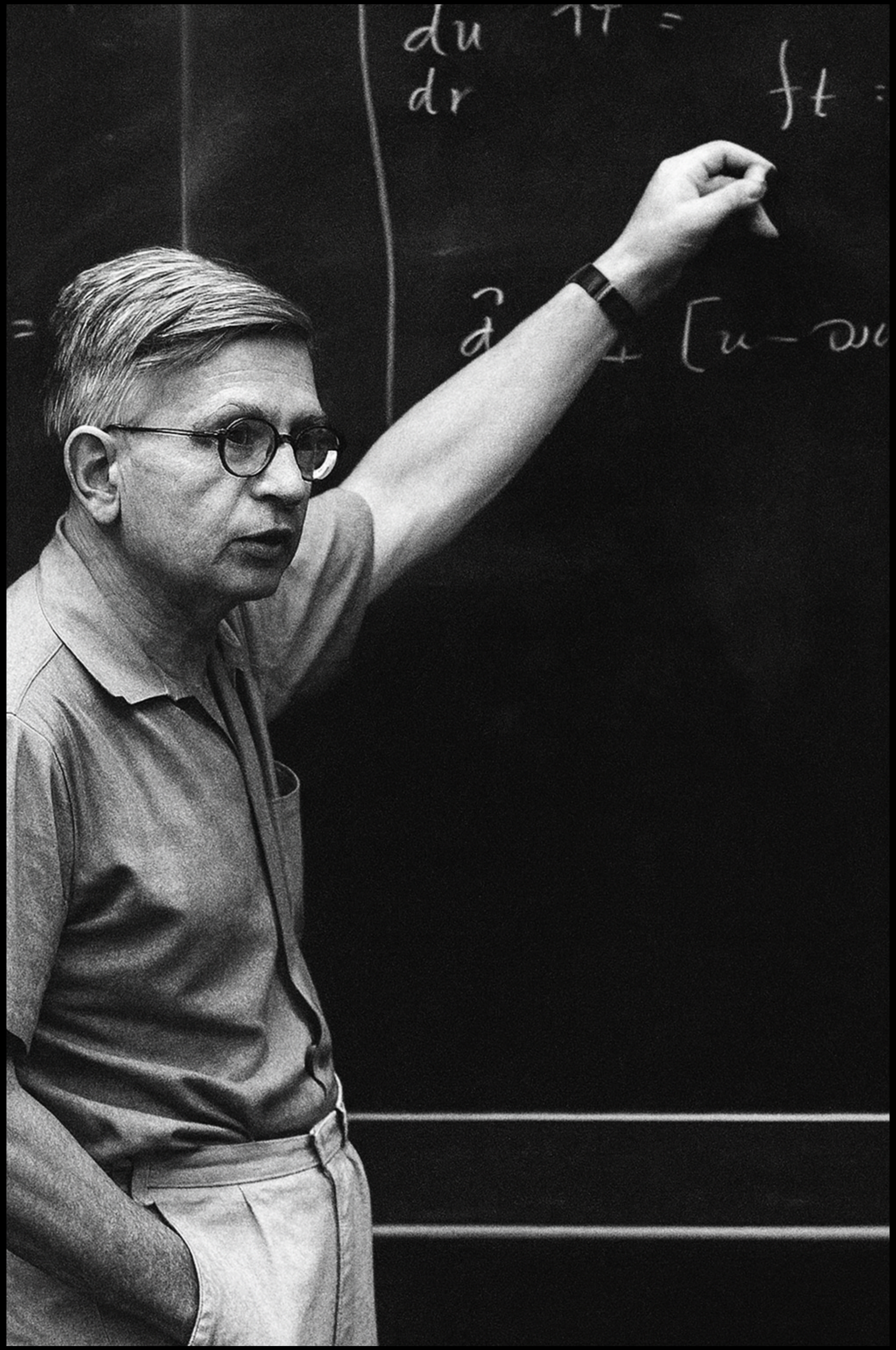
heat transport, ungauged

Stefano Baroni
Scuola Internazionale Superiore di Studi Avanzati
Trieste — Italy

talk given at the *Conference on Frontiers in Atomistic Simulations: from Physics to Chemistry and Biology,* Trieste, September 8-12, 2025



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

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

hurdles toward an ab initio Green-Kubo theory

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

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

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

MA PER SEGUIR VIRTUTE E CANOSCENZA

hurdles toward an ab initio Green-Kubo theory

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

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

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

PRL **104,** 208501 (2010) PHYSICAL REVIEW LETTERS week ending 21 MAY 2010

Thermal Conductivity of Periclase (MgO) from First Principles

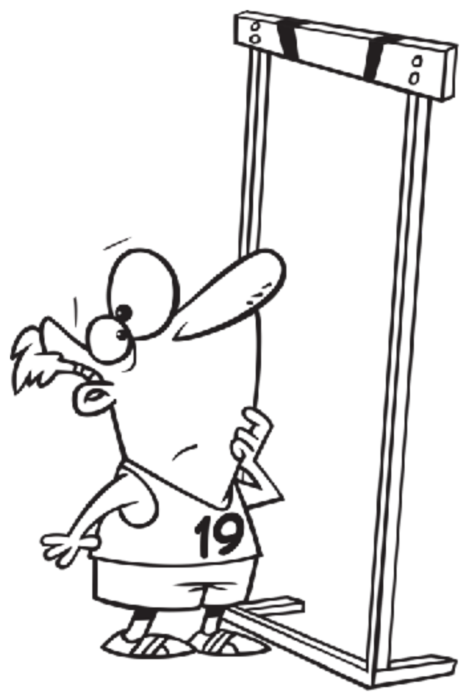
Stephen Stackhouse*
Department of Geological Sciences, University of Michigan, Ann Arbor, Michigan, 48109-1005, USA

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

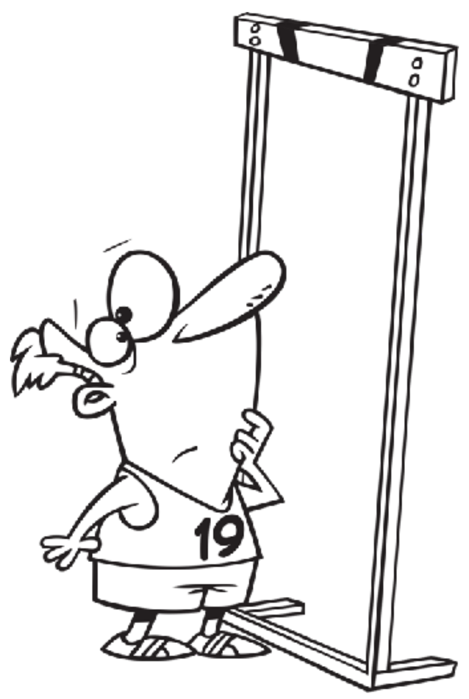
Bijaya B. Karki‡
Department of Computer Science, Louisiana State University, Baton Rouge, Louisiana 70803, USA
and Department of Geology and Geophysics, Louisiana State University, Baton Rouge, Louisiana 70803, USA

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.

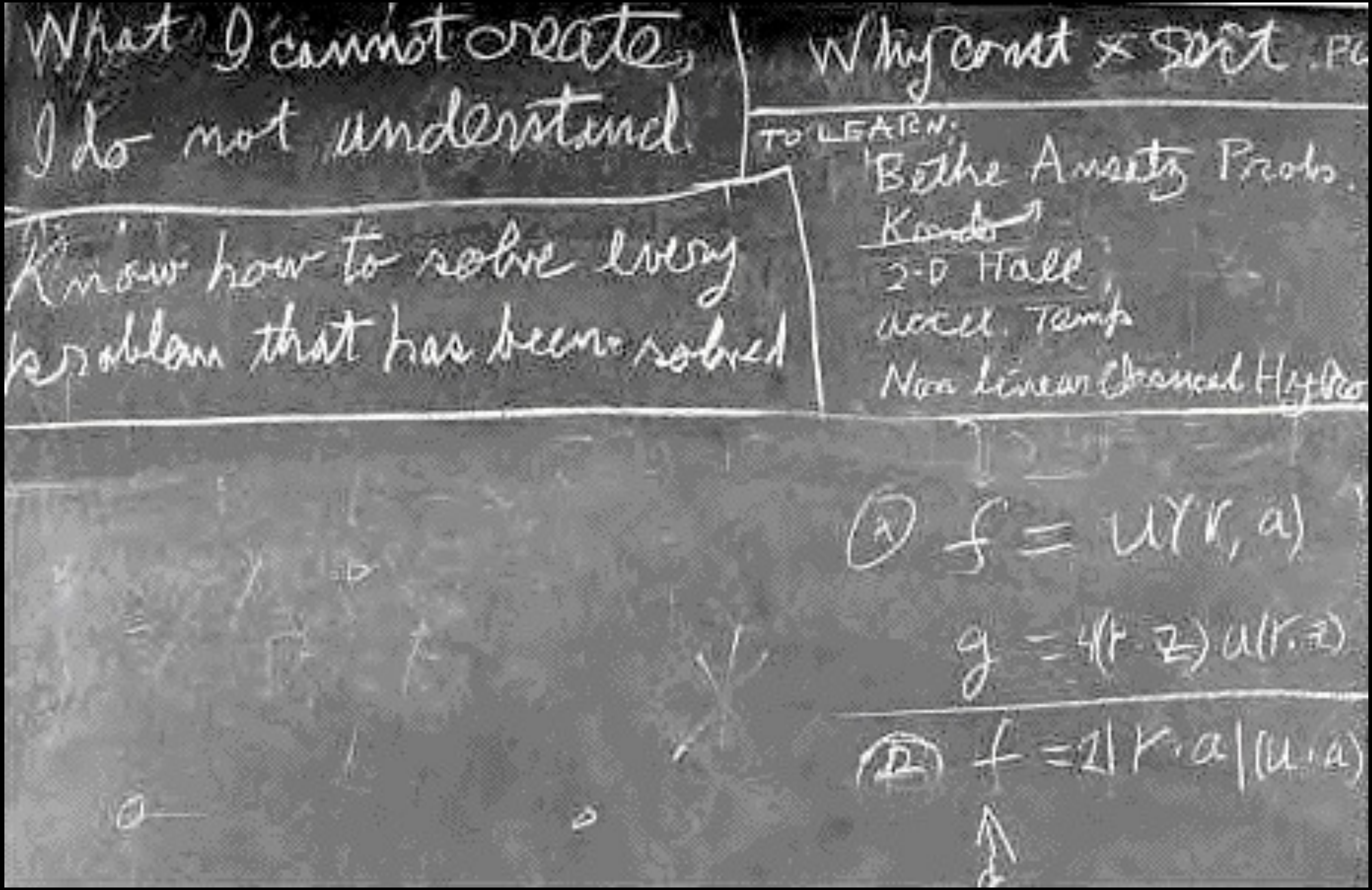
how come?

