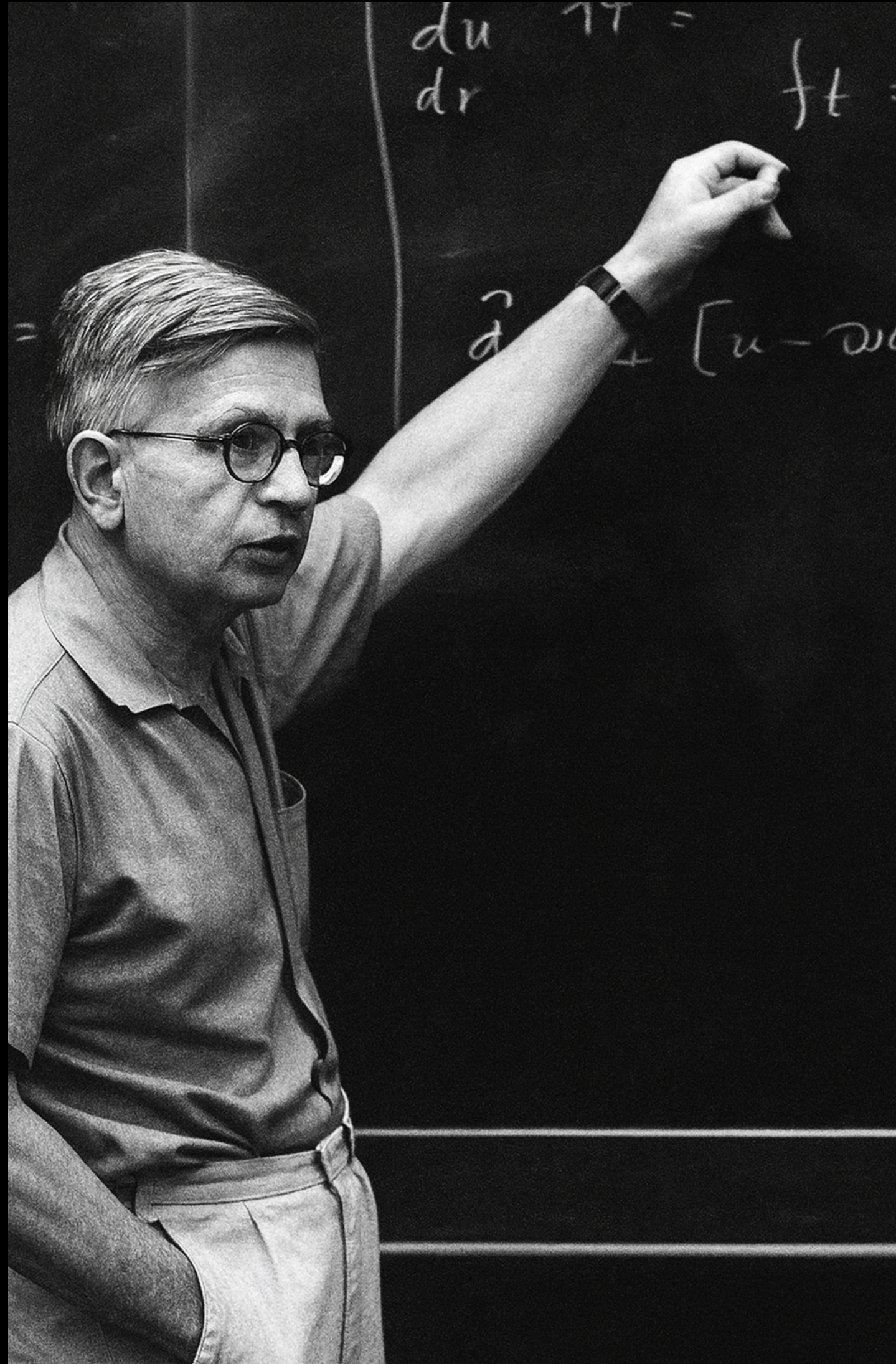




heat transport, ungauged

Stefano Baroni
Scuola Internazionale Superiore di Studi Avanzati
Trieste — Italy



It seems there is no problem in modern physics for which there are on record as many false starts, and as many theories which overlook some essential feature, as in the problem of the thermal conductivity of non-conducting [materials].

Rudolph E. Peierls [ca. 1960]

how it all started

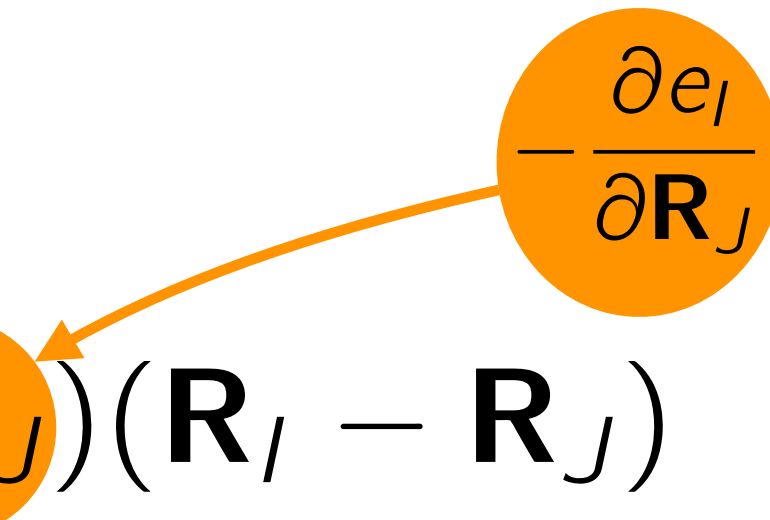
hurdles toward an ab initio Green-Kubo theory

$$\kappa = \frac{\Omega}{3k_B T^2} \int_0^\infty \langle \mathbf{J}(t) \cdot \mathbf{J}(0) \rangle dt$$



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$-\frac{\partial e_I}{\partial \mathbf{R}_J}$

PRL **104**, 208501 (2010)

PHYSICAL REVIEW LETTERS

week ending
21 MAY 2010

Thermal Conductivity of Periclase (MgO) from First Principles

Stephen Stackhouse*

Department of Geological Sciences, University of Michigan, Ann Arbor, Michigan, 48109-1005, USA

Lars Stixrude[†]

Department of Earth Sciences, University College London, Gower Street, London WC1E 6BT, United Kingdom

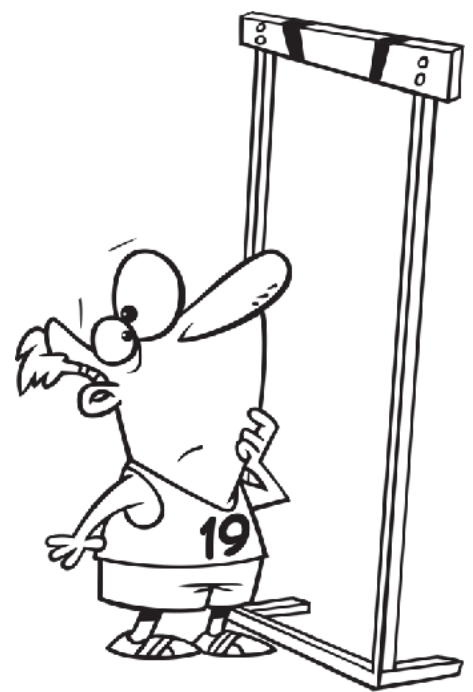
Bijaya B. Karki[‡]

*Department of Computer Science, Louisiana State University, Baton Rouge, Louisiana 70803, USA
and Department of Geology and Geophysics, Louisiana State University, Baton Rouge, Louisiana 70803, USA*

sensitive to the form of the potential. The widely used Green-Kubo relation [14] does not serve our purposes, because in first-principles calculations it is impossible to uniquely decompose the total energy into individual contributions from each atom.



how come?



how come?



how is it that a formally exact theory of the electronic ground state cannot predict *all* measurable adiabatic properties?

What I cannot create,
I do not understand

Why const $\times$ $\sqrt{\sigma T}$ Po

Know how to solve every
problem that has been solved

TO LEARN:

Bethe Ansatz Probs.

Kondo

2-D Hall

accel. Temp

Non linear classical Hydro

$$(A) f = U(r, a)$$

$$g = 4\pi \int_0^{\infty} U(r, z)$$

$$(B) f = 2|k \cdot a|(u \cdot a)$$

What I cannot create,
I do not understand.

Why const $\times$ sort. Po

TO LEARN:

Bethe Ansatz Probs.

Know how to solve every
problem that has been solve



What I cannot create,
I do not understand.

Why const $\times$ sort. Po

TO LEARN:

Bethe Ansatz Probs.

$$A \sim \int e^{-\frac{i}{\hbar} S[x(\cdot)]} \mathcal{D}[x(\cdot)]$$

Know how to solve every
problem that has been solve



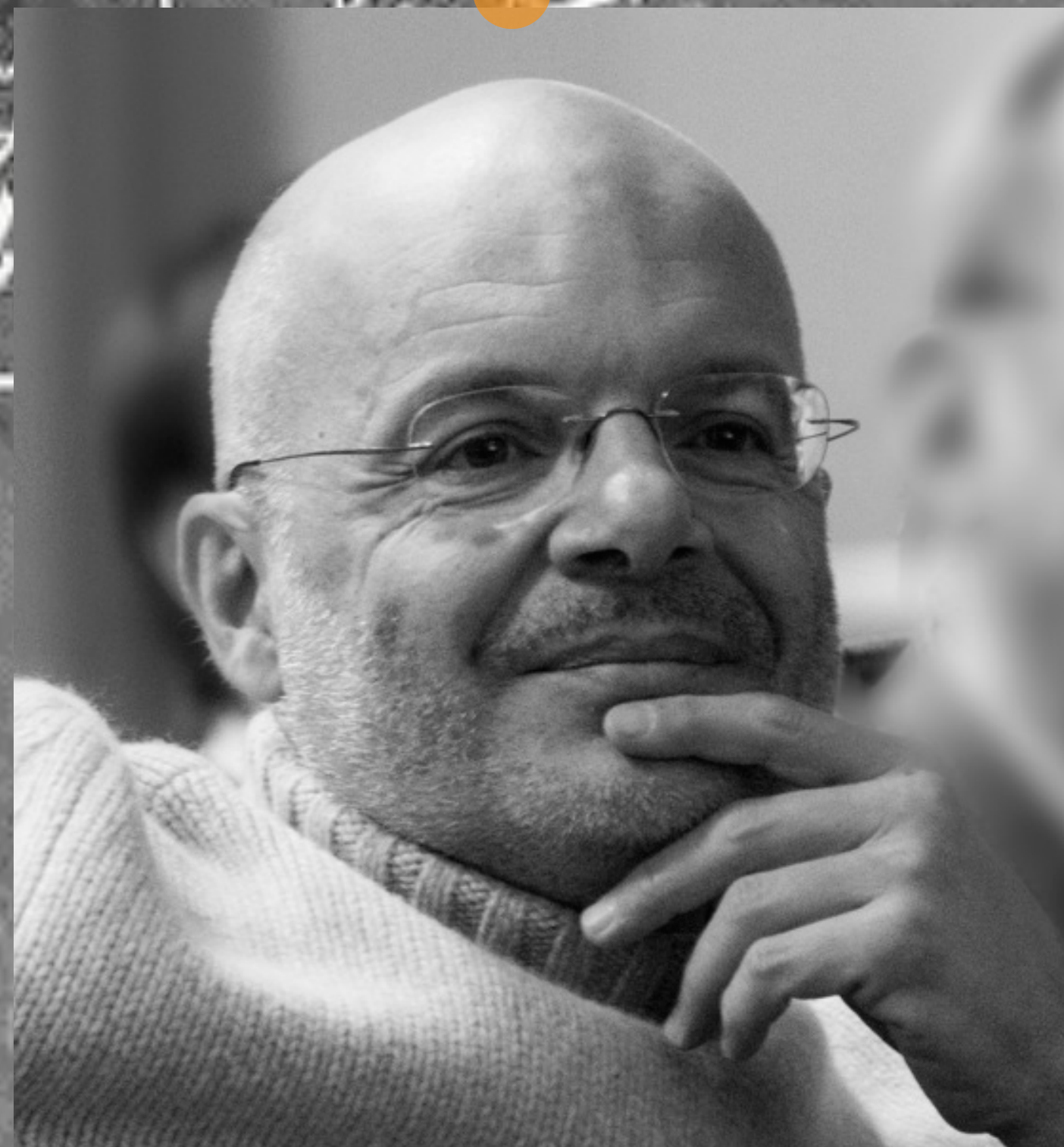
compute

What I cannot ~~create~~
I do not understand

Know how to solve every
problem that has been solved

Why const $\times$ sort . PC

Be the Anarchy Probs.



