



invariance principles in the modern theory of heat transport

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how it all started

classical and quantum adiabatic heat transport

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



classical and quantum adiabatic heat transport

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$$\kappa \propto \int_0^\infty \langle \mathbf{J}(t) \cdot \mathbf{J}(0) \rangle dt$$



classical and quantum adiabatic heat transport

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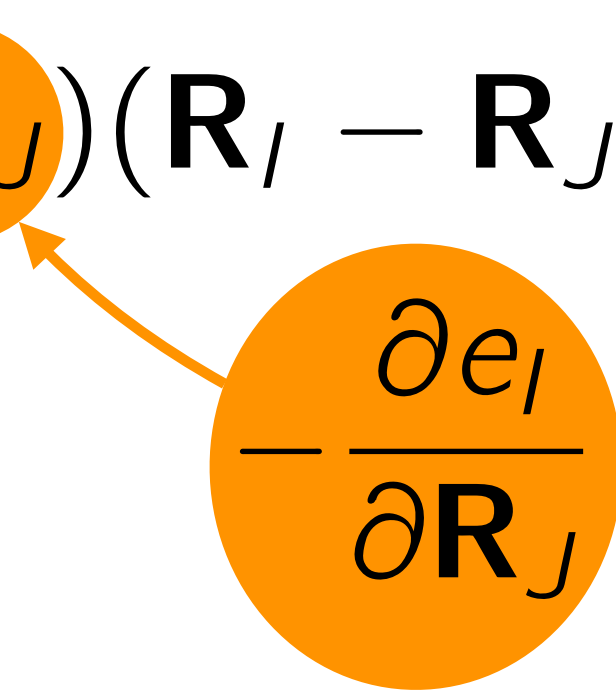
$$\mathbf{J}_\mathcal{E} = \sum_I e_I \mathbf{v}_I + \frac{1}{2} \sum_{I \neq J} (\mathbf{v}_I \cdot \mathbf{F}_{IJ}) (\mathbf{R}_I - \mathbf{R}_J)$$

hurdles toward an ab initio Green-Kubo theory

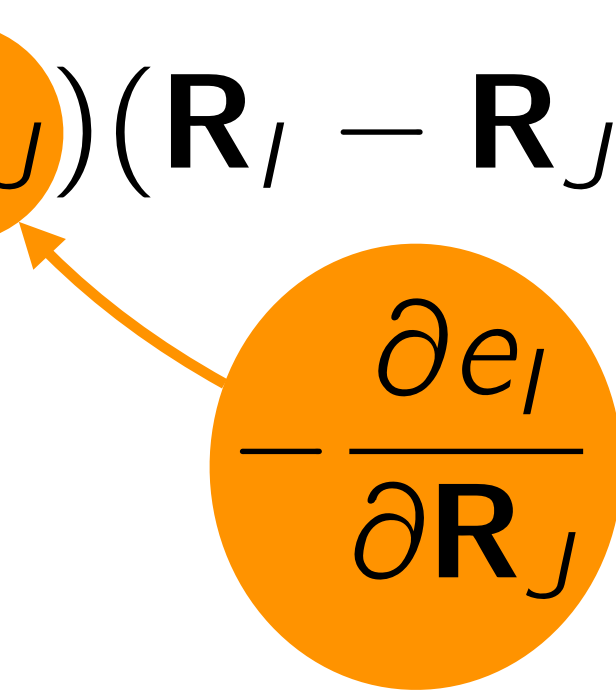
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PHYSICAL REVIEW LETTERS

week ending
21 MAY 2010

Thermal Conductivity of Periclase (MgO) from First Principles

Stephen Stackhouse*

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Lars Stixrude[†]

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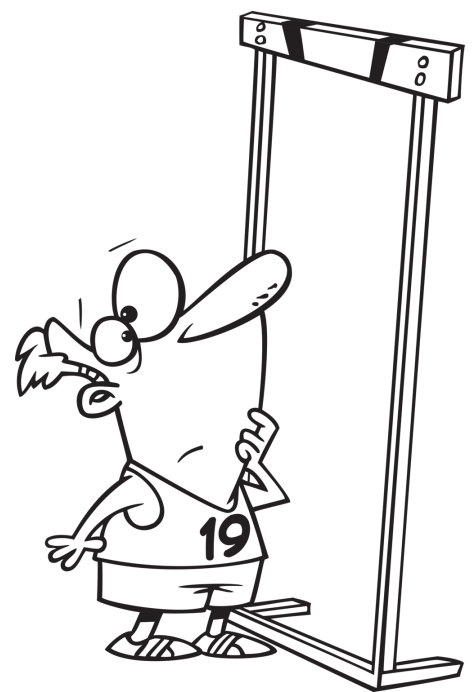
Bijaya B. Karki[‡]

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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?

the linear-response theory of transport

Fourier

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

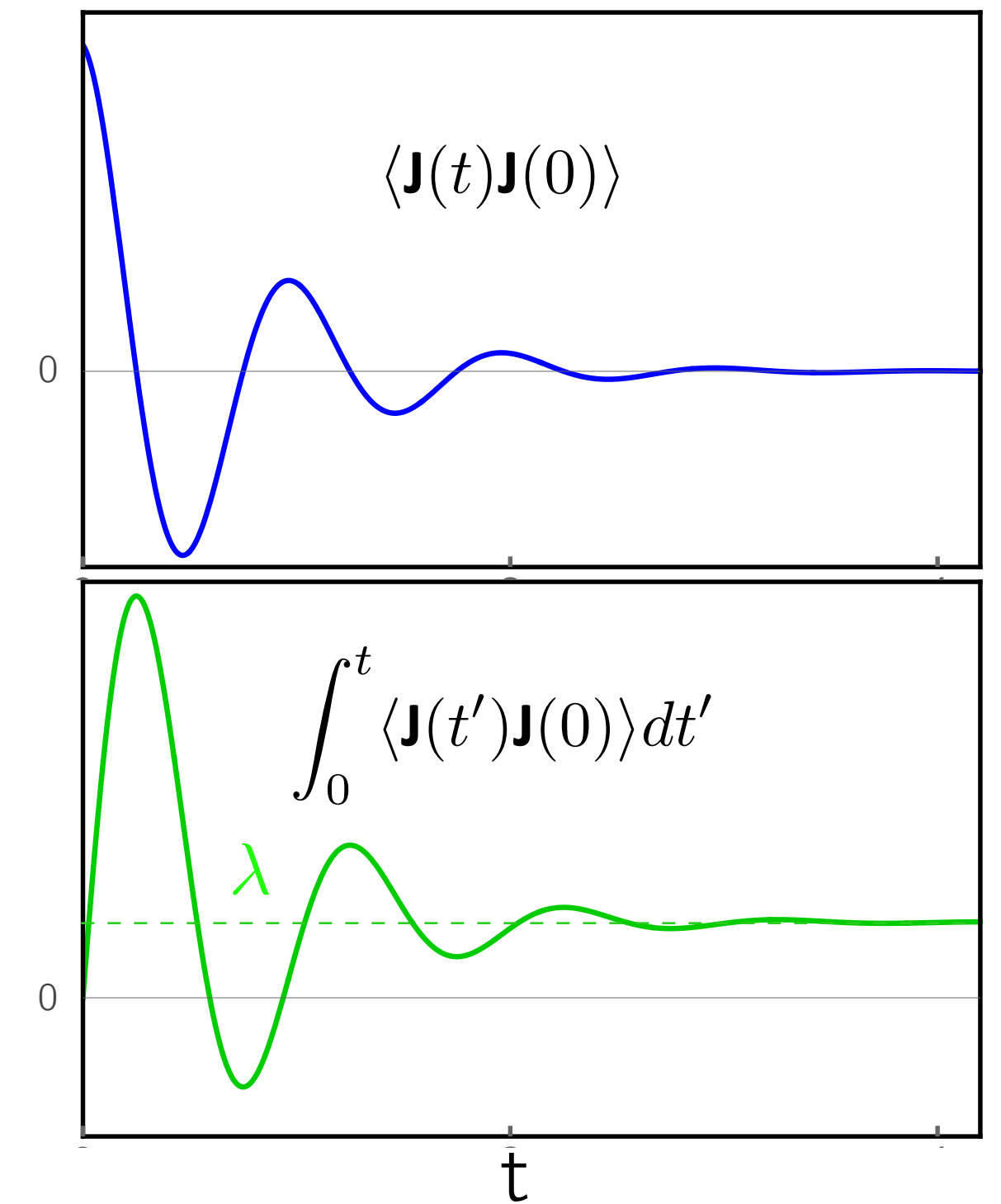
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Green-Kubo

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



t

the linear-response theory of transport

Fourier

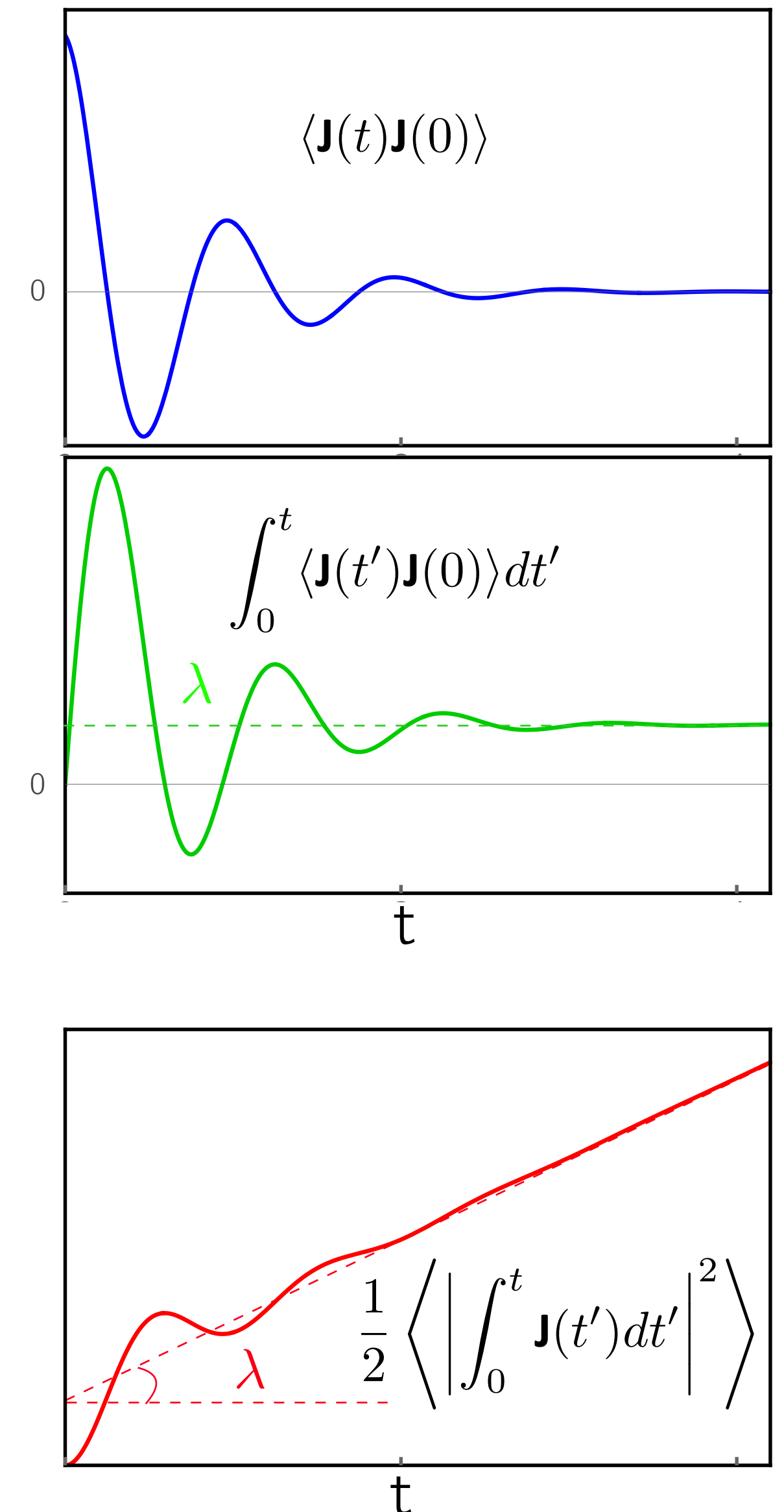
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Einstein-Helfand

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



insights from classical mechanics

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

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

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

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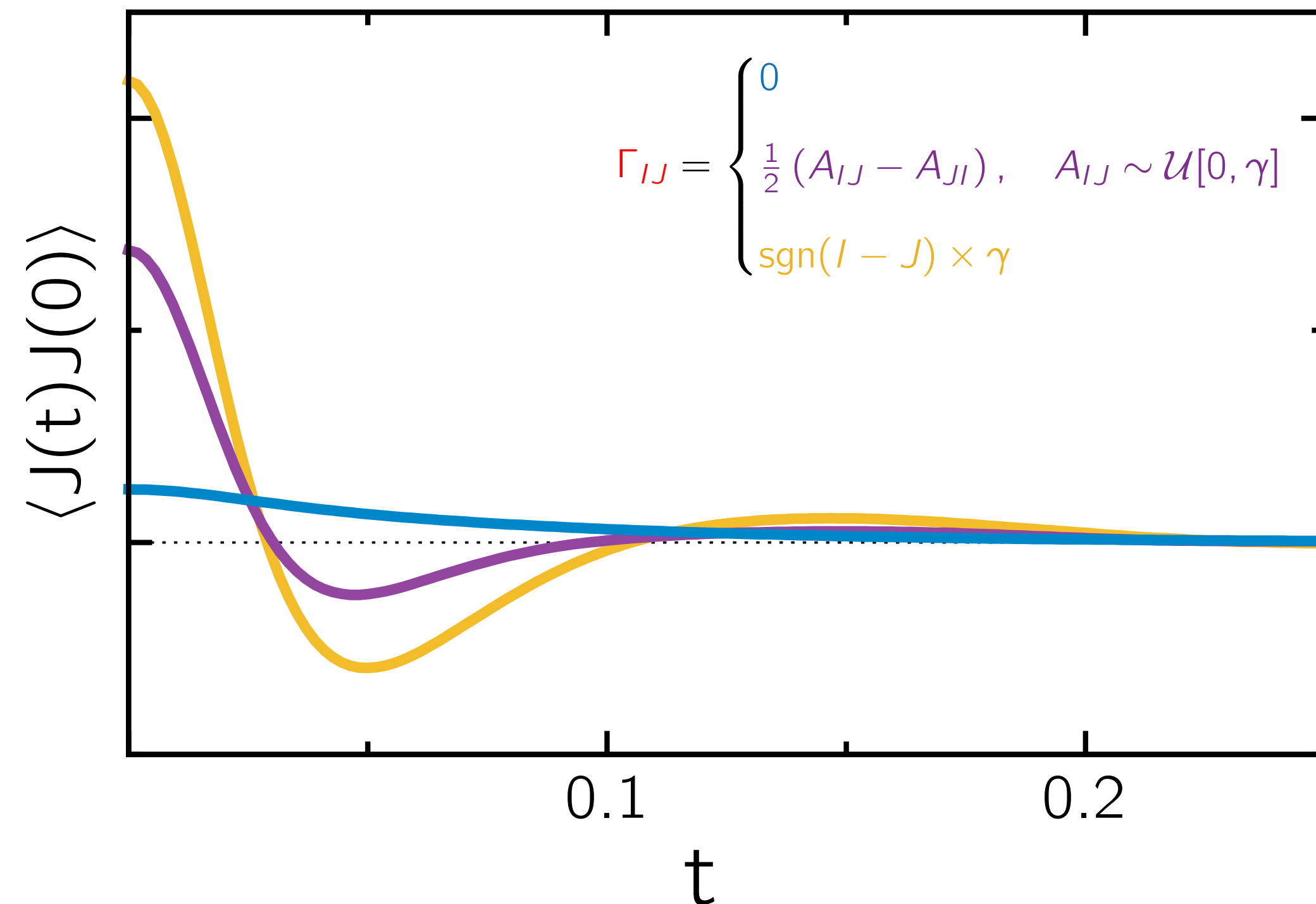
$$\begin{aligned} \mathbf{J}_e = & \sum_I \epsilon_I \mathbf{V}_I + \frac{1}{2} \sum_{I \neq J} (\mathbf{V}_I \cdot \mathbf{F}_{IJ}) (\mathbf{R}_I - \mathbf{R}_J) \\ & + \frac{1}{2} \sum_{I \neq J} \Gamma_{IJ} [\mathbf{V}_I v(|\mathbf{R}_I - \mathbf{R}_J|) + (\mathbf{V}_I \cdot \mathbf{F}_{IJ}) (\mathbf{R}_I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

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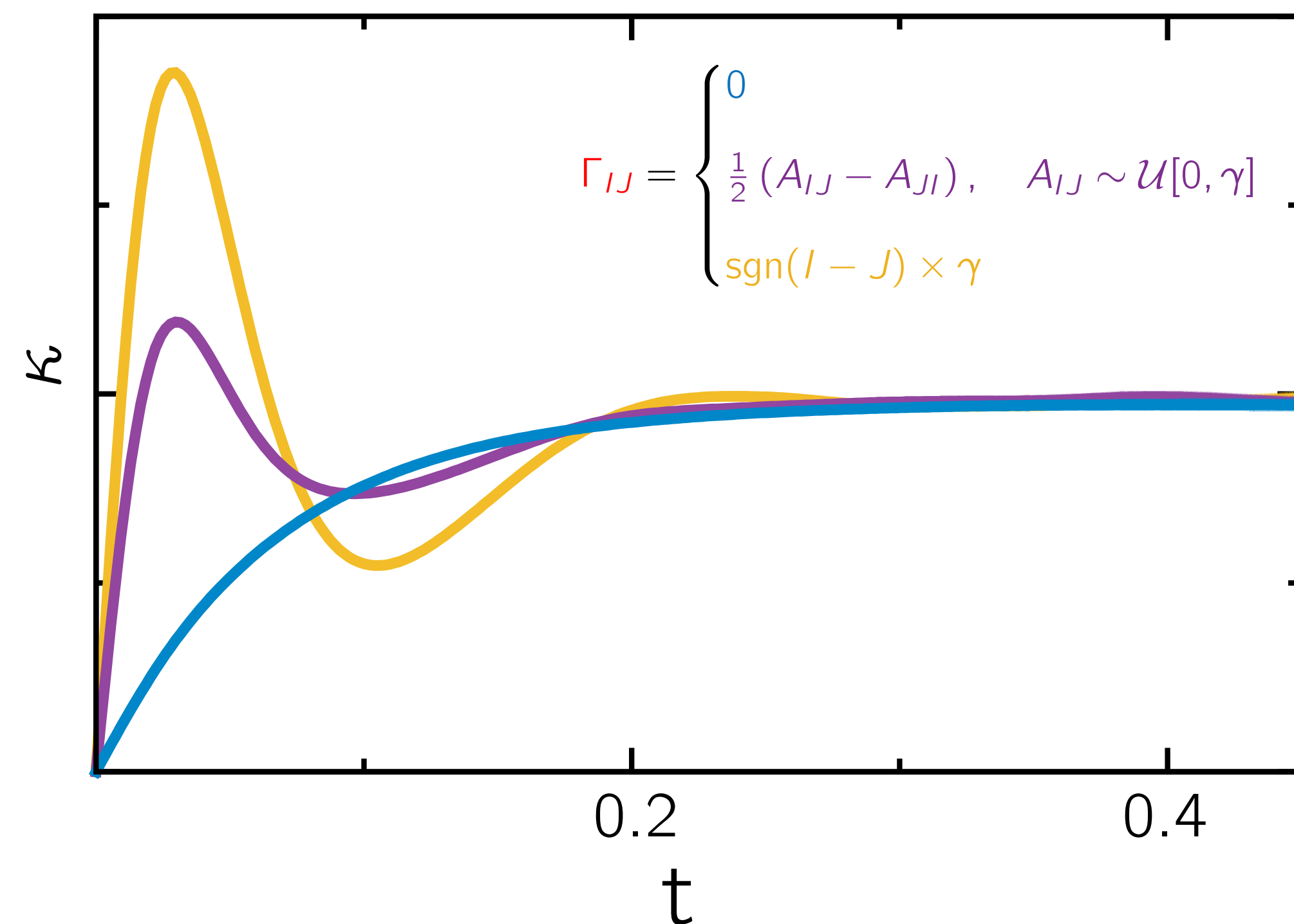
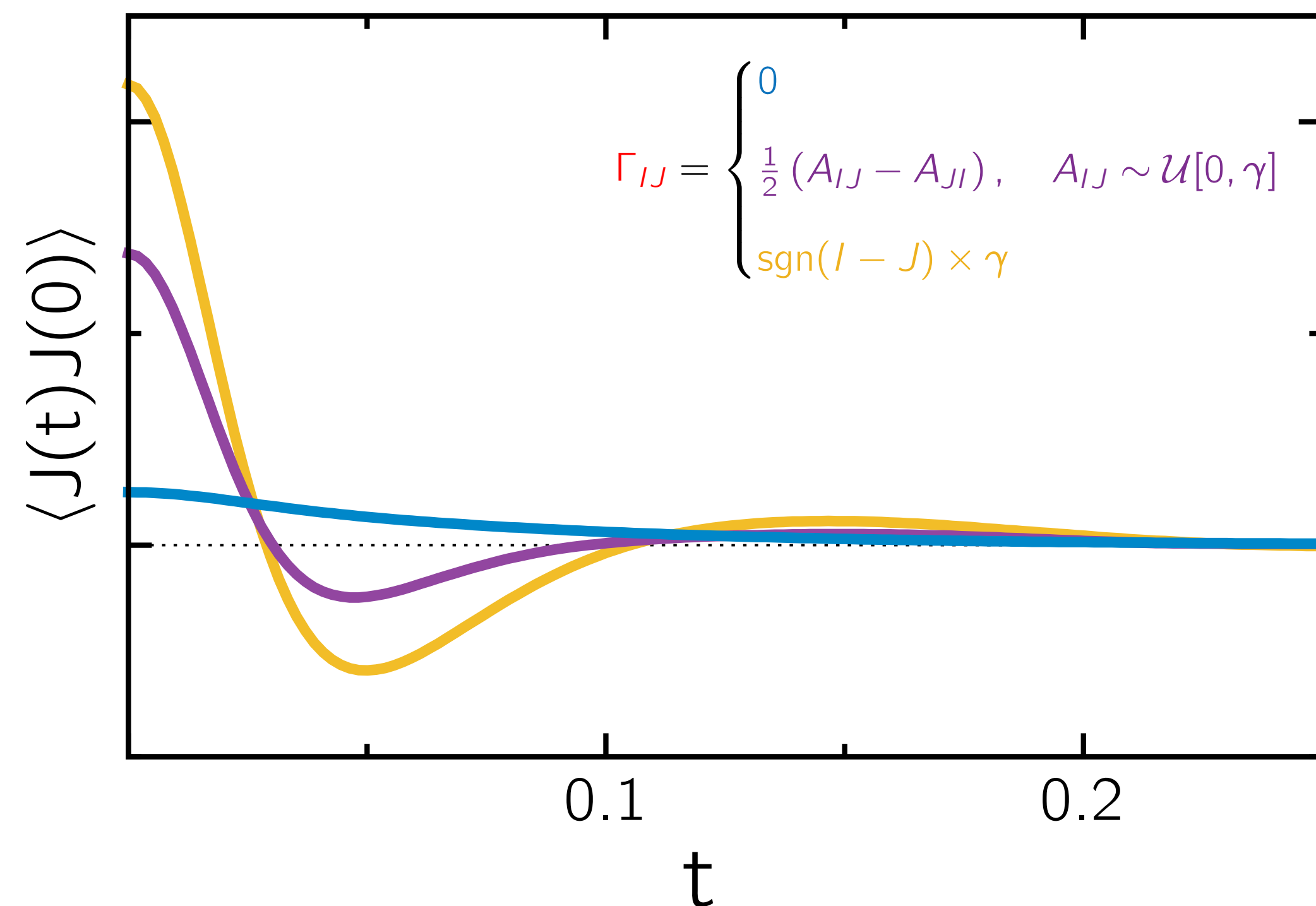
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$$\dot{\mathbf{P}} = \frac{d}{dt} \frac{1}{4} \sum_{I \neq J} \Gamma_{IJ} v(|\mathbf{R}_I - \mathbf{R}_J|) (\mathbf{R}_I - \mathbf{R}_J)$$