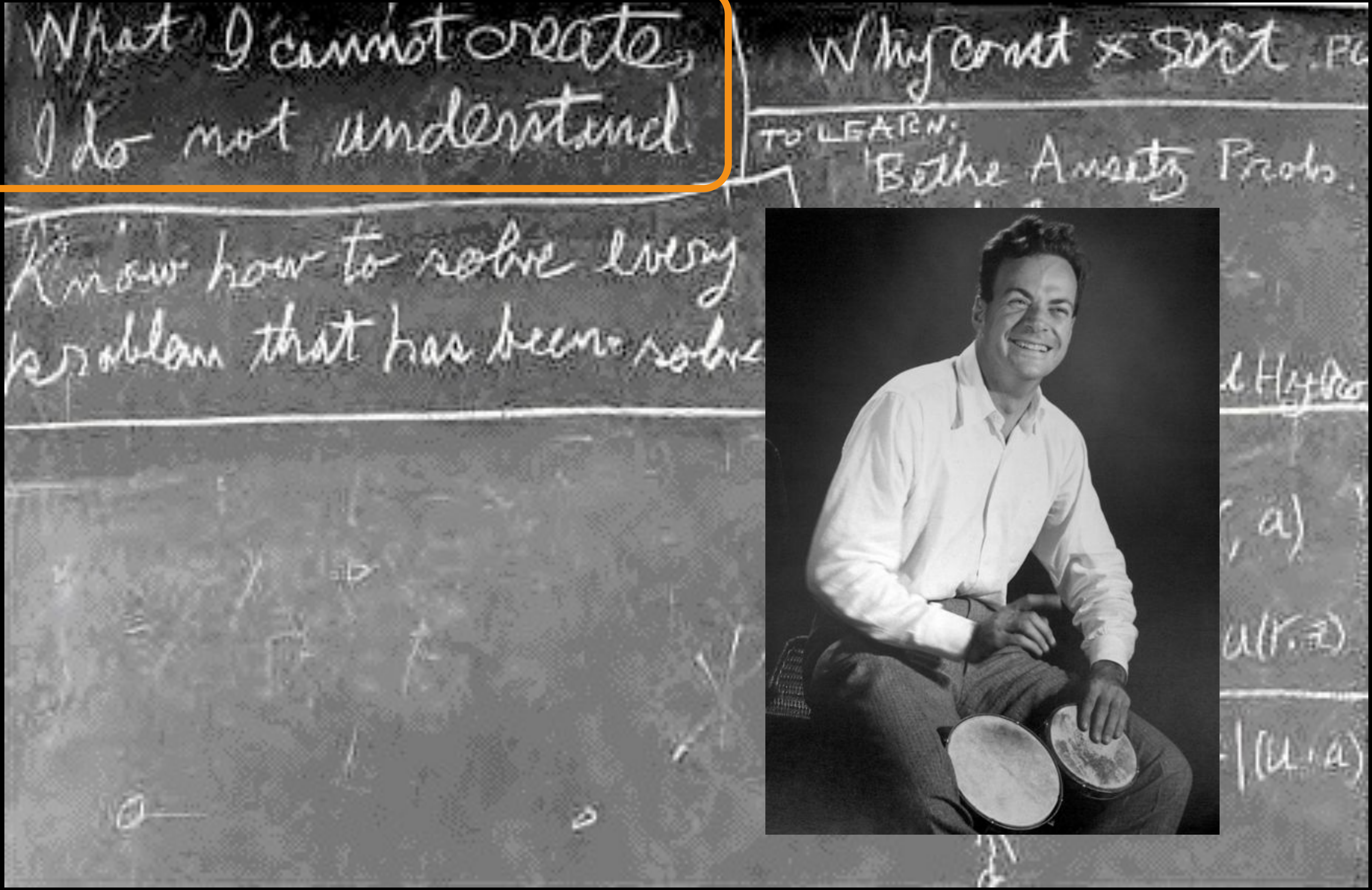


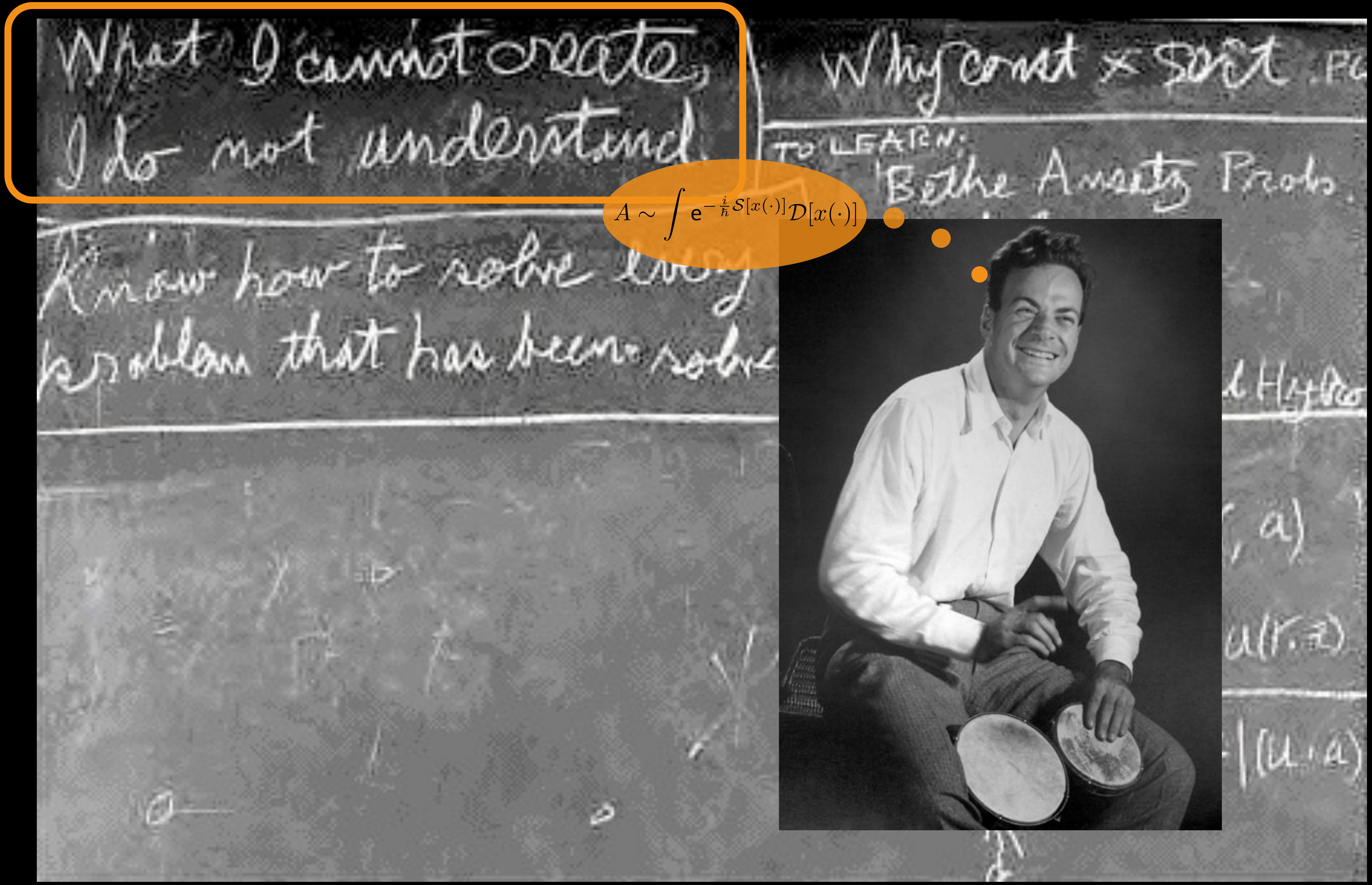
how come?



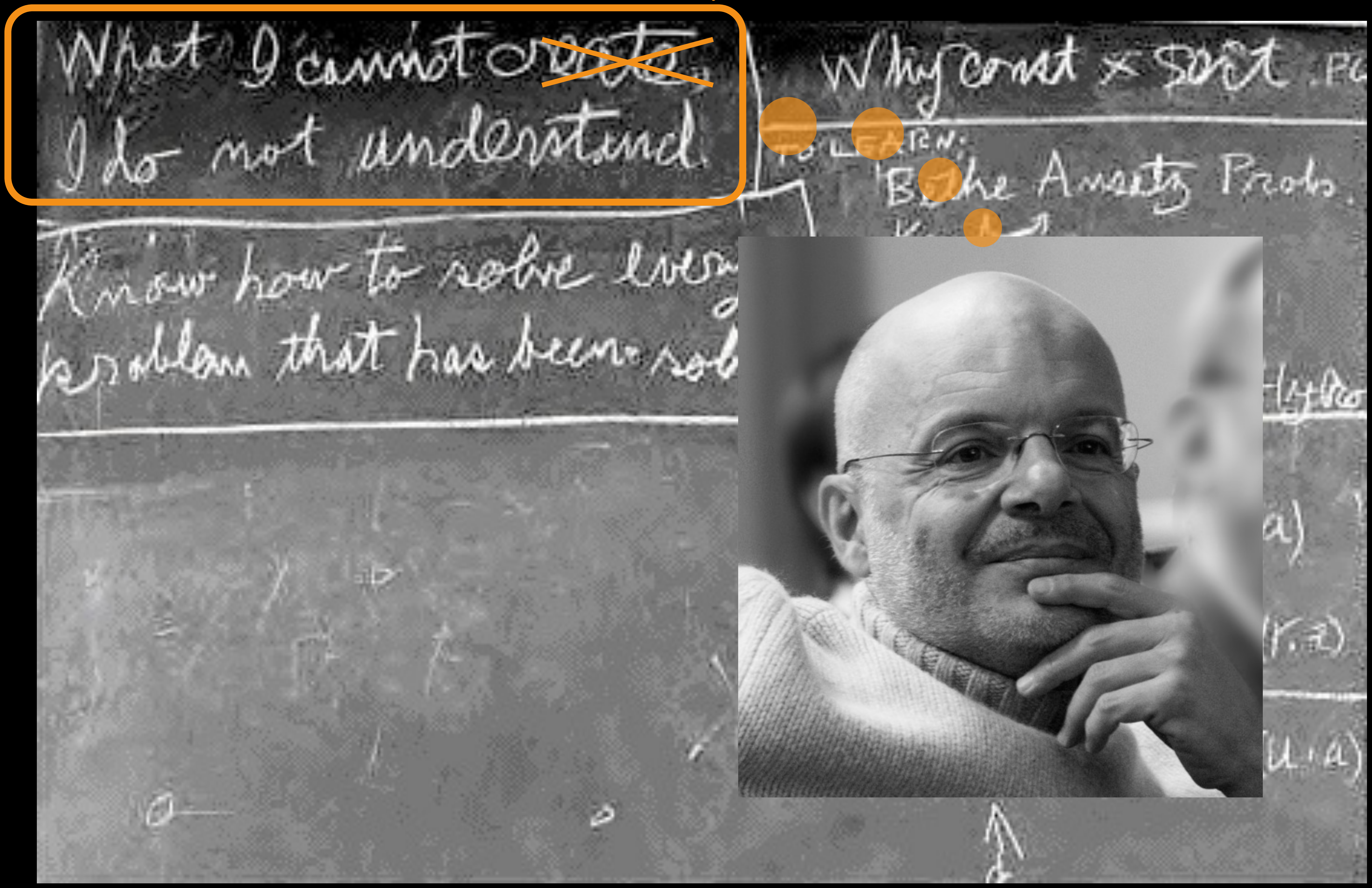
how is it that a formally exact theory of the electronic ground state cannot predict *all* measurable adiabatic properties?


What I cannot create,
I do not understand.
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


What I cannot create,
I do not understand.
Know how to solve every
problem that has been
TO LEARN:
Bethe Ansatz Probs.


What I cannot create,
I do not understand.
Know how to solve
problem that has been solve
TO LEARN:
Bethe Ansatz Probs.
$A \sim \int e^{-\frac{i}{\hbar}\mathcal{S}[x(\cdot)]}\mathcal{D}[x(\cdot)]$

compute


What I cannot create
I do not understand
TO LEARN:
Bethe Ansatz Prob.