the linear-response theory of transport

Fourier



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

the linear-response theory of transport

Fourier

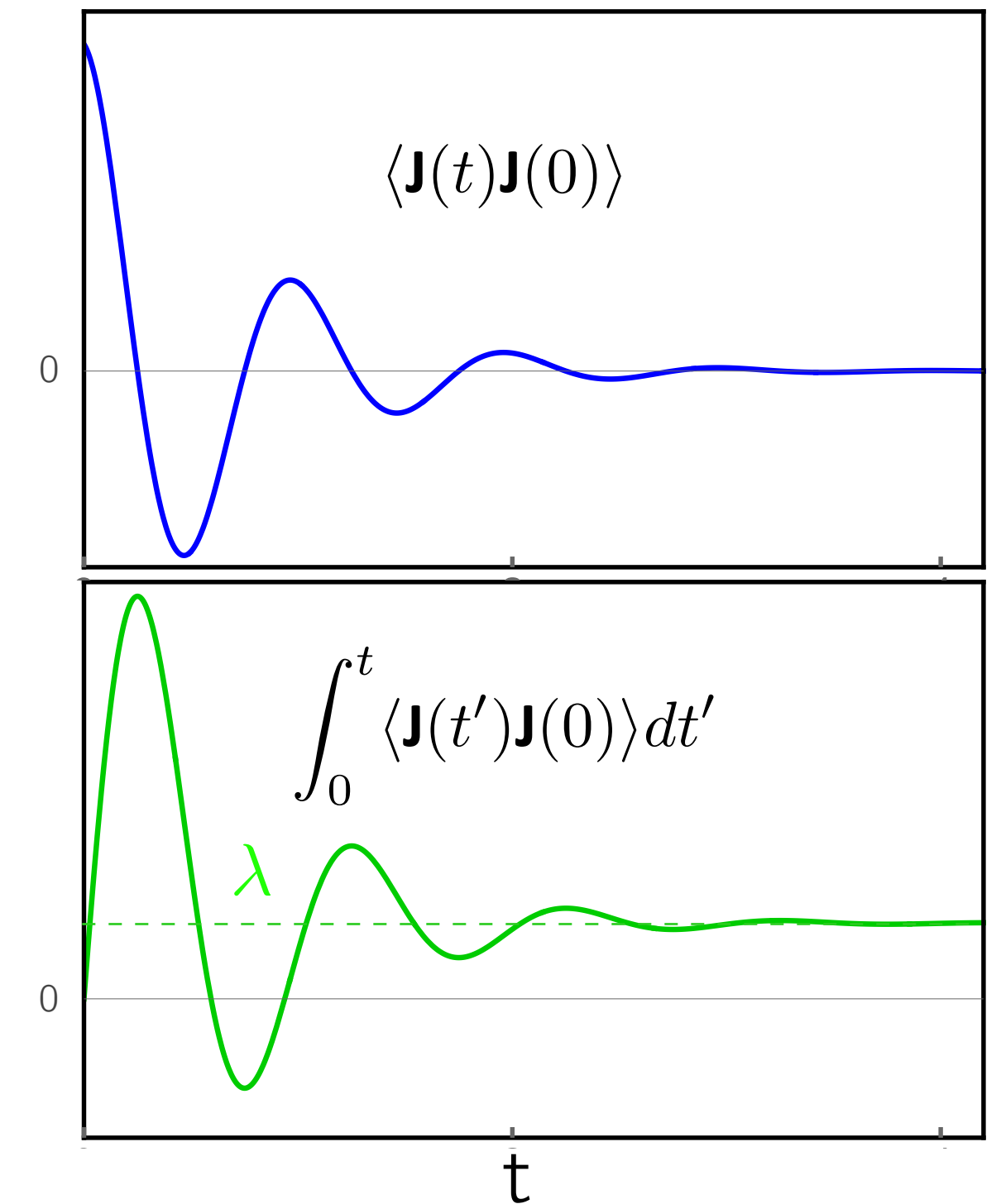


$$\mathbf{J} = -\kappa \nabla T$$

Green-Kubo



$$\kappa = \frac{\Omega}{k_B T} \underbrace{\int_0^\infty \langle J(t) J(0) \rangle dt}_{\langle J^2 \rangle \tau}$$



the linear-response theory of transport

Fourier



Green-Kubo

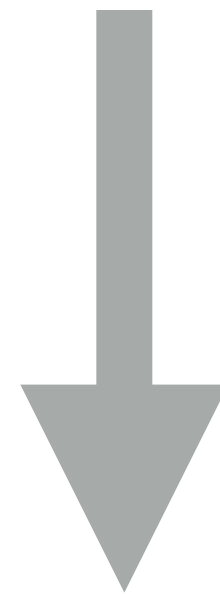


Einstein-Helfand

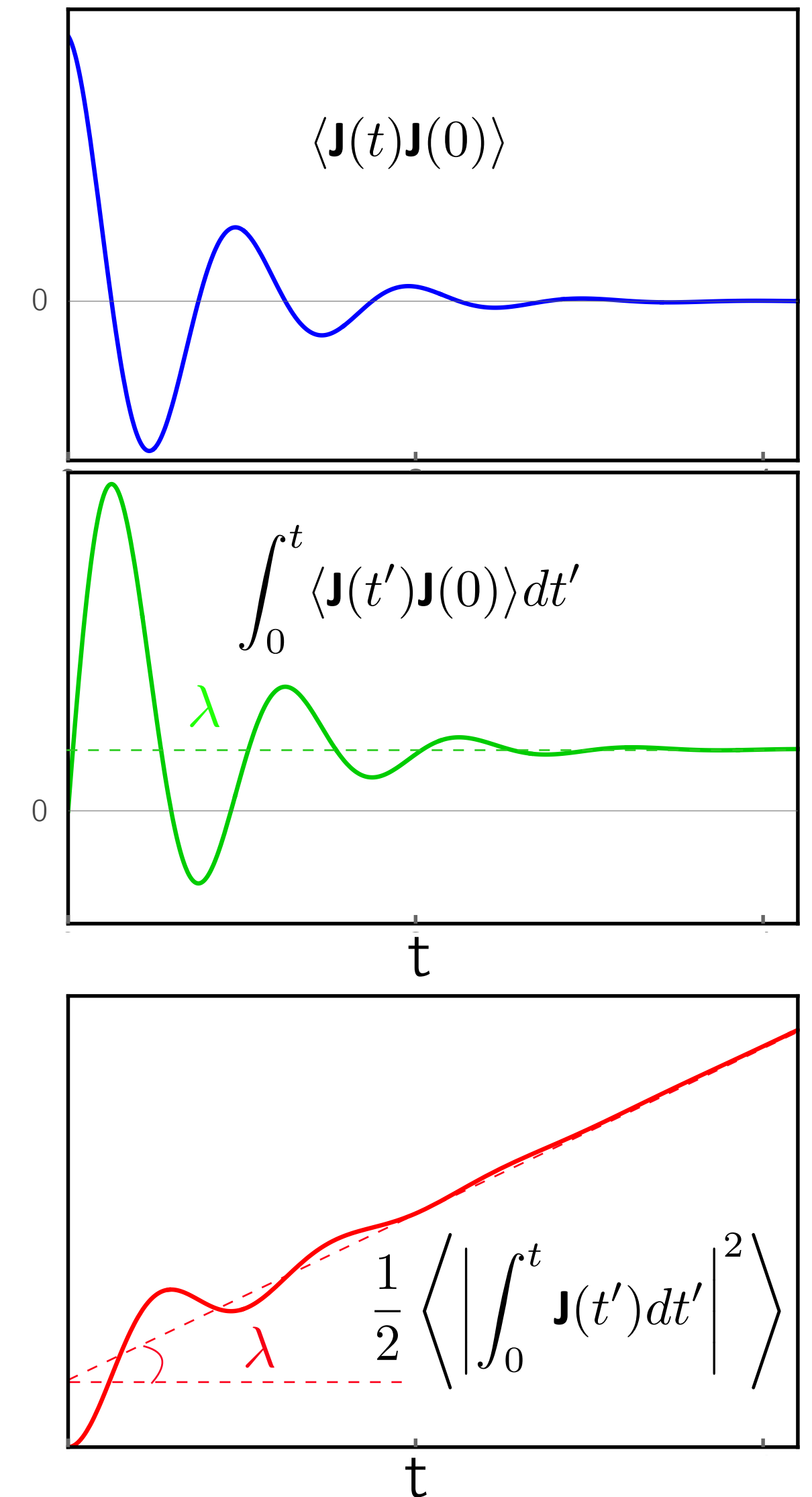


$$\mathbf{J} = -\kappa \nabla T$$

$$\kappa = \frac{\Omega}{k_B T} \underbrace{\int_0^\infty \langle J(t) J(0) \rangle dt}_{\langle J^2 \rangle \tau}$$



$$\kappa \propto \lim_{t \rightarrow \infty} \frac{1}{2t} \text{var} \left[\int_0^t J(t') dt' \right]$$



insights from classical mechanics

$$E = \sum_I \epsilon_I(\mathbf{R}, \mathbf{V})$$
$$= \text{cnst}$$

$$\epsilon_I(\mathbf{R}, \mathbf{V}) = \frac{1}{2} M_I V_I^2 + \frac{1}{2} \sum_{J \neq I} v(|\mathbf{R}_I - \mathbf{R}_J|)$$

$$\mathbf{J}_e = \sum_I \epsilon_I \mathbf{V}_I + \frac{1}{2} \sum_{I \neq J} (\mathbf{V}_I \cdot \mathbf{F}_{IJ})(\mathbf{R}_I - \mathbf{R}_J)$$

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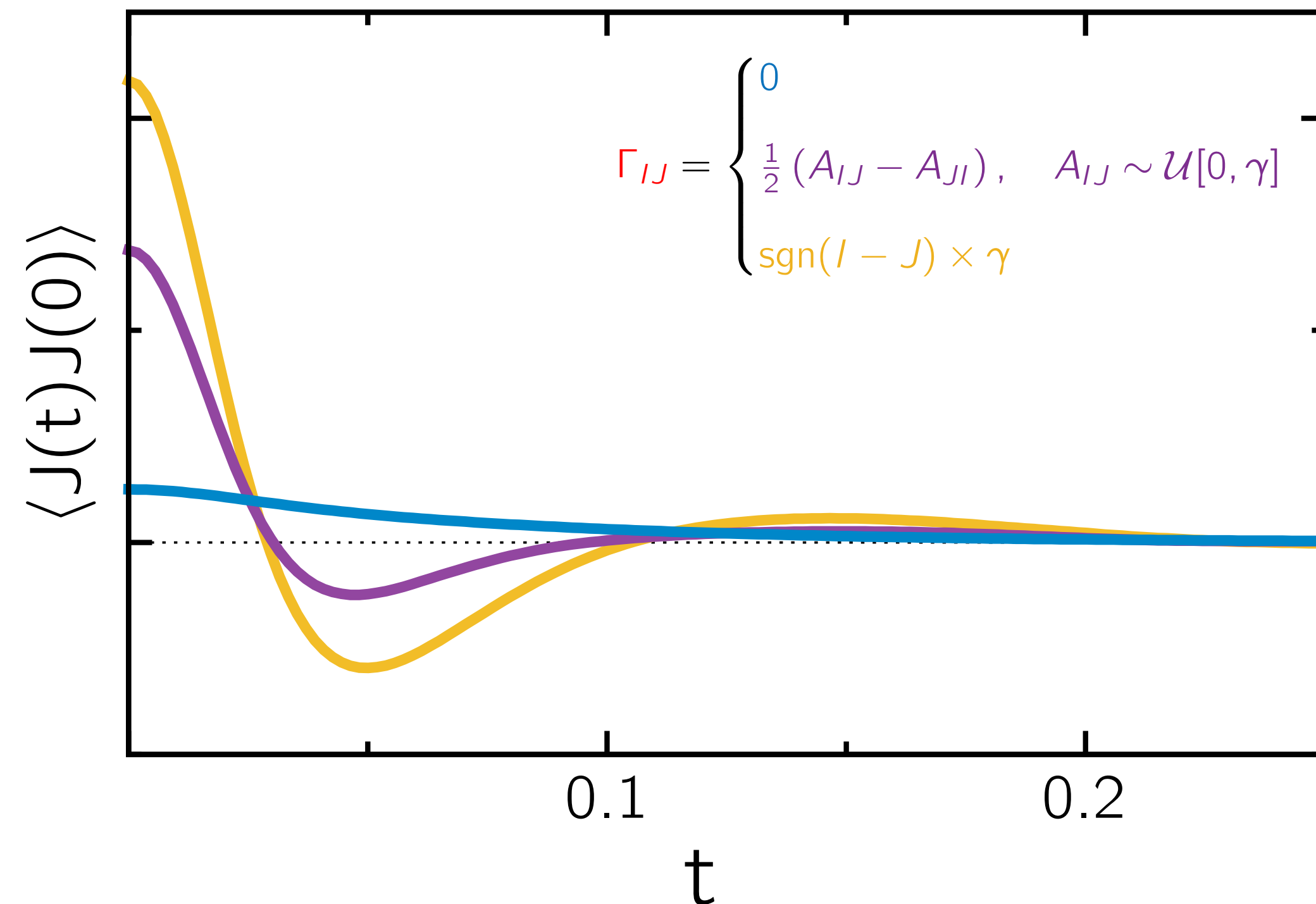
$$\begin{aligned} \mathbf{J}_e = & \sum_I \epsilon_I \mathbf{V}_I + \frac{1}{2} \sum_{I \neq J} (\mathbf{V}_I \cdot \mathbf{F}_{IJ}) (\mathbf{R}_I - \mathbf{R}_J) \\ & + \frac{1}{2} \sum_{I \neq J} \Gamma_{IJ} [\mathbf{V}_I v(|\mathbf{R}_I - \mathbf{R}_J|) + (\mathbf{V}_I \cdot \mathbf{F}_{IJ}) (\mathbf{R}_I - \mathbf{R}_J)] \end{aligned}$$