insights from classical mechanics

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

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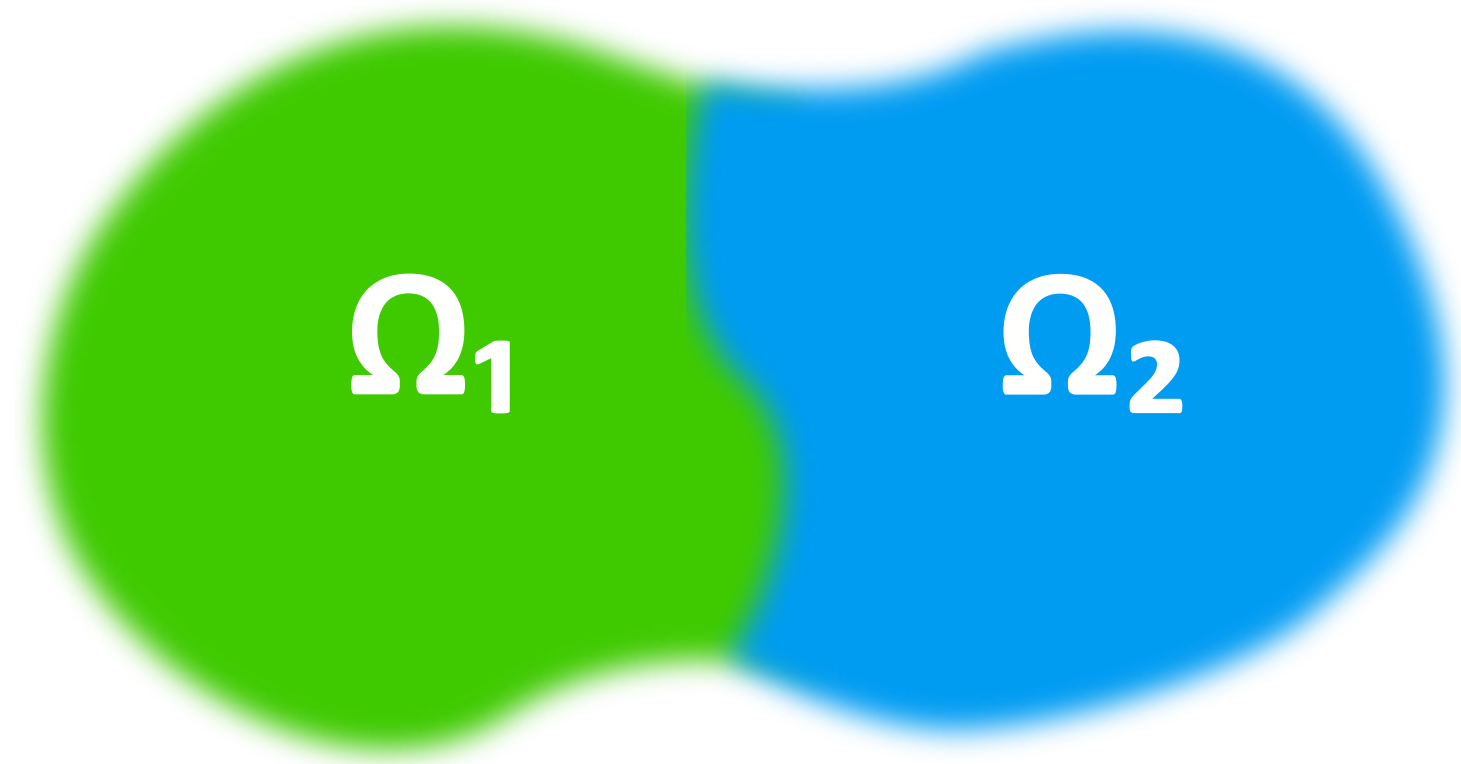


$$\mathbf{D}(t) = \mathbf{D}'(t) + \mathbf{P}(t) - \mathbf{P}(0)$$

$$\kappa' = \kappa$$

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

gauge invariance of heat transport

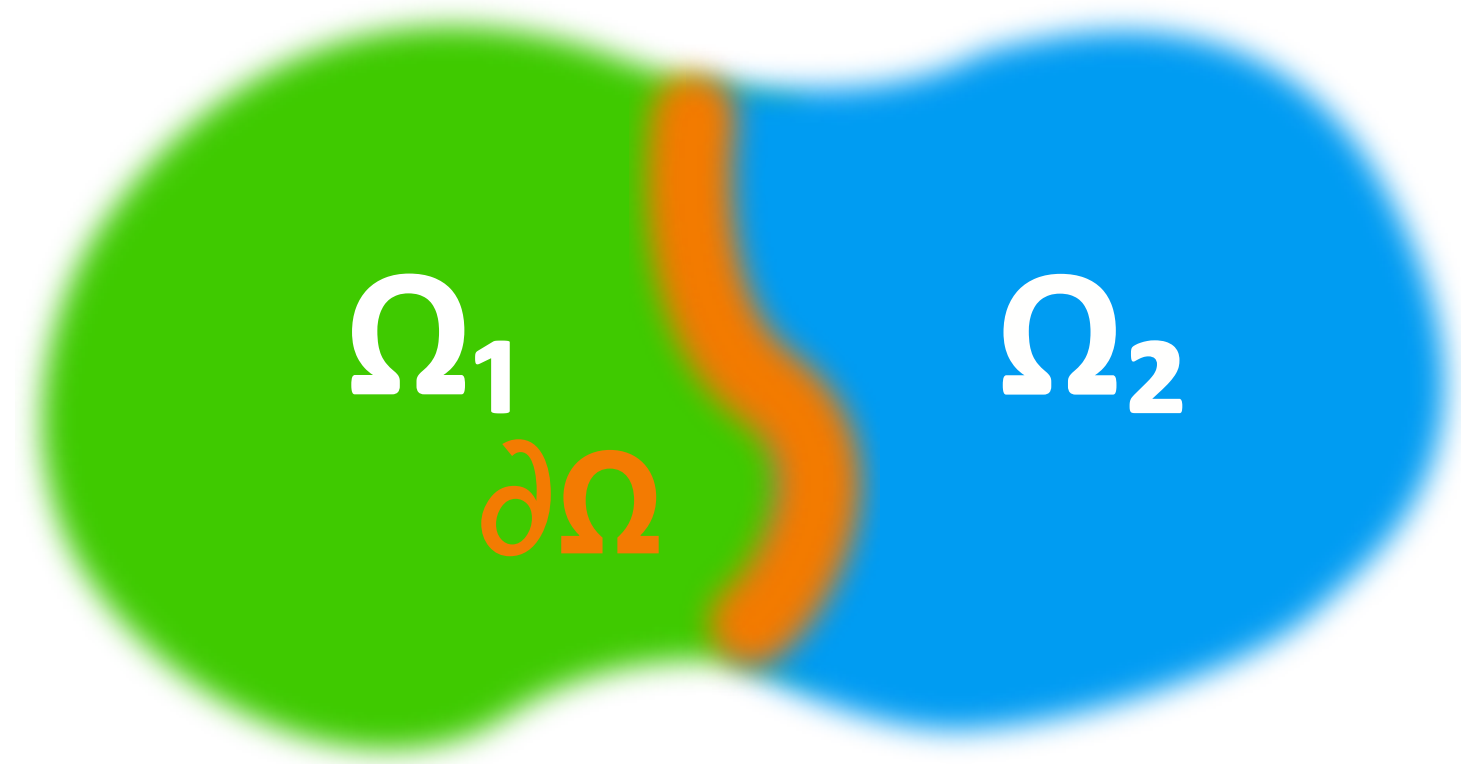


$$E[\Omega_1 \cup \Omega_2] = E[\Omega_1] + E[\Omega_2]$$

extensivity

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

gauge invariance of heat transport

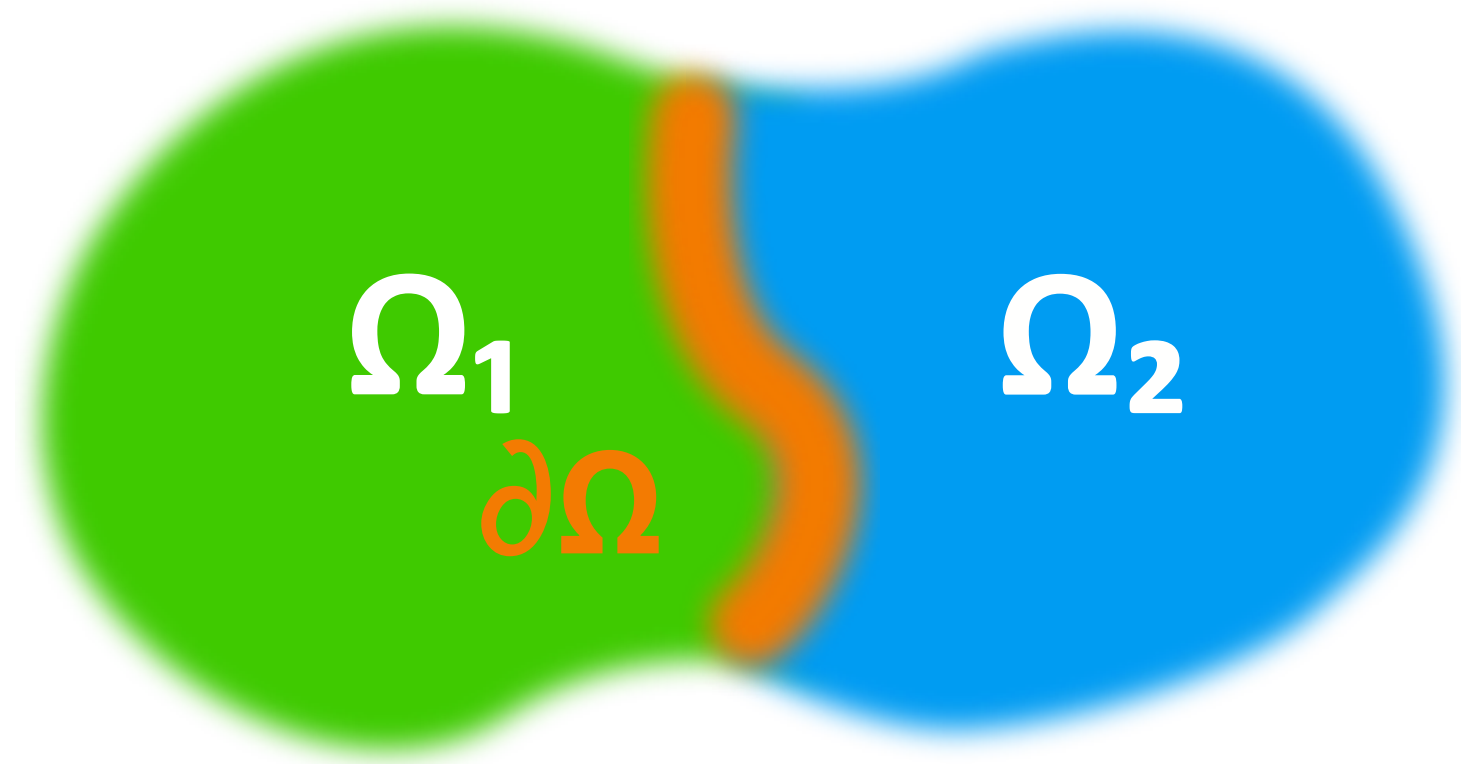


$$E[\Omega_1 \cup \Omega_2] = E[\Omega_1] + E[\Omega_2] + W[\partial\Omega]$$

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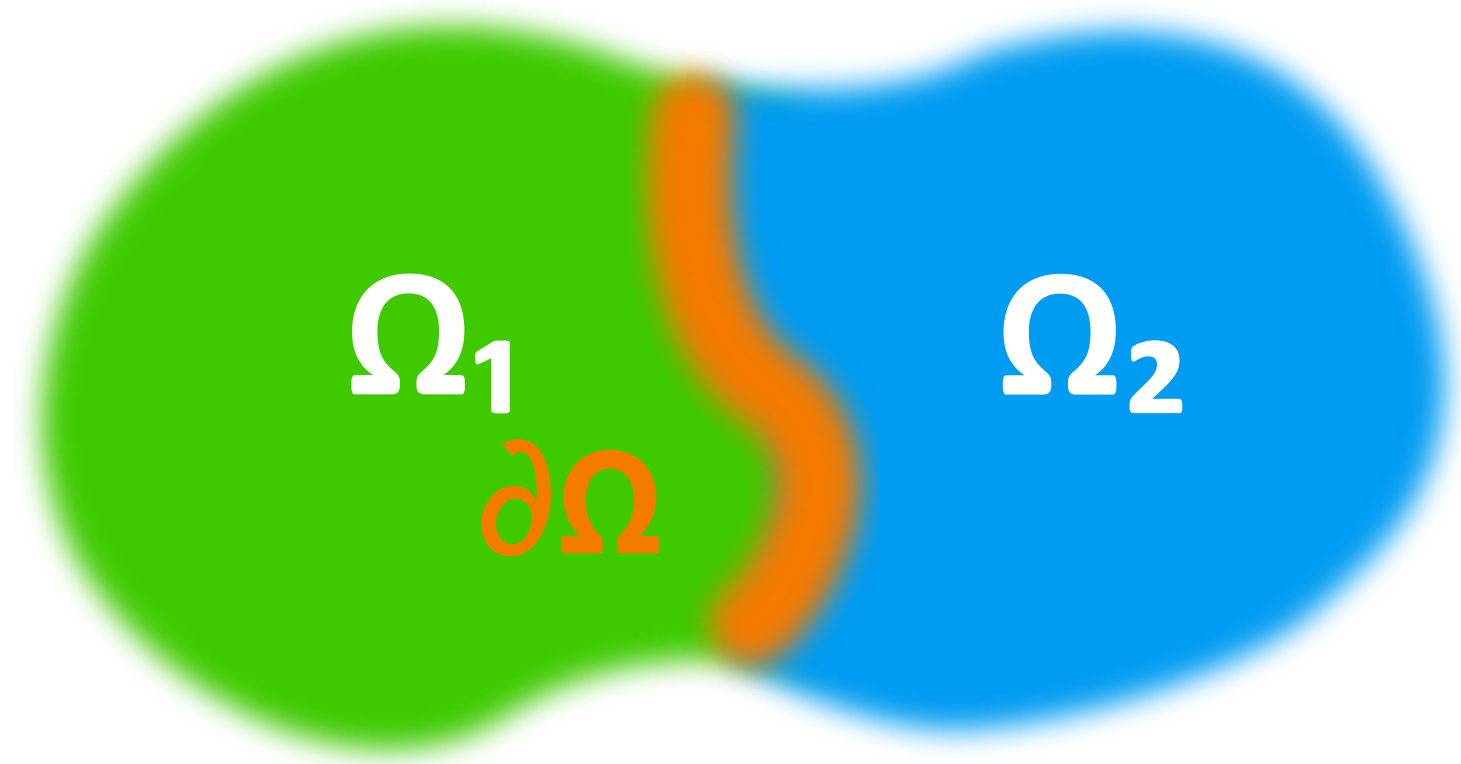


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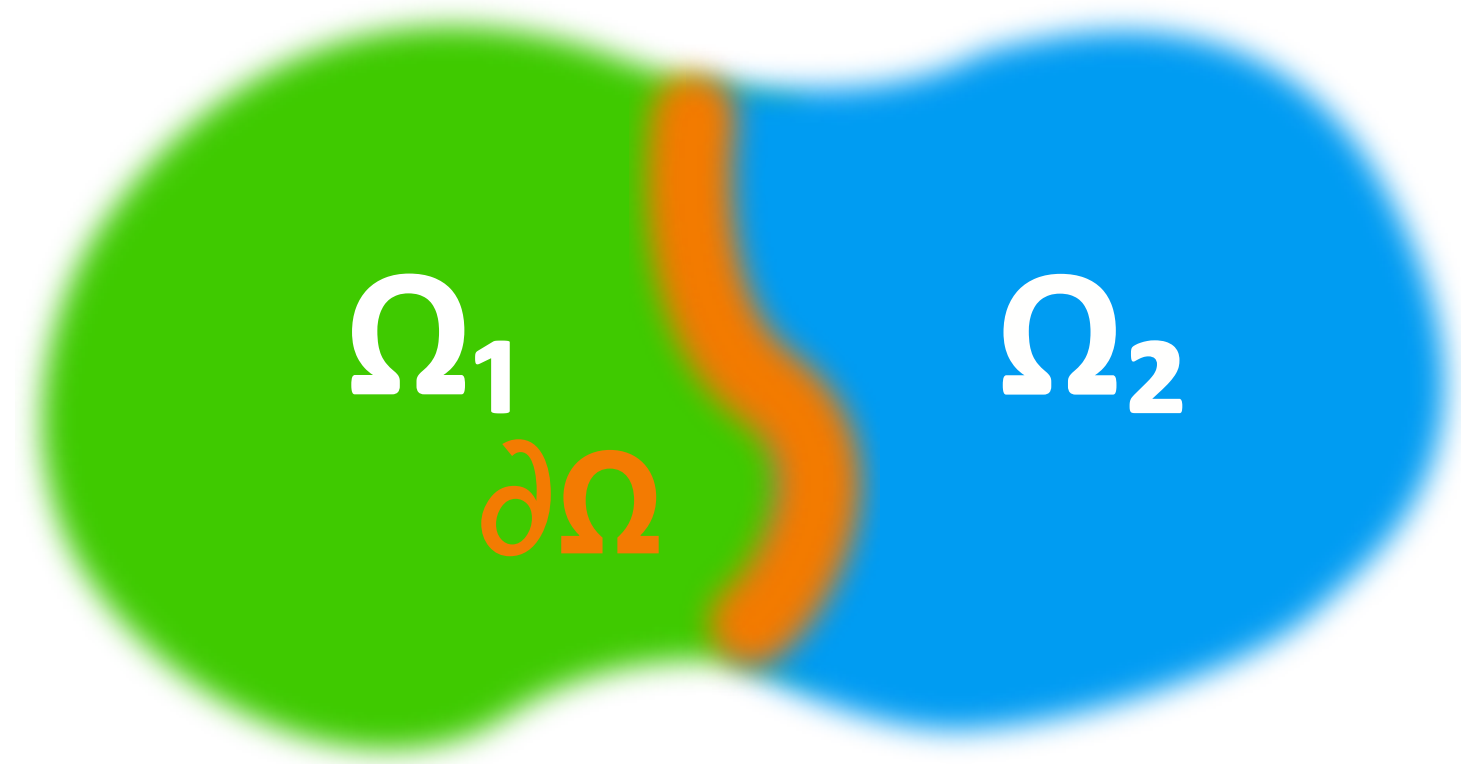
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thermodynamic invariance