the linear-response theory of transport

Fourier

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

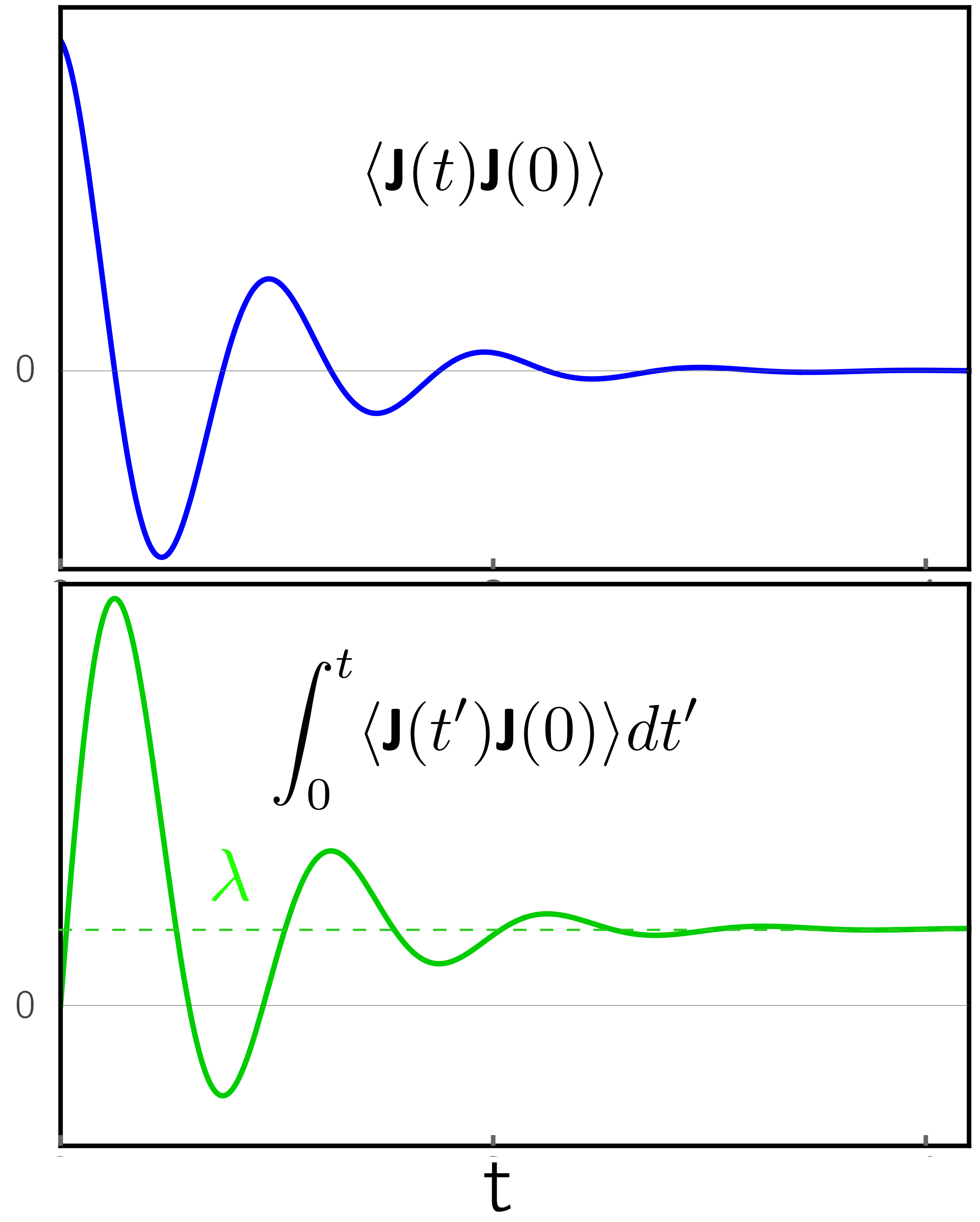
the linear-response theory of transport

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

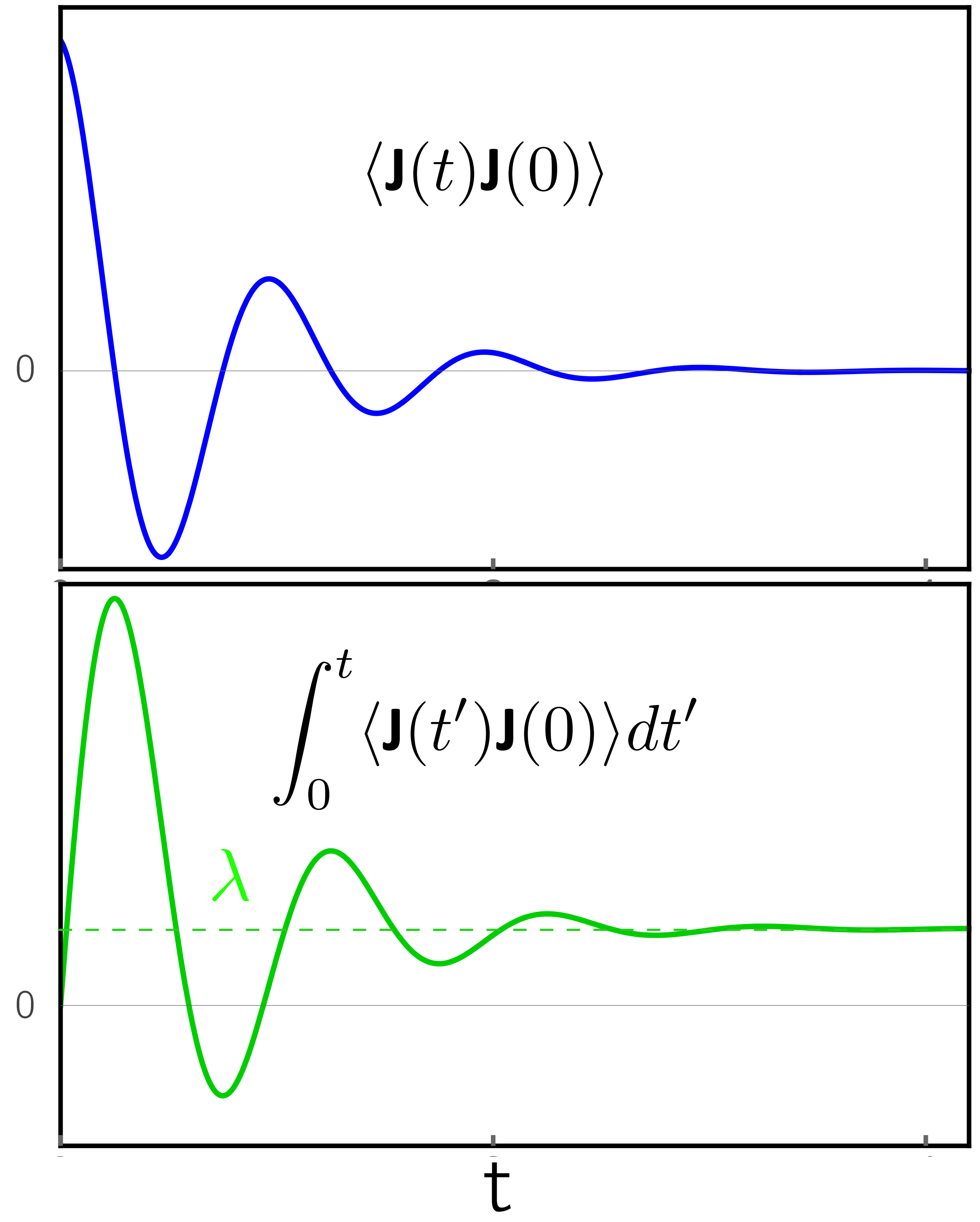
$$\mathbf{J} = -\kappa \nabla T$$

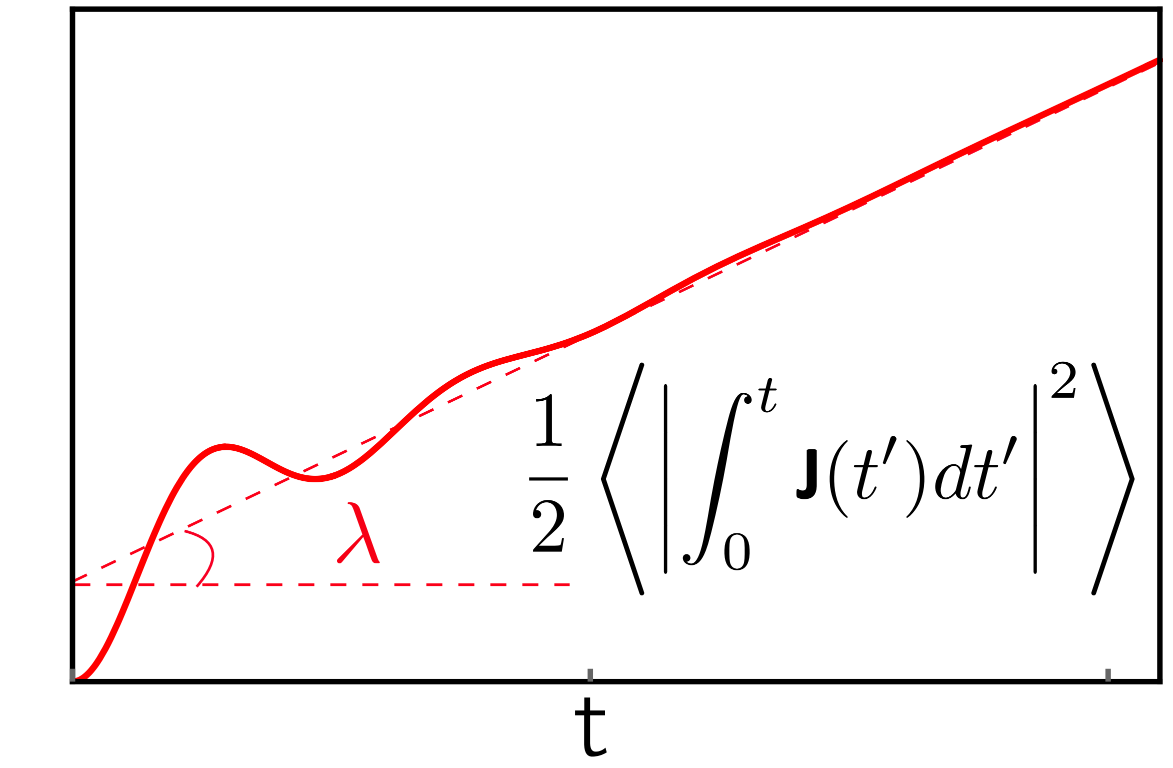
Green-Kubo

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

Einstein-Helfand

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





insights from classical mechanics

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

$$= \text{cnst}$$

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

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

MA PER SEGUIR VIRTUTE E CANOSCENZA

insights from classical mechanics

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

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

insights from classical mechanics

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

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

insights from classical mechanics

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

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

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

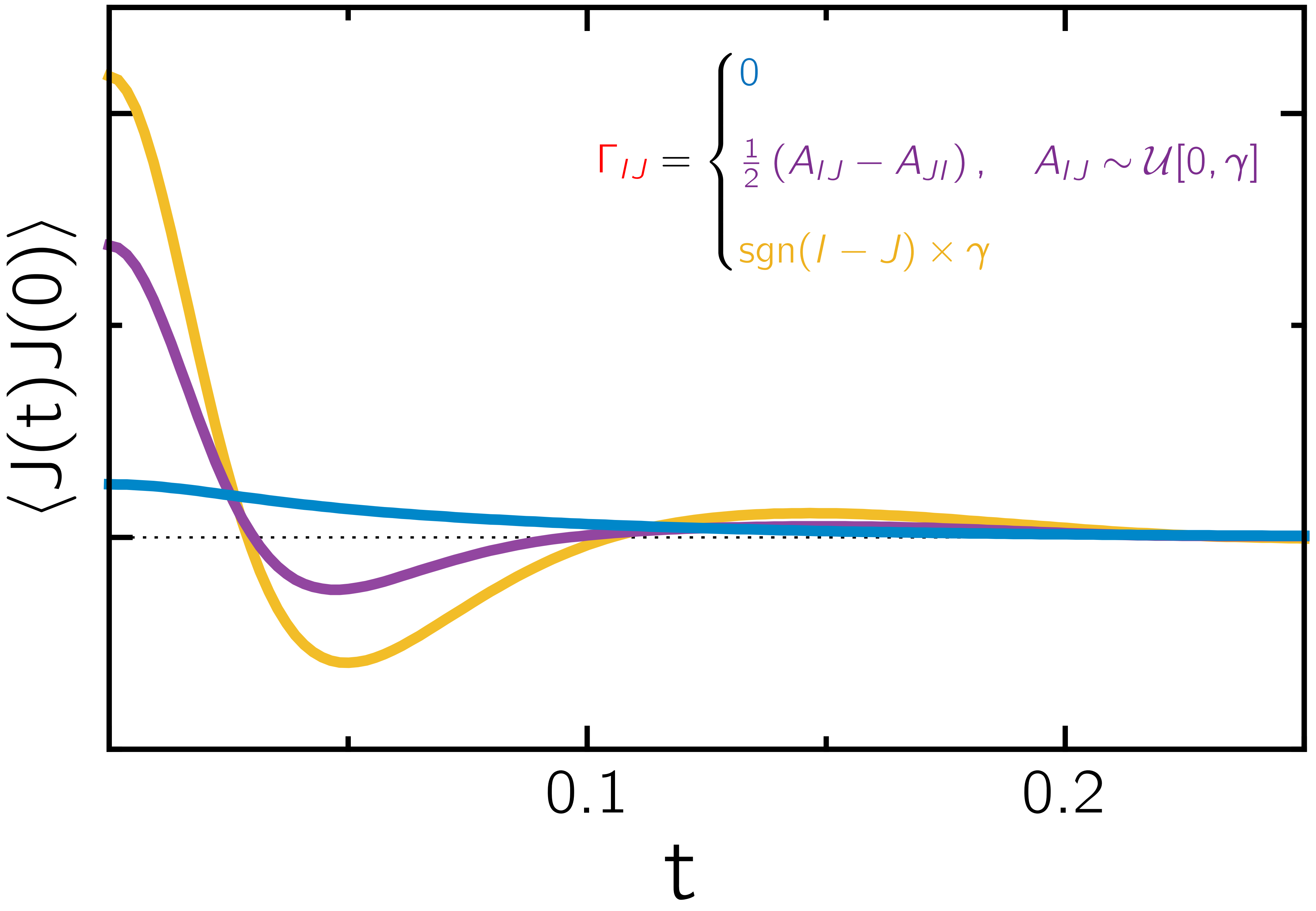
insights from classical mechanics

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

insights from classical mechanics

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

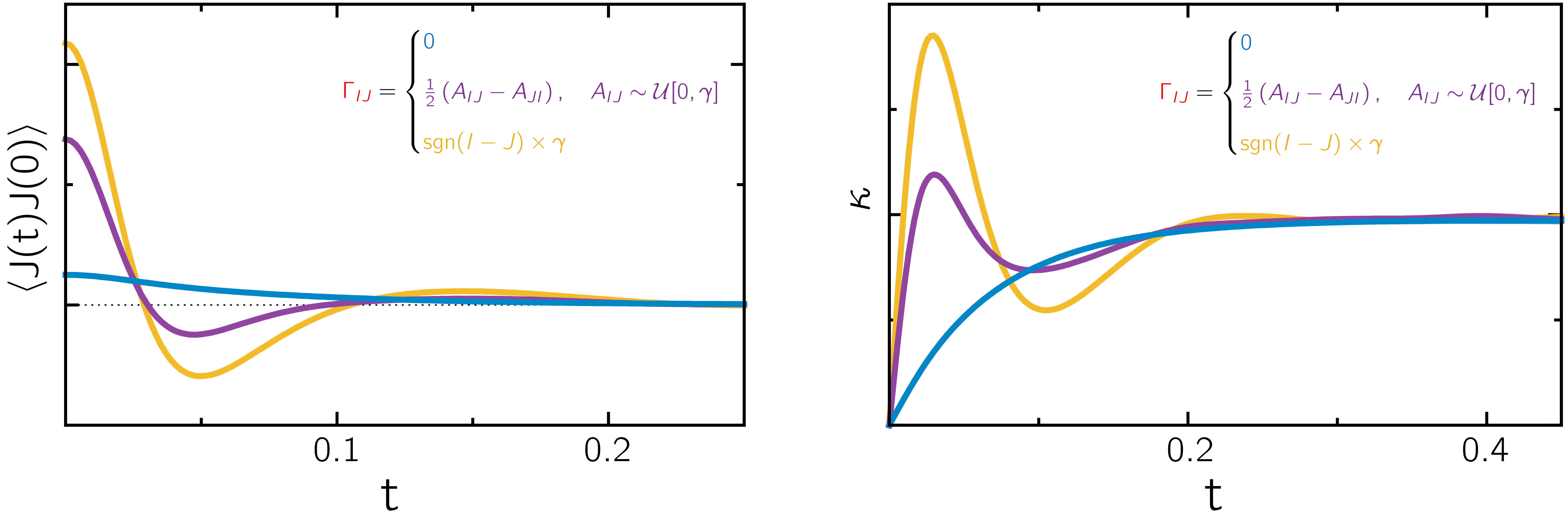
$$+ \frac{1}{2}\sum_{I\neq J}\Gamma_{IJ}\left[\mathbf{V}_I v(|\mathbf{R}_I - \mathbf{R}_J|) + (\mathbf{V}_I \cdot \mathbf{F}_{IJ})(\mathbf{R}_I - \mathbf{R}_I)\right]$$



insights from classical mechanics

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

$$+\frac{1}{2}\sum_{I\neq J}\Gamma_{IJ}\left[\mathbf{V}_I v(|\mathbf{R}_I-\mathbf{R}_J|)+(\mathbf{V}_I\cdot\mathbf{F}_{IJ})(\mathbf{R}_I-\mathbf{R}_I)\right]$$



insights from classical mechanics

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

$$+ \frac{1}{2}\sum_{I\neq J}\Gamma_{IJ}\left[\mathbf{V}_I v(|\mathbf{R}_I - \mathbf{R}_J|) + (\mathbf{V}_I \cdot \mathbf{F}_{IJ})(\mathbf{R}_I - \mathbf{R}_I)\right]$$

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

insights from classical mechanics

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

insights from classical mechanics

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

$$\kappa \sim \frac{1}{2t}\mathrm{var}\left[\mathbf{D}(t)\right] \qquad \mathbf{D}(t) = \int_0^t \mathbf{J}(t')dt'$$

insights from classical mechanics

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

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

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

insights from classical mechanics

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

$$\kappa \sim \frac{1}{2t}\mathrm{var}\left[\mathbf{D}(t)\right] \qquad \mathbf{D}(t) = \int_0^t \mathbf{J}(t')dt'$$

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

$$\mathrm{var}\left[\mathbf{D}'(t)\right] = \mathrm{var}\left[\mathbf{D}(t)\right] + \mathrm{var}\left[\Delta\mathbf{P}(t)\right] + 2\mathrm{cov}\left[\mathbf{D}(t)\cdot\Delta\mathbf{P}(t)\right]$$

MA PER SEGUIR VIRTUTE E CANOSCENZA

insights from classical mechanics

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

$$\kappa \sim \frac{1}{2t}\mathrm{var}\left[\mathbf{D}(t)\right] \qquad \mathbf{D}(t) = \int_0^t \mathbf{J}(t')dt'$$

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

$$\mathrm{var}\left[\mathbf{D}'(t)\right] = \underbrace{\mathrm{var}\left[\mathbf{D}(t)\right]}_{\mathcal{O}(t)} + \underbrace{\cancel{\mathrm{var}\left[\Delta\mathbf{P}(t)\right]}}_{\mathcal{O}(1)} + \underbrace{\cancel{2\mathrm{cov}\left[\mathbf{D}(t)\cdot\Delta\mathbf{P}(t)\right]}}_{\mathcal{O}(t^{\frac{1}{2}})}$$

insights from classical mechanics

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

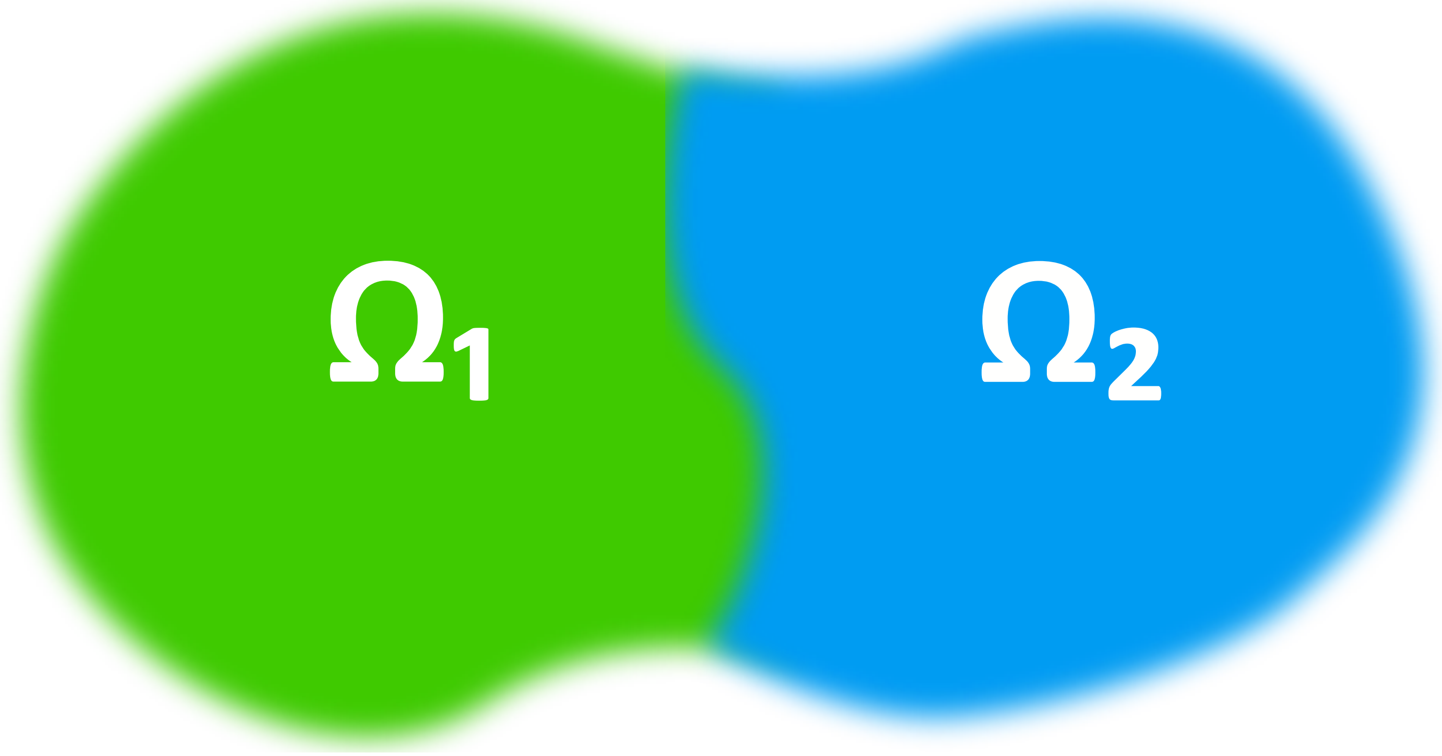
$$\kappa \sim \frac{1}{2t}\mathrm{var}\left[\mathbf{D}(t)\right] \qquad \mathbf{D}(t) = \int_0^t \mathbf{J}(t')dt'$$

