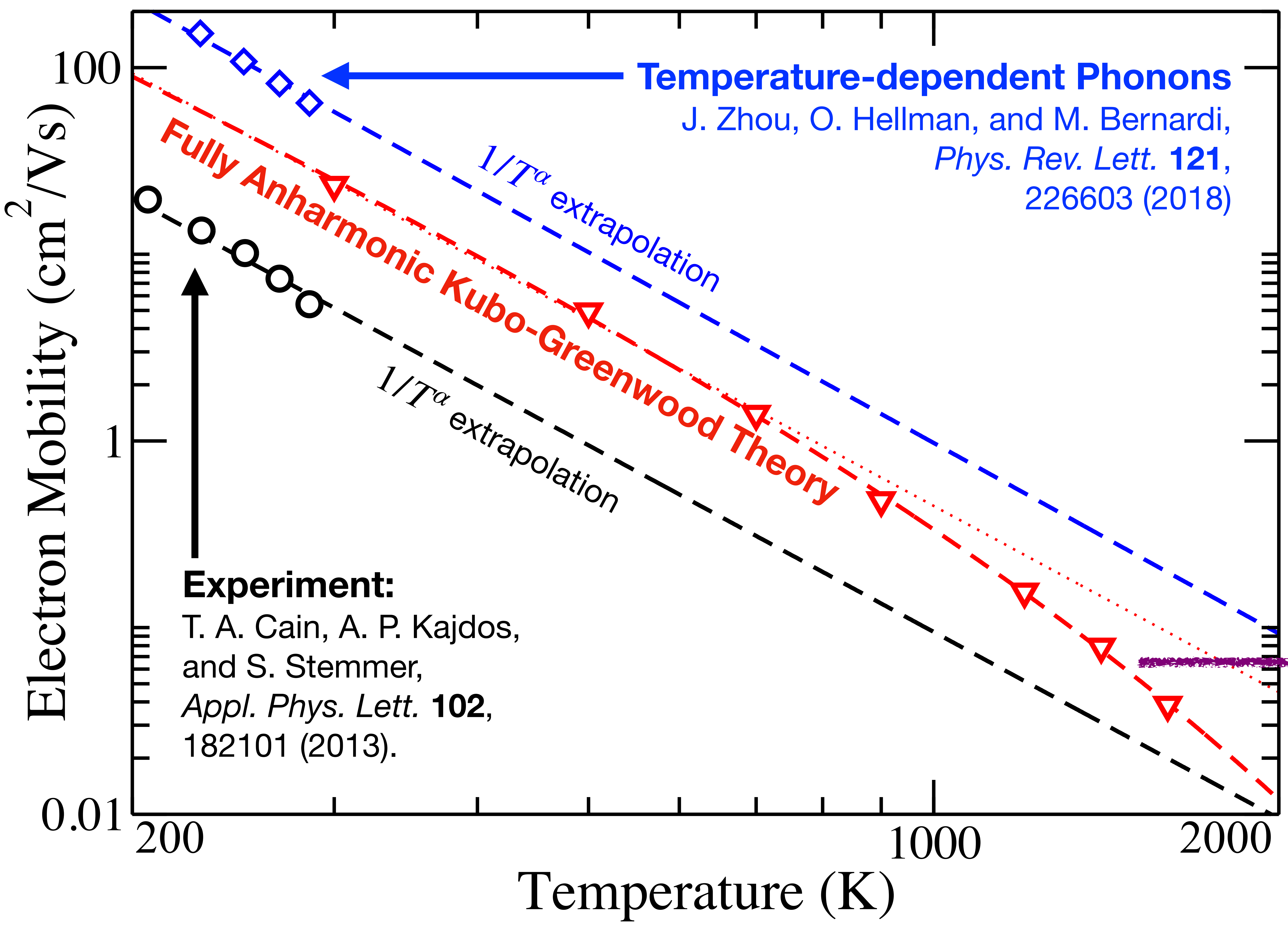

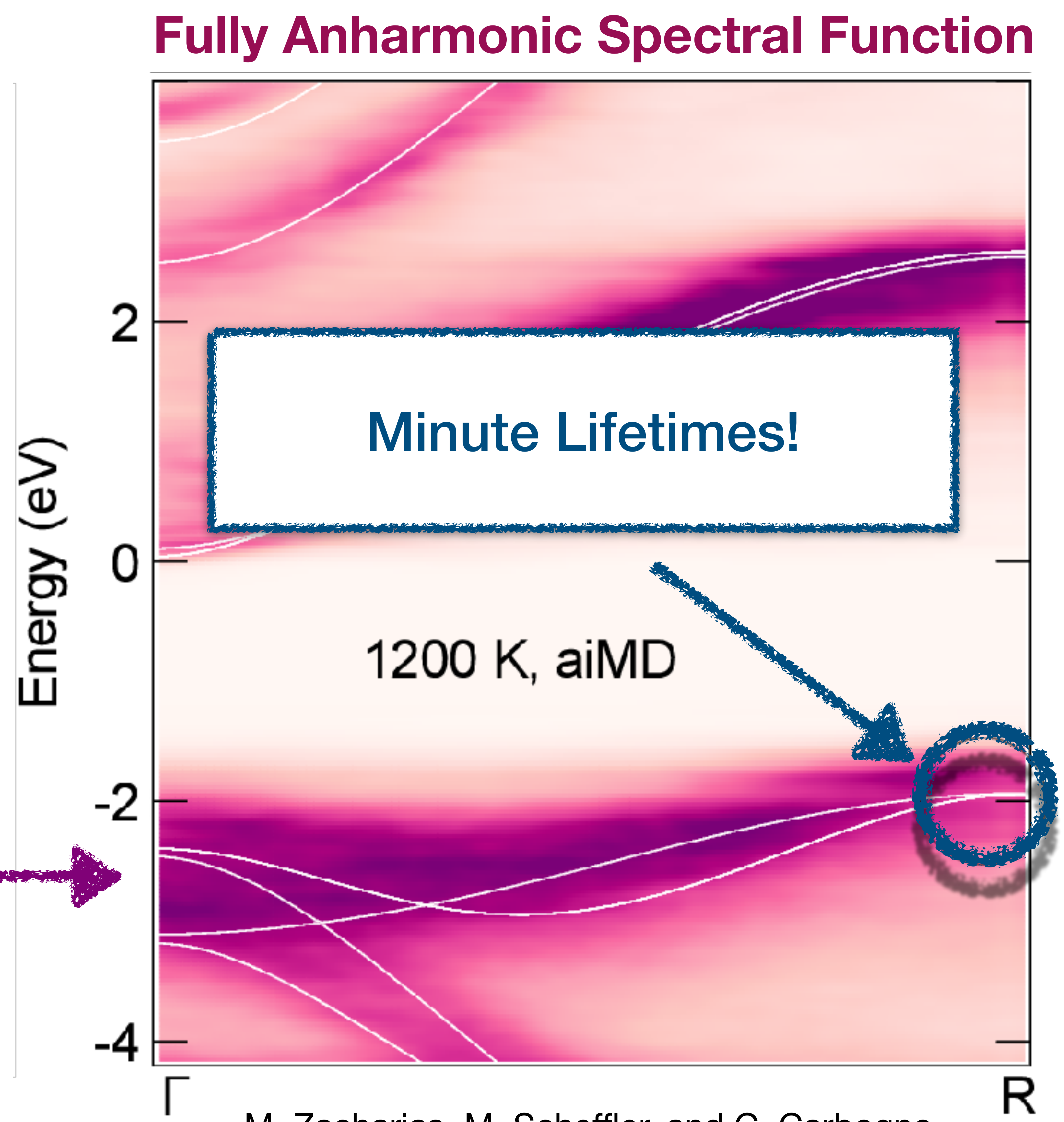

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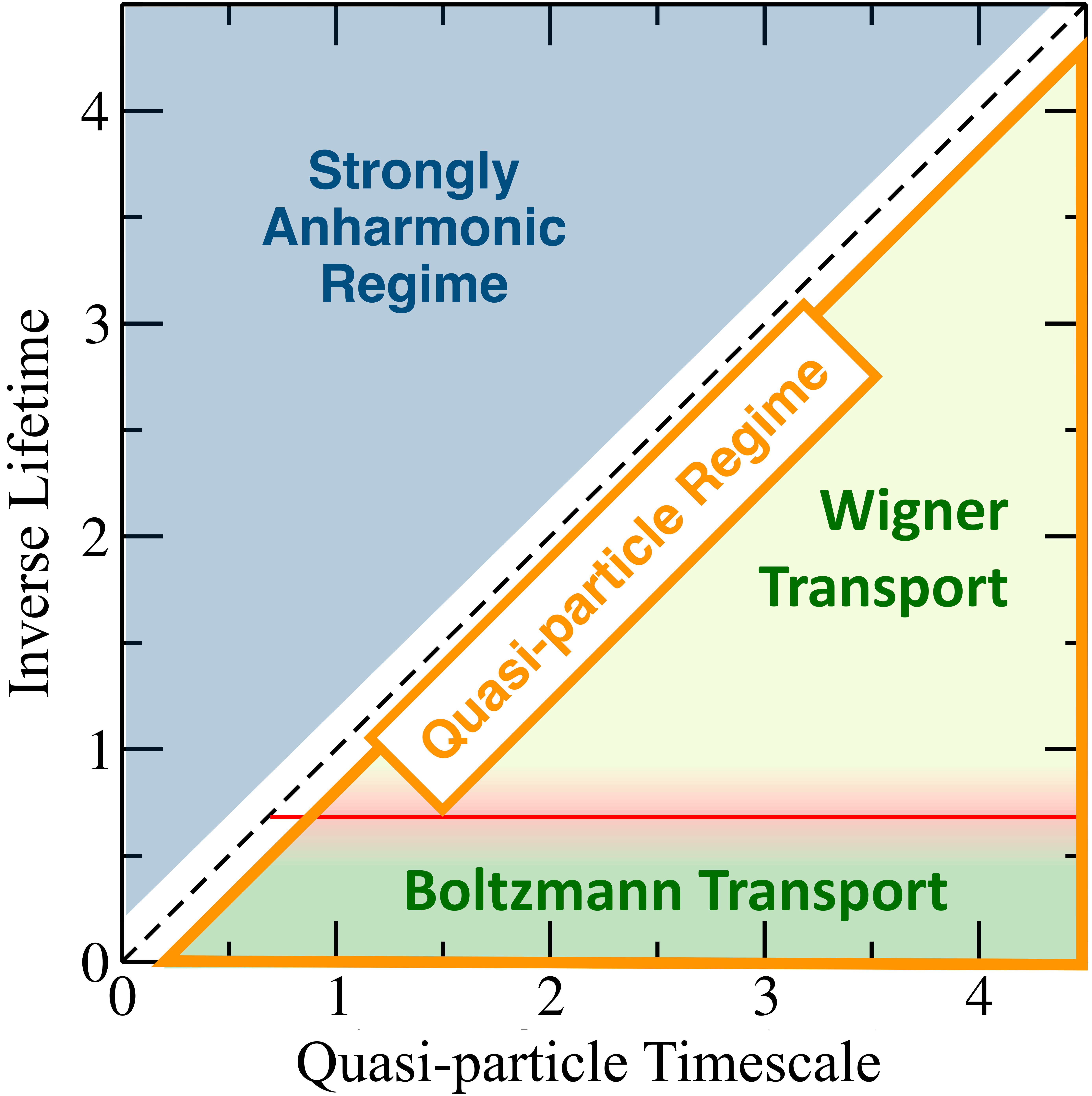

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- Going