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

gauge invariance of heat transport



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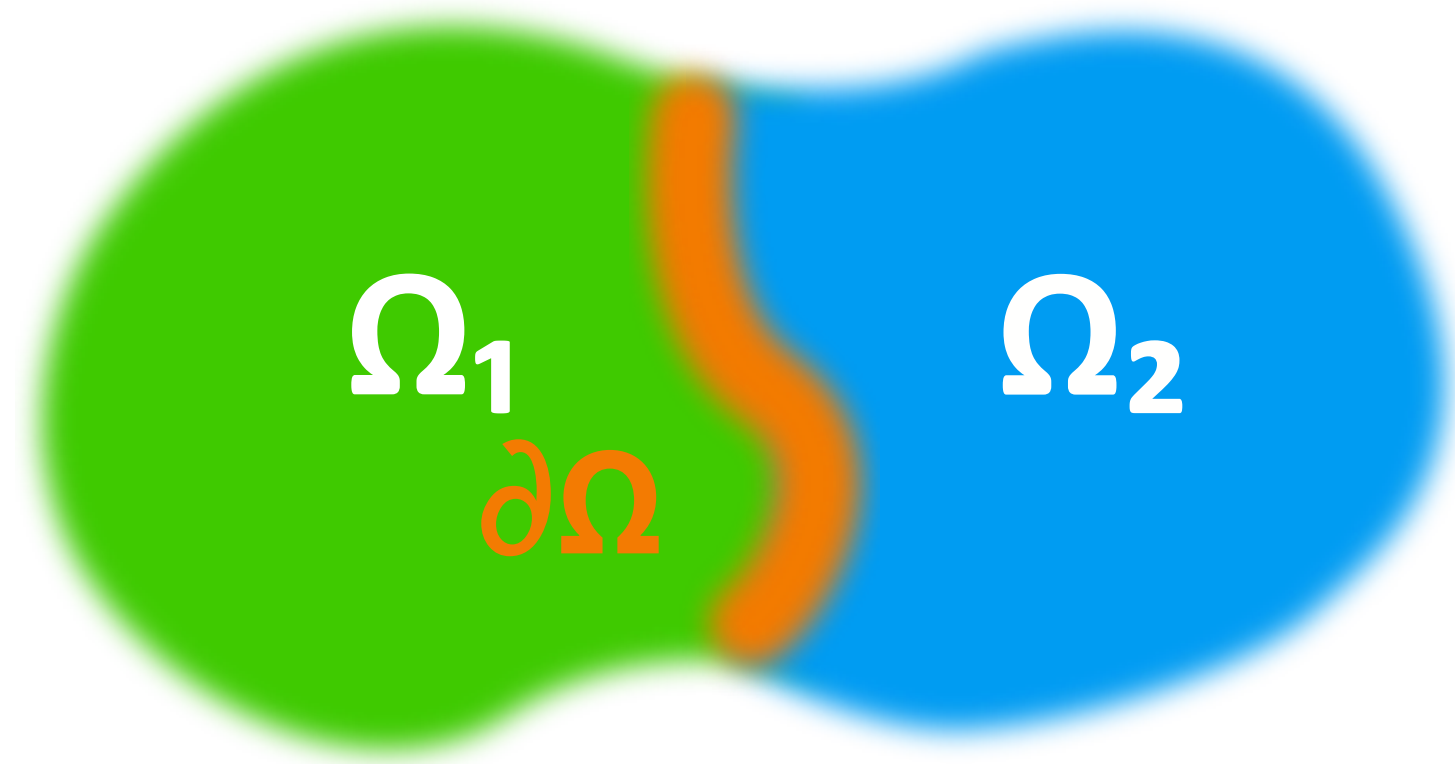
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gauge invariance

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

gauge invariance of heat transport



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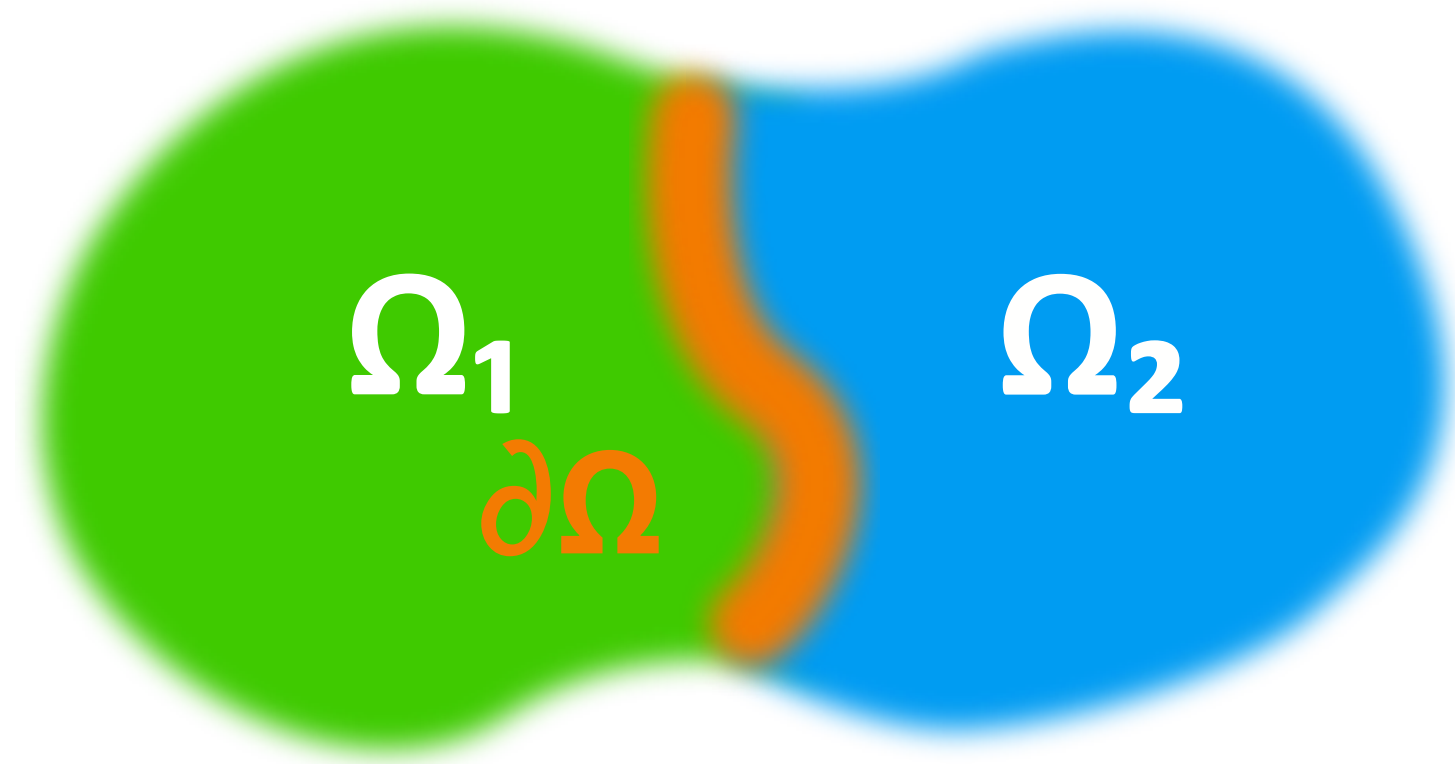
gauge invariance

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

conservation

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

gauge invariance of heat transport



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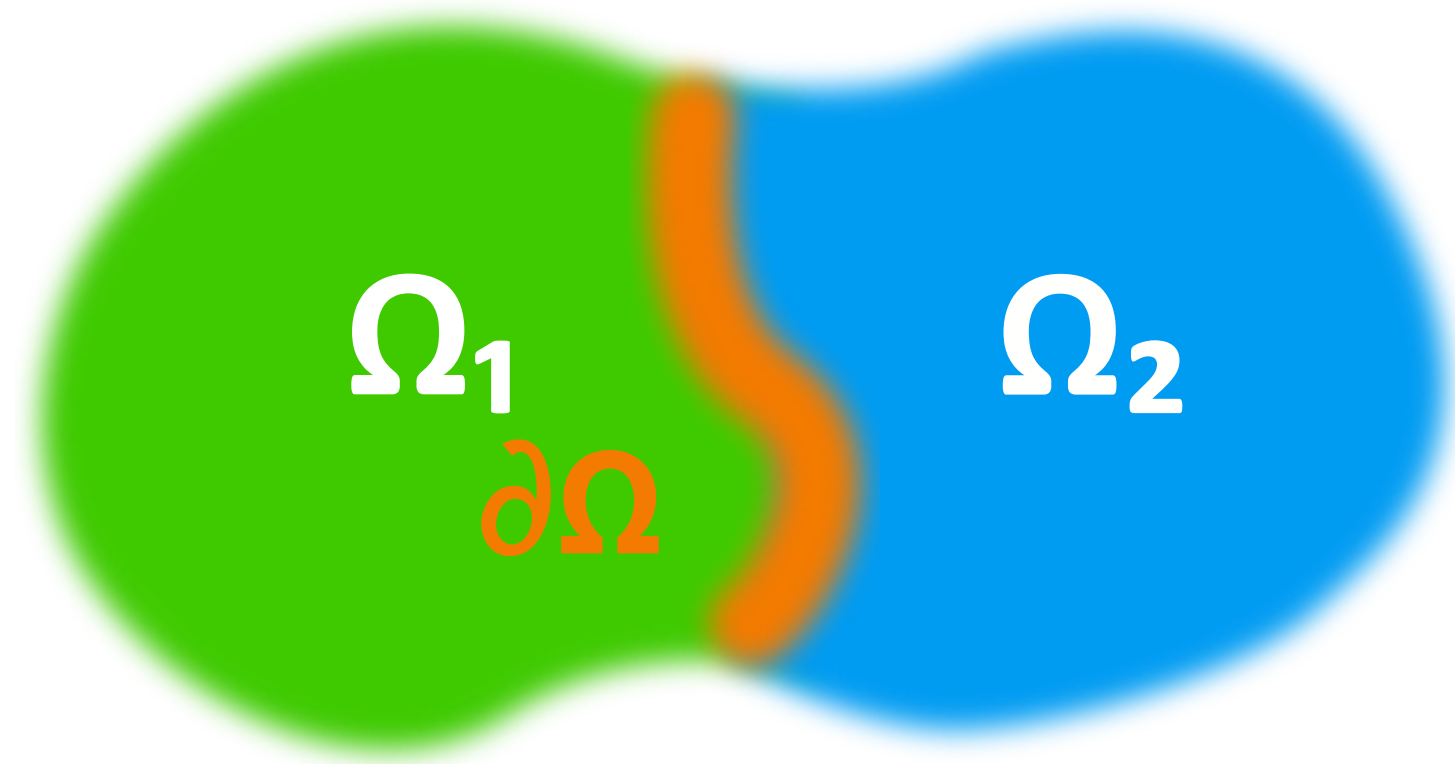
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$$e'(\mathbf{r}) = e(\mathbf{r}) - \nabla \cdot \mathbf{p}(\mathbf{r})$$
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gauge invariance of heat transport



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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

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

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

gauge invariance

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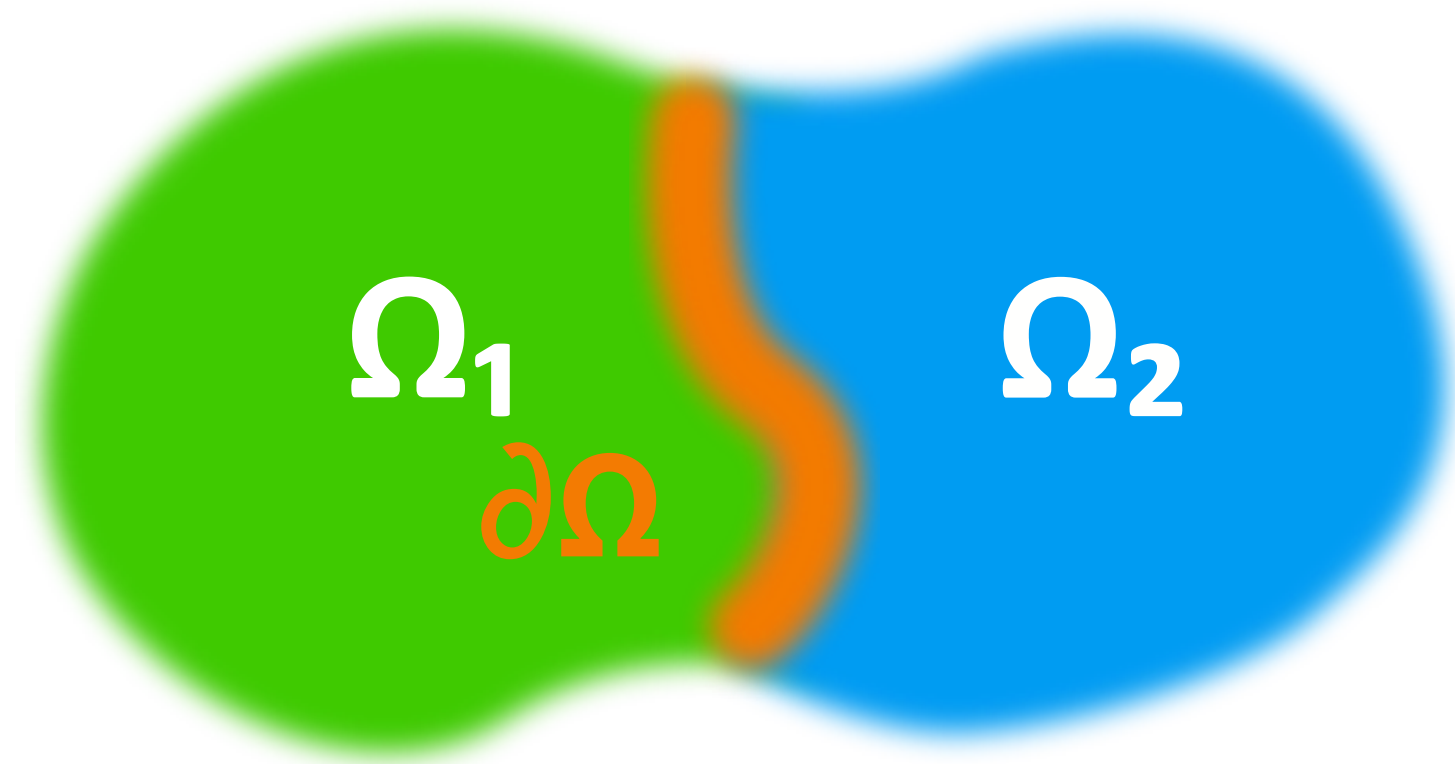
$$\mathbf{j}'(\mathbf{r}, t) = \mathbf{j}(\mathbf{r}, t) + \dot{\mathbf{p}}(\mathbf{r}, t)$$

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gauge invariance

conservation

nature
physics

ARTICLES

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Microscopic theory and quantum simulation of
atomic heat transport

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

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

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hurdles toward an ab initio Green-Kubo theory

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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

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

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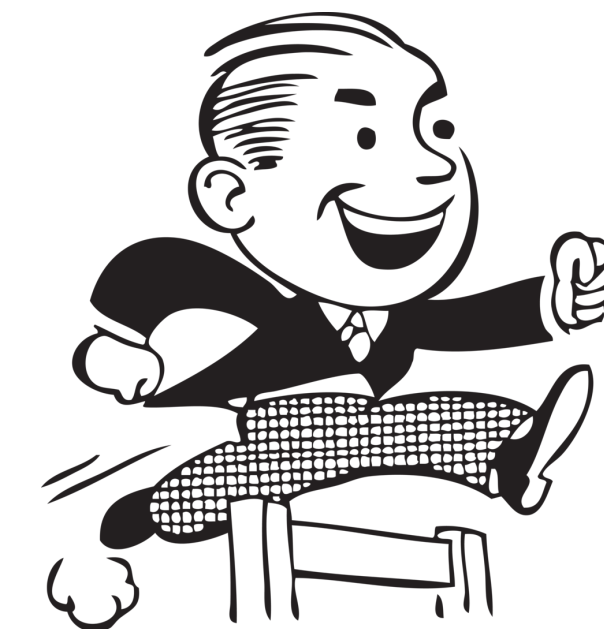
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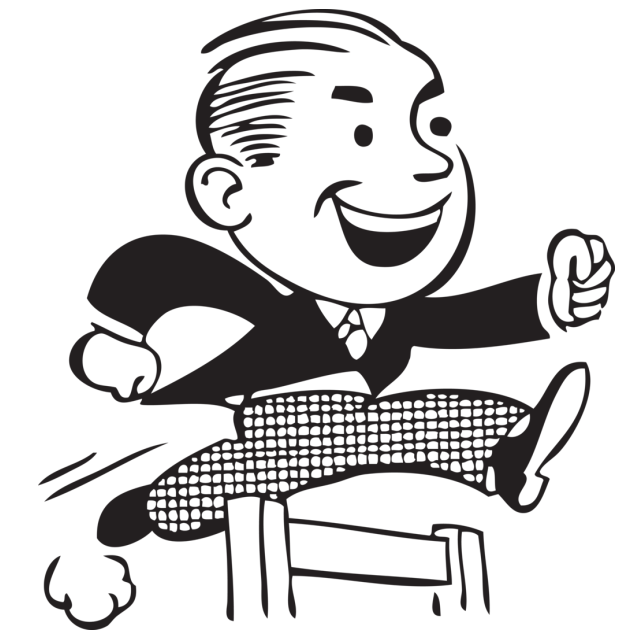
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***Ab Initio* Green-Kubo Approach for the Thermal Conductivity of Solids**

Christian Carbogno, Rampi Ramprasad, and Matthias Scheffler

ulations: Because of the limited time scales accessible in aiMD runs, thermodynamic fluctuations dominate the HFACF, which in turn prevents a reliable and numerically stable assessment of the thermal conductivity via Eq. (2).





*separating the wheat
from the chaff*

spectral analysis

$$\begin{aligned} J &= \int_V \mathbf{j}(\mathbf{r}) d\mathbf{r} \\ &= \sum_i \int_{V_i} \mathbf{j}(\mathbf{r}) d\mathbf{r} \end{aligned}$$

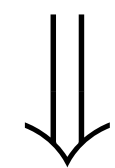
spectral analysis



$$\begin{aligned} \mathbf{J} &= \int_V \mathbf{j}(\mathbf{r}) d\mathbf{r} \\ &= \sum_i \int_{V_i} \mathbf{j}(\mathbf{r}) d\mathbf{r} \end{aligned}$$

if $\langle \mathbf{j}(\mathbf{r}) \mathbf{j}(\mathbf{r}') \rangle$ is short-range, $\mathbf{J}_i$ and $\mathbf{J}_j$ are independent stochastic variables, by the central-limit theorem,

$J(t)$ is Gaussian



$$\tilde{J}_T(\omega) = \int_0^T J(t) e^{i\omega t} dt$$

$$\tilde{J}_T(\omega_k) \sim \mathcal{CN}(0, TS(\omega_k) \times I)$$

spectral analysis

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$$\tilde{J}_T(\omega_k) \sim \mathcal{CN}(0, TS(\omega_k) \times I)$$

$$\begin{aligned} \kappa &\propto \int_0^\infty \langle \mathbf{J}(t) \mathbf{J}(0) \rangle dt \quad S(\omega) \\ &= \frac{1}{2} \int_{-\infty}^\infty \langle \mathbf{J}(t) \mathbf{J}(0) \rangle e^{i\omega t} dt \Big|_{\omega=0} \\ &= \frac{1}{2} S(0) \end{aligned}$$

spectral analysis

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$\Downarrow$

$$\tilde{J}_T(\omega) = \int_0^T J(t) e^{i\omega t} dt$$

$$\tilde{J}_T(\omega_k) \sim \mathcal{CN}(0, TS(\omega_k) \times I)$$

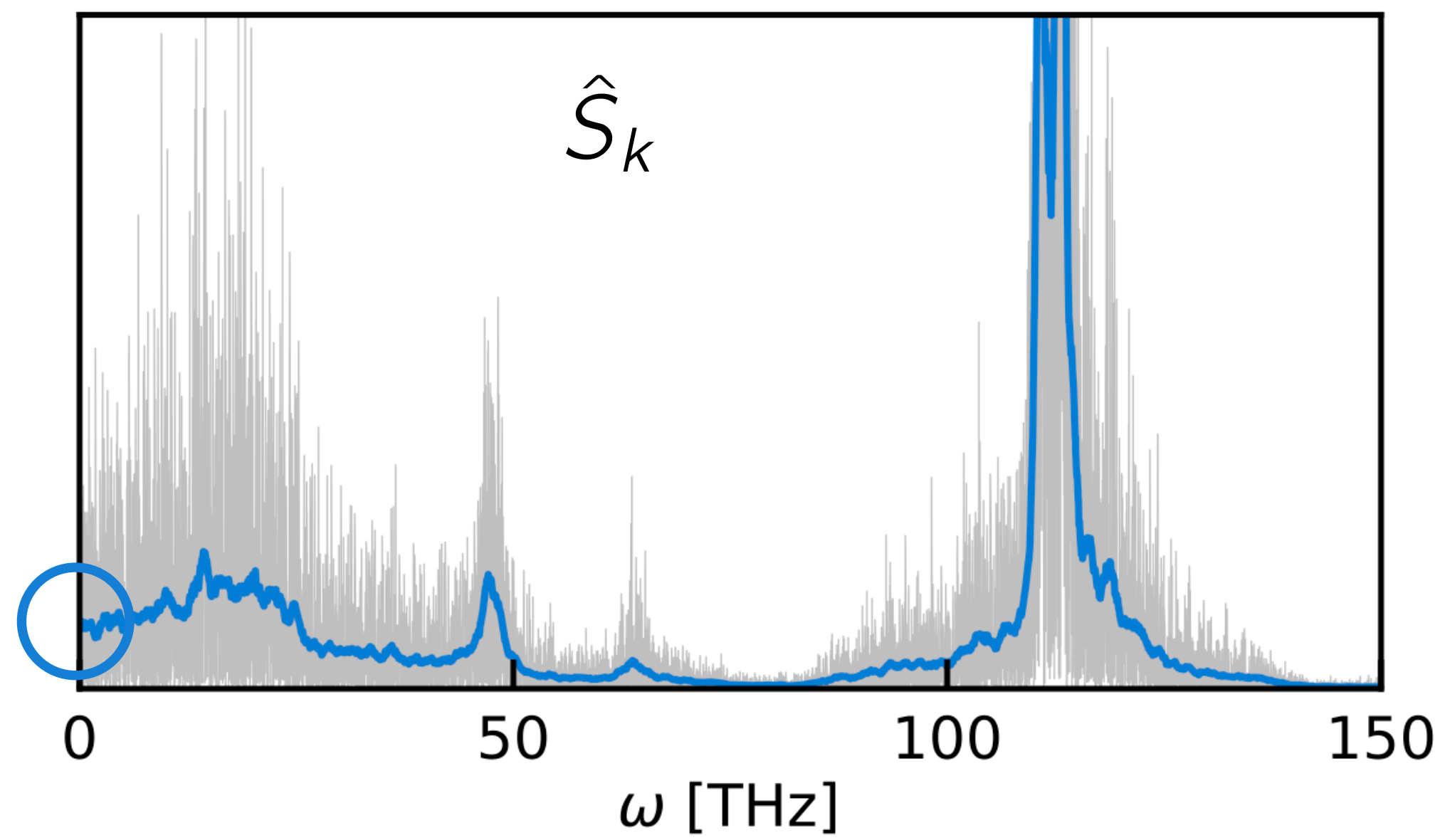
$$\begin{aligned} \kappa &\propto \int_0^\infty \langle \mathbf{J}(t) \mathbf{J}(0) \rangle dt \quad S(\omega) \\ &= \frac{1}{2} \int_{-\infty}^\infty \langle \mathbf{J}(t) \mathbf{J}(0) \rangle e^{i\omega t} dt \Big|_{\omega=0} \\ &= \frac{1}{2} S(0) \end{aligned}$$