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

$$\kappa' = \kappa$$

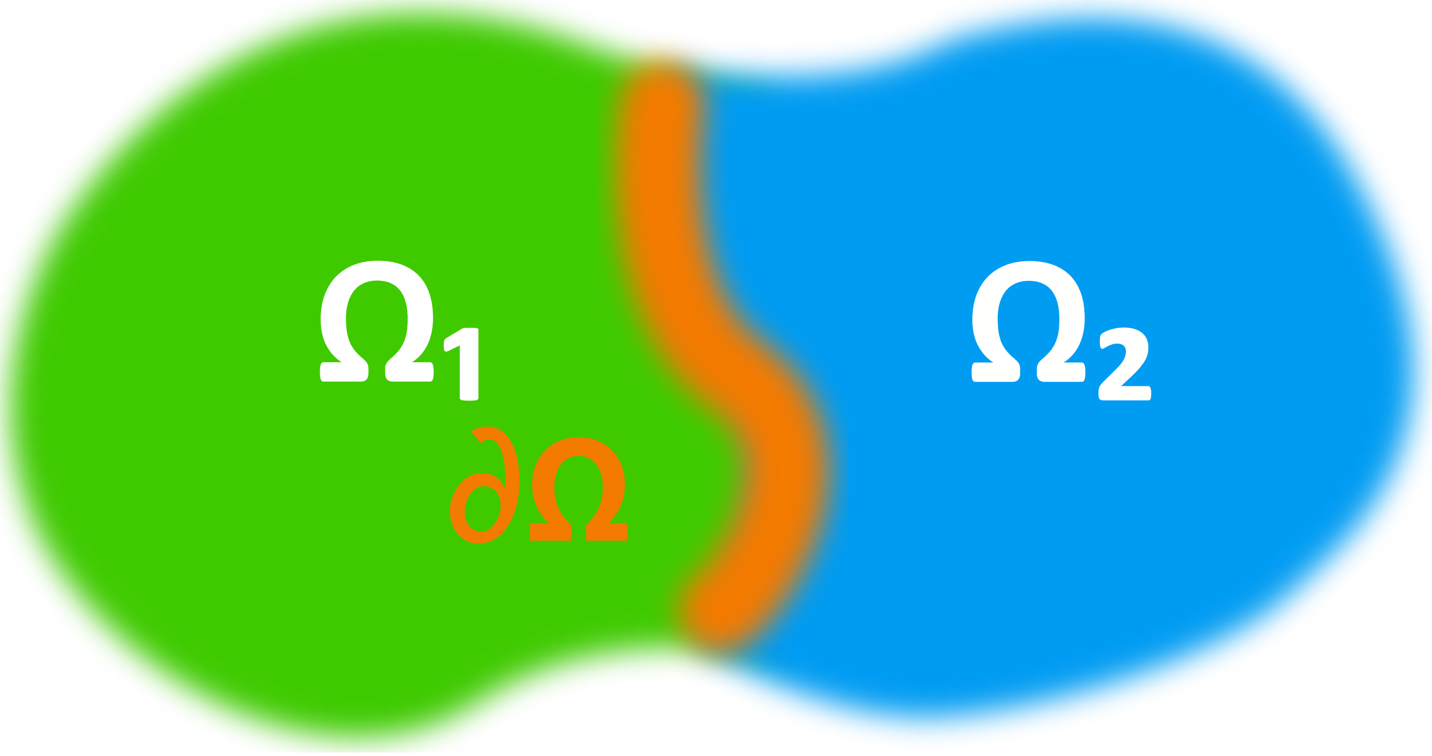
$$\mathrm{var}\left[\mathbf{D}'(t)\right] = \mathrm{var}\left[\mathbf{D}(t)\right] + \mathrm{var}\left[\Delta\mathbf{P}(t)\right] + 2\mathrm{cov}\left[\mathbf{D}\cdot\Delta\mathbf{P}(t)\right]$$

gauge invariance of heat transport



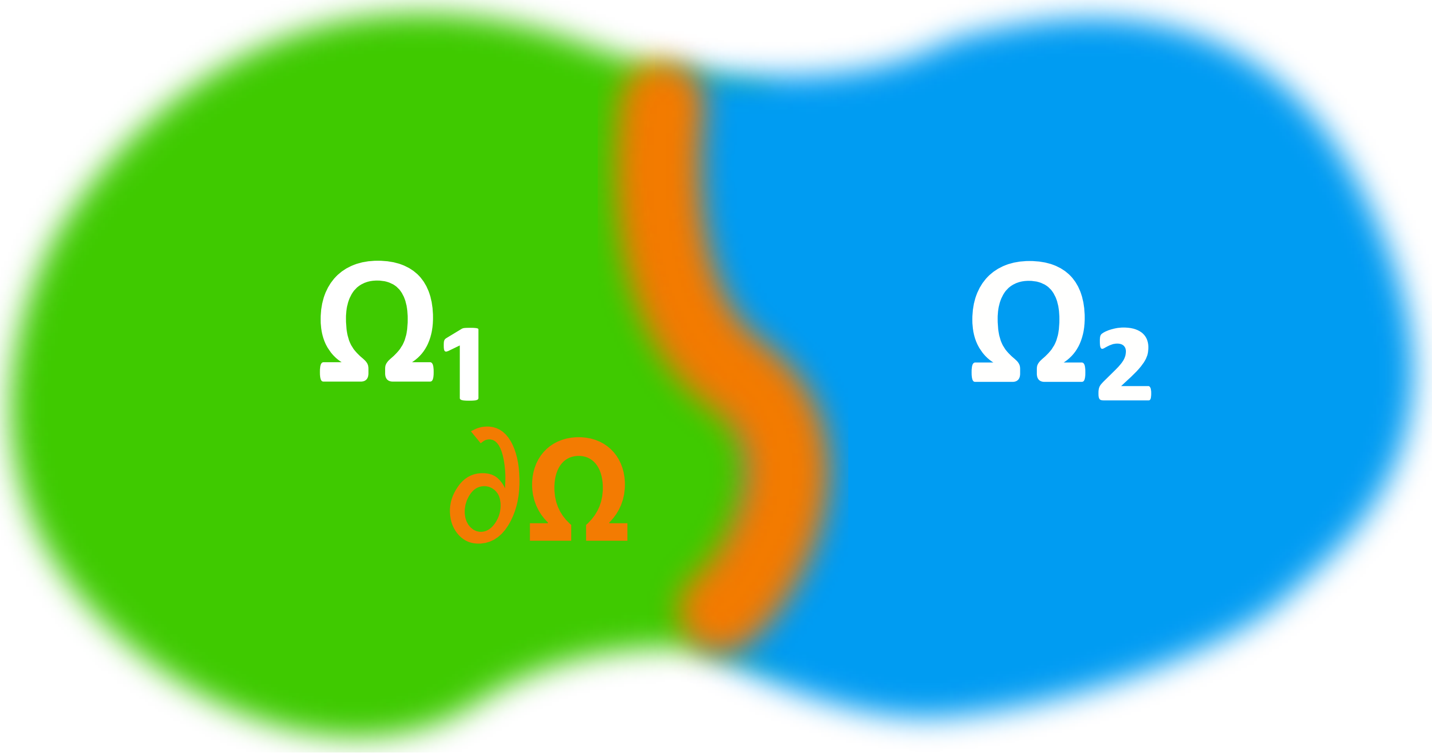
$$E[\Omega_1 \cup \Omega_2] = E[\Omega_1] + E[\Omega_2]$$

gauge invariance of heat transport



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

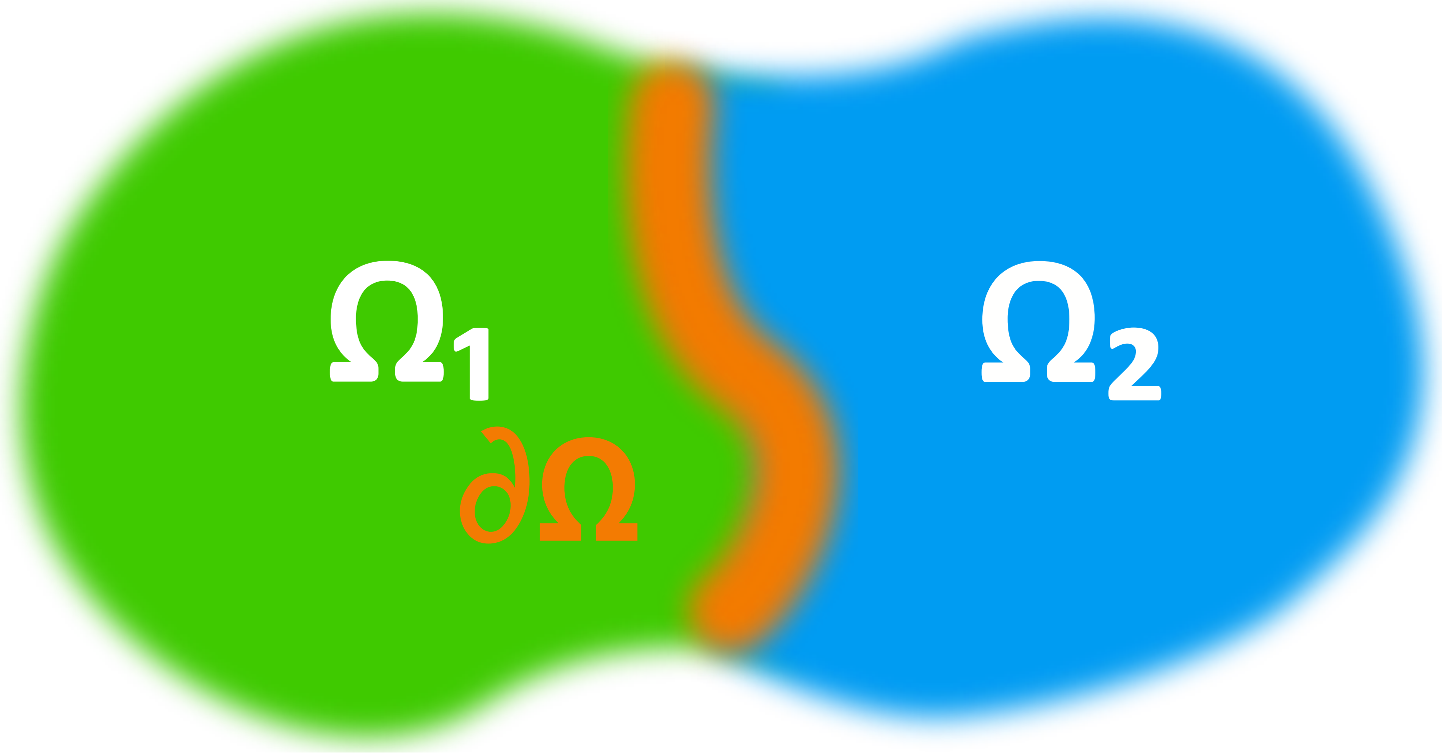
gauge invariance of heat transport



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

$$\stackrel{?}{=} \mathcal{E}[\Omega_1] + \mathcal{E}[\Omega_2]$$

gauge invariance of heat transport

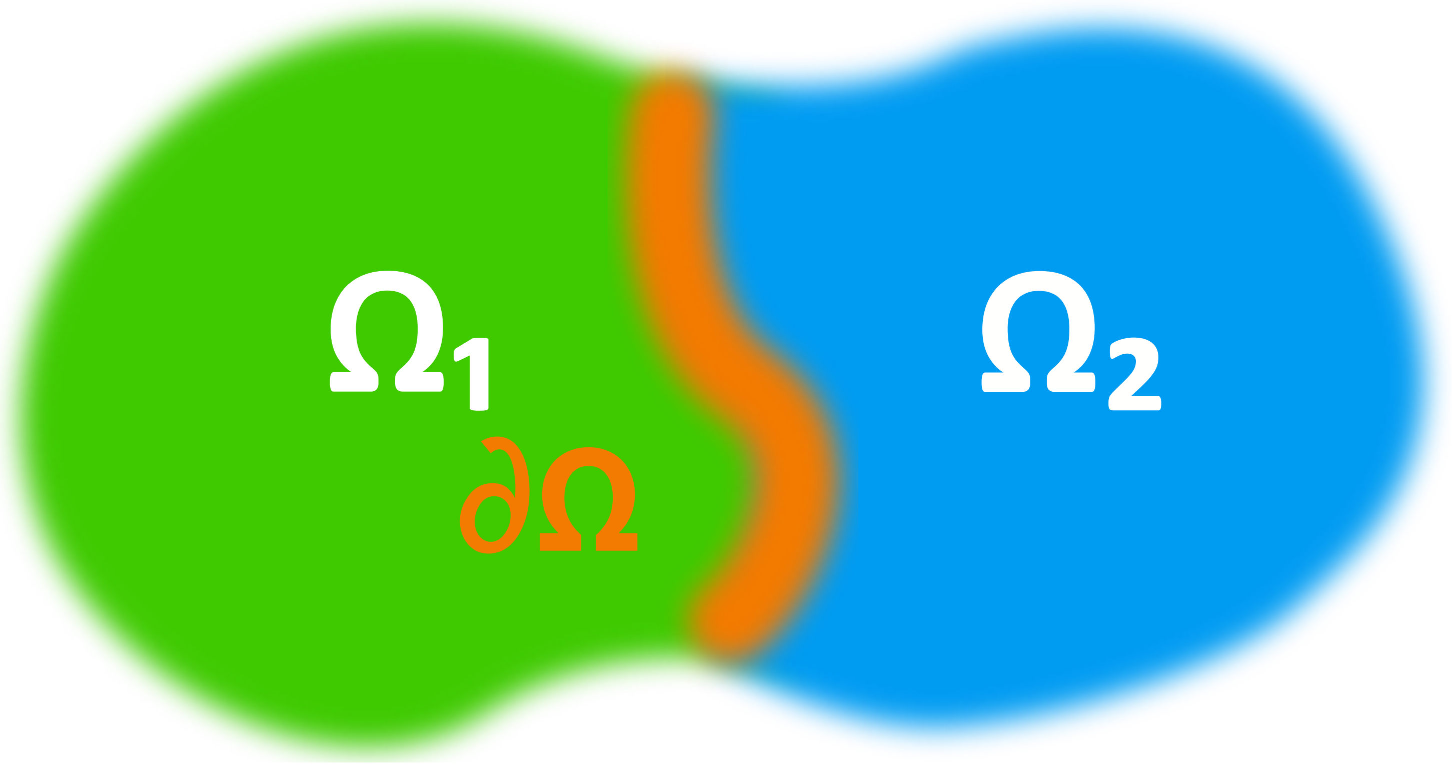


$$E[\Omega_1 \cup \Omega_2] = E[\Omega_1] + E[\Omega_2] + W[\partial\Omega]$$
$$\stackrel{?}{=} \mathcal{E}[\Omega_1] + \mathcal{E}[\Omega_2]$$