beyond the **quasi-particle picture** is crucial for computing **transport coefficients** in **complex** materials at **realistic conditions**.
- For **vibrational** transport, the implemented **Green-Kubo** formalism now allows the routine assessment of **fully anharmonic** thermal conductivities.
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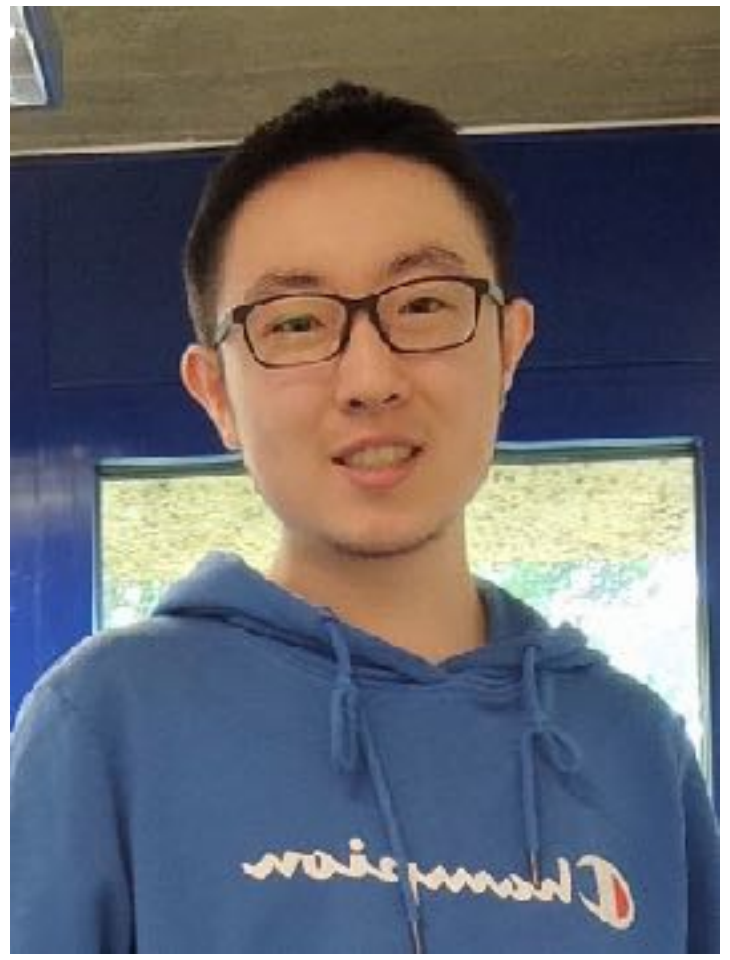