$$\begin{aligned} \hat{S}_k &\doteq \frac{1}{T} |\tilde{J}_T(\omega_k)|^2 \\ &\sim \frac{1}{2} S(\omega_k) \hat{\chi}_2^2 \quad \text{sample spectrum} \\ &\doteq S(\omega_k) \hat{\xi}_k \quad \text{aka "periodogram"} \\ &\quad \text{Wiener-Khintchine} \end{aligned}$$

separating the flour from the chaff



$$\hat{S}_k = S(\omega_k) \hat{\xi}_k$$

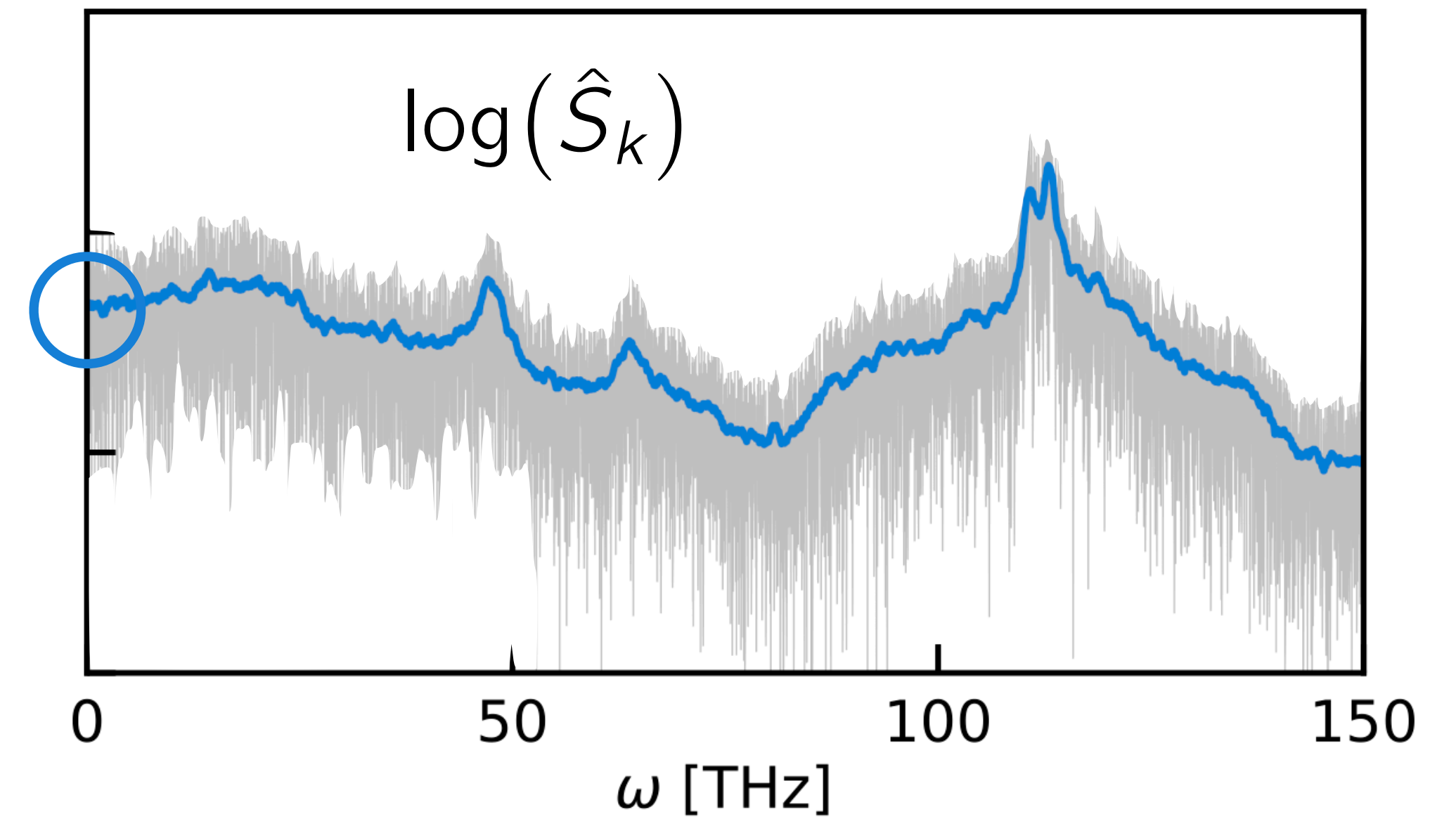
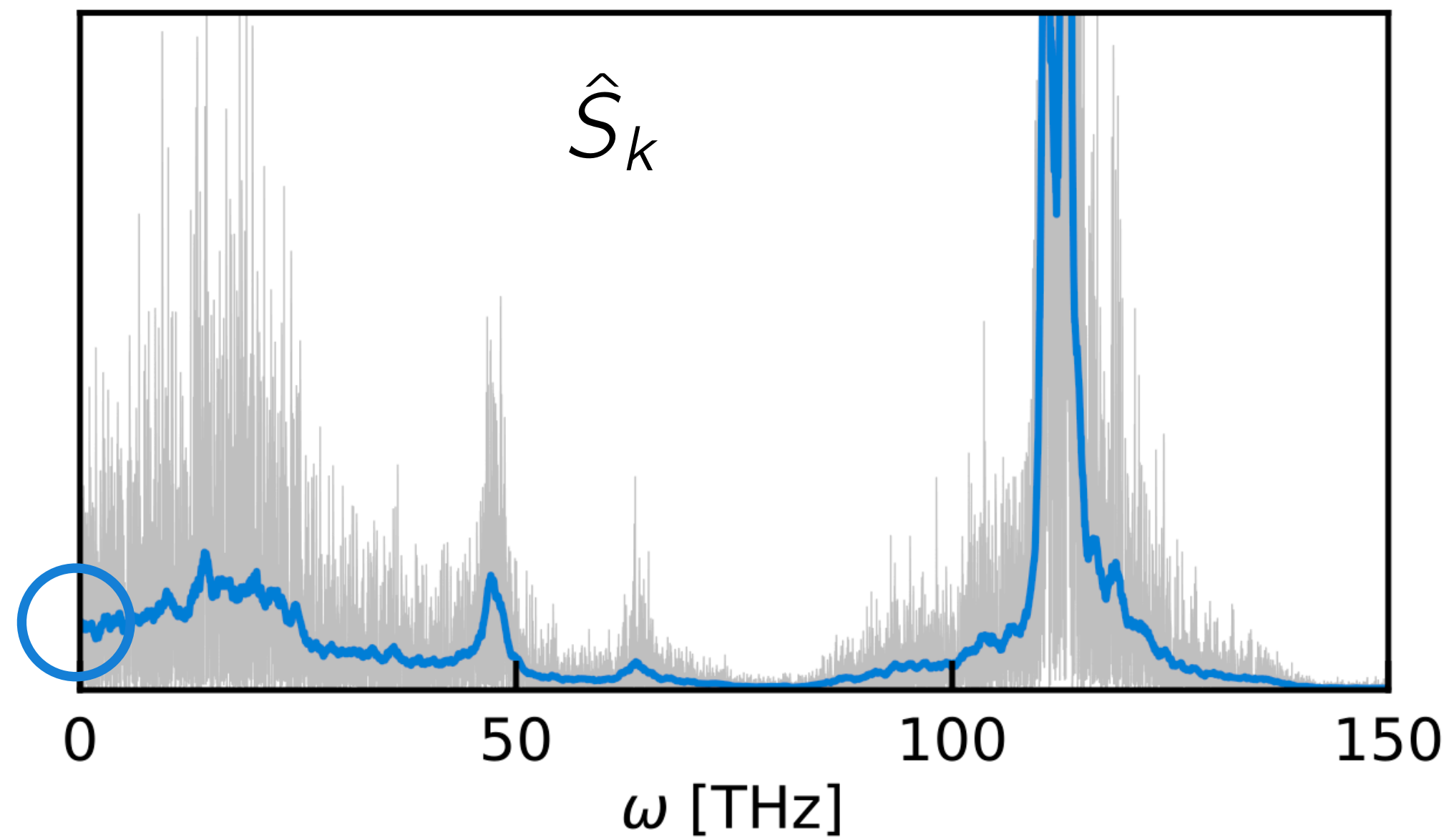


separating the flour from the chaff



$$\hat{S}_k = S(\omega_k) \hat{\xi}_k$$

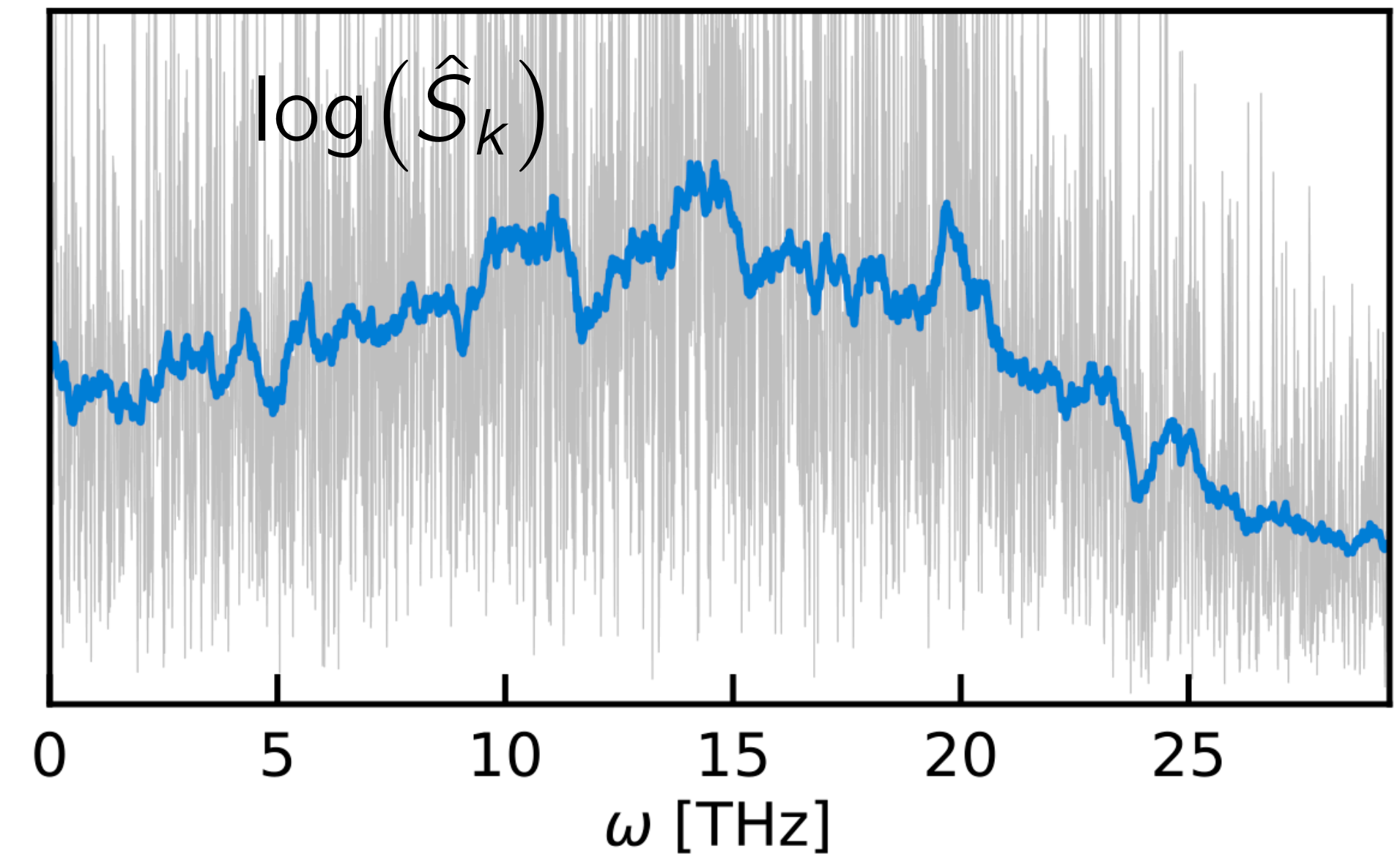
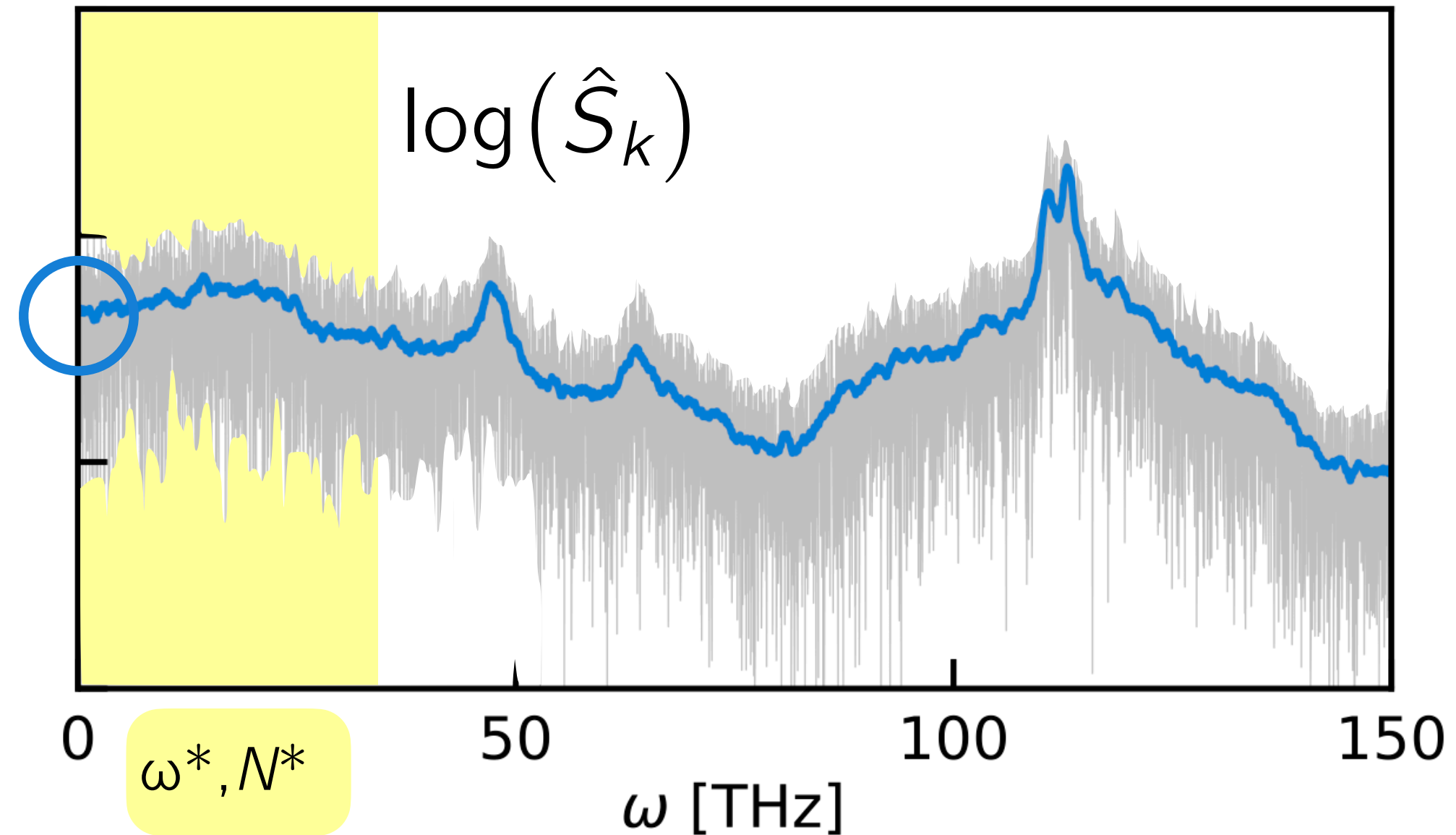
$$\log(\hat{S}_k) = \log(S(\omega_k)) + \log(\hat{\xi}_k)$$



separating the flour from the chaff

$$\log(\hat{S}_k) = \log(S(\omega_k)) + \log(\hat{\xi}_k)$$

$$\hat{C}_n \doteq \frac{1}{N^*} \sum_{k=0}^{N^*-1} \log(\hat{S}_k) e^{2\pi i \frac{kn}{N}}$$

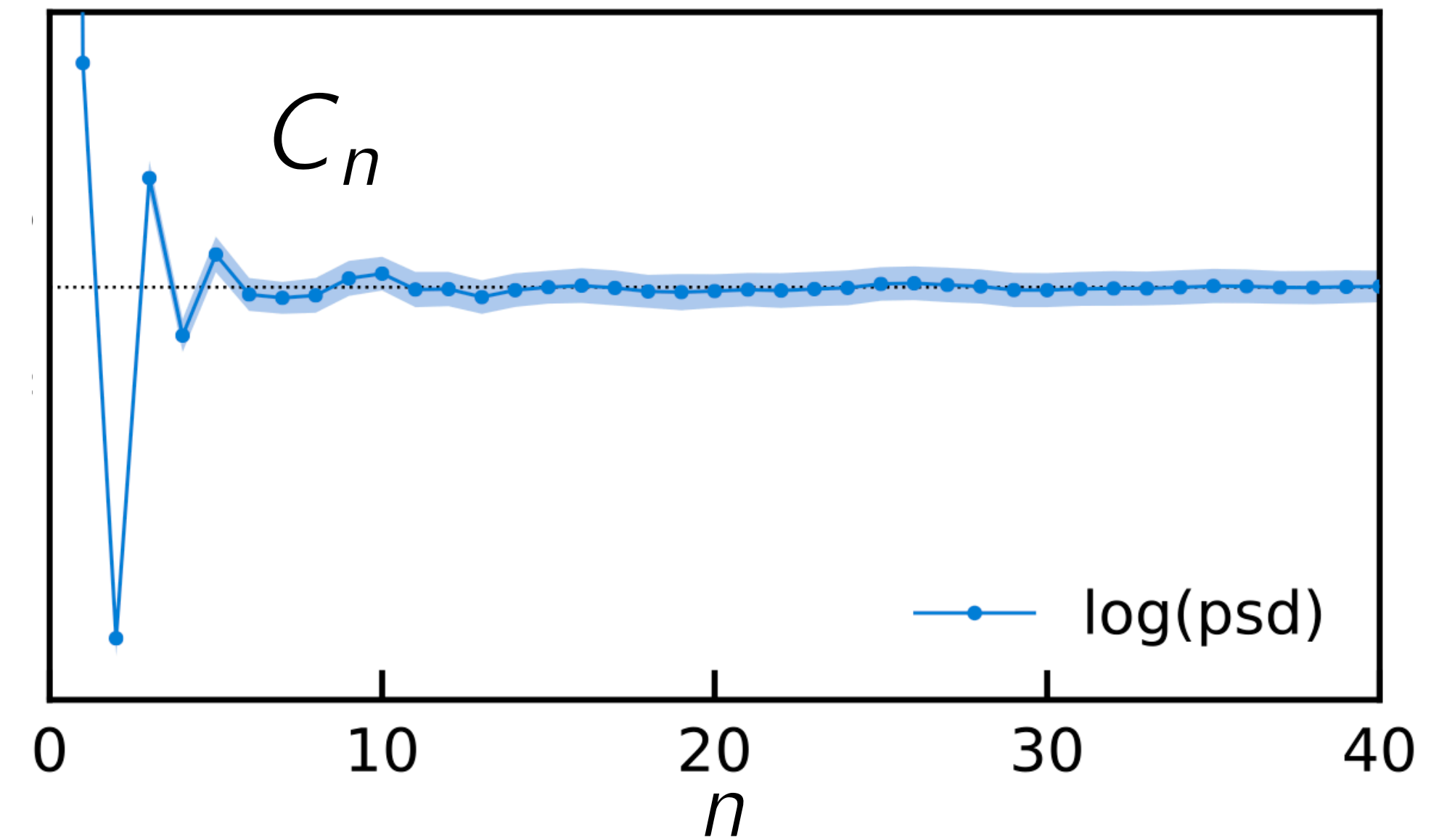
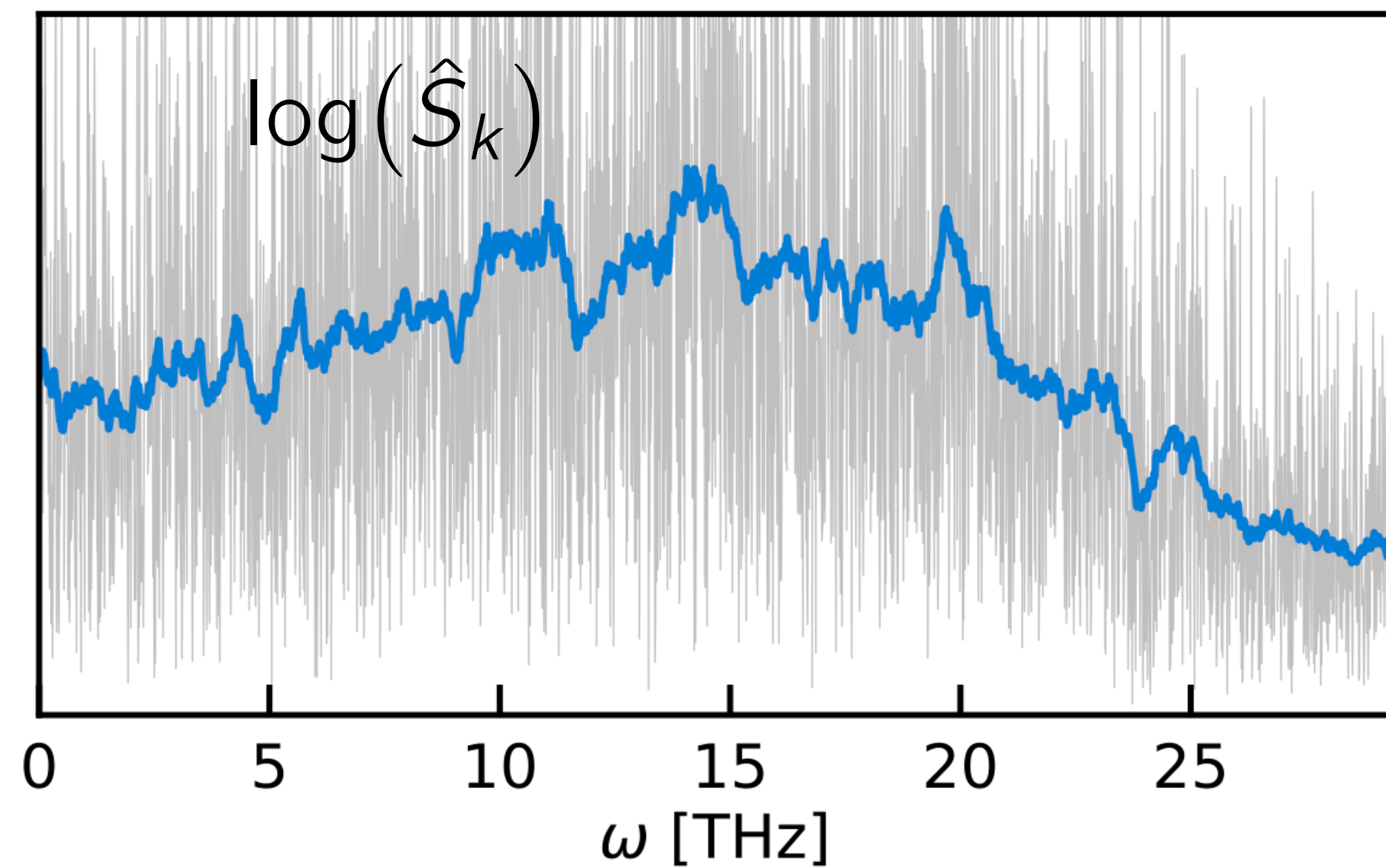


separating the flour from the chaff



$$\hat{C}_n \doteq \frac{1}{N^*} \sum_{k=0}^{N^*-1} \log(\hat{S}_k) e^{2\pi i \frac{kn}{N^*}}$$

$$\sum_{n=0}^{N^*-1} \hat{C}_n e^{2\pi i \frac{nk}{N^*}} = \log(S(\omega_k)) + \lambda + \text{noise}$$