extensivity

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

gauge invariance of heat transport



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

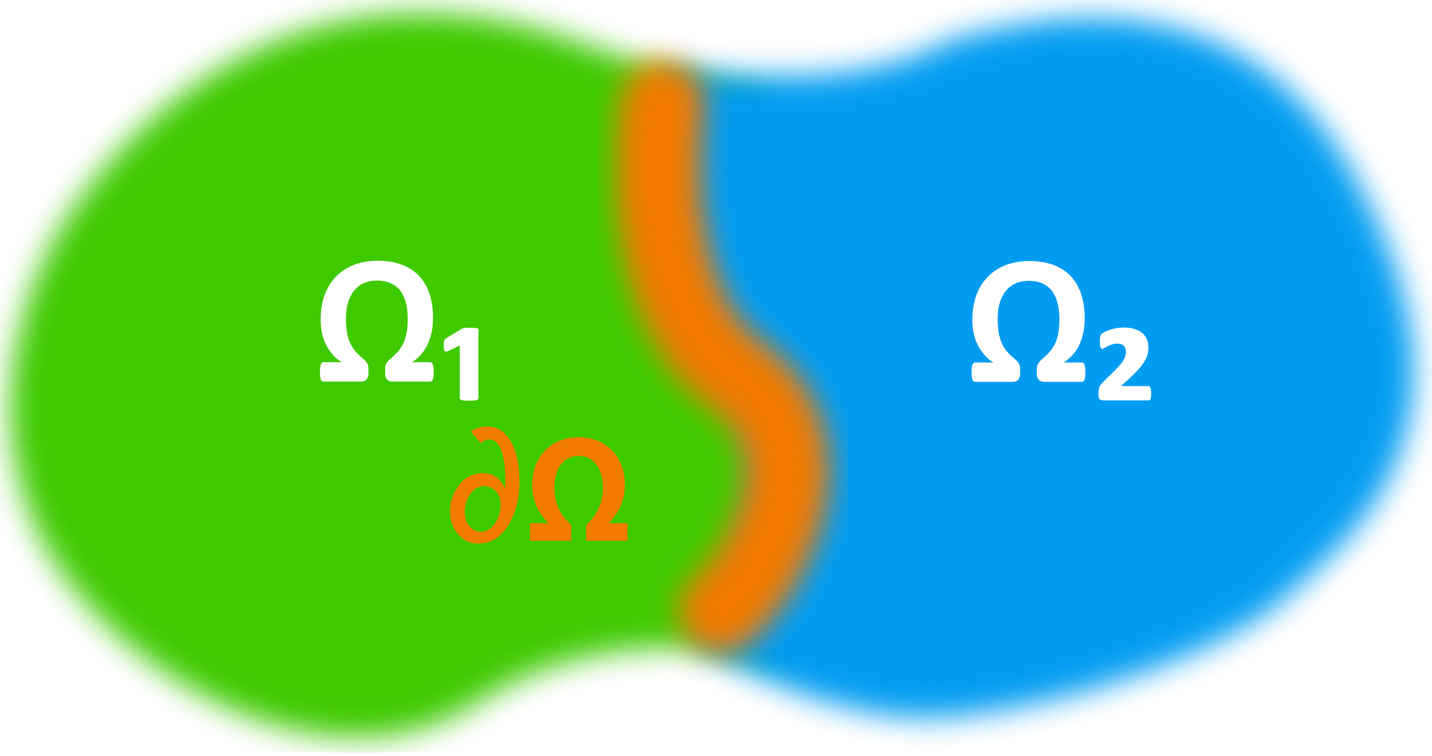
extensivity

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

thermodynamic invariance

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

gauge invariance of heat transport



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

extensivity

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

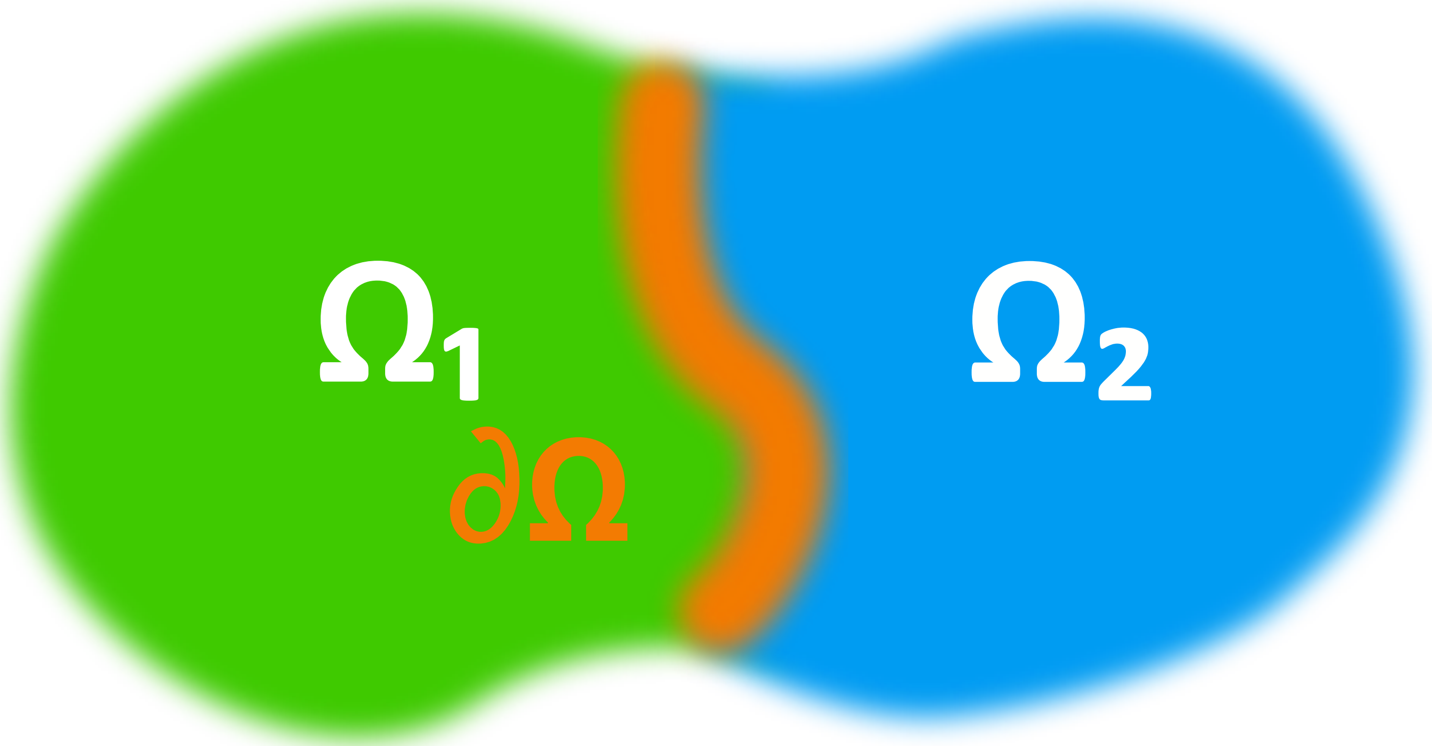
thermodynamic invariance

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

gauge invariance

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

gauge invariance of heat transport



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

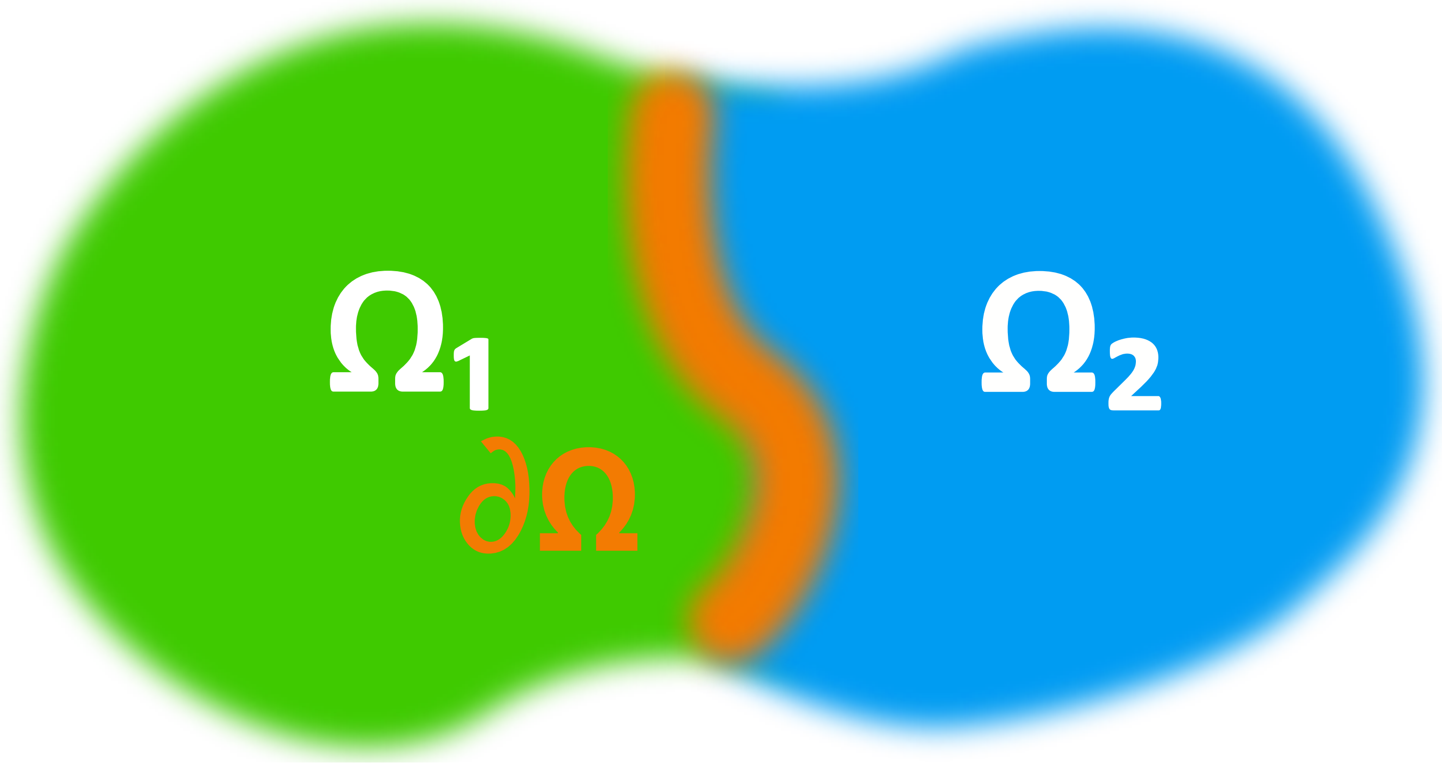
extensivity $$\mathcal{E}[\Omega] = \int_\Omega e(\mathbf{r})d\mathbf{r}$$

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

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

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

gauge invariance of heat transport



$$\mathrm{E}[\Omega_1 \cup \Omega_2] = \mathrm{E}[\Omega_1] + \mathrm{E}[\Omega_2] + \mathrm{W}[\partial\Omega]$$
$$\stackrel{?}{=} \mathcal{E}[\Omega_1] + \mathcal{E}[\Omega_2]$$

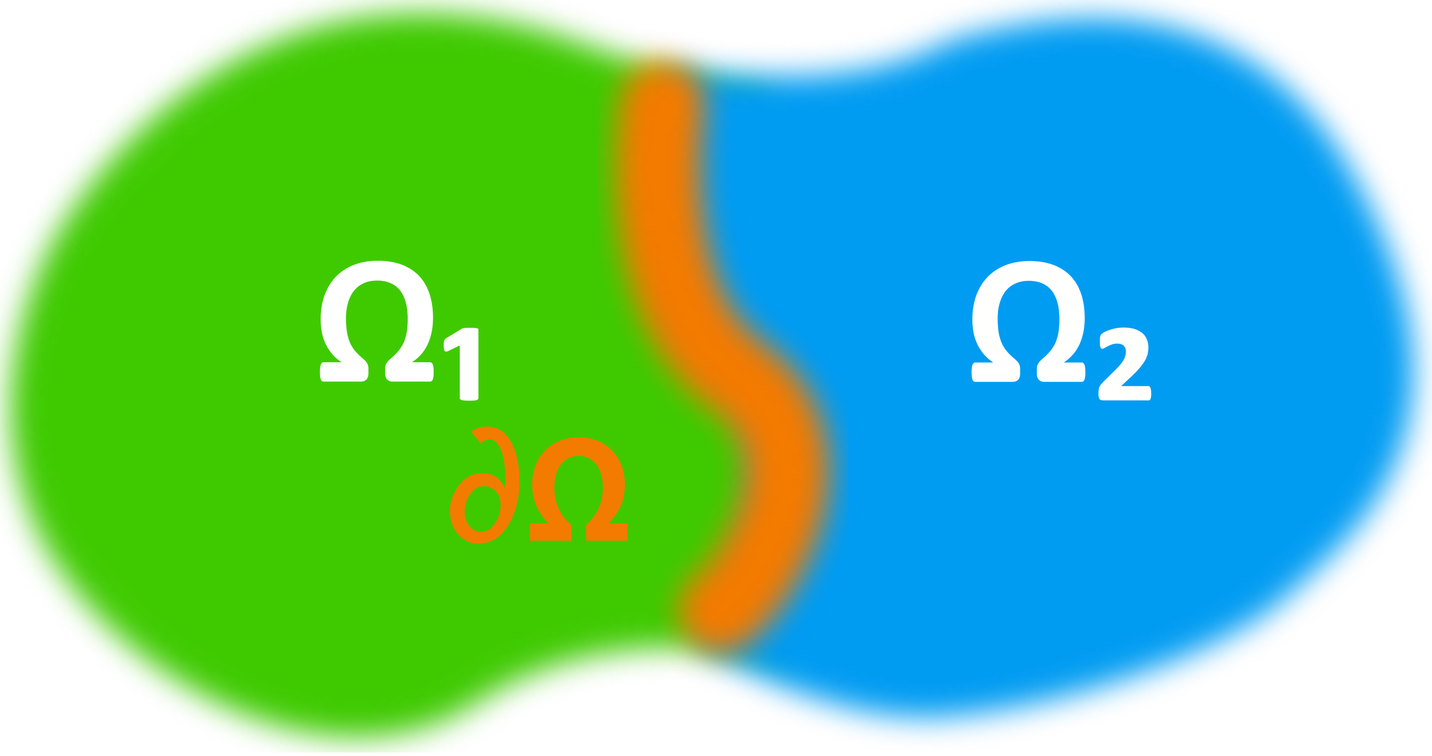
extensivity
$$\mathcal{E}[\Omega] = \int_\Omega e(\mathbf{r}) d\mathbf{r}$$