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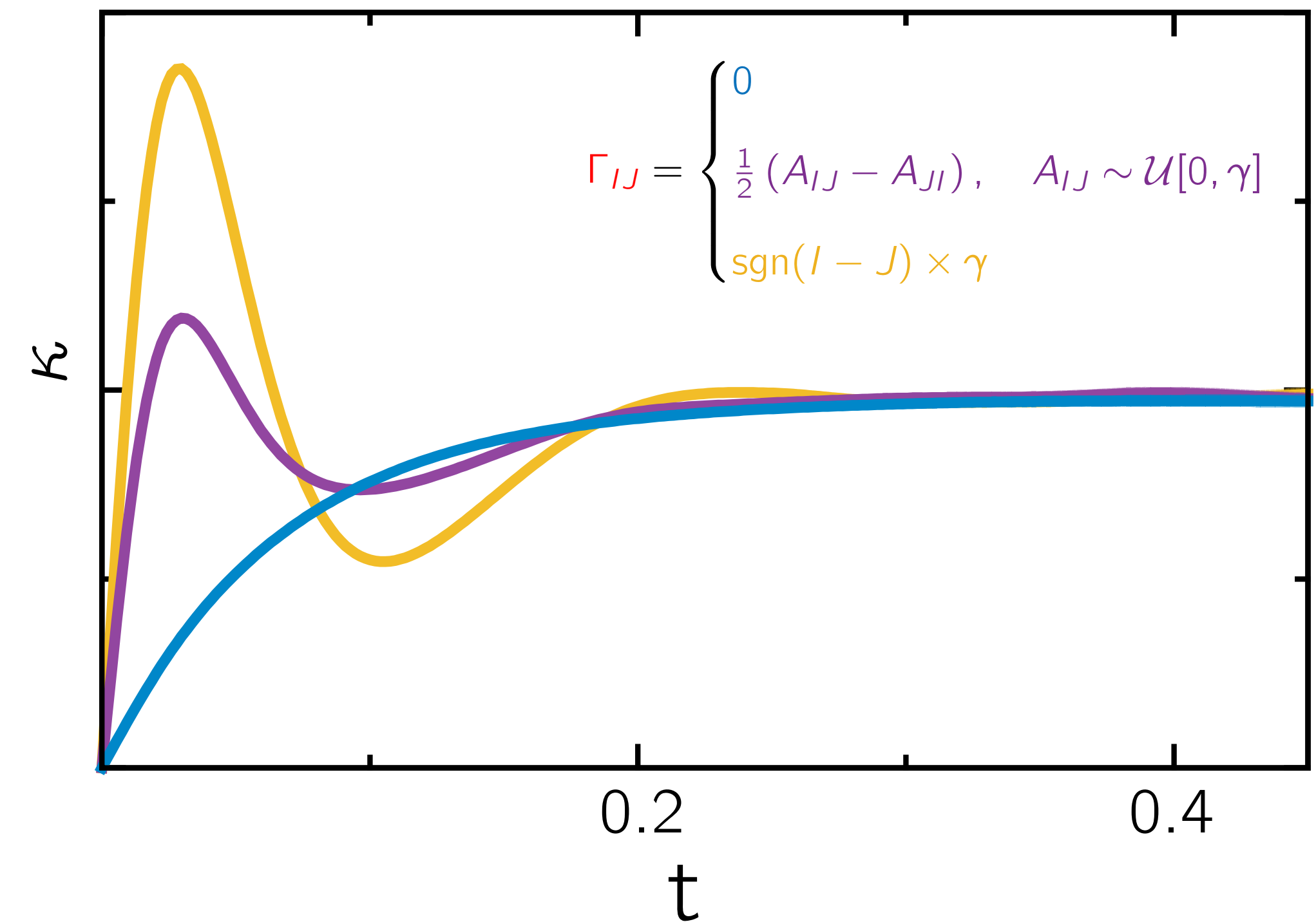
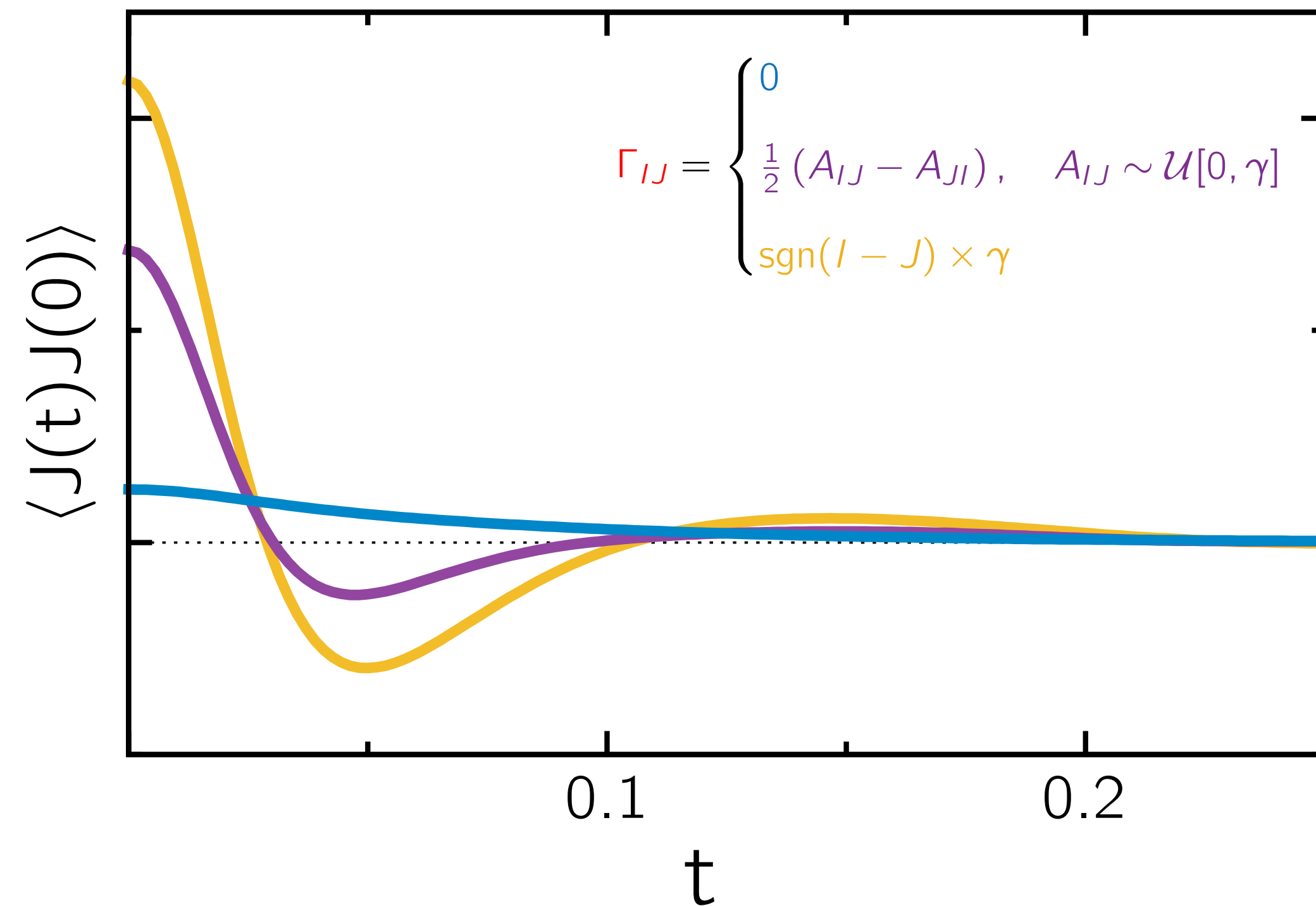
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$$\dot{\mathbf{P}} = \frac{d}{dt} \frac{1}{4} \sum_{I \neq J} \Gamma_{IJ} v(|\mathbf{R}_I - \mathbf{R}_J|) (\mathbf{R}_I - \mathbf{R}_J)$$

insights from classical mechanics

$$\mathbf{J}' = \mathbf{J} + \dot{\mathbf{P}}$$

insights from classical mechanics

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$$\kappa \sim \frac{1}{2t} \text{var}[\mathbf{D}(t)] \quad \mathbf{D}(t) = \int_0^t \mathbf{J}(t') dt'$$

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$$\mathbf{D}'(t) = \mathbf{D}(t) + \mathbf{P}(t) - \mathbf{P}(0)$$

insights from classical mechanics

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insights from classical mechanics

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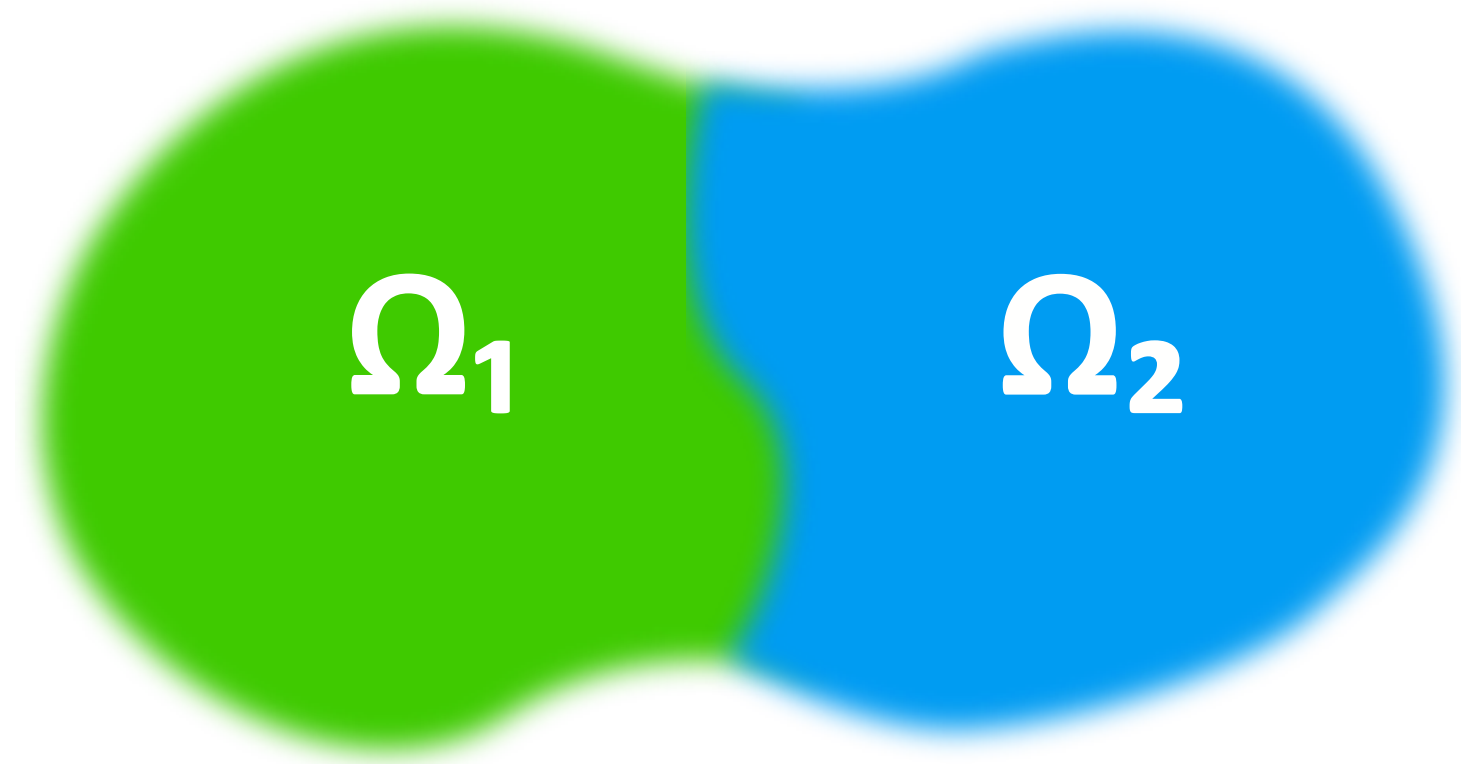


$$\mathbf{D}(t) = \mathbf{D}'(t) + \mathbf{P}(t) - \mathbf{P}(0)$$

$$\kappa' = \kappa$$

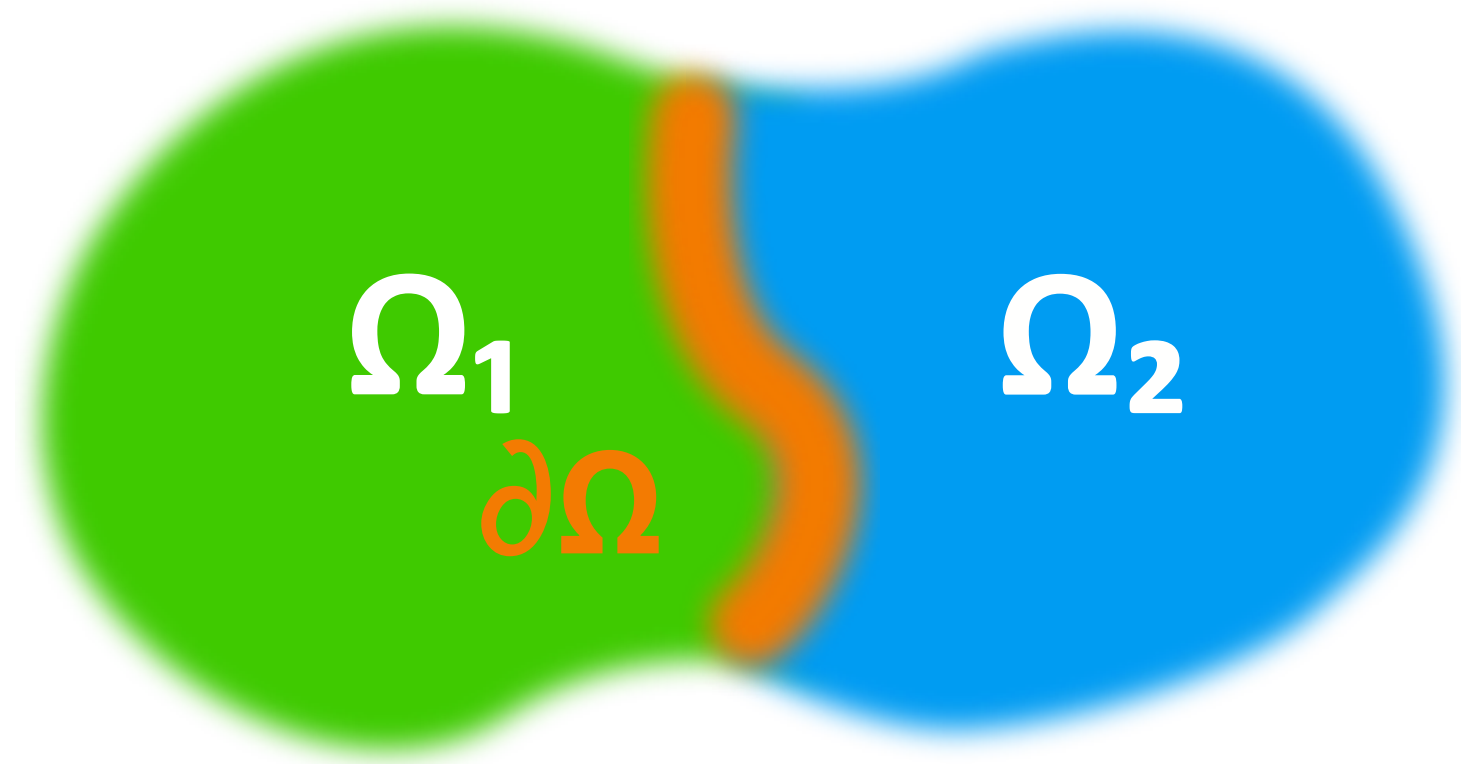
$$\text{var} [\mathbf{D}'(t)] = \text{var} [\mathbf{D}(t)] + \text{var} [\mathbf{P}(t)] + 2\text{cov} [\mathbf{D}, \mathbf{P}(t)]$$