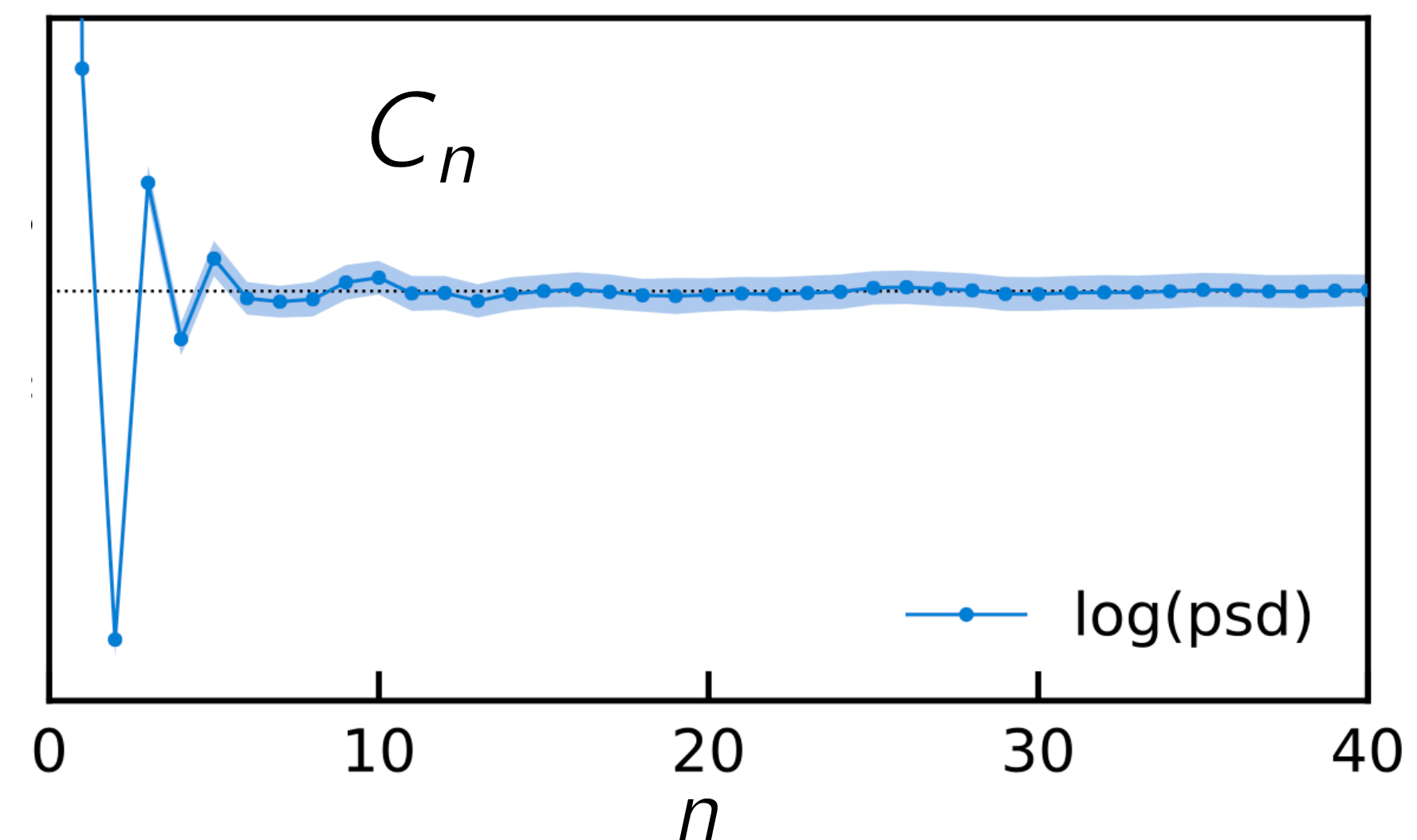
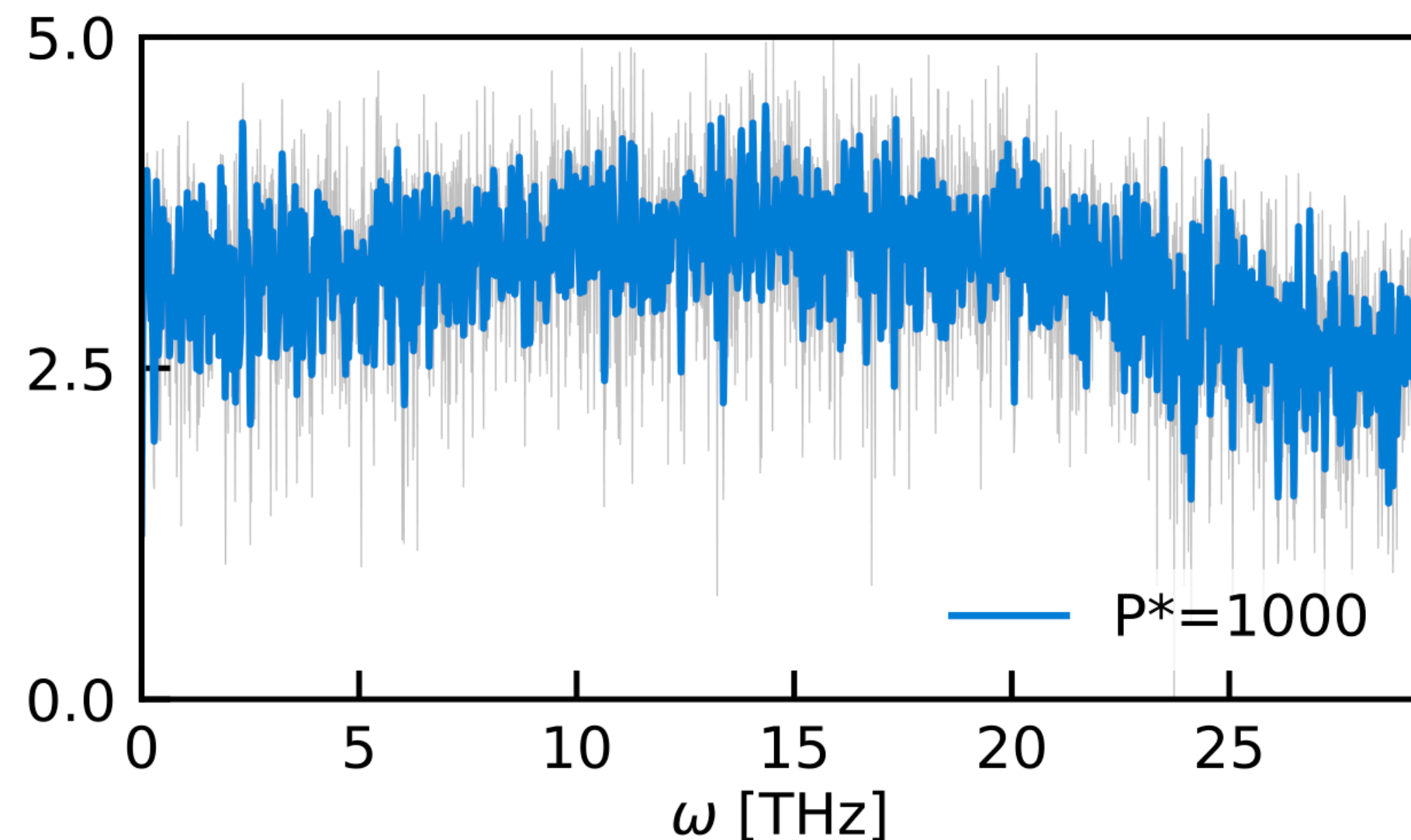


separating the flour from the chaff

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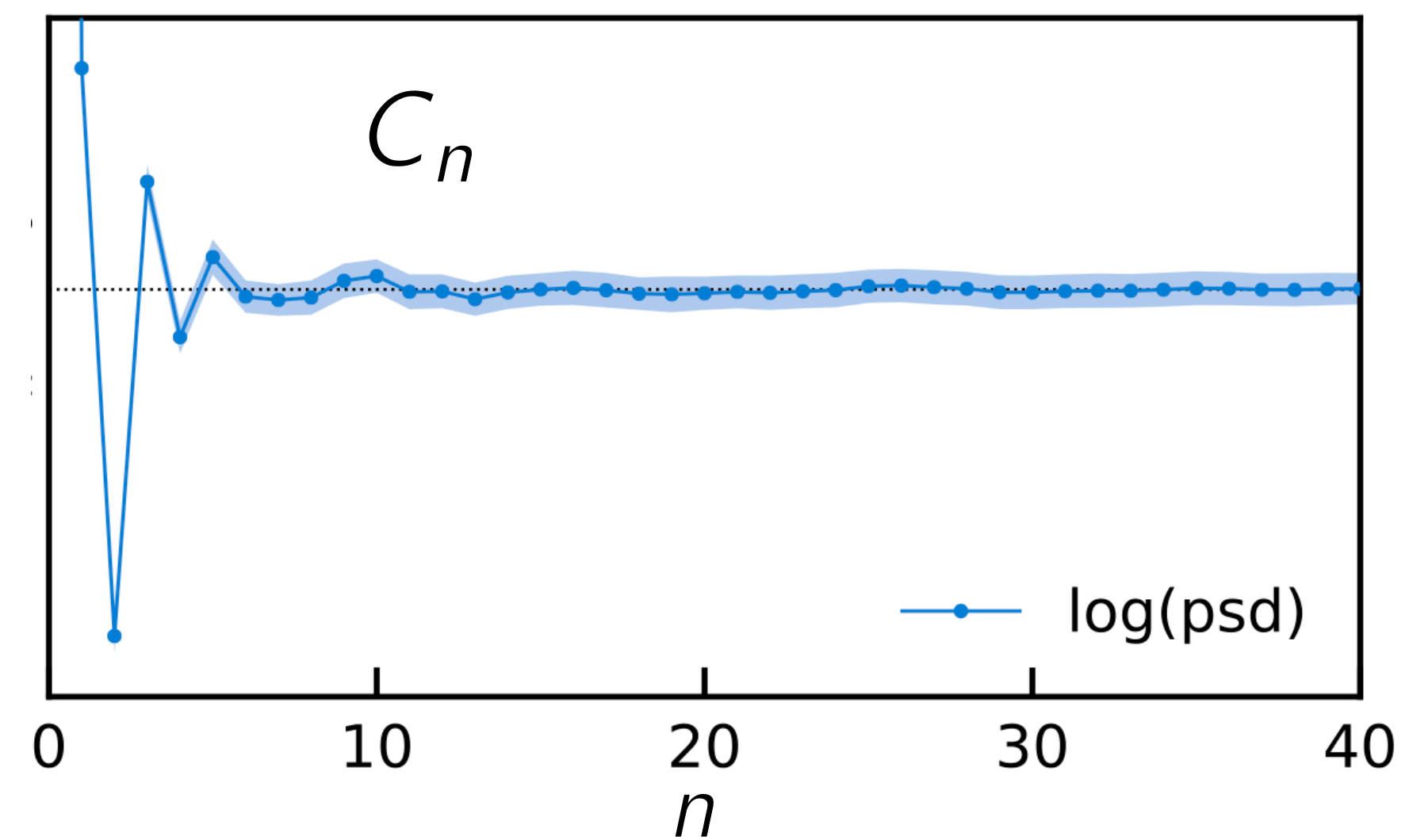
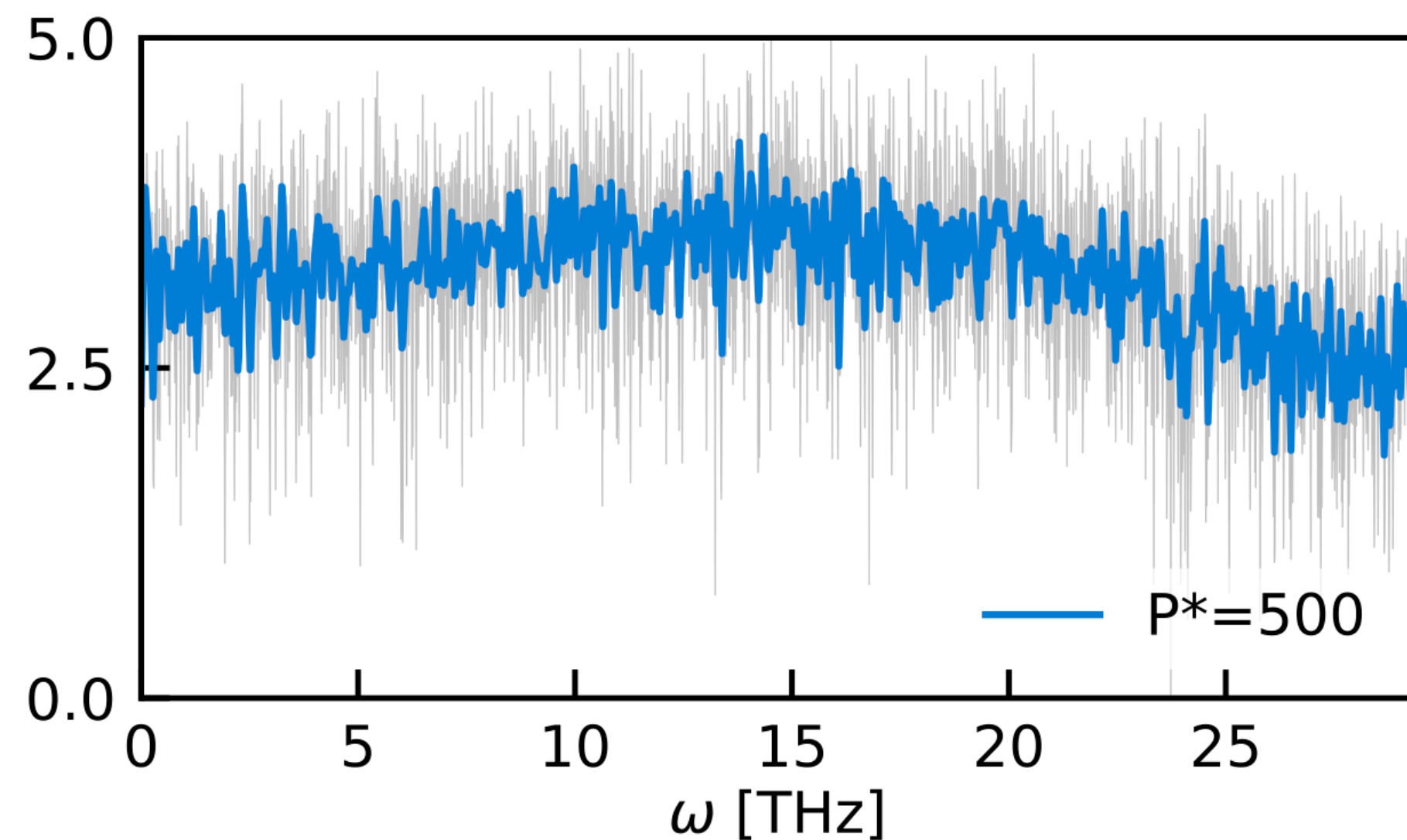


separating the flour from the chaff

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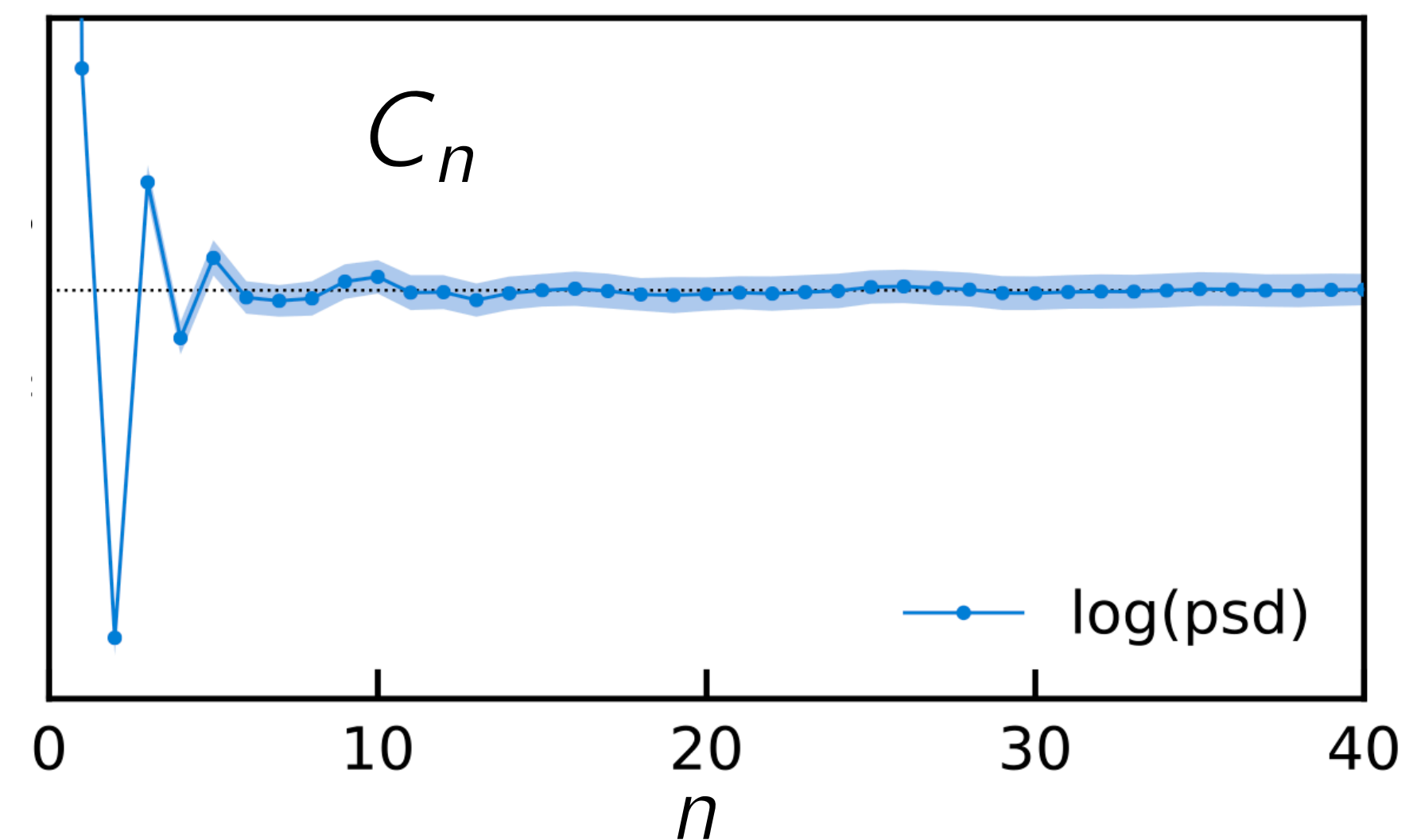
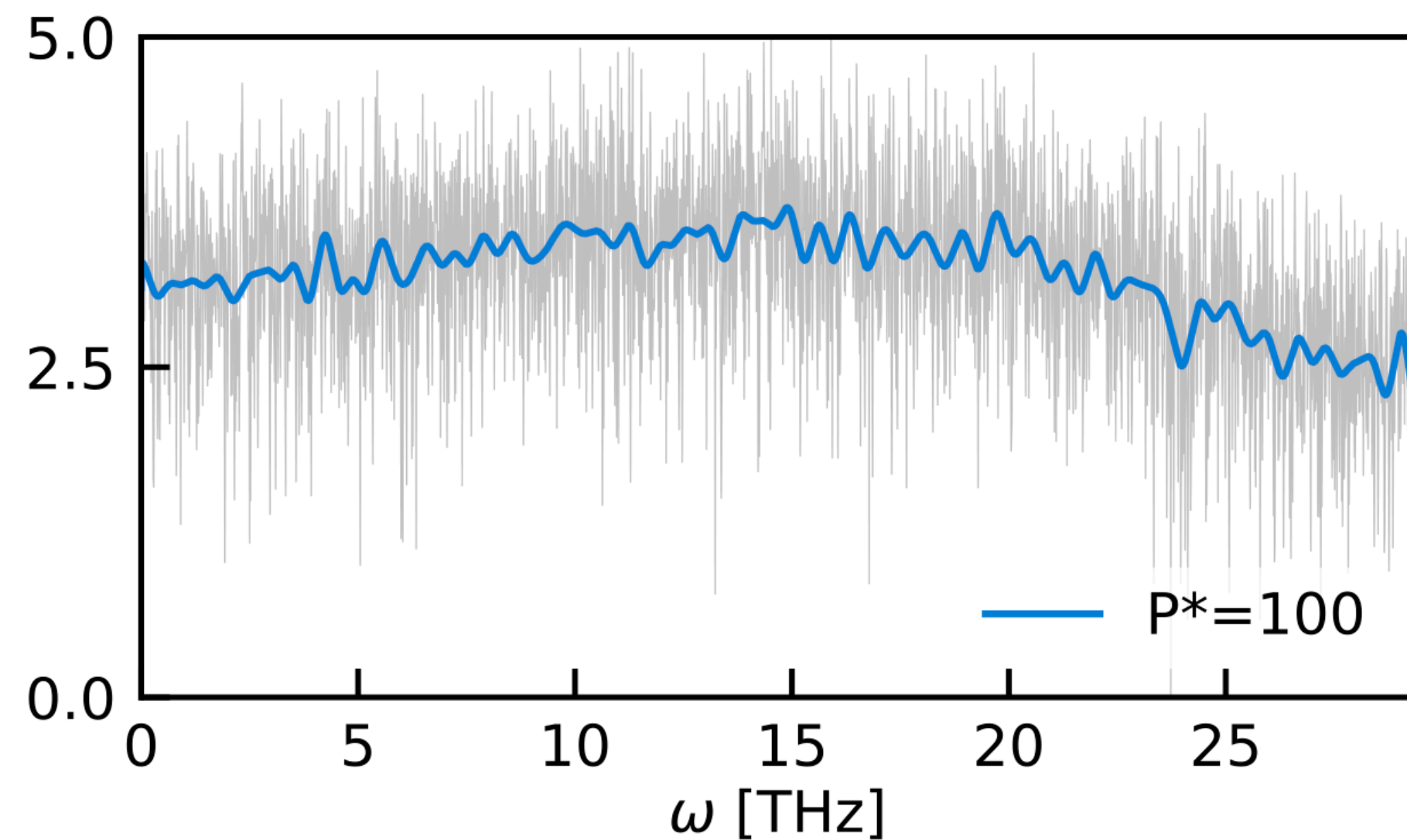