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

gauge invariance
$$e'(\mathbf{r}) = e(\mathbf{r}) - \nabla \cdot \mathbf{p}(\mathbf{r})$$
$$\mathbf{j}'(\mathbf{r}, t) = \mathbf{j}(\mathbf{r}, t) + \dot{\mathbf{p}}(\mathbf{r}, t)$$

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

gauge invariance of heat transport



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

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

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

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

gauge invariance

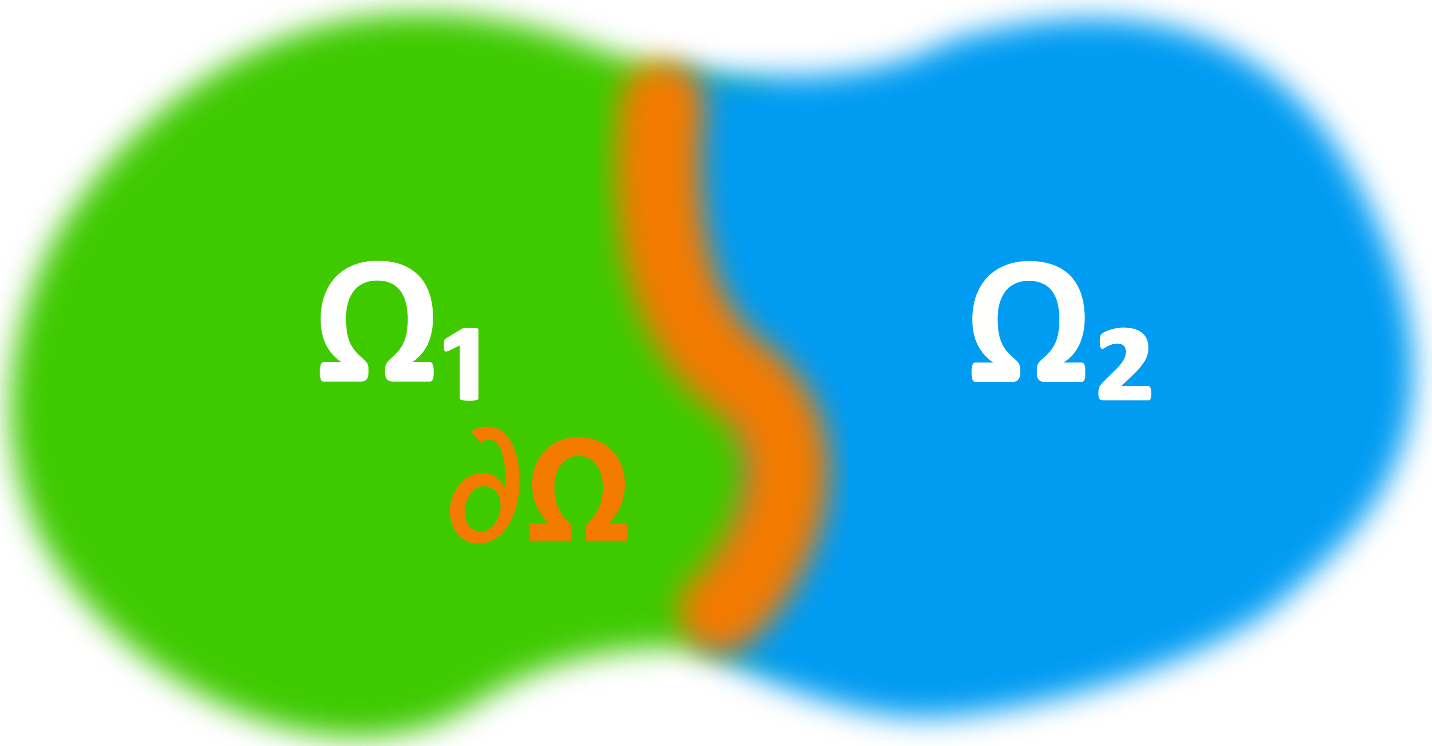
$$e'(\mathbf{r}) = e(\mathbf{r}) - \nabla\cdot\mathbf{p}(\mathbf{r})$$
$$\mathbf{j}'(\mathbf{r},t) = \mathbf{j}(\mathbf{r},t) + \dot{\mathbf{p}}(\mathbf{r},t)$$

$$\mathbf{J}'(t) = \mathbf{J}(t) + \dot{\mathbf{P}}(t)$$

conservation

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

gauge invariance of heat transport



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

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

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

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

gauge invariance

nature physics ARTICLES
PUBLISHED ONLINE: 19 OCTOBER 2015 | DOI: 10.1038/NPHYS3509

Microscopic theory and quantum simulation of atomic heat transport

Aris Marcolongo[1], Paolo Umari[2] and Stefano Baroni[1]*

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

$$\mathbf{J}'(t) = \mathbf{J}(t) + \dot{\mathbf{P}}(t)$$

conservation

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

hurdles toward an ab initio Green-Kubo theory

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

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.

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

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

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

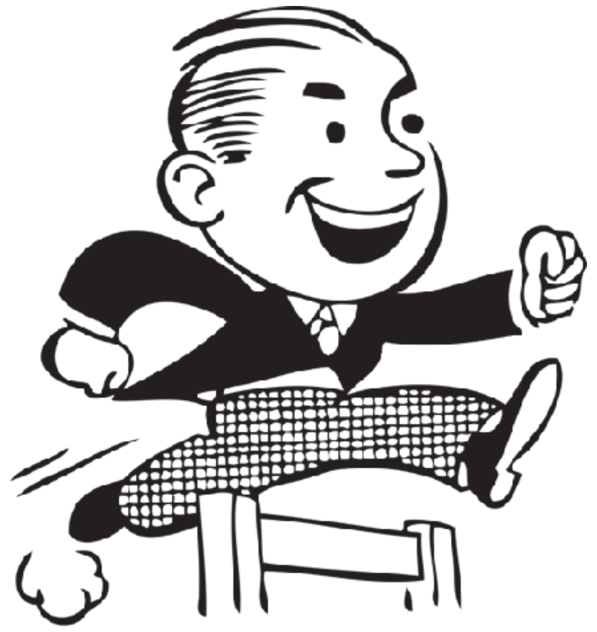
Lars Stixrude†
Department of Earth Sciences, University College London, Gower Street, London WC1E 6BT, United Kingdom

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.

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.



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:

- [x] energy
- [x] water mass
- [ ] ethanol mass

multi-component systems

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

conserved quantities:

- [x] energy
- [x] water mass
- [ ] ethanol mass

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

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

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

multi-component systems

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

conserved quantities:

- [x] energy
- [x] water mass
- [ ] ethanol mass

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

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

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

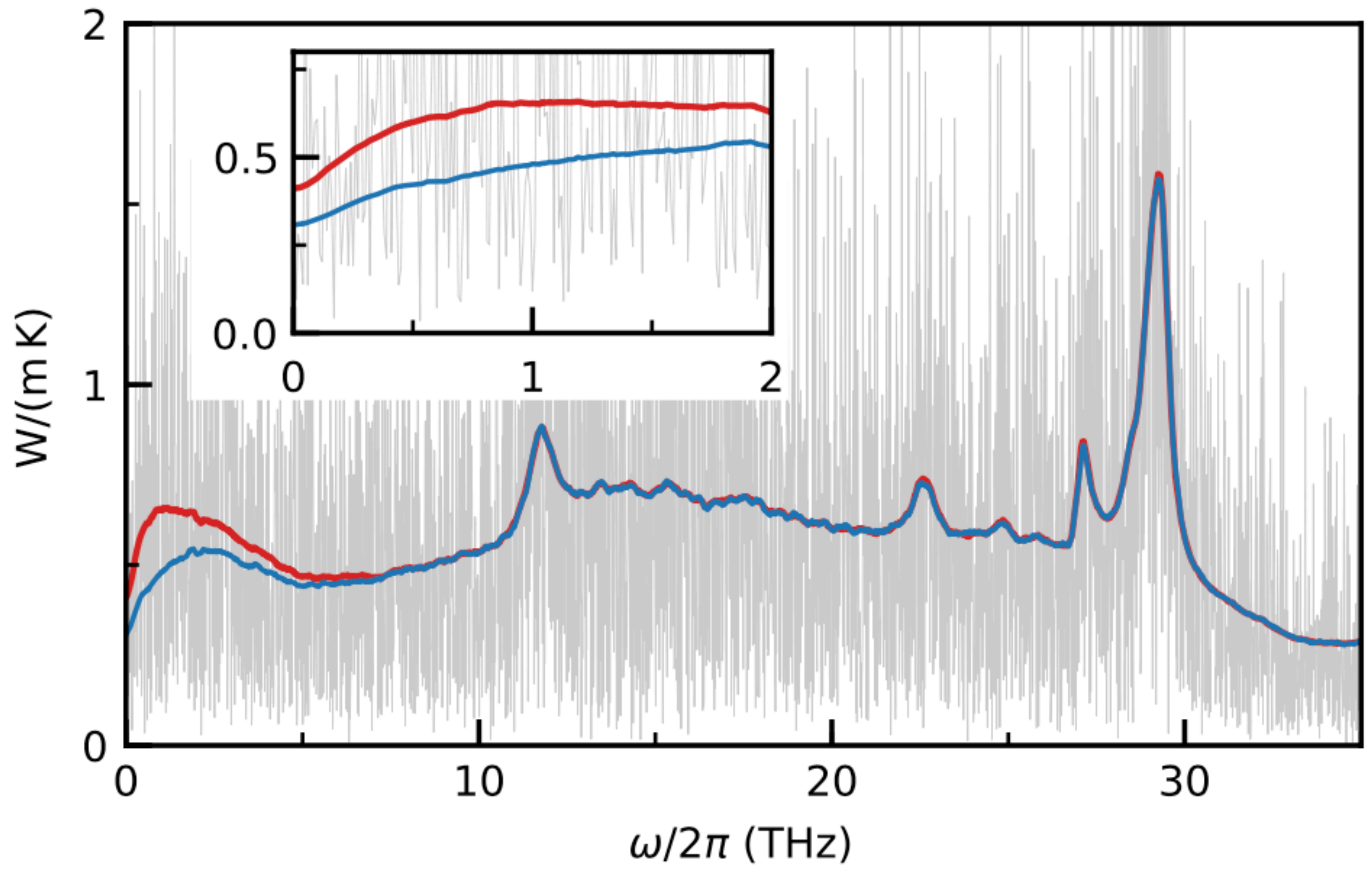
$$J_M = 0 \longrightarrow \kappa = \frac{1}{T^2} \left(\Lambda_{EE} - \frac{\Lambda_{EM}^2}{\Lambda_{MM}} \right)$$

$\kappa = \Lambda / \Lambda_{MM}$: *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

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

$$\boldsymbol{J}'_E = \boldsymbol{J}_E + c\boldsymbol{J}_M$$

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

$$= \kappa$$

multi-component systems

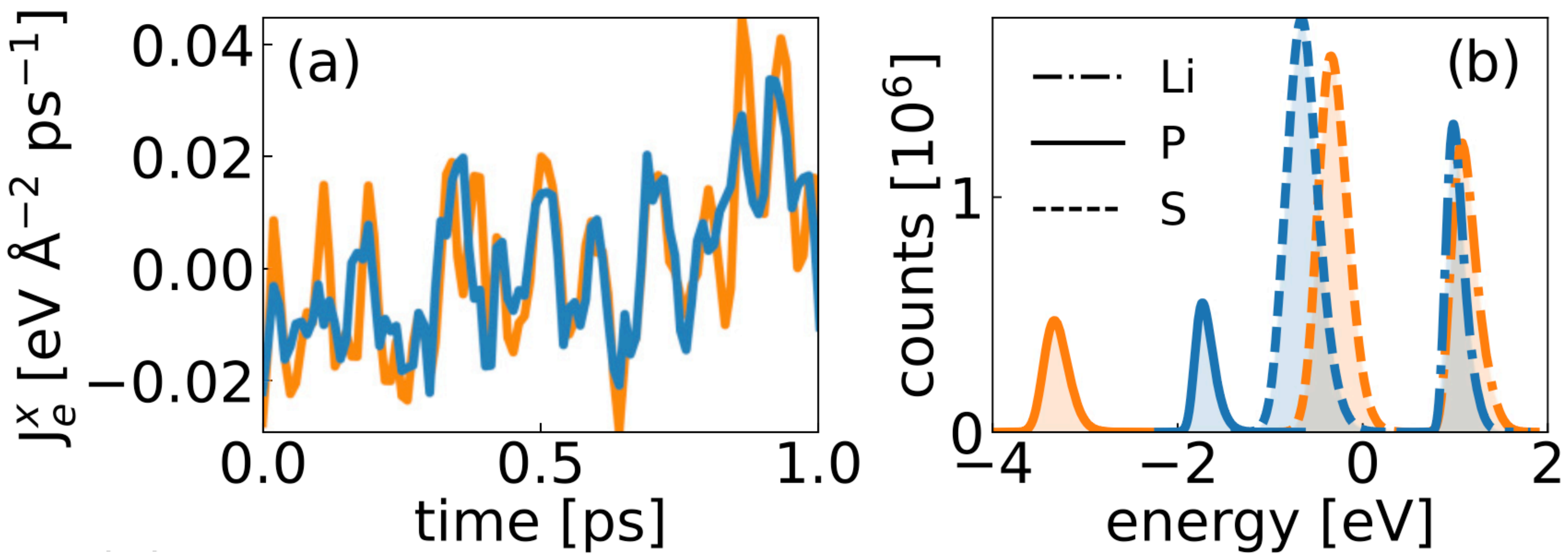
$$\kappa = \frac{1}{T^2}\left(\Lambda_{EE} - \frac{\Lambda_{EM}^2}{\Lambda_{MM}}\right)$$