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now @ CNRS Rennes

Jingkai Quan,
FHI

Matthias Scheffler,
FHI

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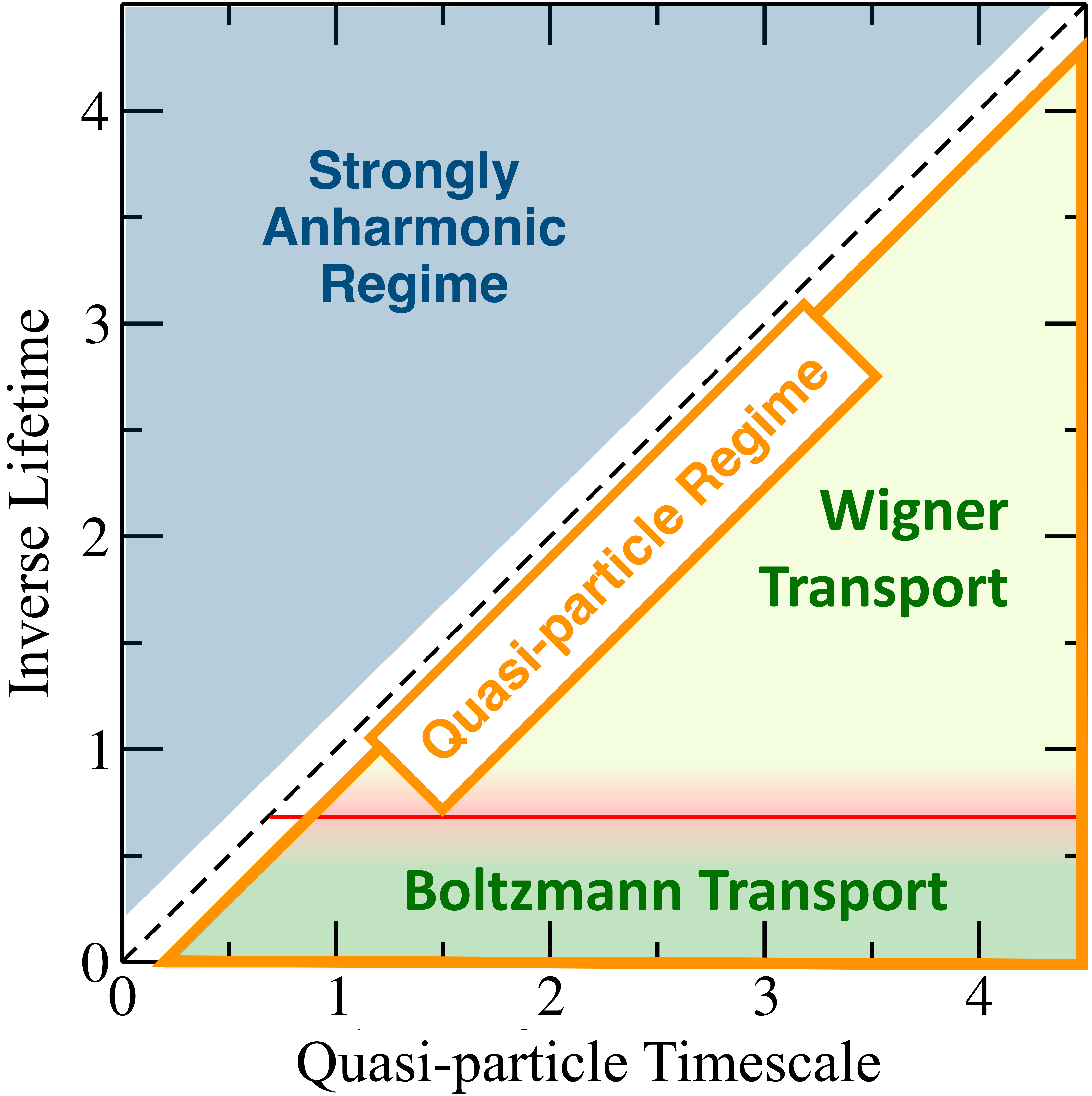

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