separating the flour from the chaff

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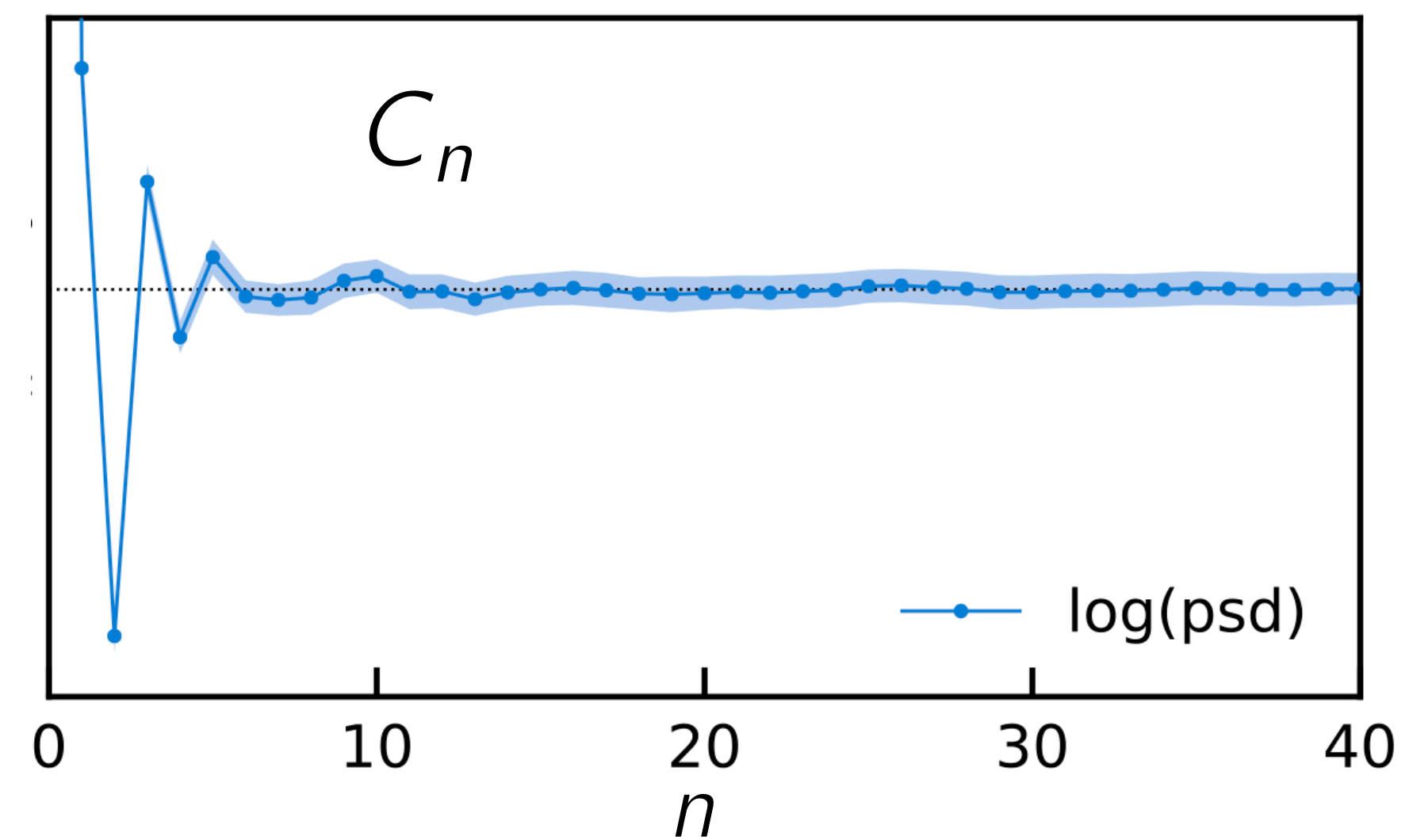
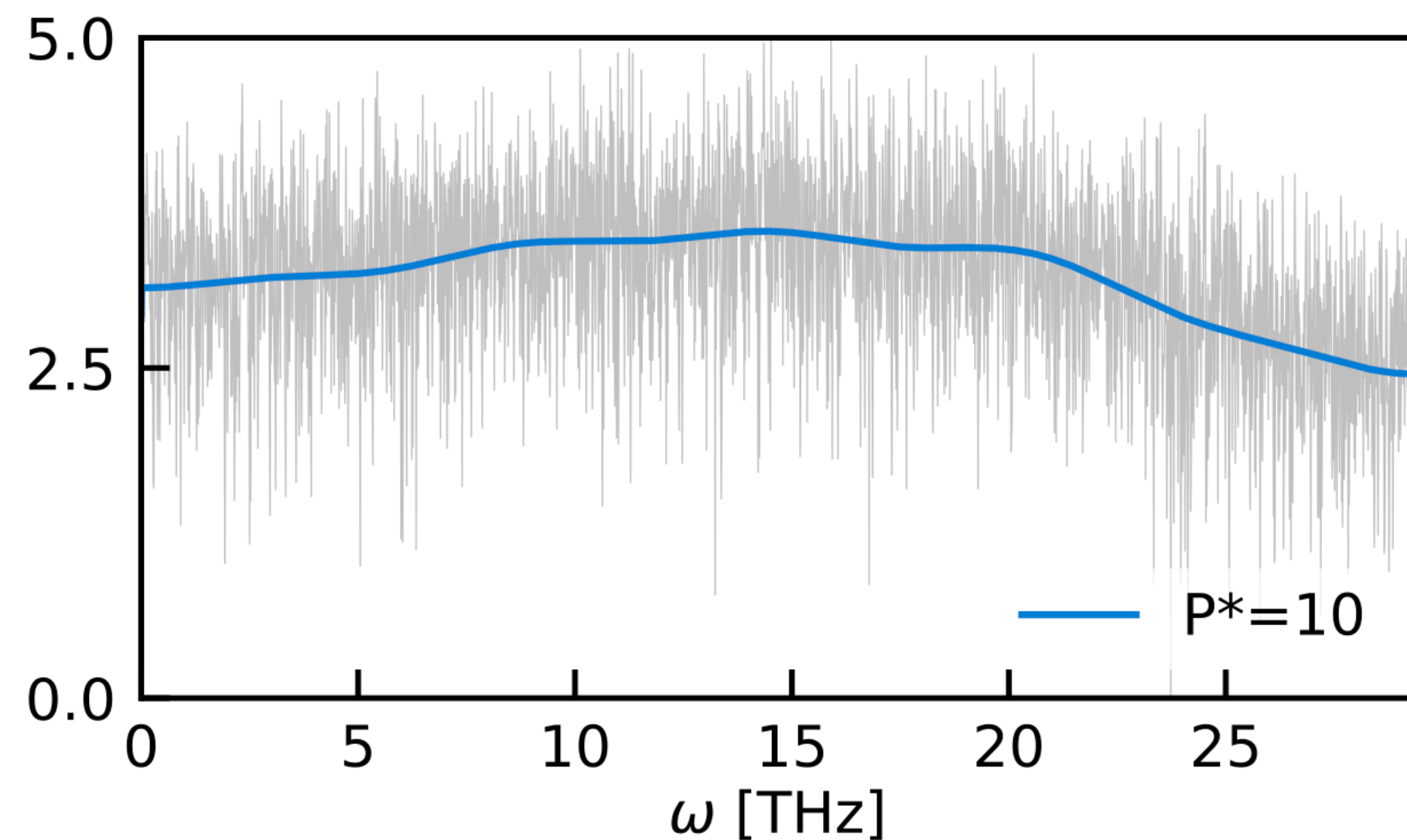


separating the flour from the chaff

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separating the flour from the chaff



$$\sum_{n=-P^*+1}^{P^*-1} \hat{C}_n e^{2\pi i \frac{nk}{N^*}} = \log(S(\omega_k)) + \lambda + \text{less noise}$$

optimal number of
coefficients, to be determined

separating the flour from the chaff



$$\sum_{n=-P^*+1}^{P^*-1} \hat{C}_n e^{2\pi i \frac{nk}{N^*}} = \log(S(\omega_k)) + \lambda + \text{less noise}$$

optimal number of
coefficients, to be determined

$$\log(S(0)) = -\lambda + C_0 + 2 \sum_{n=1}^{P^*-1} C_n \pm \sigma \sqrt{\frac{4P^* - 2}{N^*}}$$

constants independent of the time series being sampled

hurdles toward an ab initio Green-Kubo theory

PRL **104**, 208501 (2010)

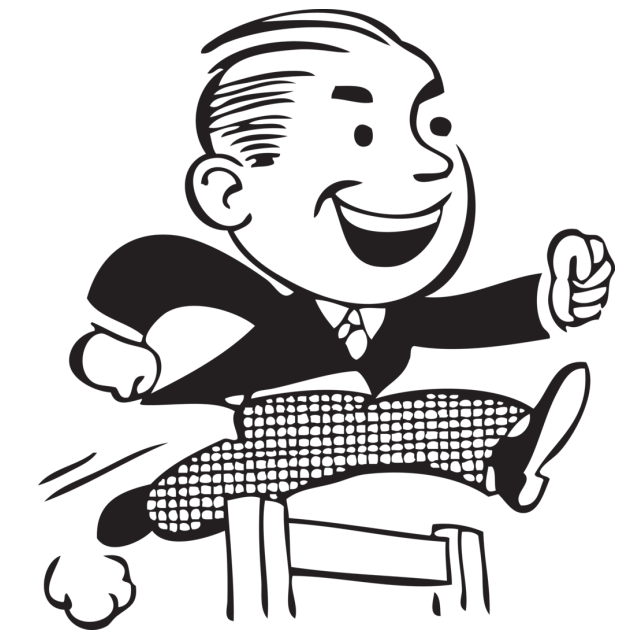
PHYSICAL REVIEW LETTERS

week ending
21 MAY 2010

Thermal Conductivity of Periclase (MgO) from First Principles

Stephen Stackhouse, Lars Stixrude, and Bijaya B. Karki

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.



PRL **118**, 175901 (2017)

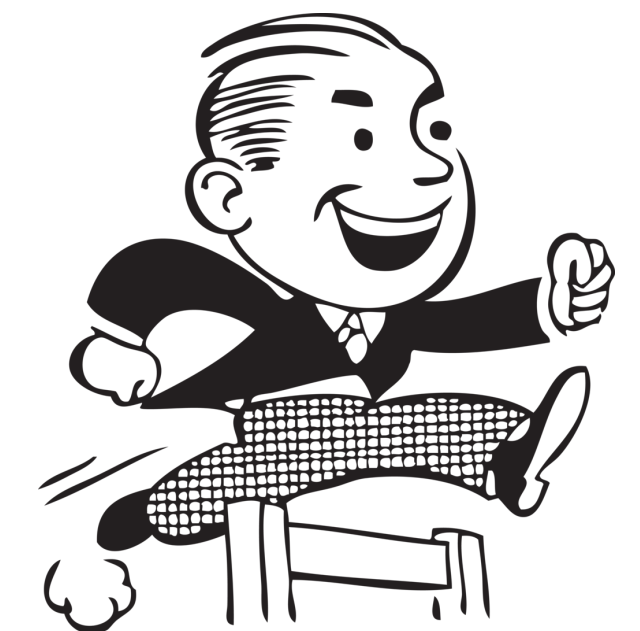
PHYSICAL REVIEW LETTERS

week ending
28 APRIL 2017

***Ab Initio* Green-Kubo Approach for the Thermal Conductivity of Solids**

Christian Carbogno, Rampi Ramprasad, and Matthias Scheffler

ulations: Because of the limited time scales accessible in aiMD runs, thermodynamic fluctuations dominate the HFACF, which in turn prevents a reliable and numerically stable assessment of the thermal conductivity via Eq. (2).



multi-component systems



50% water
50% ethanol

白酒

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

白酒

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



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conserved quantities:

- ☒ energy
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$$\begin{aligned} J_E &= \Lambda_{EE} \nabla \left(\frac{1}{T} \right) + \Lambda_{ME} \left(\frac{\mu}{T} \right) \\ J_M &= \Lambda_{EM} \left(\frac{1}{T} \right) + \Lambda_{MM} \left(\frac{\mu}{T} \right) \end{aligned}$$

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

$$J_M = 0 \rightarrow$$

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

multi-component systems

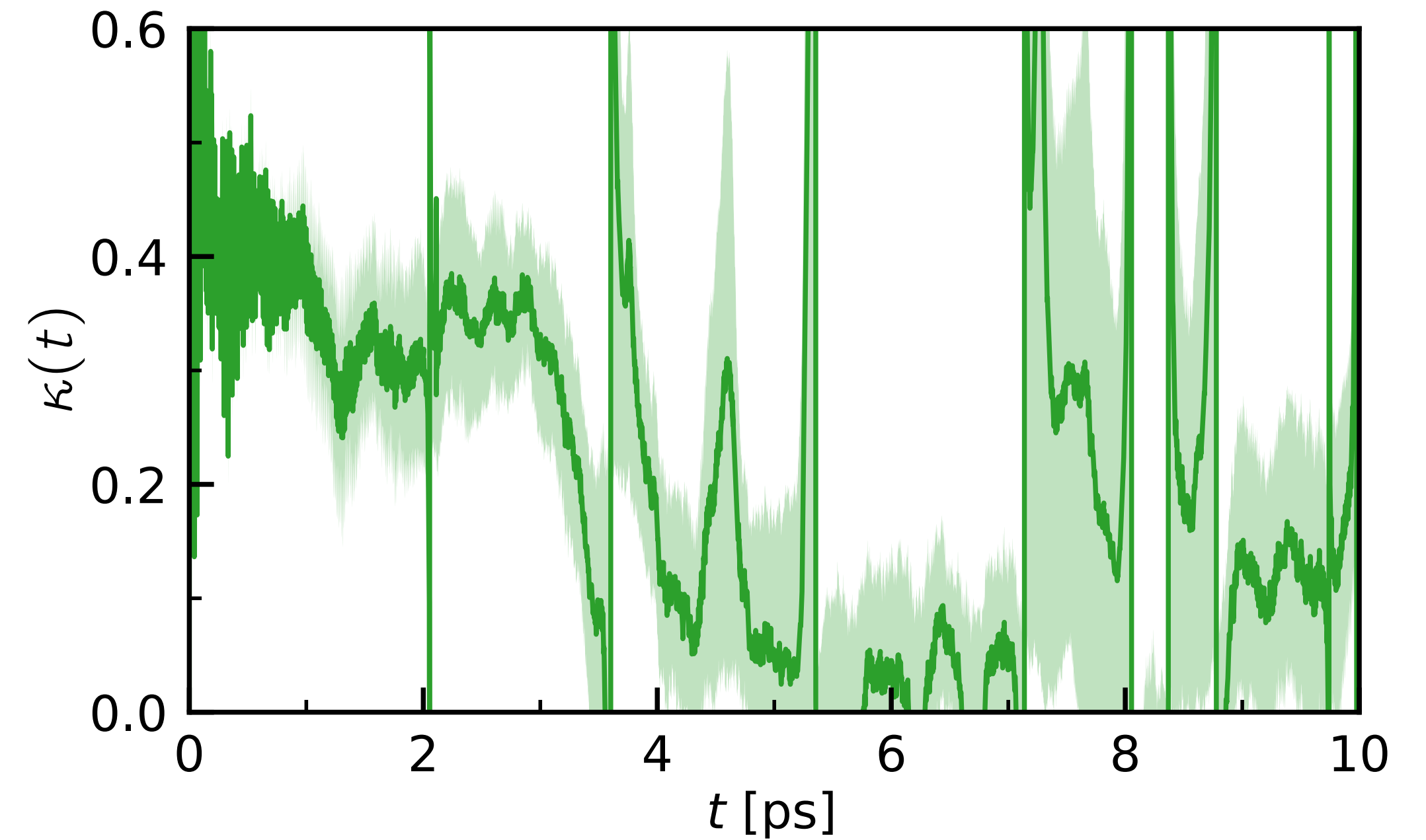


白酒

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

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

$$\Lambda_{ik}(t) \propto \int_0^t \langle J_i(t') J_k(0) \rangle dt'$$



multi-component systems

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

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

multi-component systems

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$$\Lambda_{ik} = \frac{1}{2} S_{ik}(0)$$

$$S_{ik}(\omega) = \int_{-\infty}^{\infty} \langle J_i(t) J_k(0) \rangle e^{i\omega t} dt$$

$$= \lim_{T \rightarrow \infty} \langle \hat{S}_{T,ik}(\omega) \rangle$$

Wishart matrix

$$\hat{S}_{T,ik}(\omega) = \frac{1}{T} \tilde{J}_{T,i}(\omega) \tilde{J}_{T,k}(-\omega) \sim \mathcal{CW}(S_{ik}(\omega), 1, 2)$$

multi-component systems

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the Schur complement of a block in a Wishart matrix, $\widehat{W}$, is itself Wishart distributed with expectation equal to the Schur complement of the corresponding block in $\langle \widehat{W} \rangle$

multi-component systems

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do cepstral analysis on the
Schur complement!

multi-component systems

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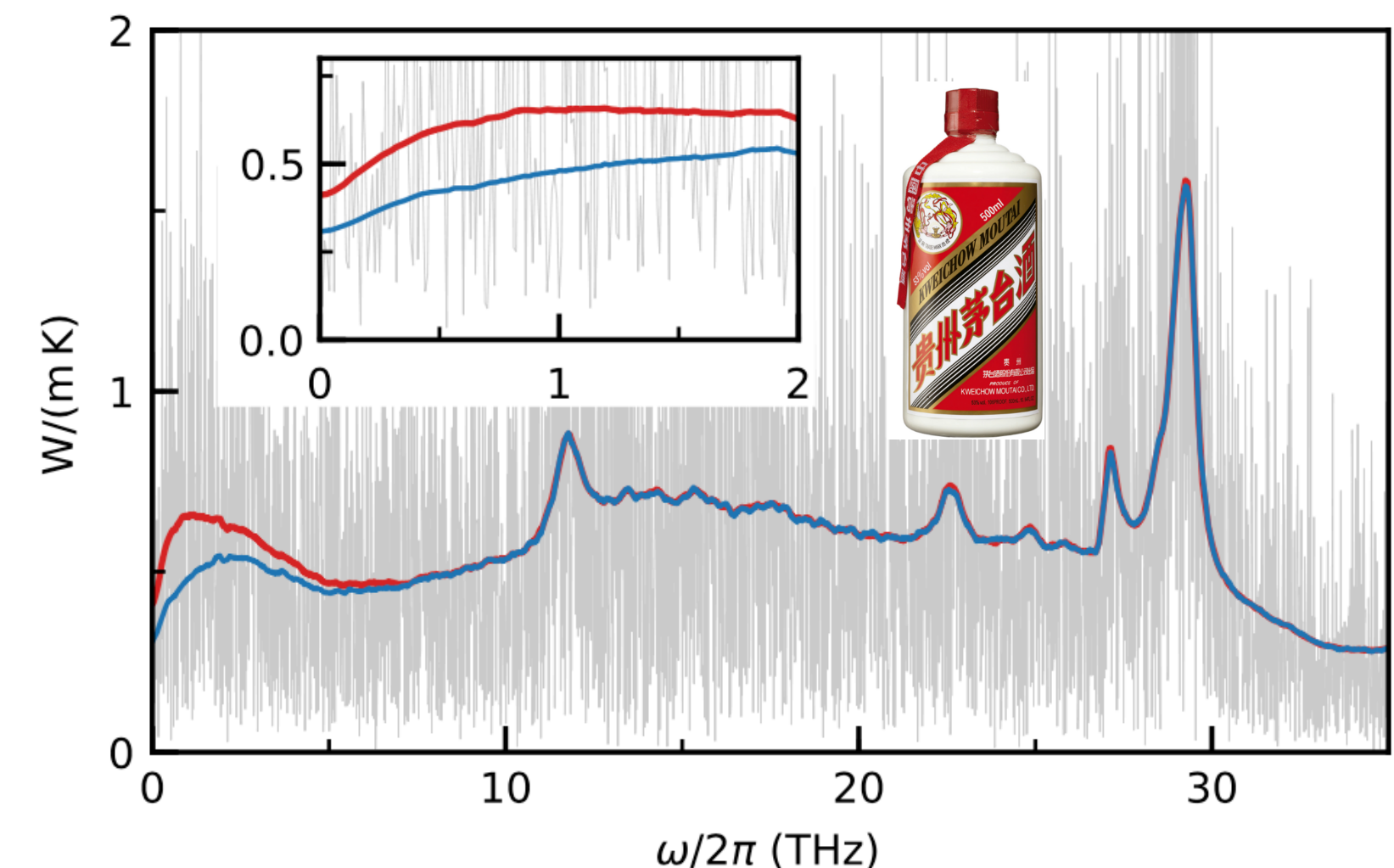
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do cepstral analysis on the Schur complement!