gauge invariance of heat transport



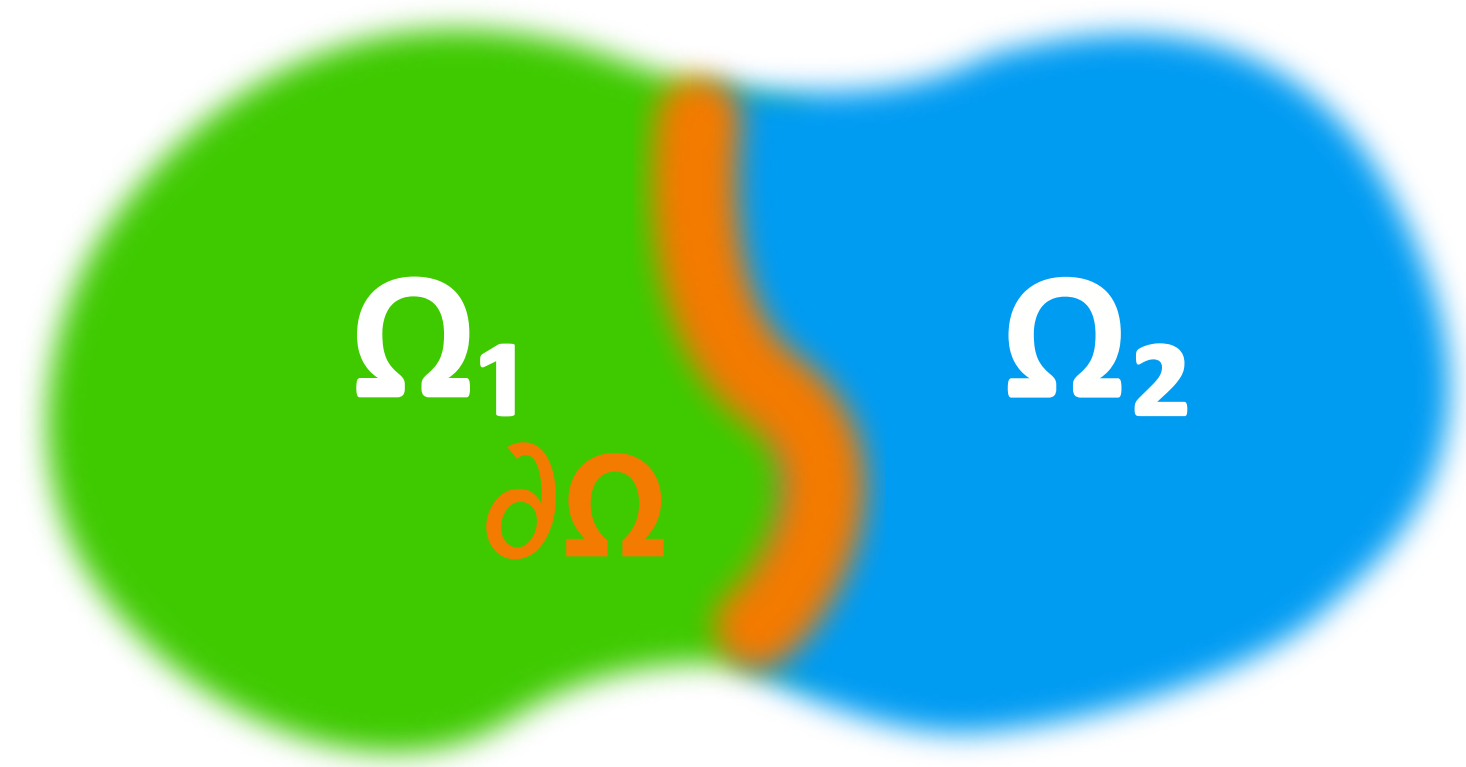
$$E[\Omega_1 \cup \Omega_2] = E[\Omega_1] + E[\Omega_2]$$

gauge invariance of heat transport



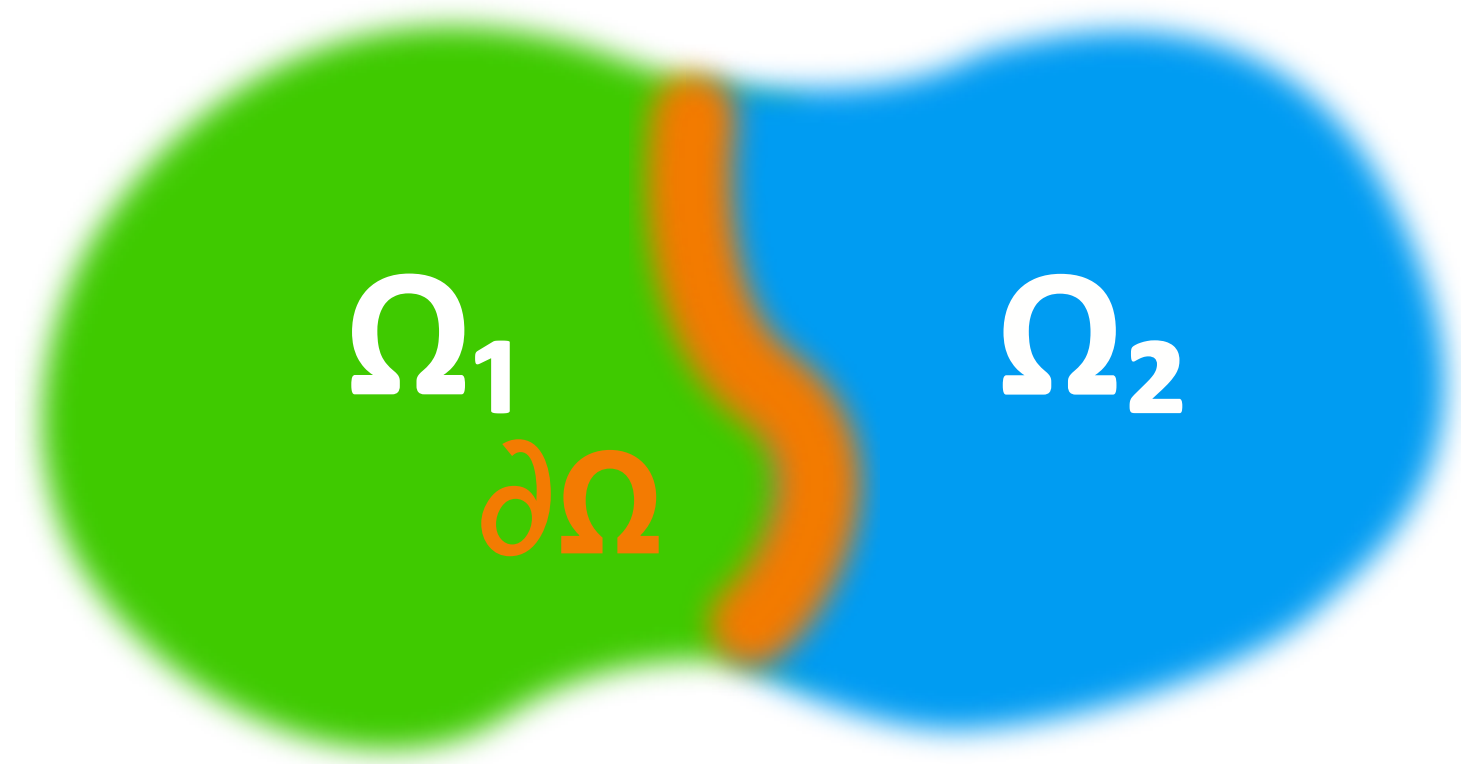
$$E[\Omega_1 \cup \Omega_2] = E[\Omega_1] + E[\Omega_2] + W[\partial\Omega]$$

gauge invariance of heat transport



$$\begin{aligned} E[\Omega_1 \cup \Omega_2] &= E[\Omega_1] + E[\Omega_2] + W[\partial\Omega] \\ &\stackrel{?}{=} \mathcal{E}[\Omega_1] + \mathcal{E}[\Omega_2] \end{aligned}$$

gauge invariance of heat transport

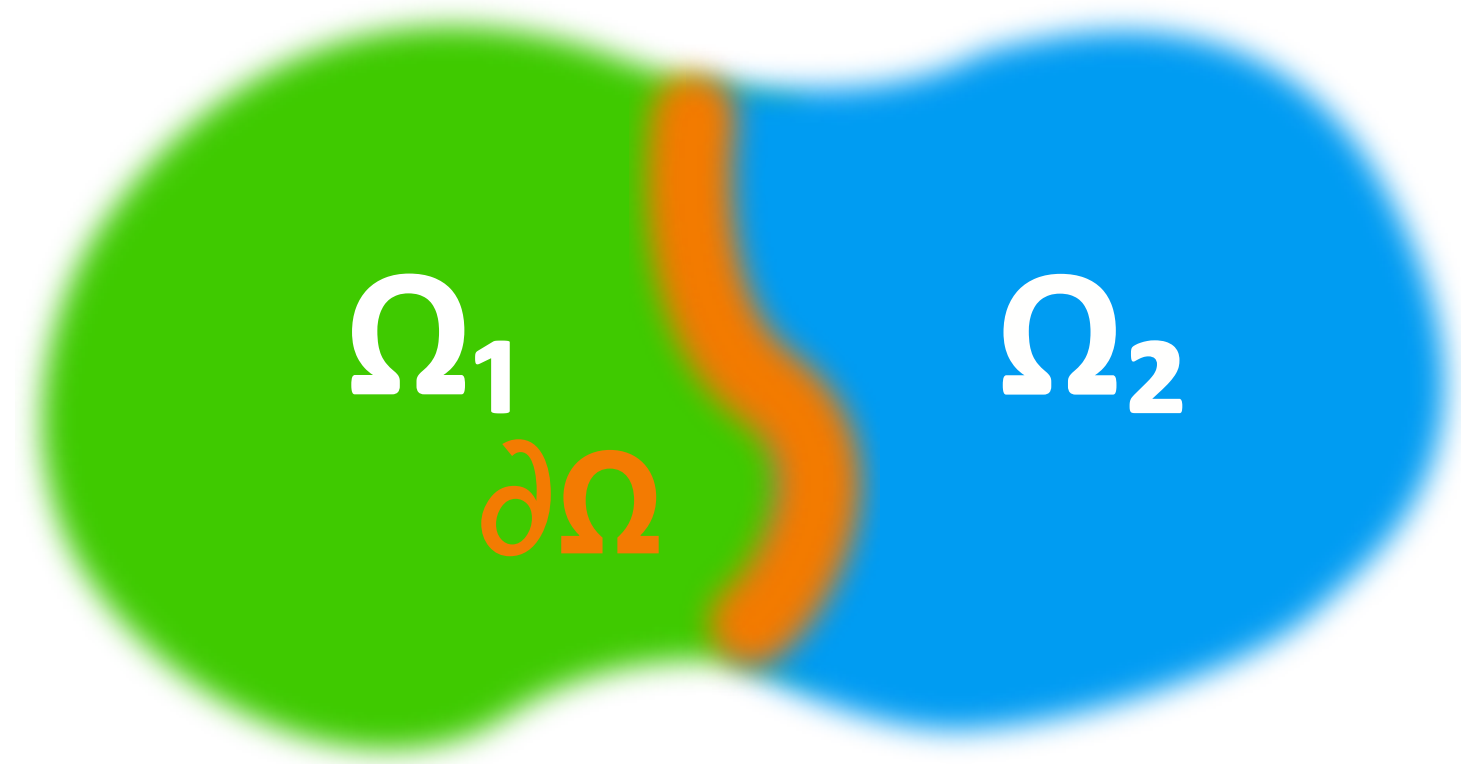


extensivity

$$E[\Omega_1 \cup \Omega_2] = E[\Omega_1] + E[\Omega_2] + W[\partial\Omega]$$
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$$\mathcal{E}[\Omega] = \int_{\Omega} e(\mathbf{r}) d\mathbf{r}$$

gauge invariance of heat transport



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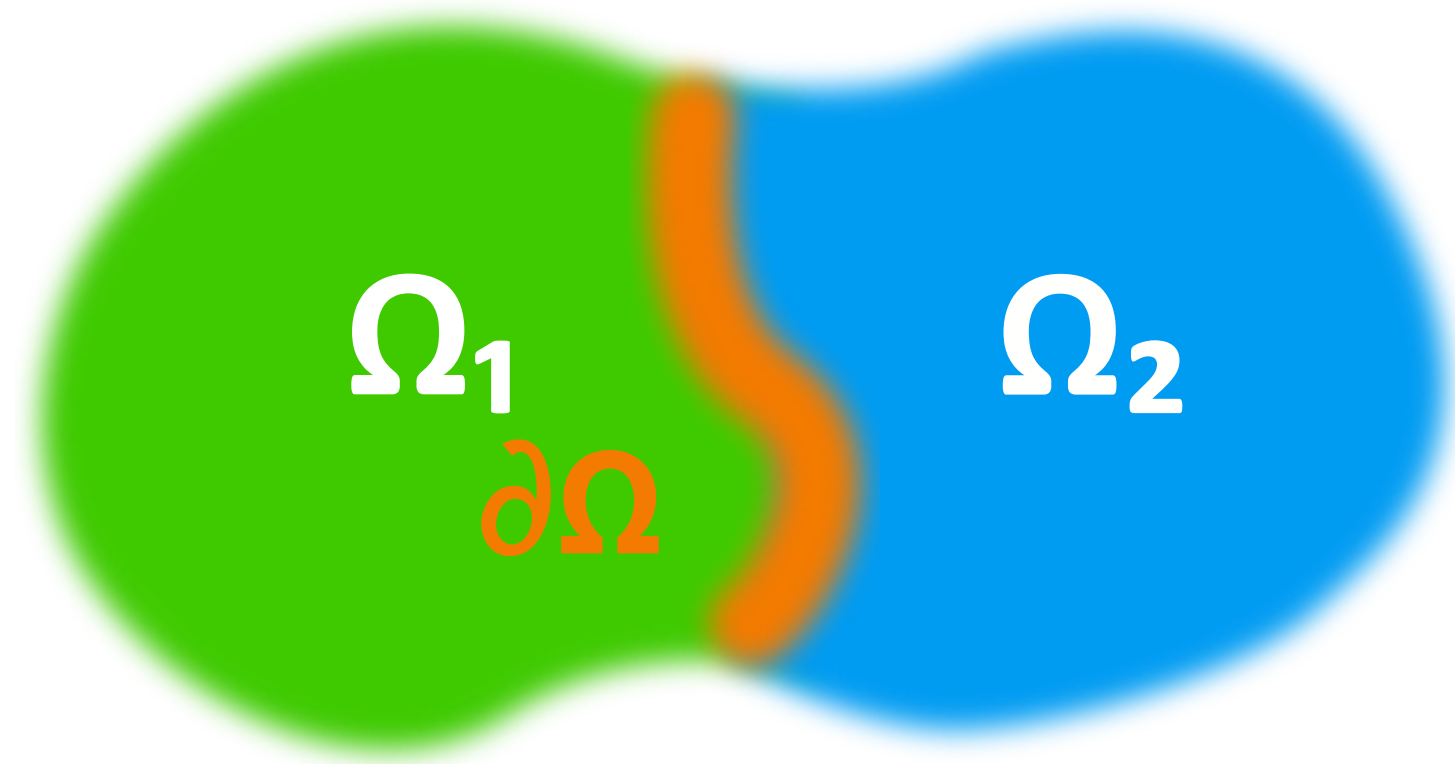
extensivity