$$\boldsymbol{J}'_E = \boldsymbol{J}_E + c\boldsymbol{J}_M$$

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

convective invariance

impact on ML MD simulations



Li_3PS_4

ML model A

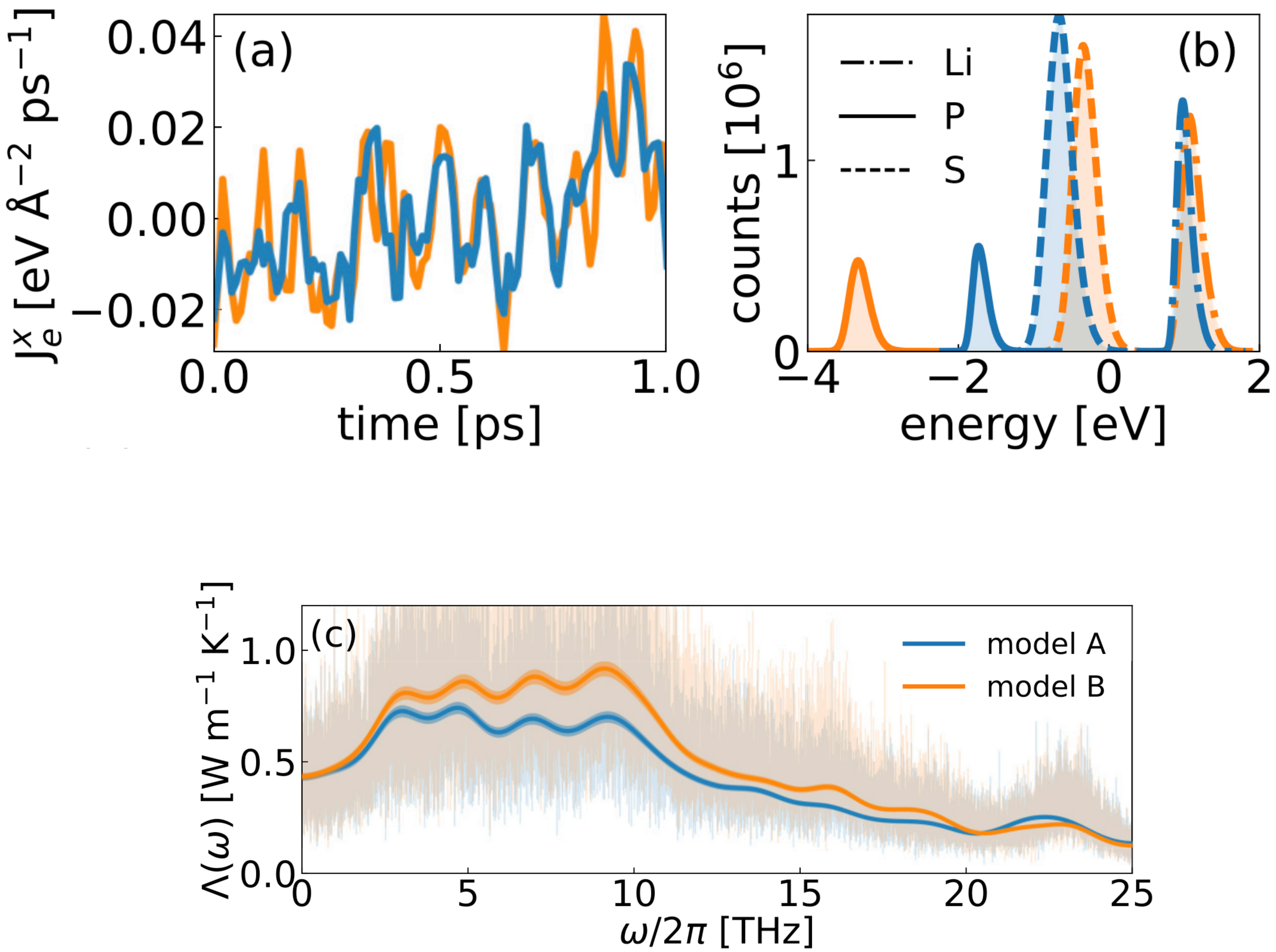
ML model B

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

Thermal conductivity of Li_3PS_4 solid electrolytes with *ab initio* accuracy

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

impact on ML MD simulations



Li_3PS_4

ML model A

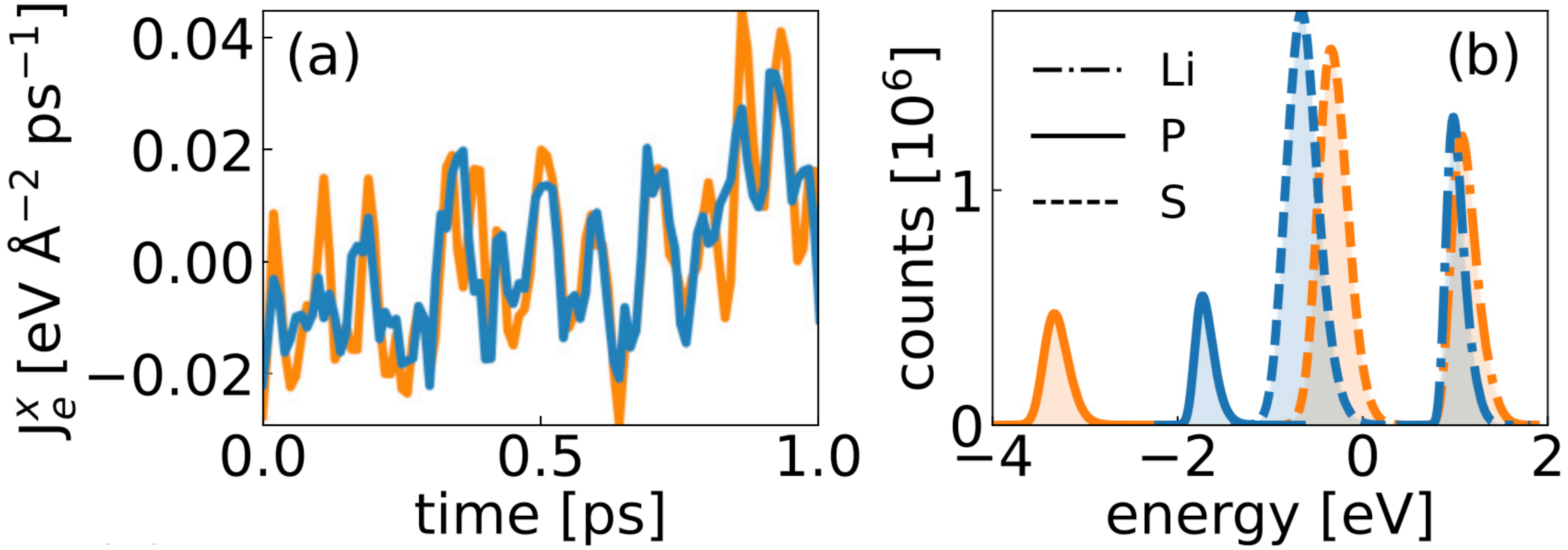
ML model B

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

Thermal conductivity of Li_3PS_4 solid electrolytes with *ab initio* accuracy

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

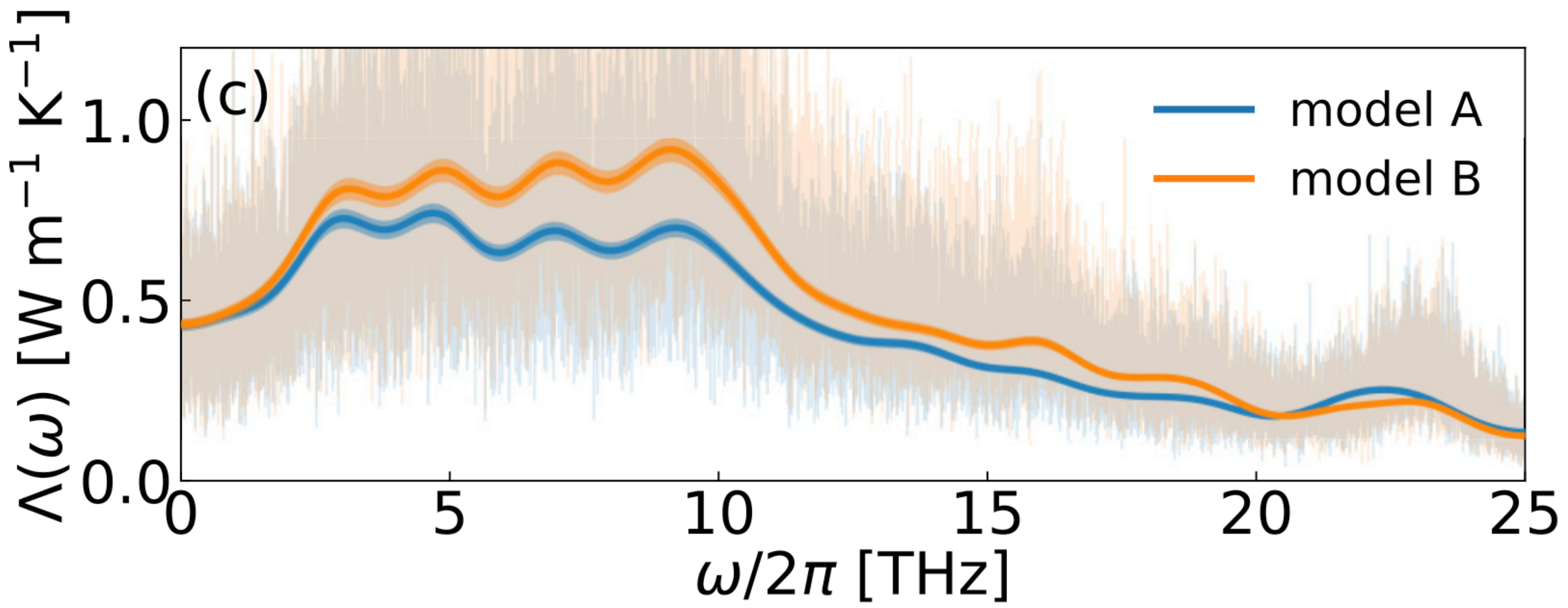
impact on ML MD simulations

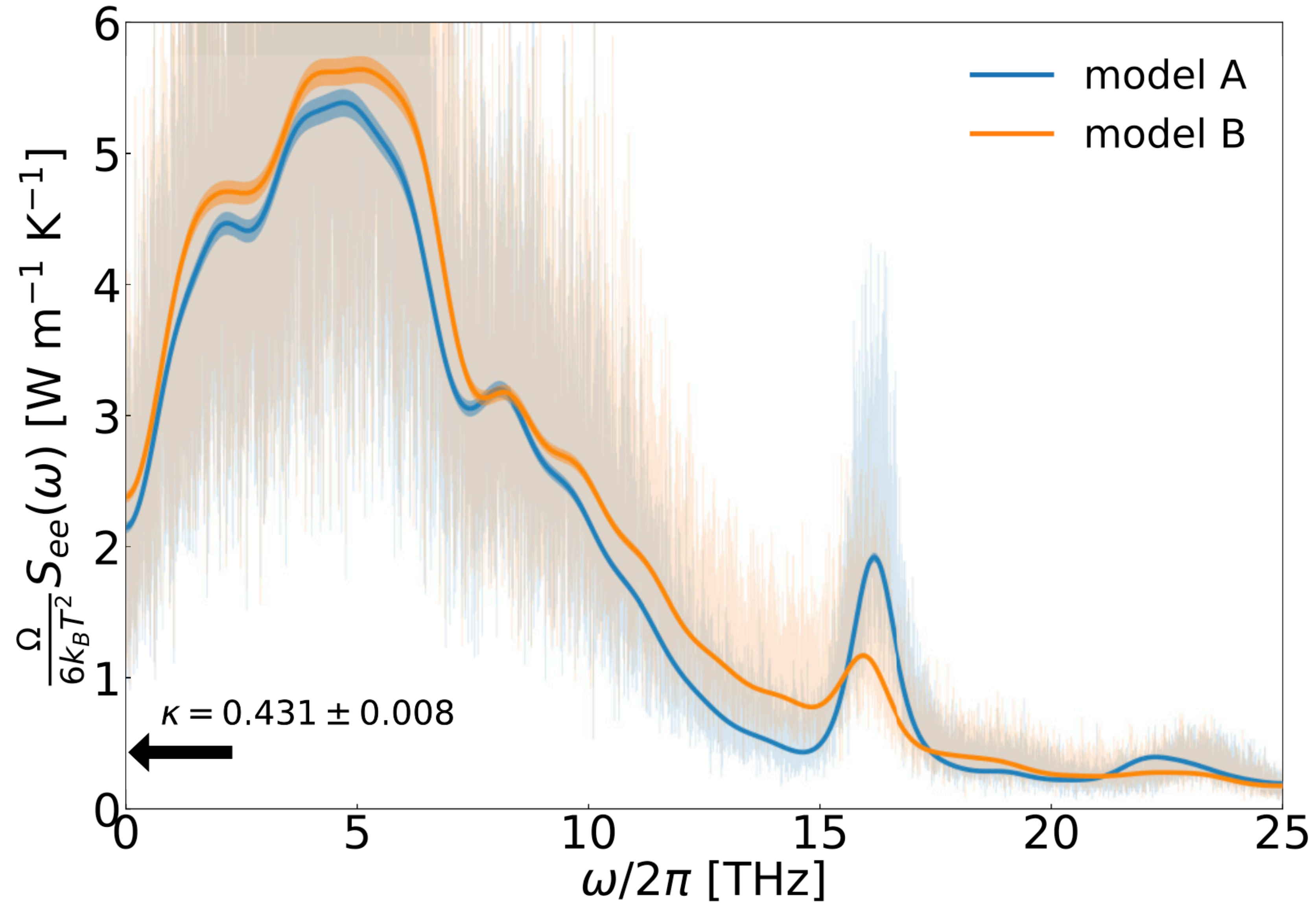


Li_3PS_4

ML model A

ML model B



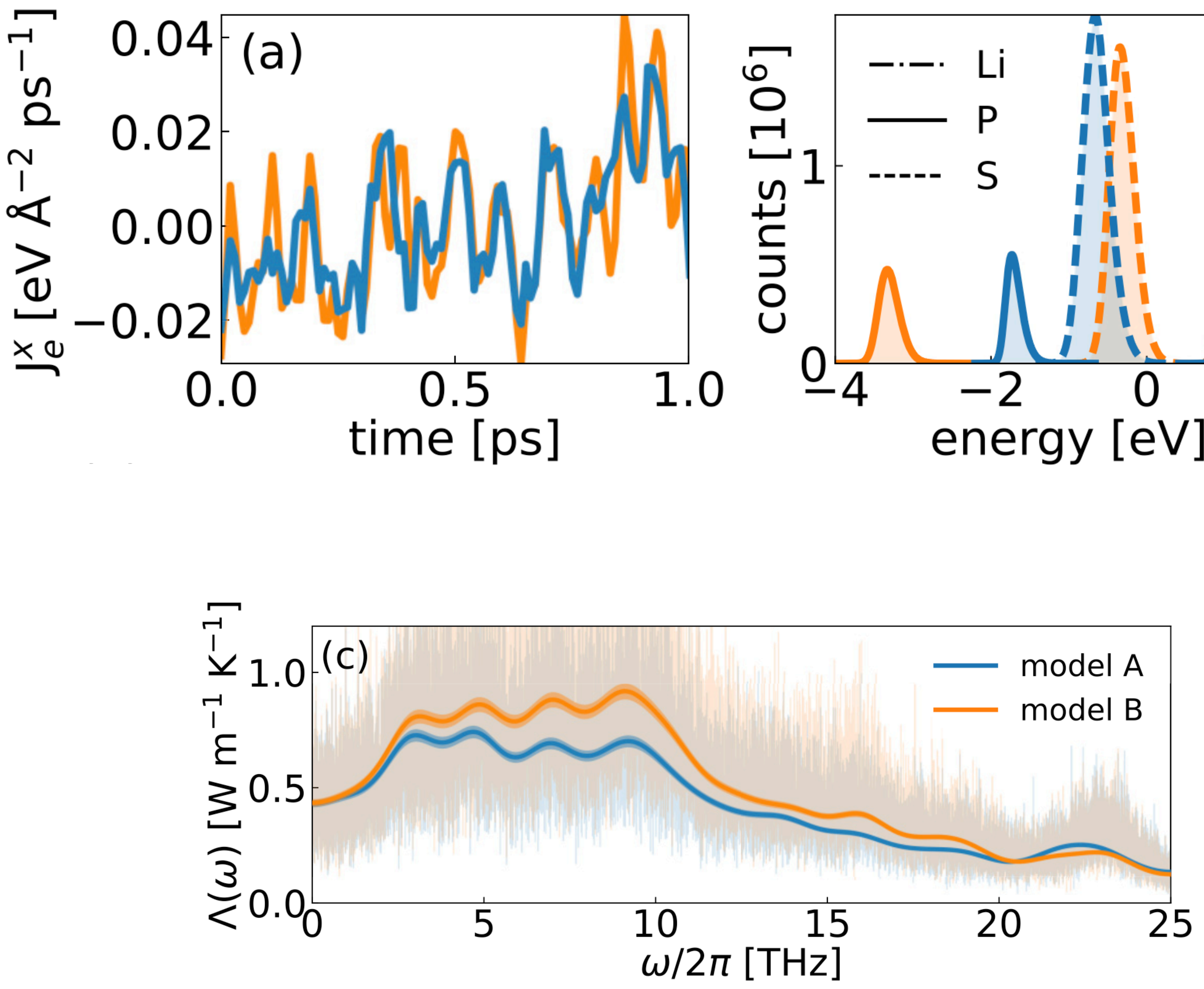


PHYSICAL REVIEW MATERIALS **8**, 065403 (2024)