convective invariance & noise reduction

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

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



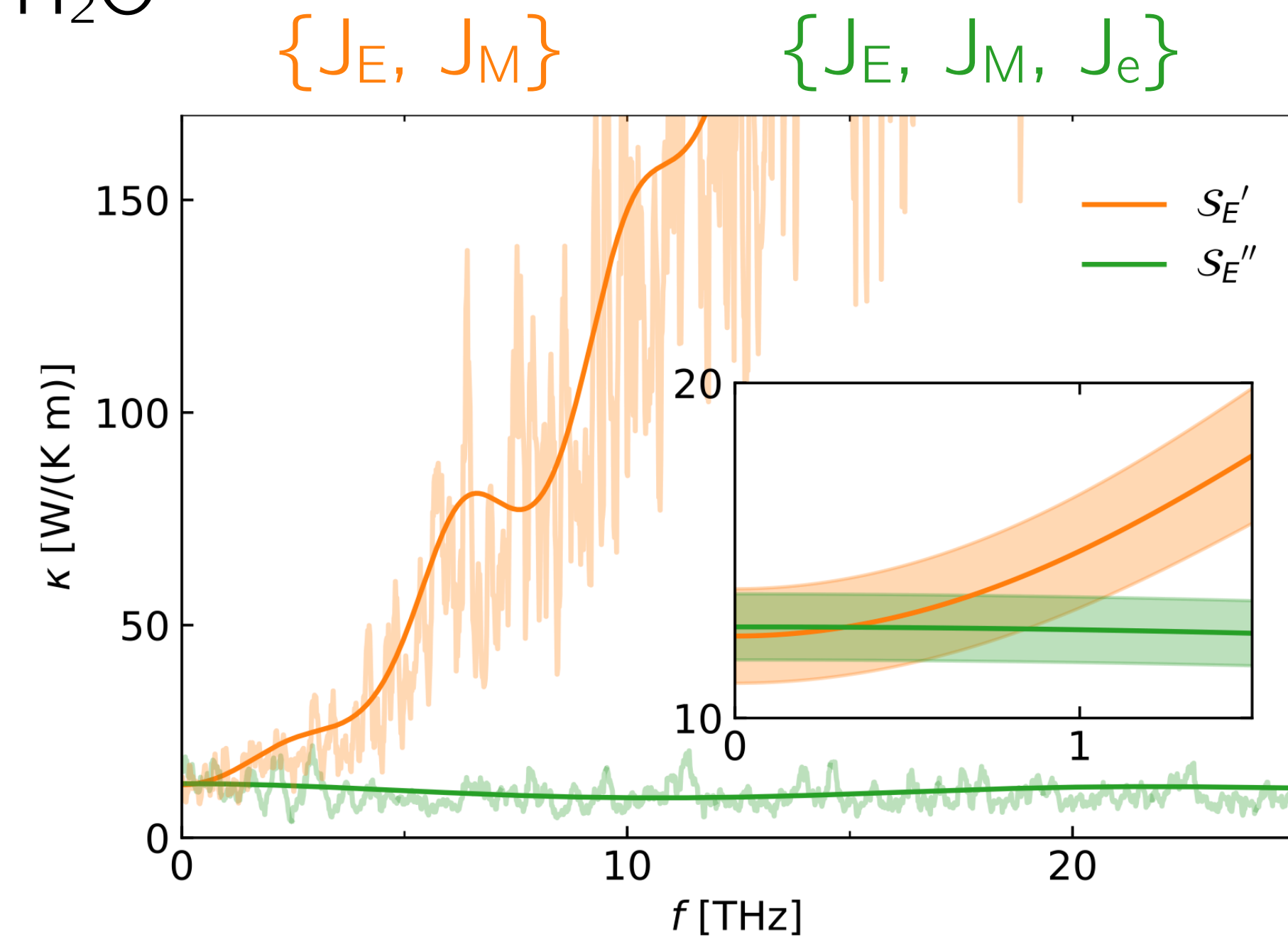
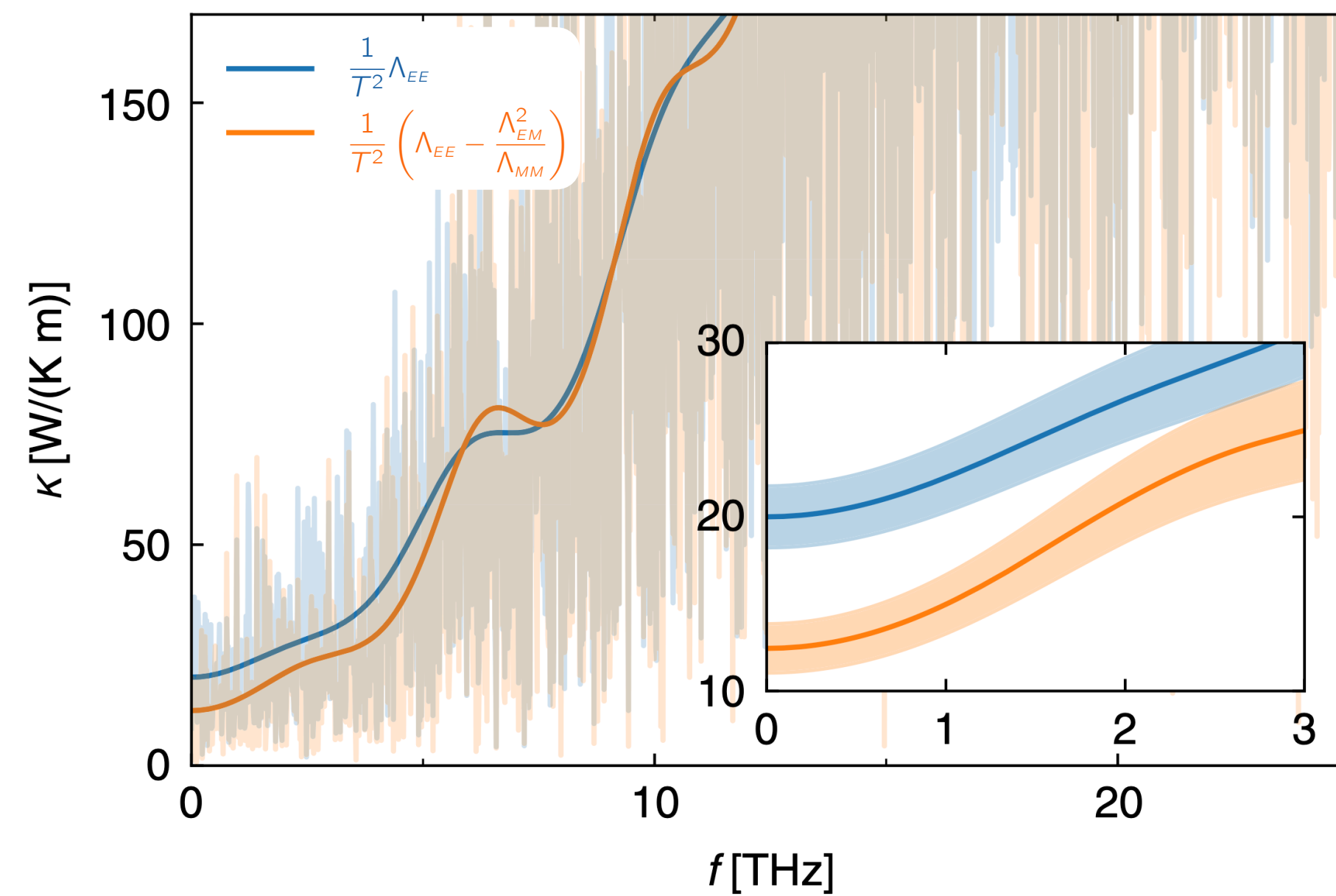
convective invariance & noise reduction

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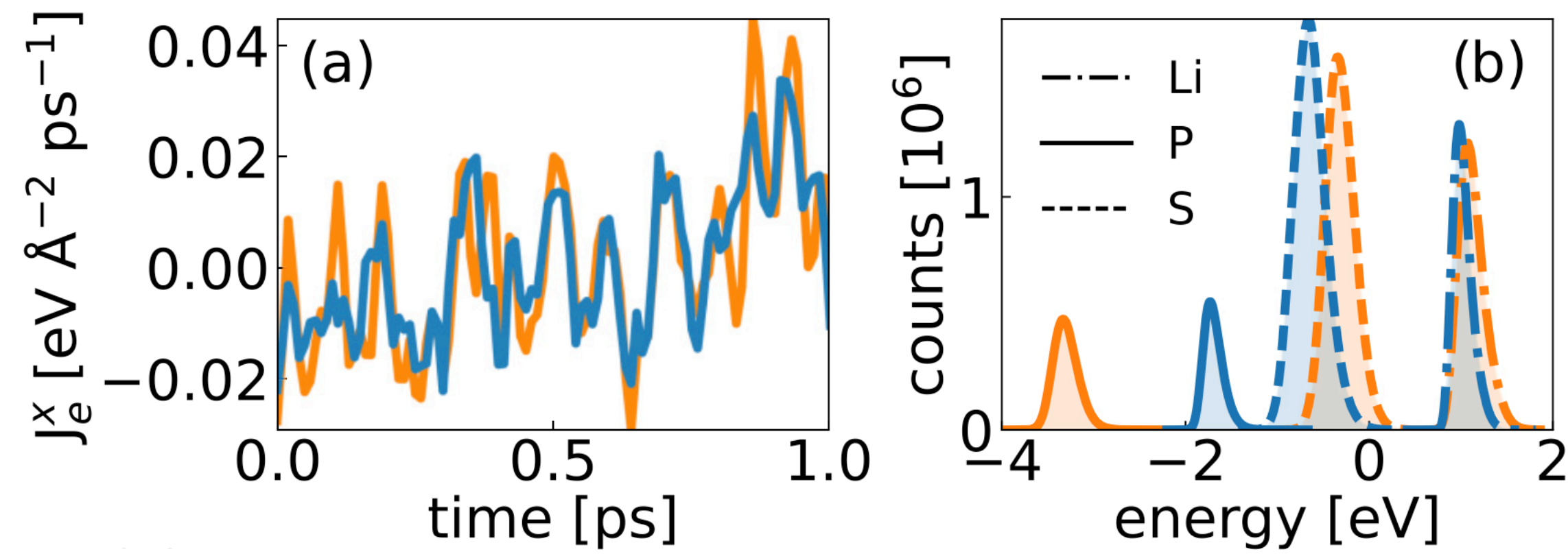
$$\kappa' = \frac{1}{T^2} \left(\Lambda'_{EE} - \frac{\Lambda'^2_{EM}}{\Lambda'_{MM}} \right)$$