$$\mathcal{E}[\Omega] = \int_{\Omega} e(\mathbf{r}) d\mathbf{r}$$

thermodynamic invariance

$$\mathcal{E}'[\Omega] = \mathcal{E}[\Omega] + \mathcal{O}[\partial\Omega]$$

gauge invariance of heat transport



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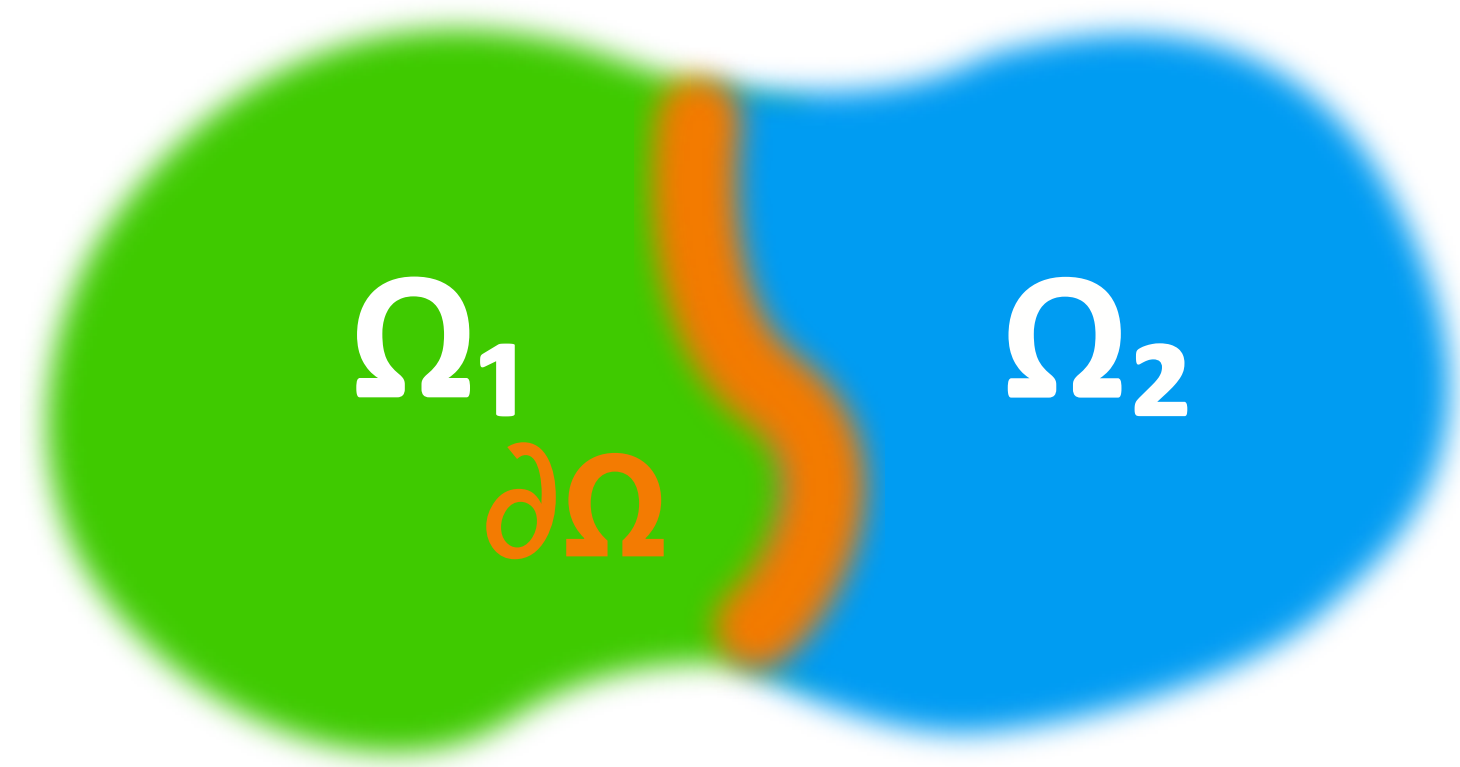
thermodynamic invariance

$$\mathcal{E}'[\Omega] = \mathcal{E}[\Omega] + \mathcal{O}[\partial\Omega]$$

gauge invariance

$$e'(\mathbf{r}) = e(\mathbf{r}) - \nabla \cdot \mathbf{p}(\mathbf{r})$$

gauge invariance of heat transport



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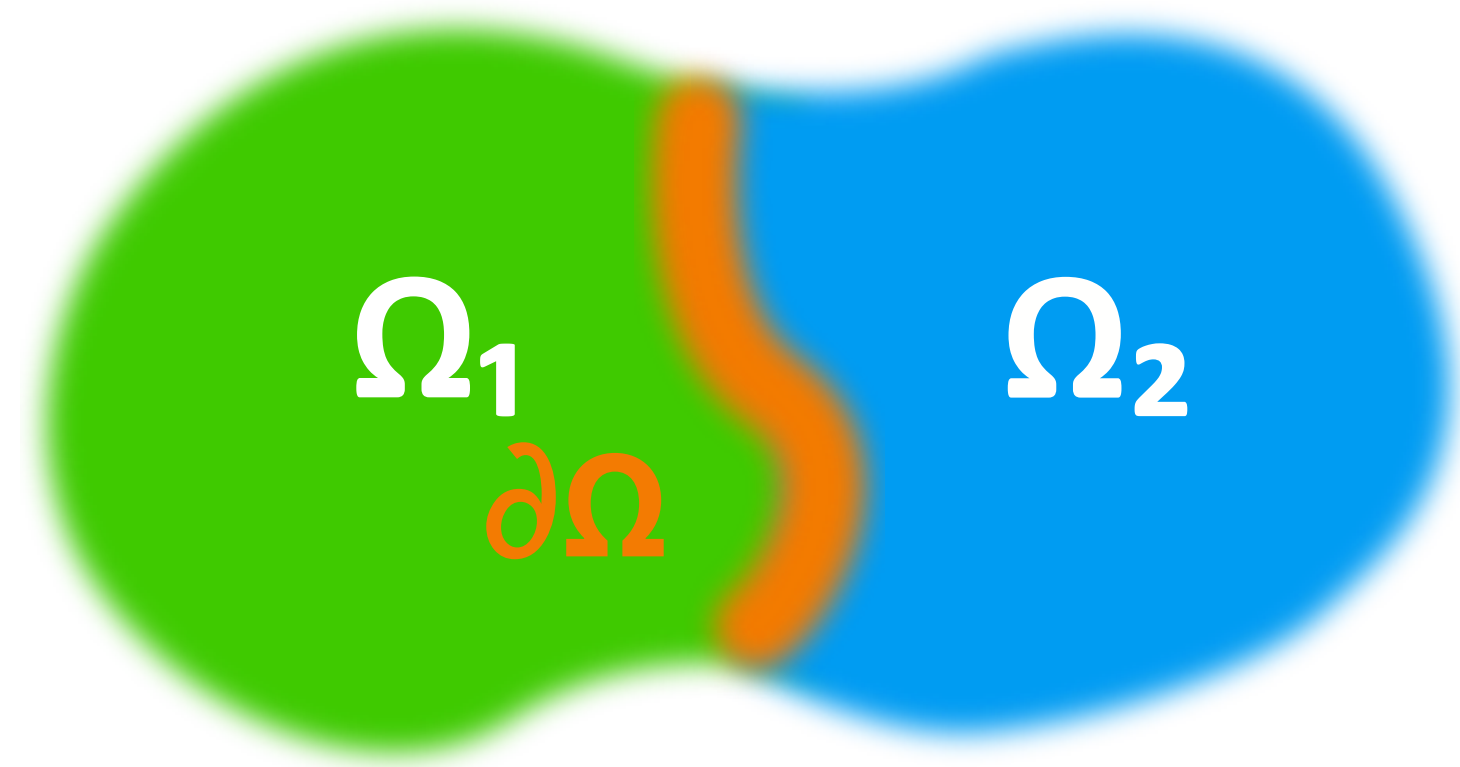
gauge invariance

$$e'(\mathbf{r}) = e(\mathbf{r}) - \nabla \cdot \mathbf{p}(\mathbf{r})$$

conservation

$$\dot{e}(\mathbf{r}, t) = -\nabla \cdot \mathbf{j}(\mathbf{r}, t)$$

gauge invariance of heat transport



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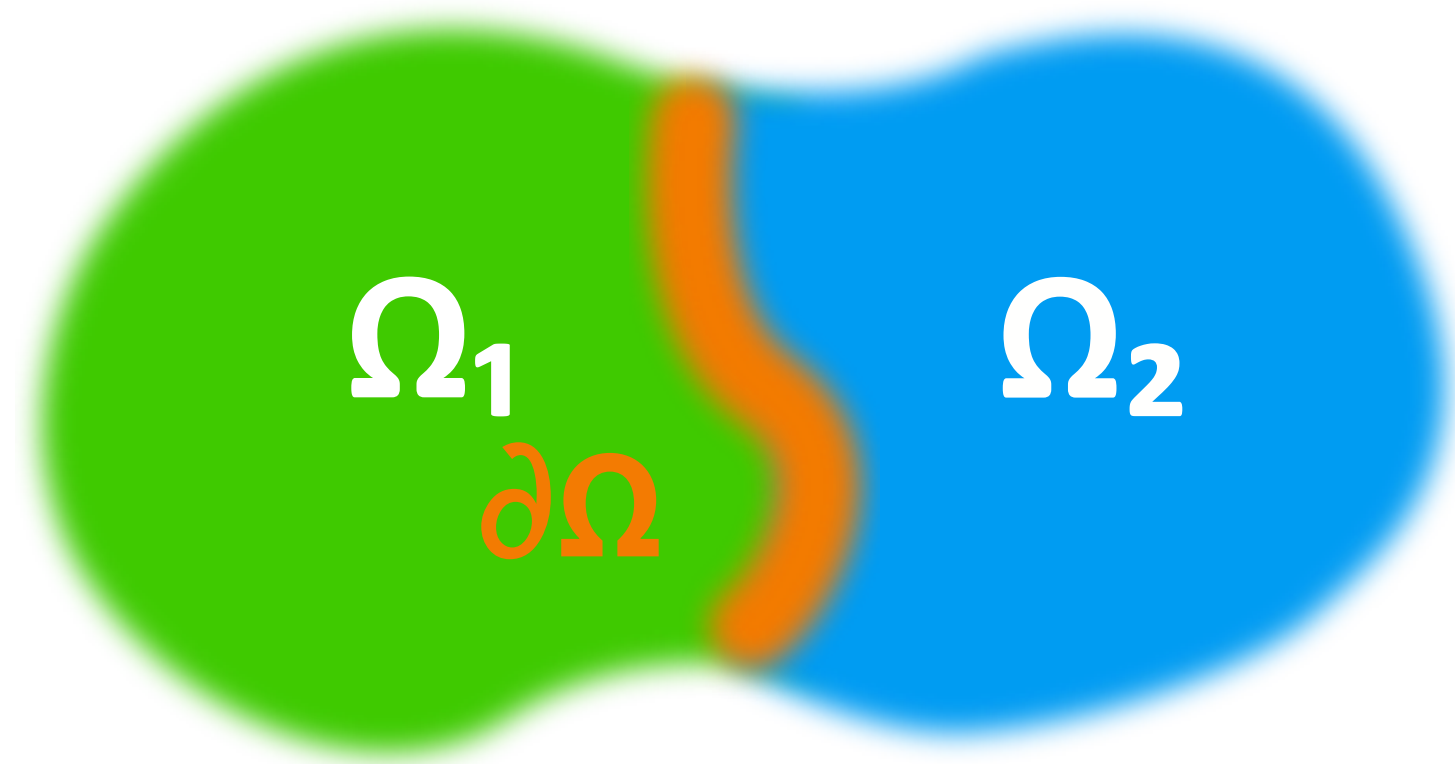
gauge invariance

$$e'(\mathbf{r}) = e(\mathbf{r}) - \nabla \cdot \mathbf{p}(\mathbf{r})$$
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gauge invariance of heat transport



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extensivity

$$\mathcal{E}[\Omega] = \int_{\Omega} e(\mathbf{r}) d\mathbf{r}$$

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

thermodynamic invariance

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$$\mathbf{P}(t) = \frac{1}{\Omega} \int \mathbf{p}(\mathbf{r}, t) d\mathbf{r}$$

gauge invariance

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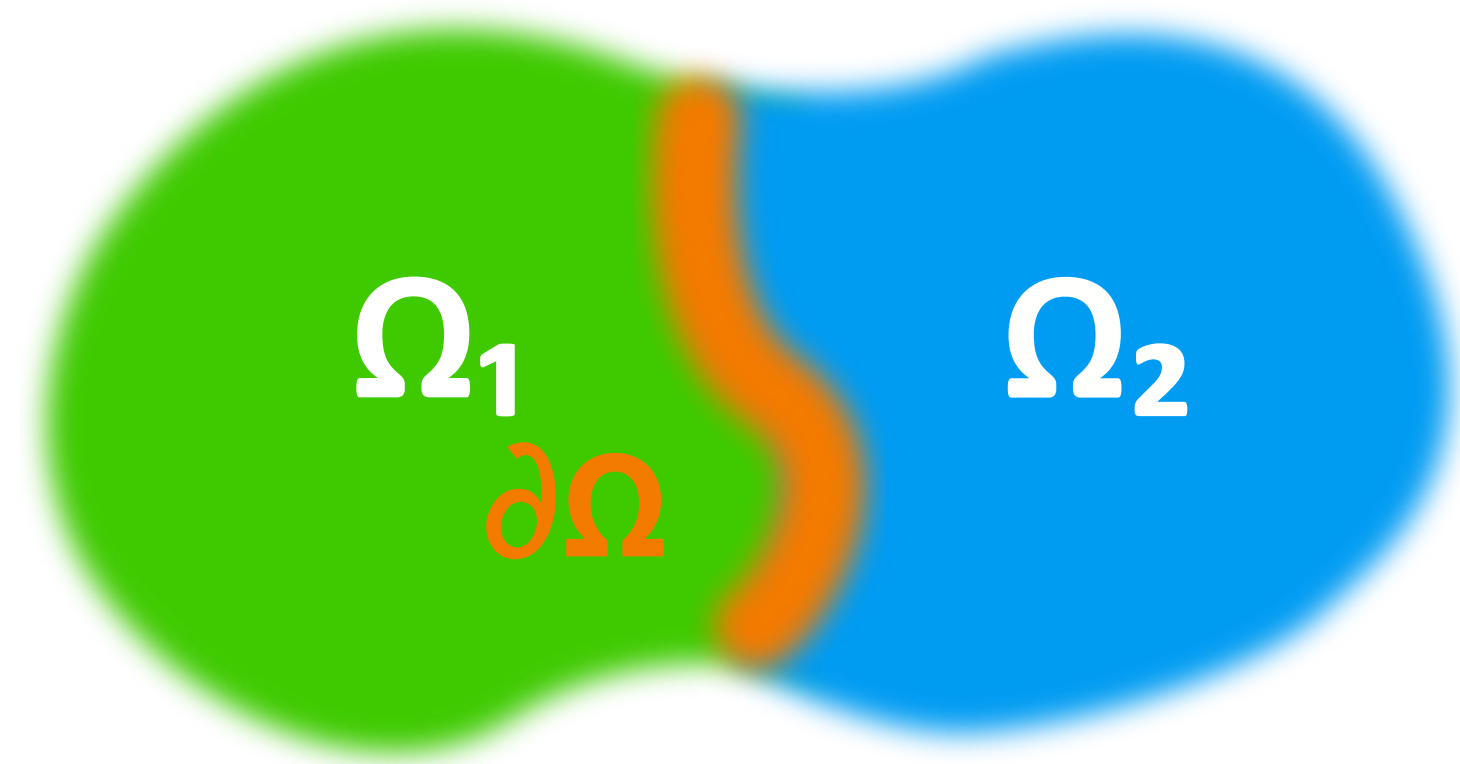
$$\mathbf{j}'(\mathbf{r}, t) = \mathbf{j}(\mathbf{r}, t) + \dot{\mathbf{p}}(\mathbf{r}, t)$$