Thermal conductivity of Li_3PS_4 solid electrolytes with *ab initio* accuracy

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

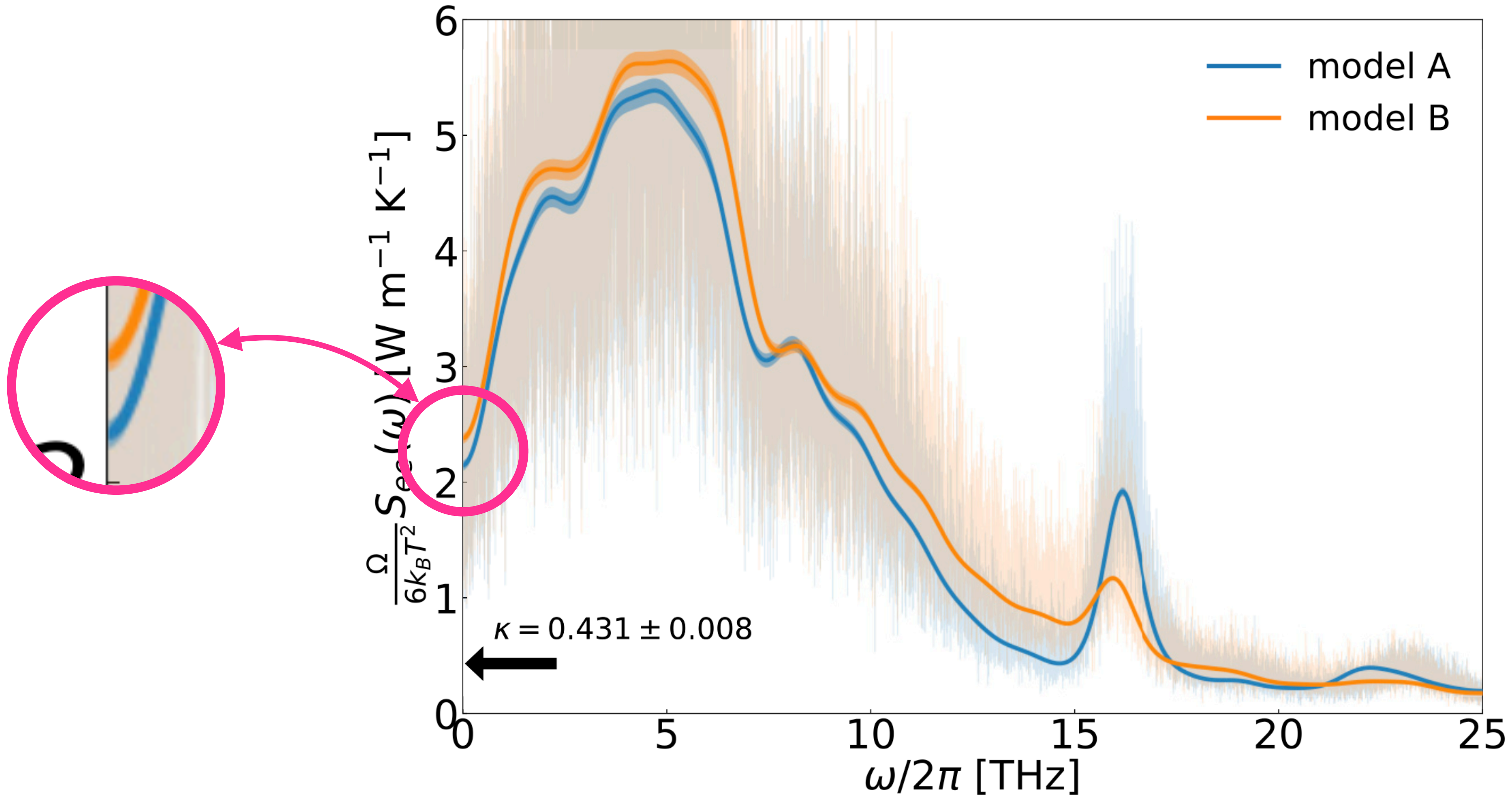
impact on ML MD simulations



Li_3PS_4

ML model A

ML model B

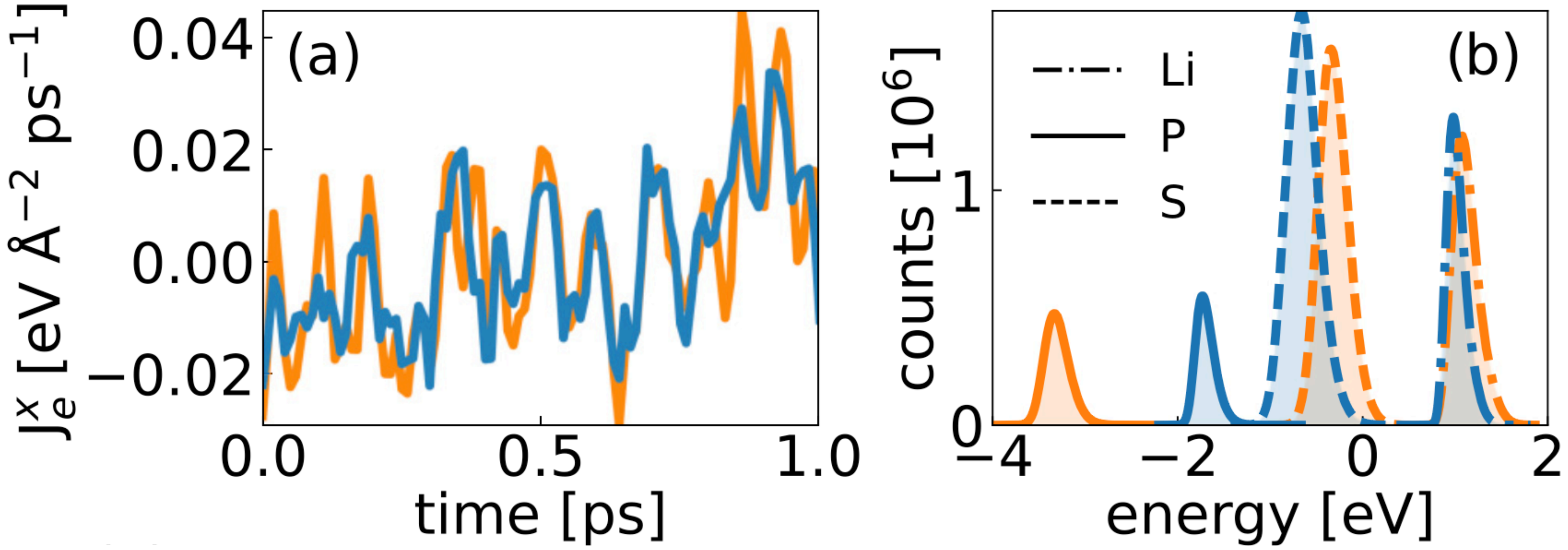


PHYSICAL REVIEW MATERIALS **8**, 065403 (2024)

Thermal conductivity of Li_3PS_4 solid electrolytes with *ab initio* accuracy

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

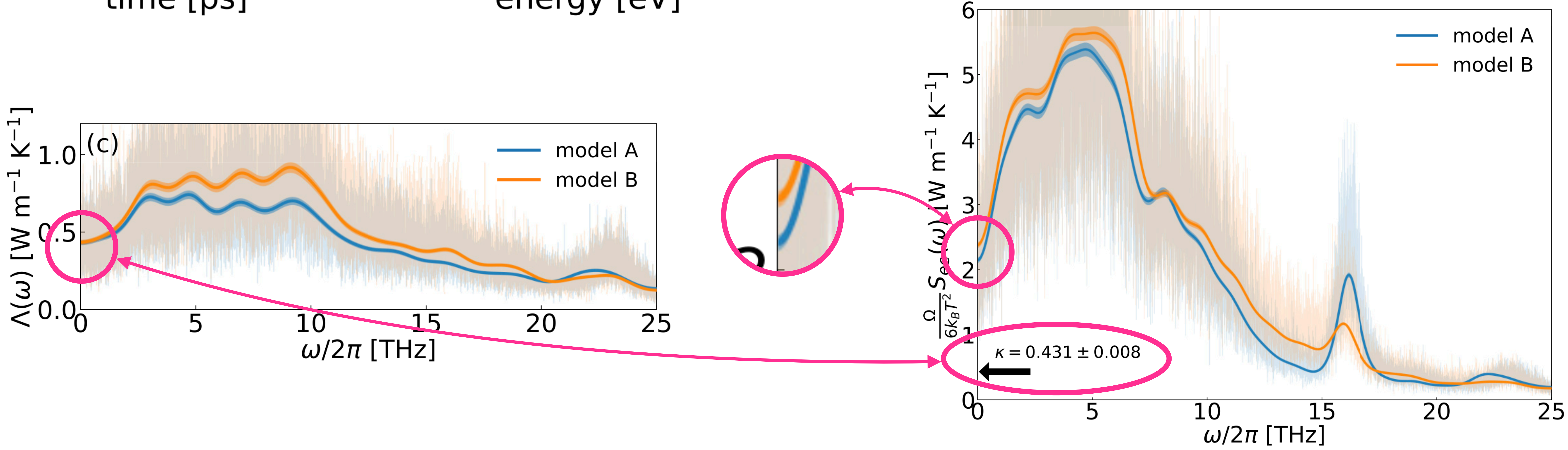
impact on ML MD simulations



Li_3PS_4

ML model A

ML model B



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

Thermal conductivity of Li_3PS_4 solid electrolytes with *ab initio* accuracy

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

MA PER SEGUIR VIRTUTE E CANOSCENZA

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

$$\mathbf{F}_I(\mathbf{R}) = -\frac{\partial}{\partial \mathbf{R}_I} \sum_J e_J(\mathbf{R})$$

$$= \sum_J \mathbf{f}_{IJ}; \quad \mathbf{f}_{IJ} = -\frac{\partial e_J}{\partial \mathbf{R}_I}$$

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

$$\mathbf{F}_I(\mathbf{R}) = -\frac{\partial}{\partial \mathbf{R}_I} \sum_J e_J(\mathbf{R})$$

$$= \sum_J \mathbf{f}_{IJ}; \quad \mathbf{f}_{IJ} = -\frac{\partial e_J}{\partial \mathbf{R}_I}$$

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

$$\sum_J \mathbf{f}'_{IJ}(\mathbf{R}) = 0; \qquad \mathbf{f}'_{IJ} = \mathbf{f}^2_{IJ} - \mathbf{f}^1_{IJ}$$

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

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

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

$$\sum_J \mathbf{f}'_{IJ}(\mathbf{R}) = 0; \qquad \mathbf{f}'_{IJ} = \mathbf{f}^2_{IJ} - \mathbf{f}^1_{IJ}$$

is this enough to guarantee equality of the transport coefficients?

MA PER SEGUIR VIRTUTE E CANOSCENZA

the nuts and bolts of gauge invariance

$$\kappa_2 = \kappa_1$$

iff

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

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

the nuts and bolts of gauge invariance

$$\kappa_2 = \kappa_1$$

iff

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

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

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

the nuts and bolts of gauge invariance

$$\kappa_2 = \kappa_1$$

iff

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

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

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

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

$$f'_{IJ} = 0 \quad \text{for} |R_I - R_J| > R_c$$

$\Rightarrow$

$$\sum_I \int_0^T \Big(\big[\mathcal{D}_I\big(R(t)\big) + \delta e'\big(R(t)\big) \big] \cdot V_I(t) dt =$$

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

independent of path and periodic in R^T

the nuts and bolts of gauge invariance

$$J'(t) = \sum_I \Big(\xcancel{\boldsymbol{\mathcal{D}}'_I(\boldsymbol{R}(t))} + e'_I(\infty) + \xcancel{\delta e'_I(\boldsymbol{R}(t))} \Big) \cdot \boldsymbol{V}_I(t); \qquad \boldsymbol{\mathcal{D}}'_I(\boldsymbol{R}) = \sum_J \boldsymbol{R}_J \otimes \boldsymbol{f}'_{IJ}(\boldsymbol{R})$$

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

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

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

the nuts and bolts of gauge invariance

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

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

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

independent of path and periodic in R^T

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

the nuts and bolts of gauge invariance

$$\kappa_2 = \kappa_1$$

iff

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

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

$$\sum_J \frac{\partial e_I^1}{\partial \mathbf{R}_J} = \sum_J \frac{\partial e_I^2}{\partial \mathbf{R}_J}$$

$$\frac{\partial e_I}{\partial \mathbf{R}_J} = 0 \quad \text{for } |\mathbf{R}_I - \mathbf{R}_J| > R_c$$

$\Rightarrow$

$$\kappa^1 = \kappa^2$$

$(\Lambda_{EE}^1 \neq \Lambda_{EE}^2$, in general)

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

supported by:

MAX

http://www.max-centre.eu

ICSC
Centro Nazionale di Ricerca in HPC,
Big Data and Quantum Computing

https://www.supercomputing-icsc.it

QUANTUM ESPRESSO
FOUNDATION

http://foundation.quantum-espresso.org

MA PER SEGUIR VIRTUTE E CANOSCENZA

thanks to:


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!
(ca. 2016)

this is the best stuff
you've ever done!
(ca. 2016)

Happy Birthday, Michele! 80 more years of mind-blowing science!