$$= \kappa$$

super-ionic H₂O



impact on ML MD simulations

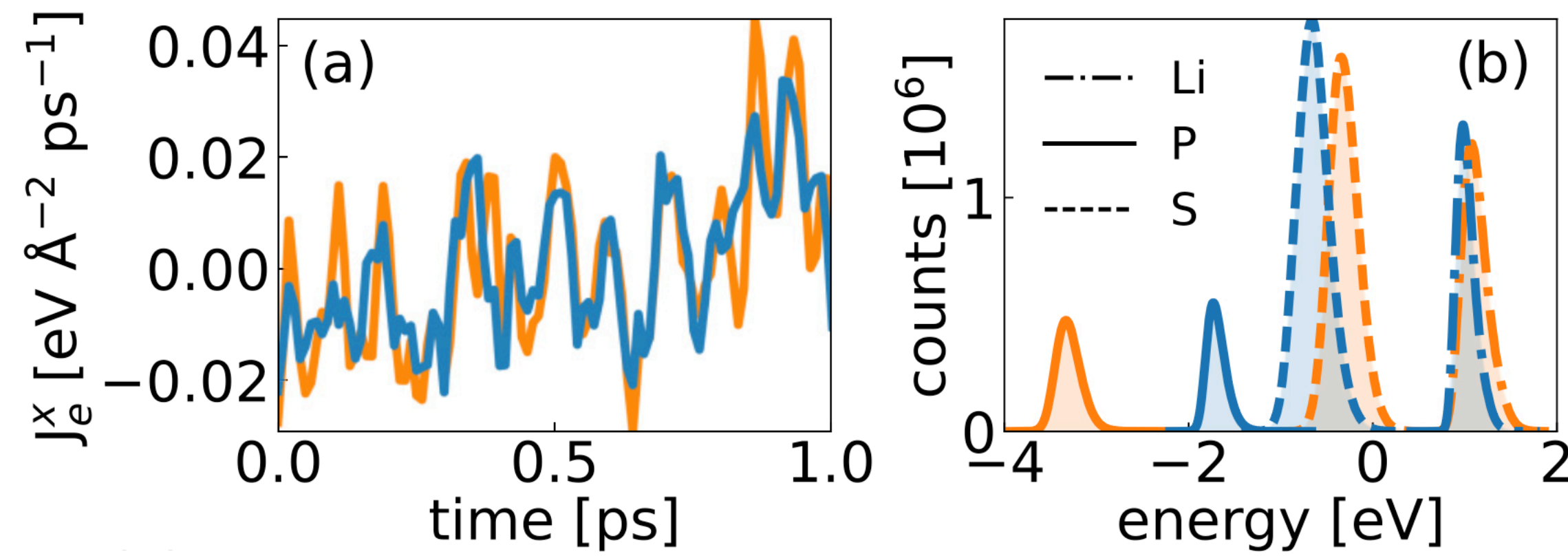


Li_3PS_4

ML model A

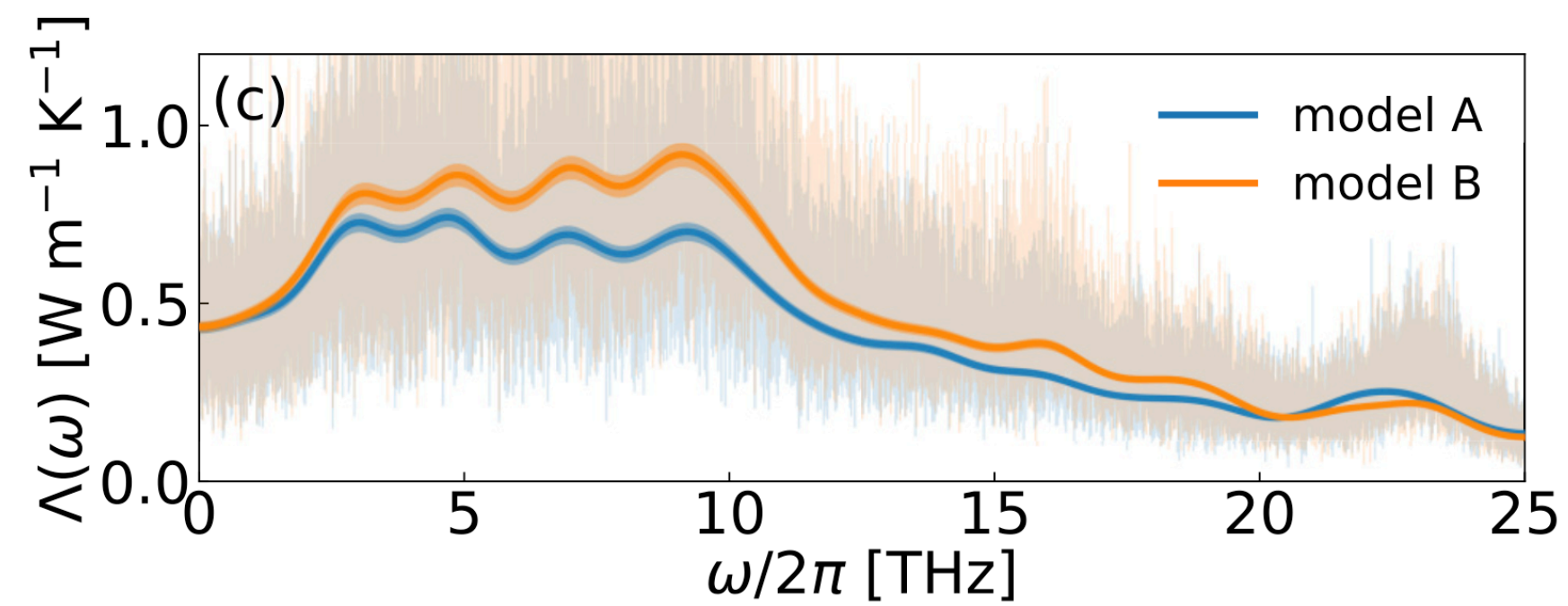
ML model B

impact on ML MD simulations

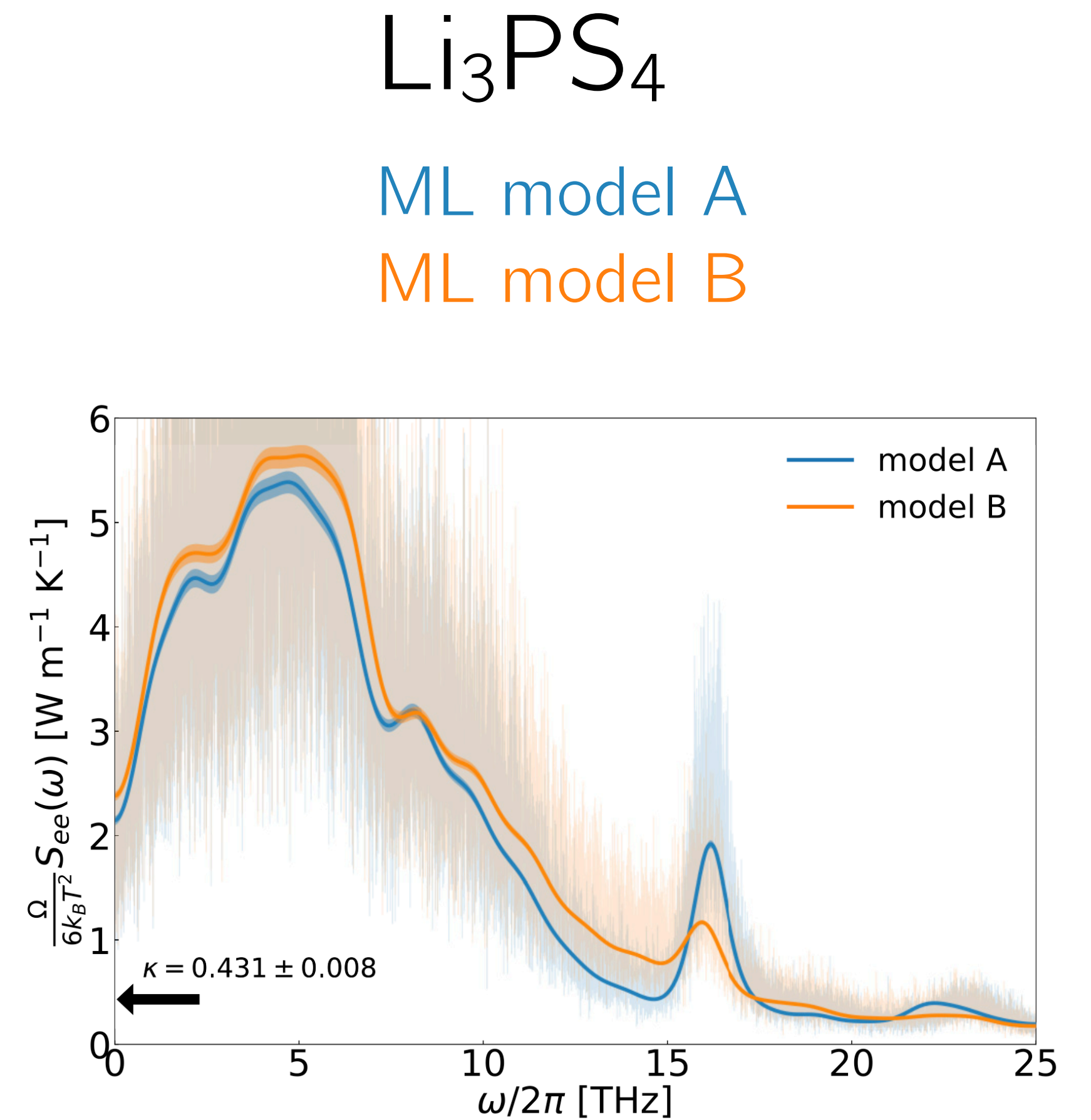
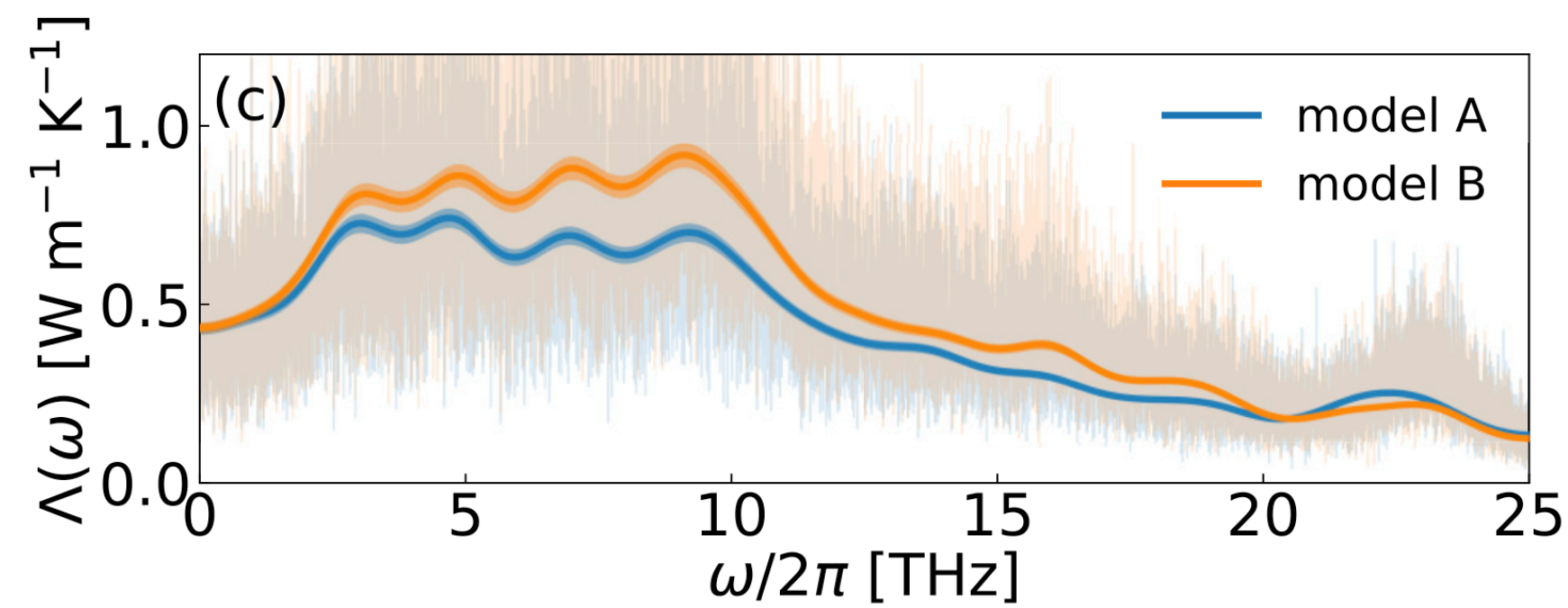
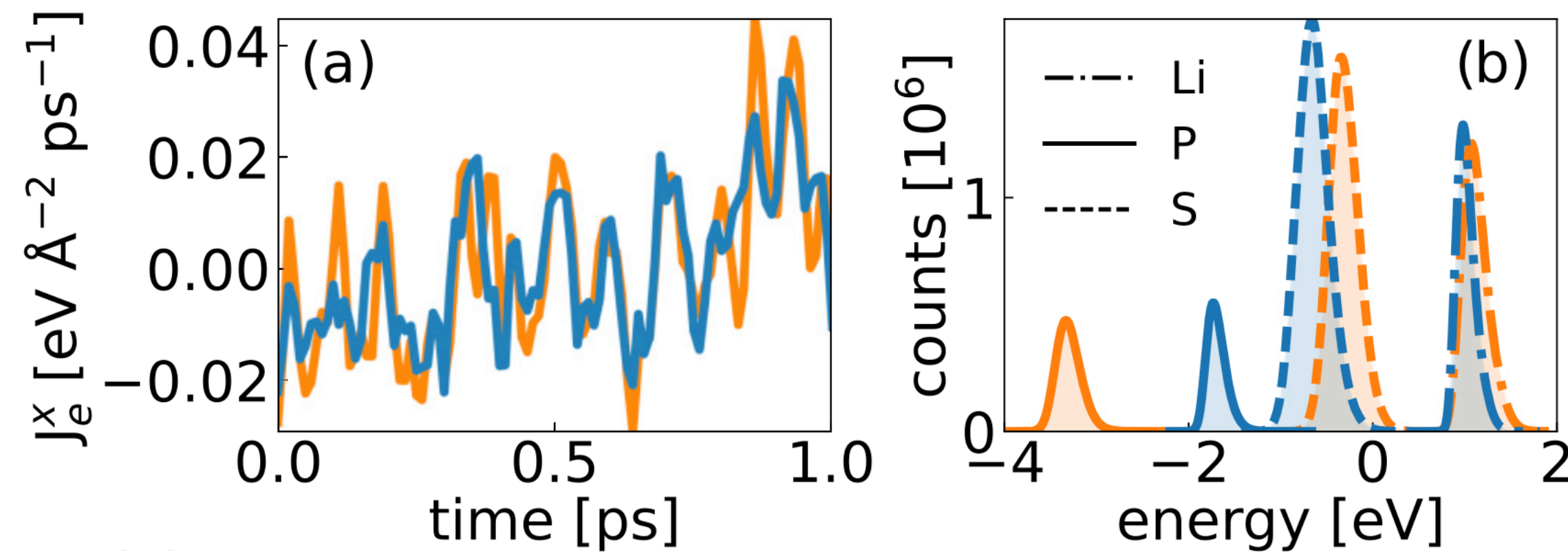


ML model A

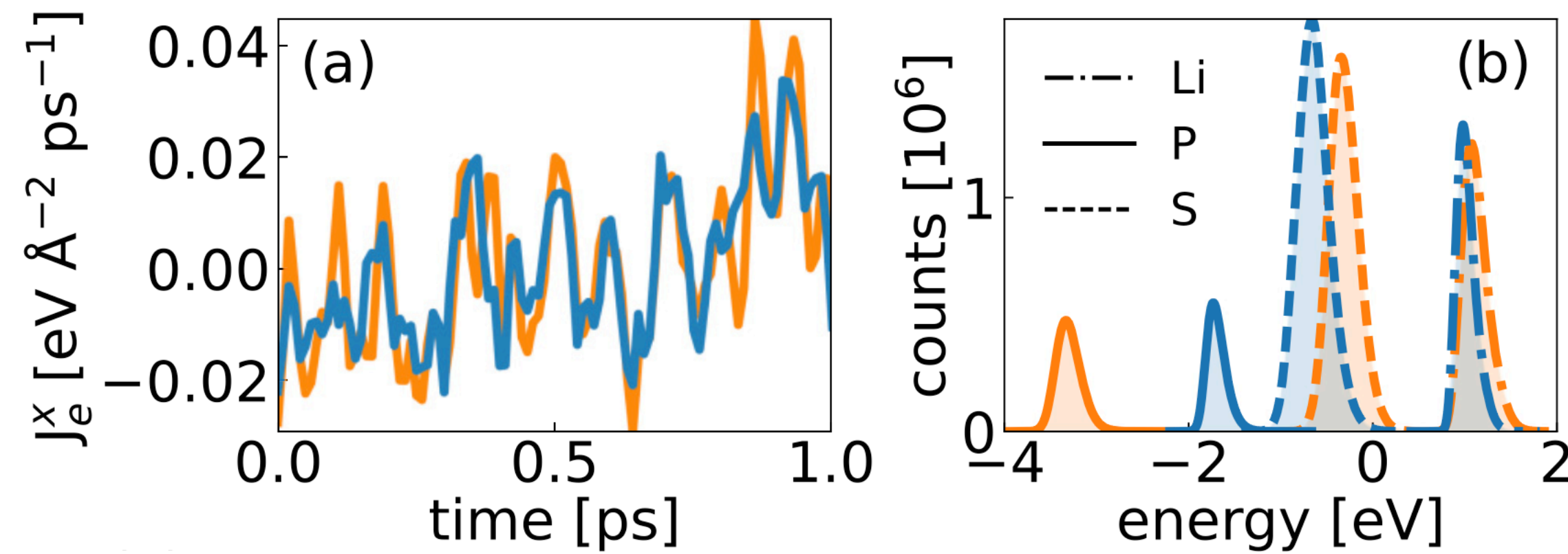
ML model B



impact on ML MD simulations



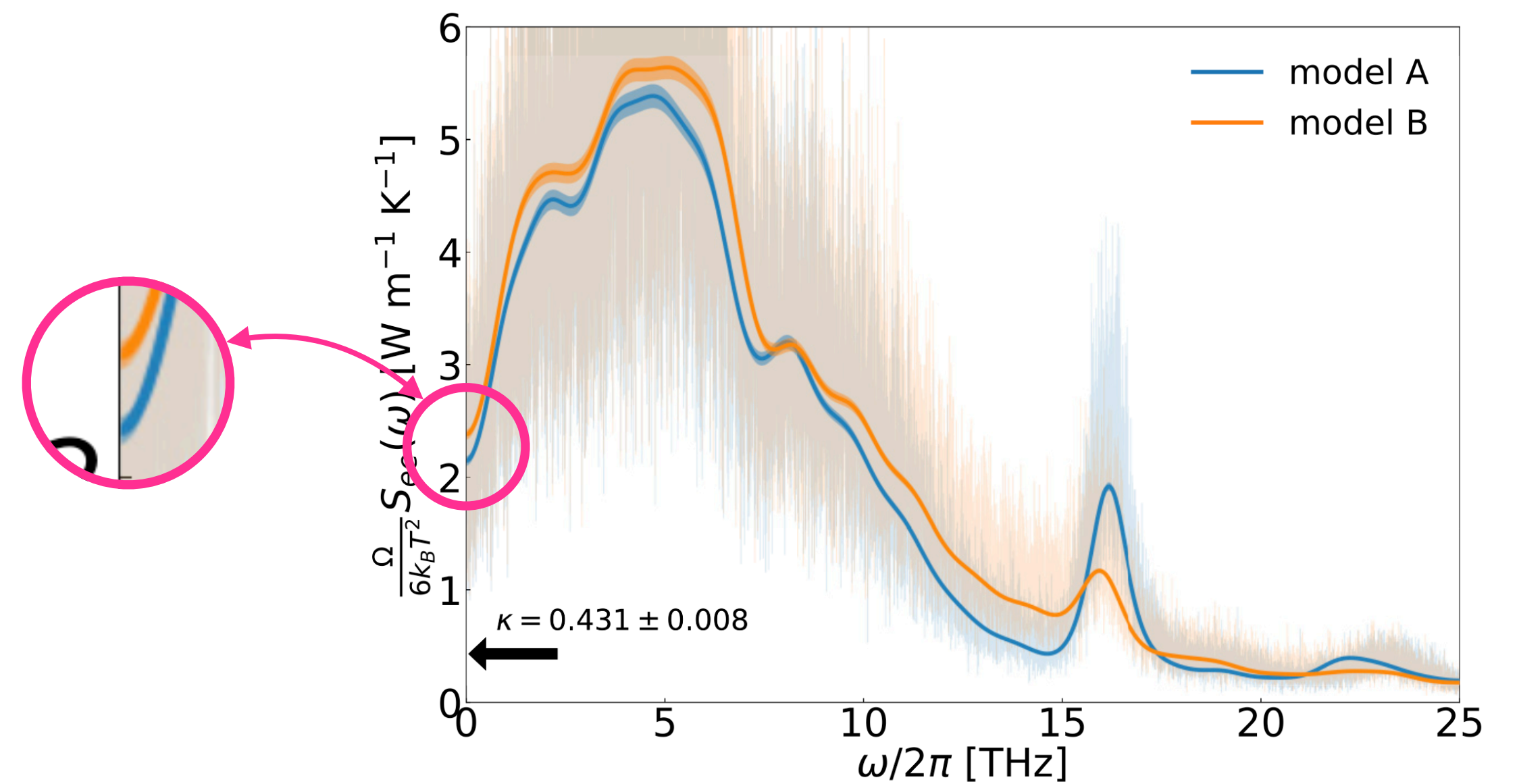
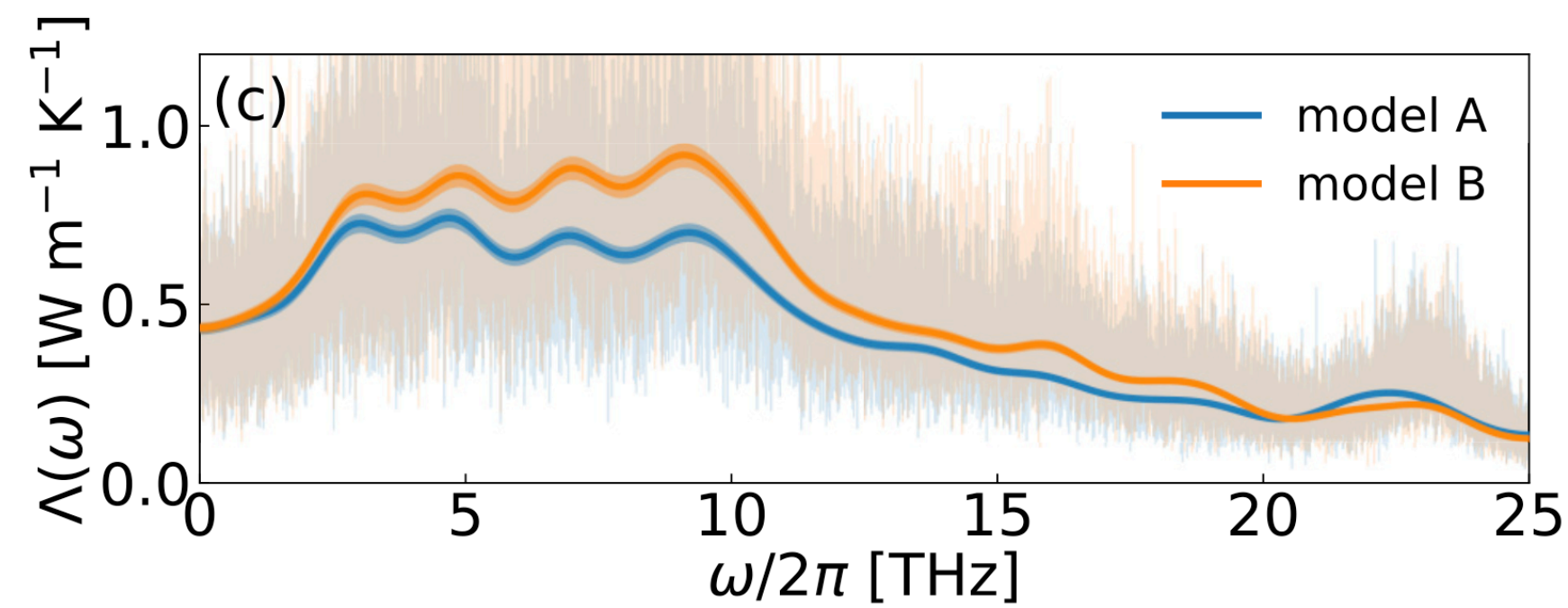
impact on ML MD simulations



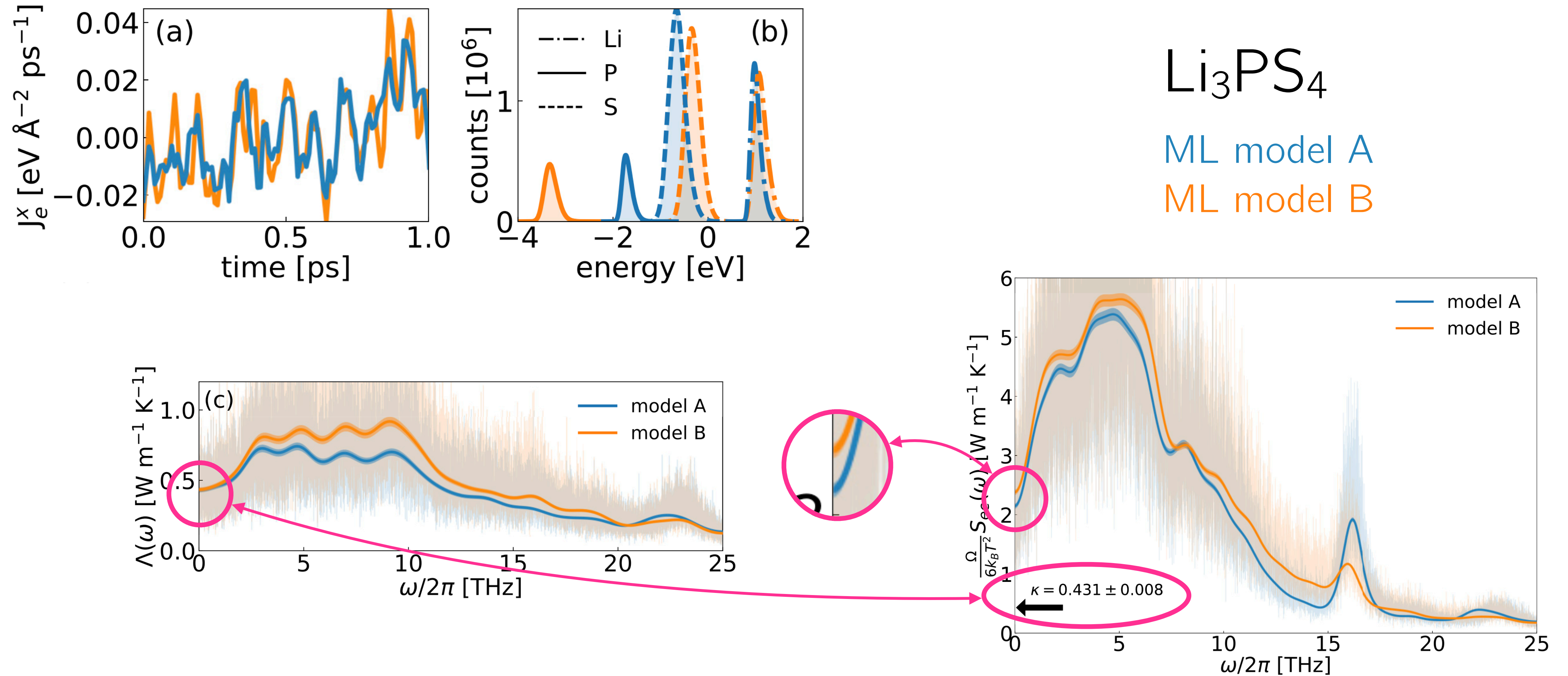
Li₃PS₄

ML model A

ML model B



impact on ML MD simulations



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



conclusions

- The definition of energy densities and currents is largely arbitrary, whereas transport coefficients are not.
- Adding any linear combination of mass currents to the energy current does not alter the estimate of the heat conductivity.
- These principles, together with cepstral analysis, can be used to effectively denoise the estimate of transport coefficients.
- In multi-component systems, energy/heat current autocorrelations alone do not yield the heat conductivity; a proper multivariate analysis is required.



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thanks to:



Aris Marcolongo



Loris Ercole



Riccardo Bertossa



Cesare Malosso



Leyla Isaeva



Giuseppe Barbalinardo



Davide Donadio



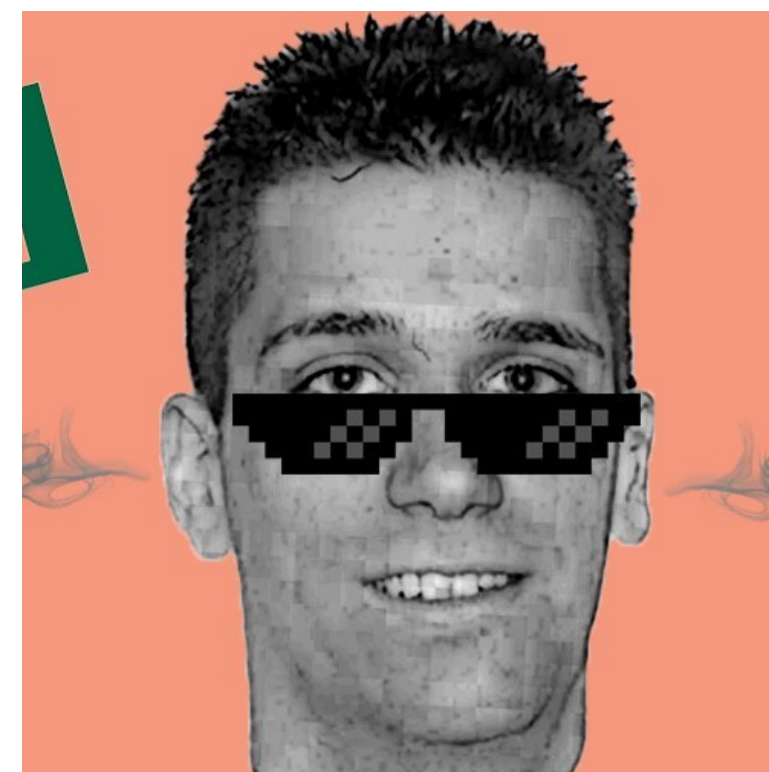
Alfredo Fiorentino



Federico Grasselli



Paolo Pegolo



Davide Tisi



Enrico Drigo

thanks to:



Aris Marcolongo



Loris Ercole



Riccardo Bertossa



Davide Tisi



Federico Grasselli



Paolo Pegolo

Microscopic theory and quantum simulation of atomic heat transport

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

SCIENTIFIC REPORTS | 7: 15835 | DOI:10.1038/s41598-017-15843-2

OPEN

Accurate thermal conductivities from optimally short molecular dynamics simulations

14 August 2017

Loris Ercole¹, Aris Marcolongo² & Stefano Baroni¹

PHYSICAL REVIEW LETTERS **122**, 255901 (2019)

Theory and Numerical Simulation of Heat Transport in Multicomponent Systems

Riccardo Bertossa,¹ Federico Grasselli,¹ Loris Ercole,^{1,*} and Stefano Baroni^{1,2,†}



Heat and charge transport in H₂O at ice-giant conditions from ab initio molecular dynamics simulations

Federico Grasselli^{1,4}, Lars Stixrude² & Stefano Baroni^{1,3}

Eur. Phys. J. B (2021) 94:160
<https://doi.org/10.1140/epjb/s10051-021-00152-5>

THE EUROPEAN
PHYSICAL JOURNAL B

Regular Article - Computational Methods

Invariance principles in the theory and computation of transport coefficients

Federico Grasselli^{1,a} and Stefano Baroni^{2,3}