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gauge invariance

conservation

nature
physics

ARTICLES

PUBLISHED ONLINE: 19 OCTOBER 2015 | DOI: 10.1038/NPHYS3509

Microscopic theory and quantum simulation of
atomic heat transport

Aris Marcolongo¹, Paolo Umari² and Stefano Baroni^{1*}

$$e(\mathbf{r}, t) = -\nabla \cdot \mathbf{j}(\mathbf{r}, t)$$

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hurdles toward an ab initio Green-Kubo theory

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PRL **104**, 208501 (2010)

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Thermal Conductivity of Periclase (MgO) from First Principles

Stephen Stackhouse*

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sensitive to the form of the potential. The widely used Green-Kubo relation [14] does not serve our purposes, because in first-principles calculations it is impossible to uniquely decompose the total energy into individual contributions from each atom.

solution:

choose *any* local representation of the energy that integrates to the correct value and whose correlations decay at large distance — the conductivity computed from the resulting current will be *independent* of the chosen representation.

hurdles toward an ab initio Green-Kubo theory

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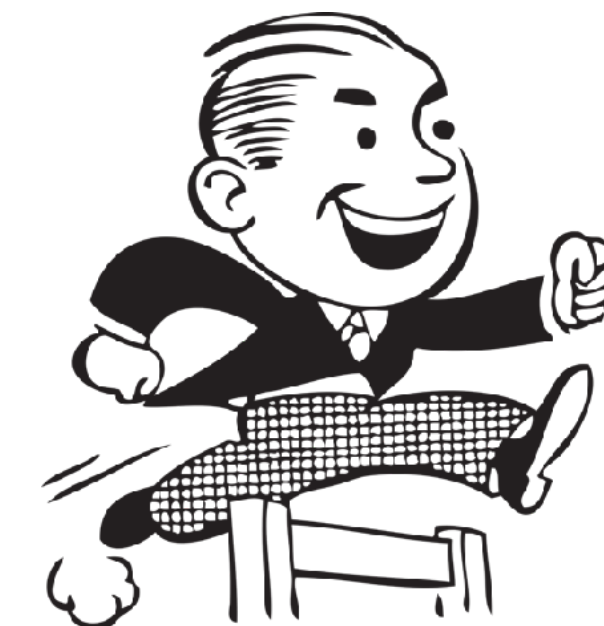
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multi-component systems



50% water
50% ethanol

multi-component systems

Conserved currents are adiabatically decoupled from the myriad fast atomic modes, while retaining mutual interaction



conserved quantities:

- ☒ energy
- ☒ water mass
- ☐ ethanol mass

multi-component systems

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$$J_M = \Lambda_{EM} \left(\frac{1}{T} \right) + \Lambda_{MM} \left(\frac{\mu}{T} \right)$$

$$\Lambda_{ik} \propto \int_0^\infty \langle J_i(t) J_k(0) \rangle dt$$

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$$J_M = 0 \rightarrow$$

$$\kappa = \frac{1}{T^2} \left(\Lambda_{EE} - \frac{\Lambda_{EM}^2}{\Lambda_{MM}} \right)$$

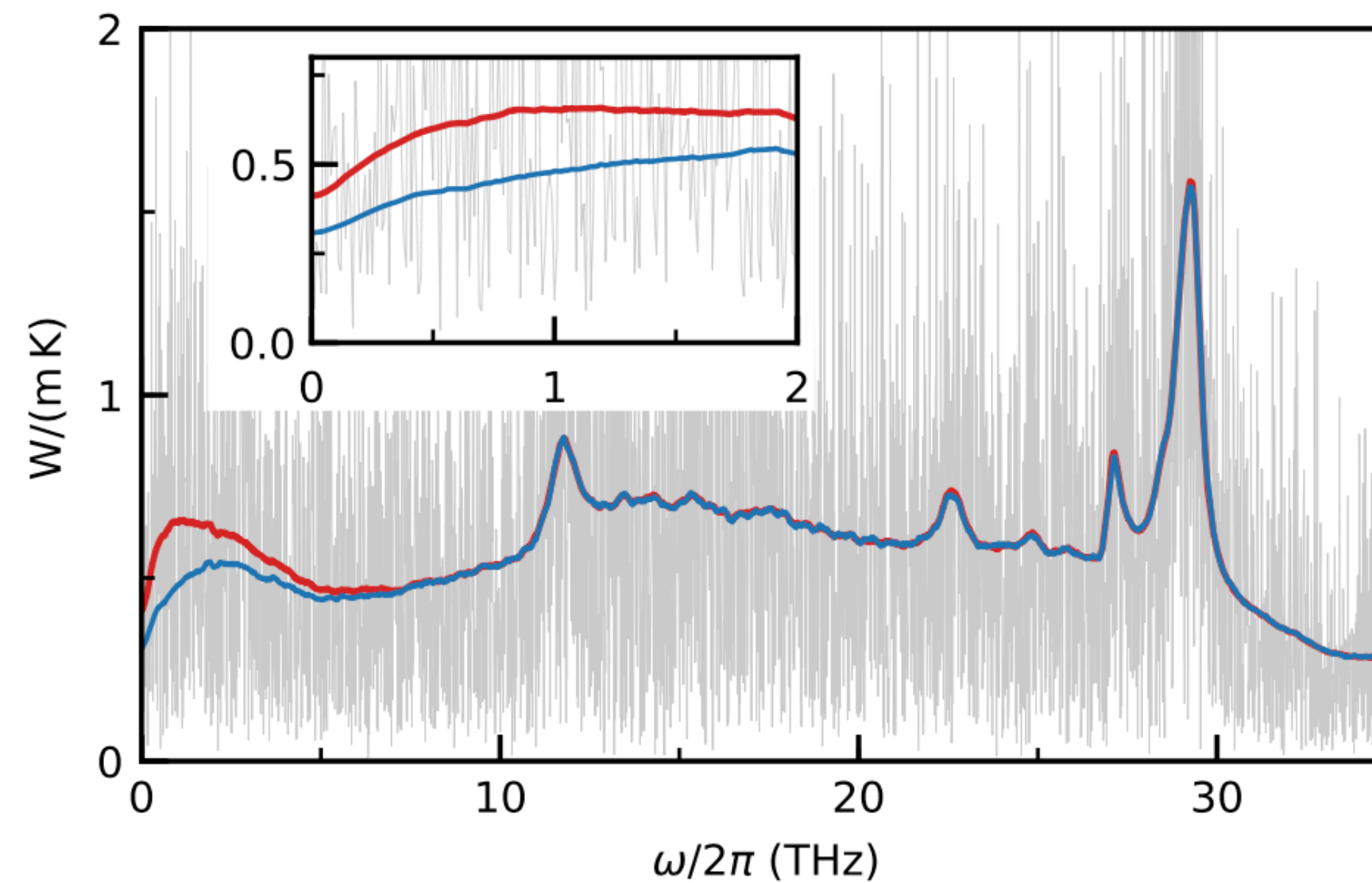
$\kappa = \Lambda / \Lambda_{MM}$: Schur complement
of Λ_{MM} in Λ
 $= 1 / (\Lambda^{-1})_{EE}$

multi-component systems



$$J_E = \Lambda_{EE} \nabla \left(\frac{1}{T} \right) + \Lambda_{ME} \left(\frac{\mu}{T} \right)$$
$$J_M = \Lambda_{EM} \left(\frac{1}{T} \right) + \Lambda_{MM} \left(\frac{\mu}{T} \right)$$

$$\kappa = \frac{1}{T^2} \left(\Lambda_{EE} - \frac{\Lambda_{EM}^2}{\Lambda_{MM}} \right)$$



multi-component systems

$$\kappa = \frac{1}{T^2} \left(\Lambda_{EE} - \frac{\Lambda_{EM}^2}{\Lambda_{MM}} \right)$$

$$J'_E = J_E + c J_M$$

$$\begin{aligned} \kappa' &= \frac{1}{T^2} \left(\Lambda'_{EE} - \frac{\Lambda'^2_{EM}}{\Lambda'_{MM}} \right) \\ &= \kappa \end{aligned}$$

multi-component systems

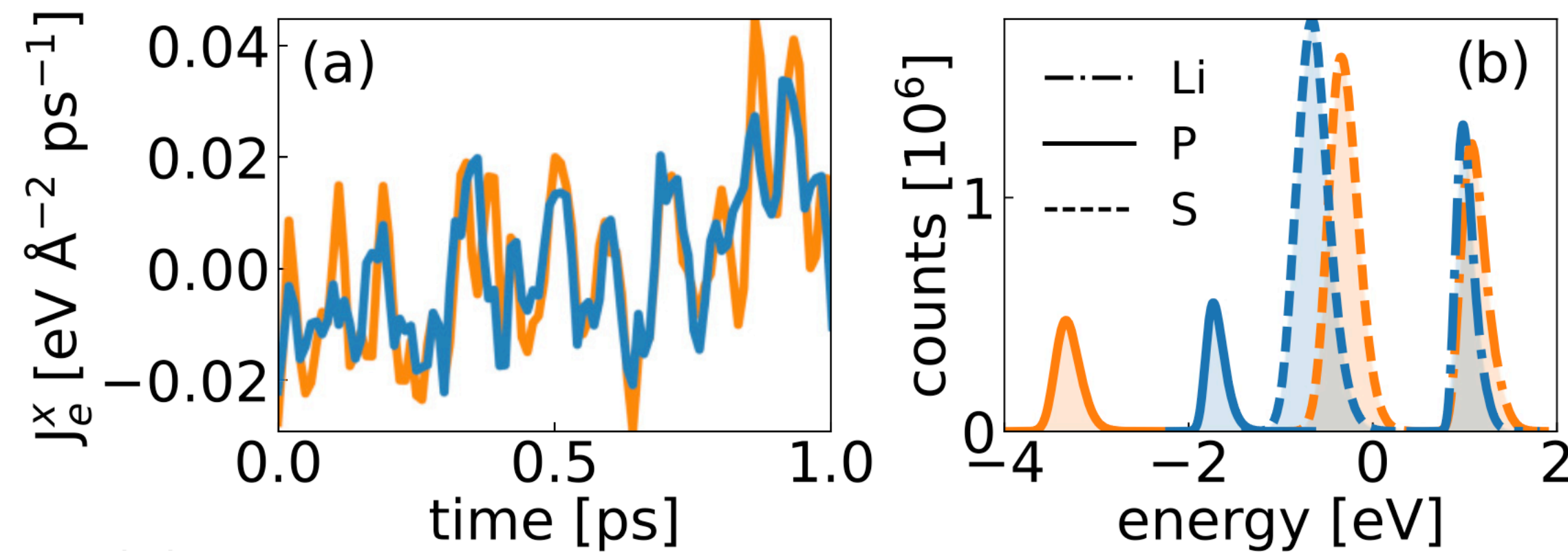
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convective invariance

impact on ML MD simulations



Li_3PS_4

ML model A

ML model B

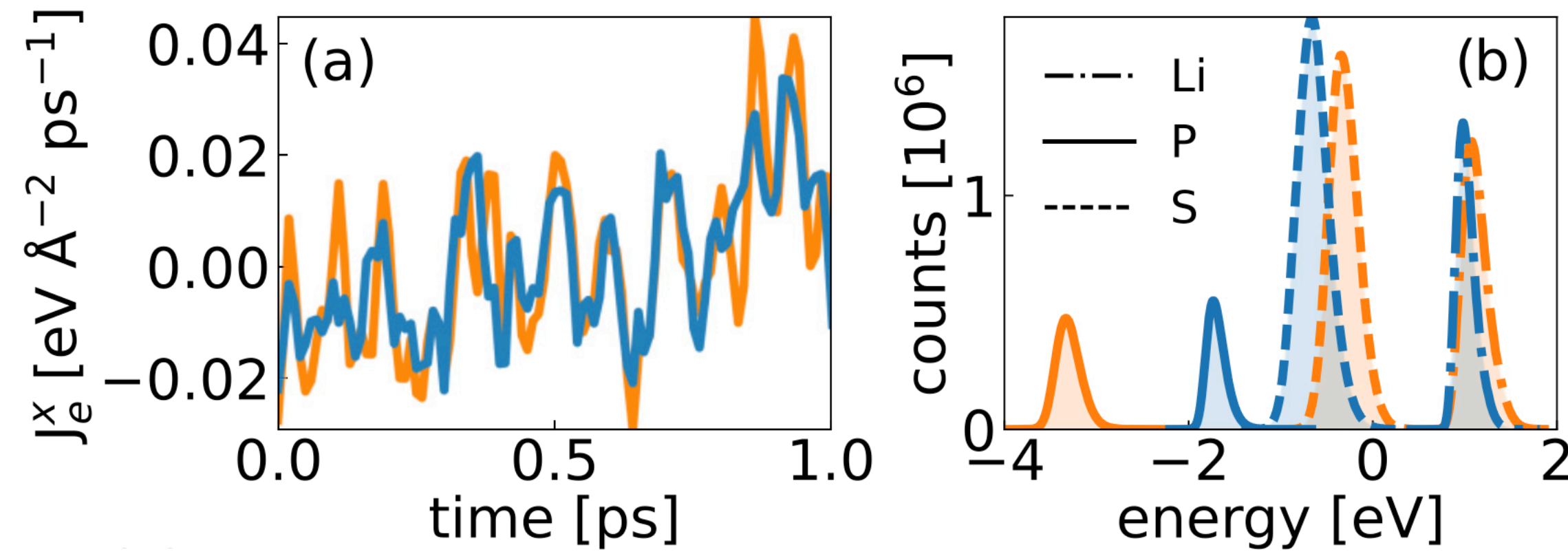
PHYSICAL REVIEW MATERIALS **8**, 065403 (2024)

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Davide Tisi , Federico Grasselli , Lorenzo Gigli , and Michele Ceriotti 

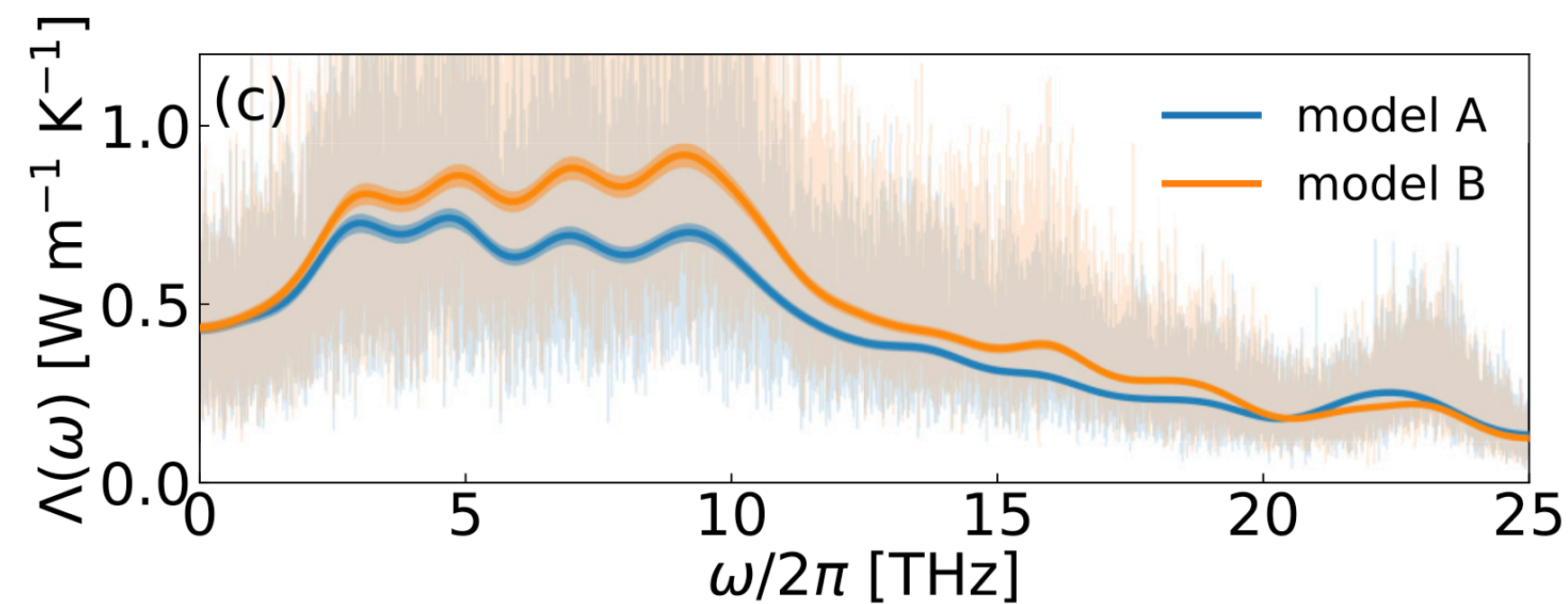


impact on ML MD simulations



ML model A

ML model B



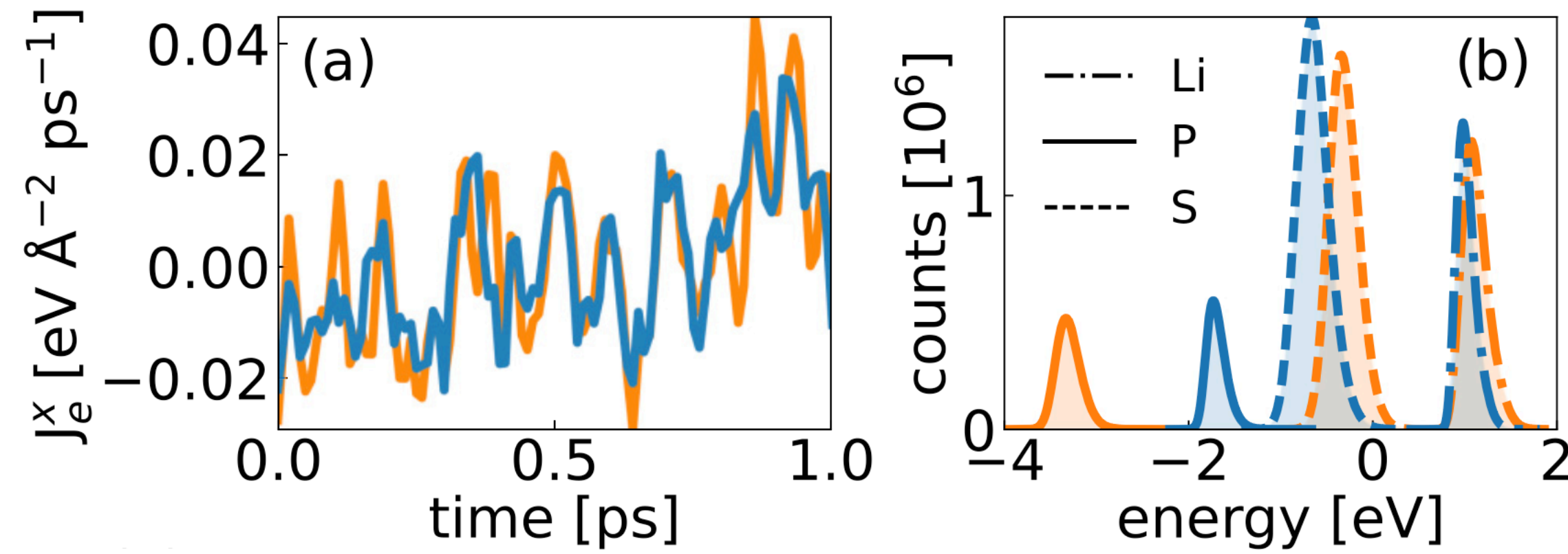
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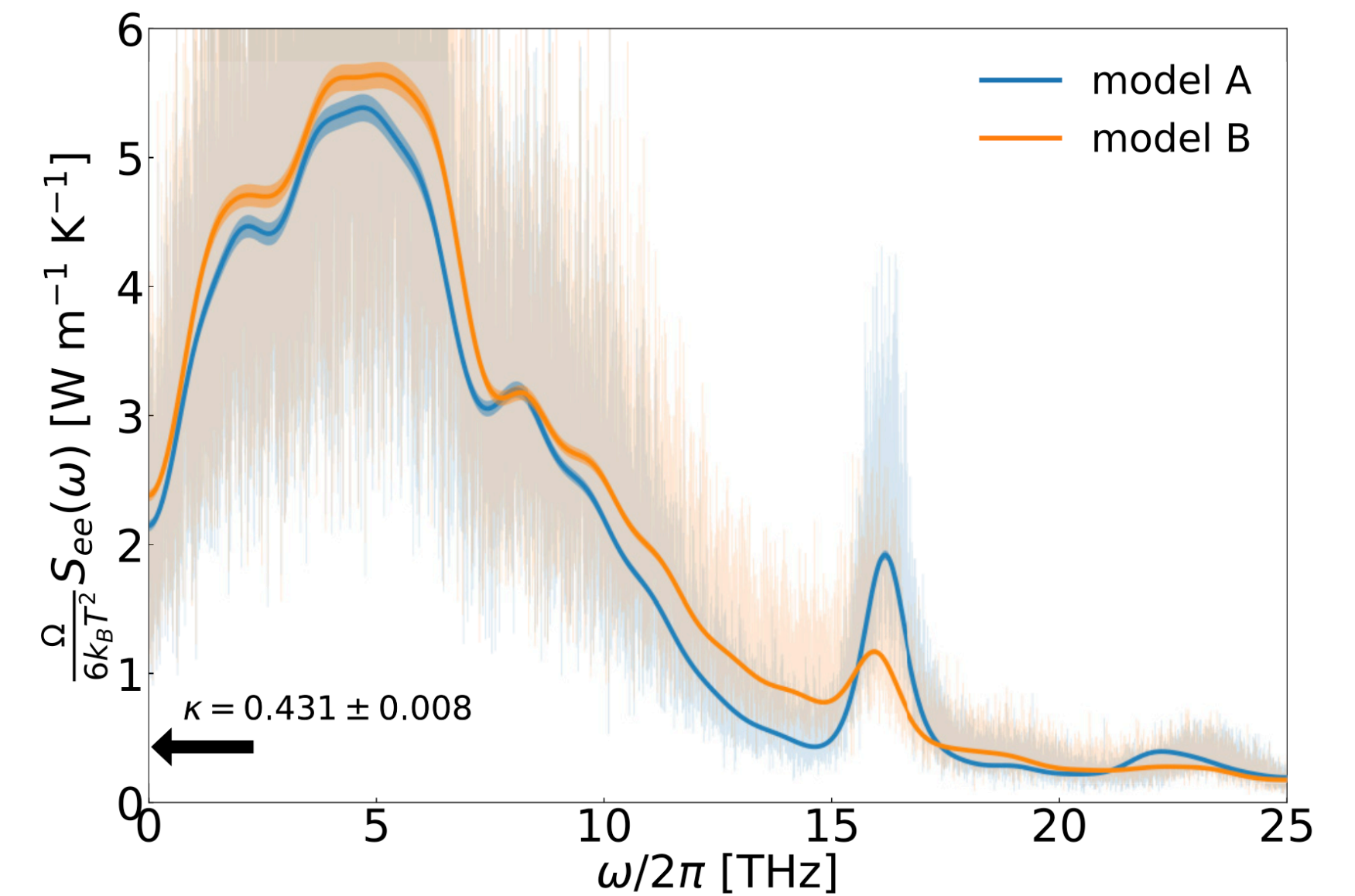
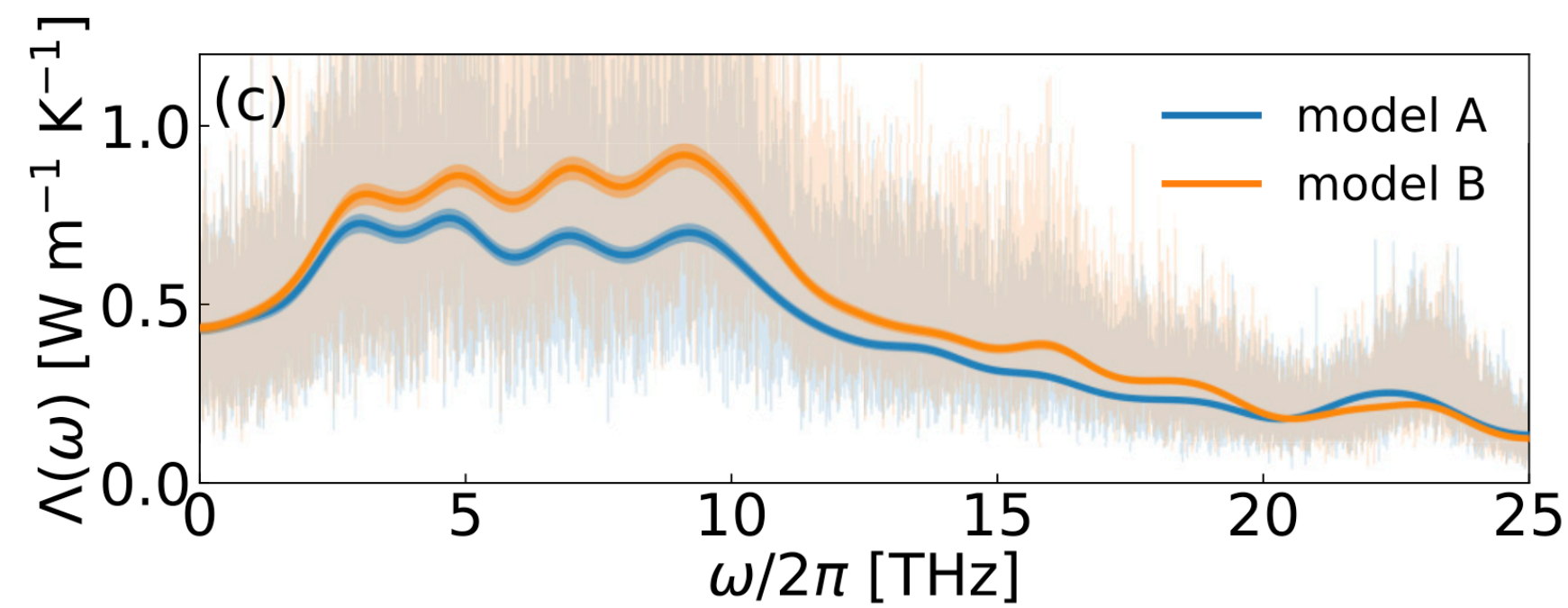


impact on ML MD simulations



ML model A

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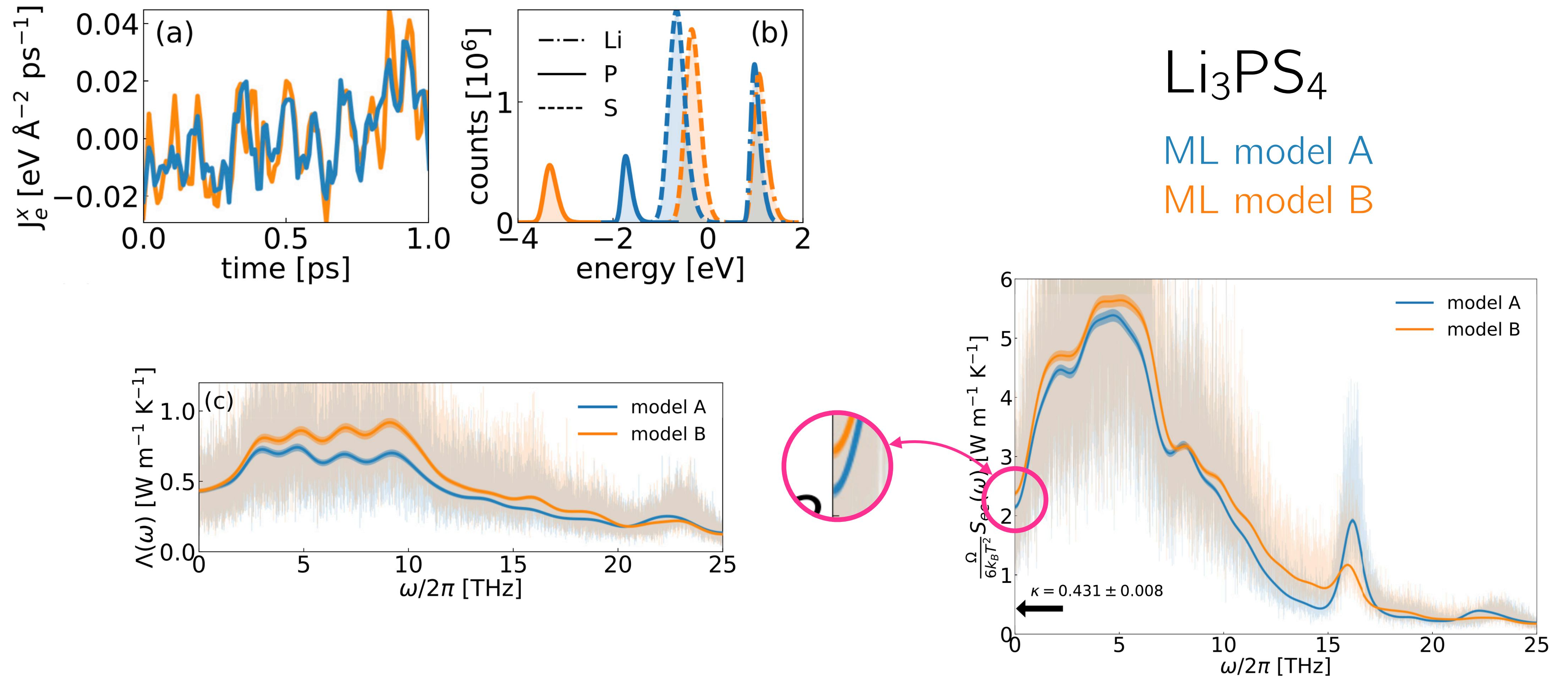
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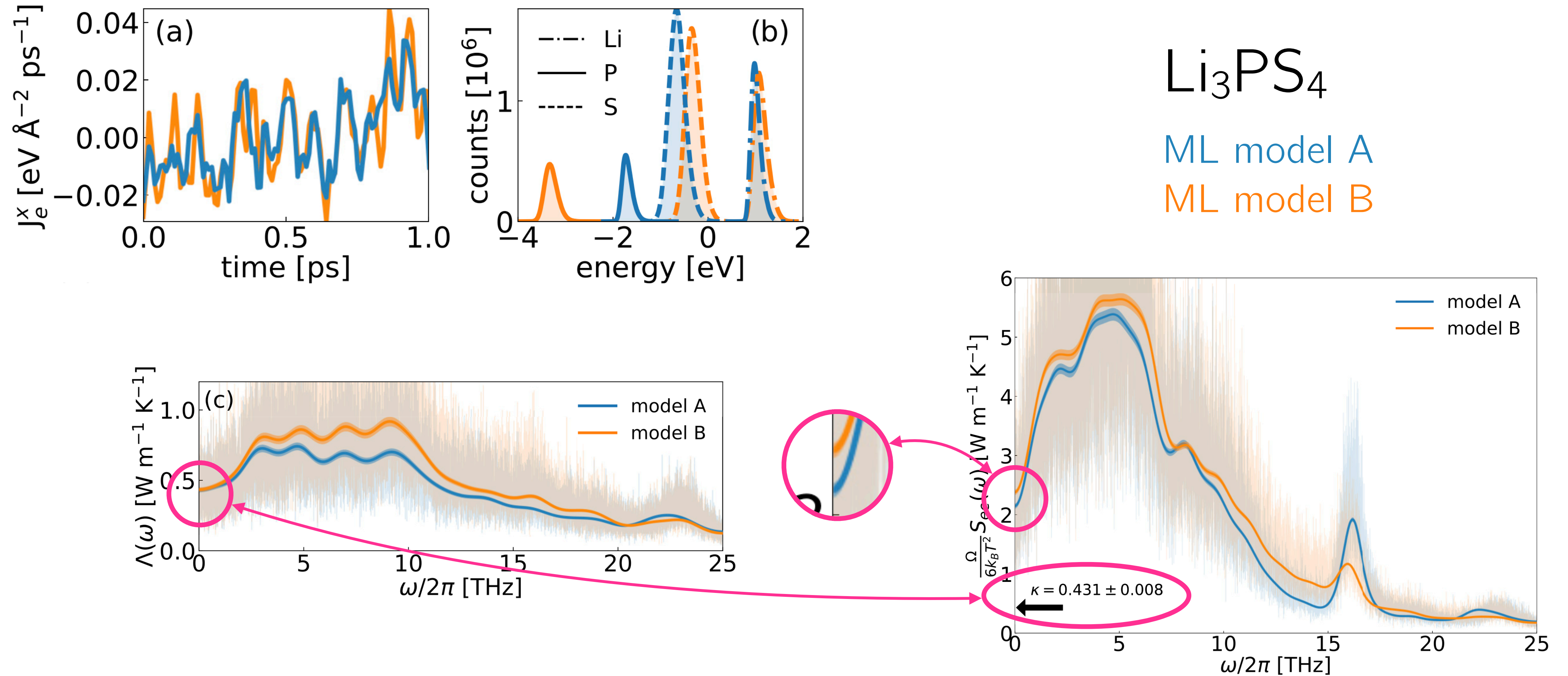
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the nuts and bolts of gauge invariance

the physical requirement that a local representation of the energy must possess is that it gives rise to the physical forces from some reference accurate level of theory

$$\begin{aligned}\mathbf{F}_I(\mathbf{R}) &= -\frac{\partial}{\partial \mathbf{R}_I} \sum_J e_J(\mathbf{R}) \\ &= \sum_J \mathbf{f}_{IJ}; \quad \mathbf{f}_{IJ} = -\frac{\partial e_J}{\partial \mathbf{R}_I}\end{aligned}$$

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the condition that two such local representations the same atomic forces is that the sum of the difference of the local representation of the atomic forces vanishes

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is this enough to guarantee equality of the transport coefficients?



the nuts and bolts of gauge invariance

$$\kappa_2 = \kappa_1$$

iff

$$\left\langle \left| \int_0^T J'(t) dt \right|^2 \right\rangle \sim o(T)$$

$$\mathbf{J}_e = \sum_I e_I \mathbf{V}_I + \frac{1}{2} \sum_{I \neq J} (\mathbf{V}_I \cdot \mathbf{f}_{IJ}) (\mathbf{R}_I - \mathbf{R}_J)$$

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$$J'(t) = \sum_I \left(\mathcal{D}'_I(R(t)) + e'_I(\infty) + \delta e'_I(R(t)) \right) \cdot V_I(t); \quad \mathcal{D}'_I(R) = \sum_J R_J \otimes f'_{IJ}(R)$$

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$$\sum_J \mathbf{f}'_{IJ} = 0$$

$$\mathbf{f}'_{IJ} = 0 \quad \text{for } |\mathbf{R}_I - \mathbf{R}_J| > R_c$$

$\Rightarrow$

$$\sum_I \int_0^T \left([\mathcal{D}_I(\mathbf{R}(t)) + \delta e'_I(\mathbf{R}(t))] \cdot \mathbf{V}_I(t) \right) dt =$$

$$\sum_I \int_{R^0}^{R^T} (\mathcal{D}_I(\mathbf{R}) + \delta e'_I(\mathbf{R})) \cdot d\mathbf{R}_I$$

independent of path
and periodic in $\mathbf{R}^T$

the nuts and bolts of gauge invariance

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$$\int_0^T J'(t) dt = \underbrace{D(R(t))}_{\text{periodic, bounded}} + \underbrace{\sum_I e_I(\infty) \int_0^T V_I(t) dt}_{\text{does contribute to } \Lambda_{EE}, \text{ but not to } \kappa}$$

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$$\sum_J \frac{\partial e_I^1}{\partial R_J} = \sum_J \frac{\partial e_I^2}{\partial R_J} \quad \Rightarrow \quad \begin{matrix} \kappa^1 = \kappa^2 \\ (\Lambda_{EE}^1 \neq \Lambda_{EE}^2, \text{ in general}) \end{matrix}$$

$$\frac{\partial e_I}{\partial R_J} = 0 \quad \text{for } |R_I - R_J| > R_c$$

conclusions

- different local representations of a system's potential energy that yield the same atomic forces give rise to the same heat conductivity
- the resulting energy-energy diagonal elements of the Onsager matrix, though, may differ
- the correct multi-component formula for the heat conductivity must always be used when computing the thermal conductivity of a system with diffusing mass currents
- long-range forces should behave the same way, but I am not sure I know why



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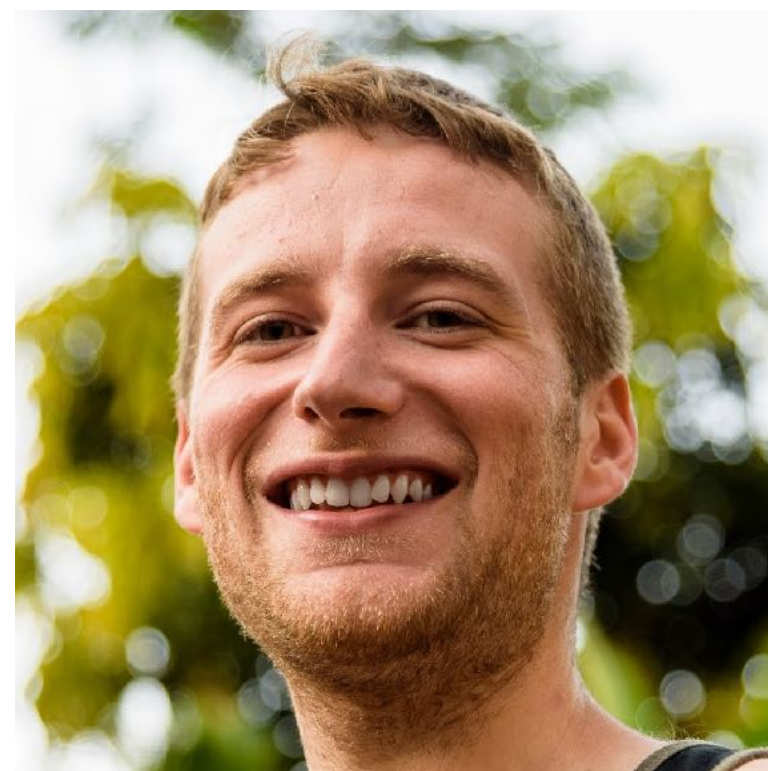
<http://foundation.quantum-espresso.org>



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Aris Marcolongo



Loris Ercole



Riccardo Bertossa



Cesare Malosso



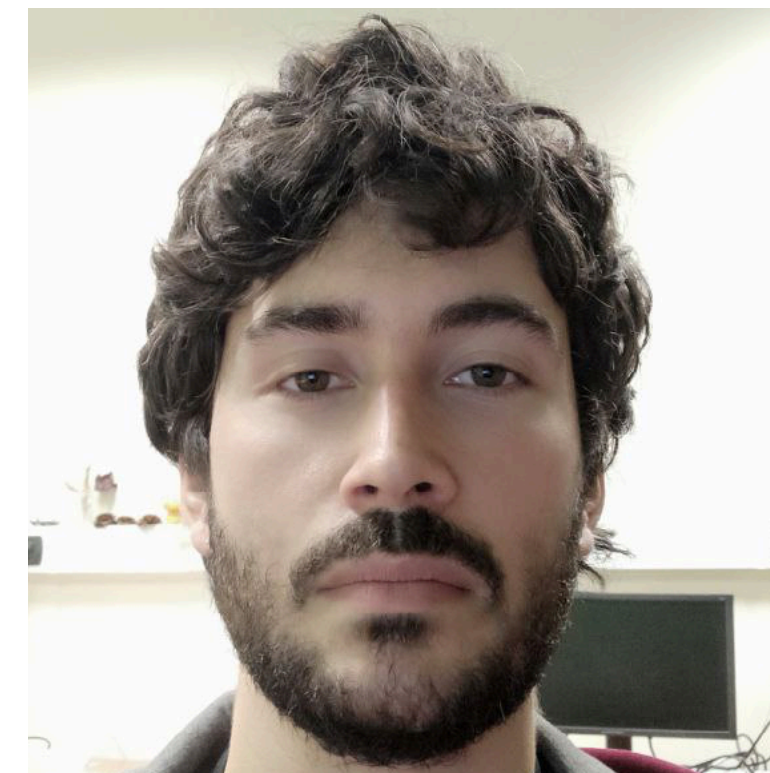
Leyla Isaeva



Giuseppe Barbalinardo



Davide Donadio



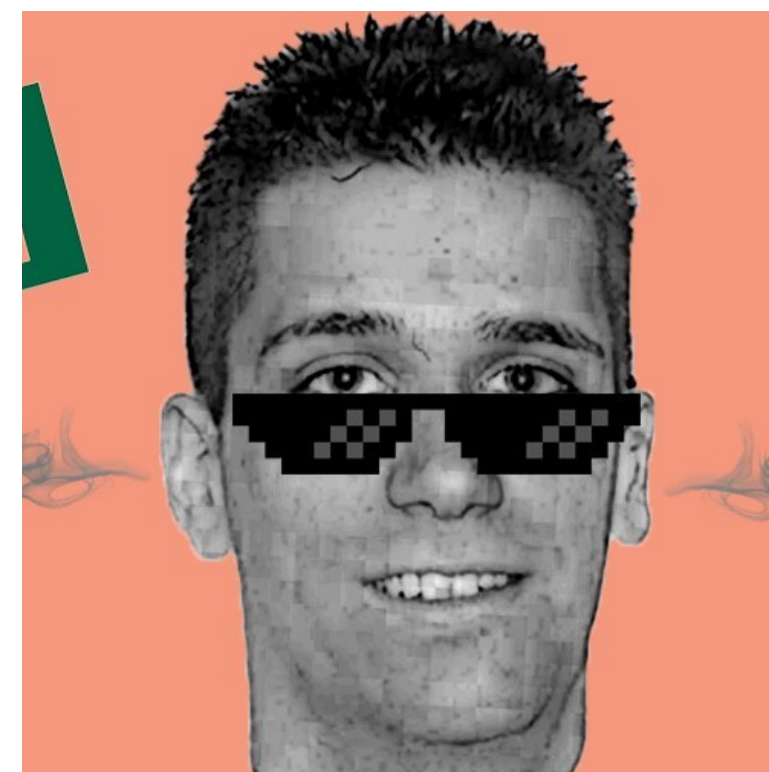
Alfredo Fiorentino



Federico Grasselli



Paolo Pegolo



Davide Tisi



Enrico Drigo





this is the best stuff
you've ever done!
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Happy Birthday, Michele! 80 more years of mind-blowing science!