gauge invariance of heat transport coefficients

fathoming heat transport from the struggle to simulate it

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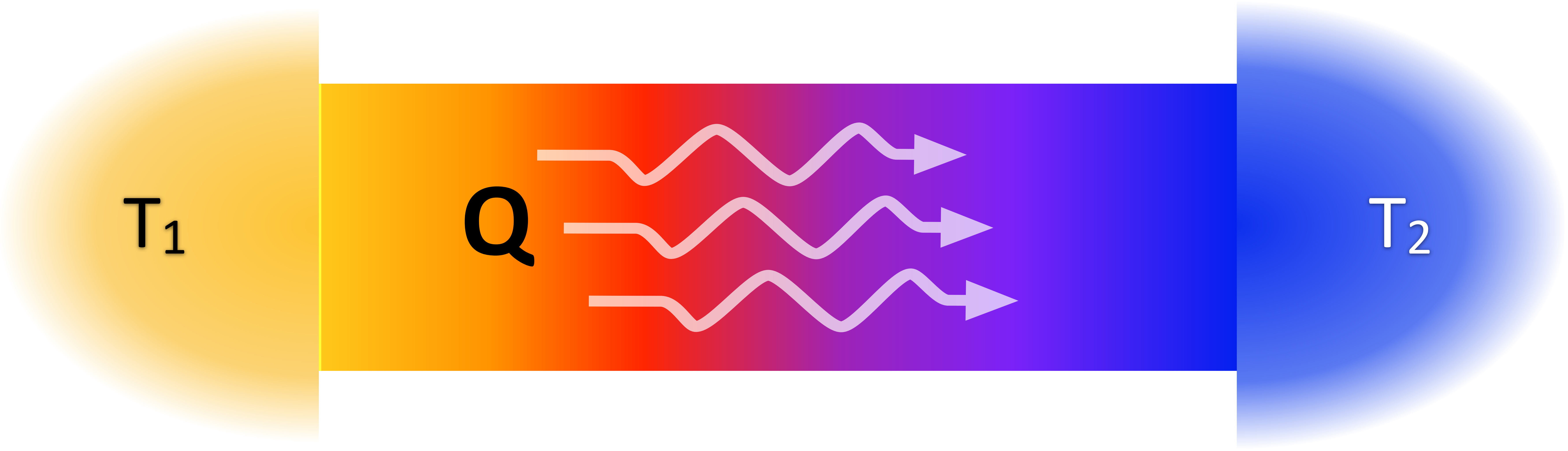
Trieste — Italy

CECAM *Mixed-Gen* webinar, December 15, 2022

what heat transport is all about



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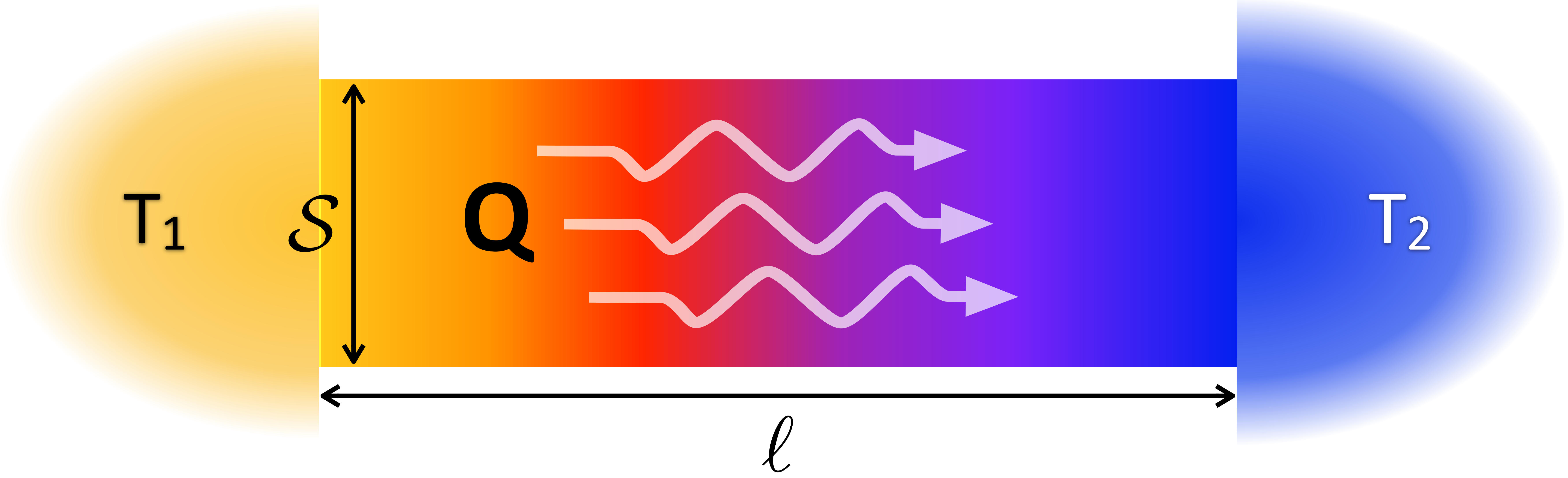
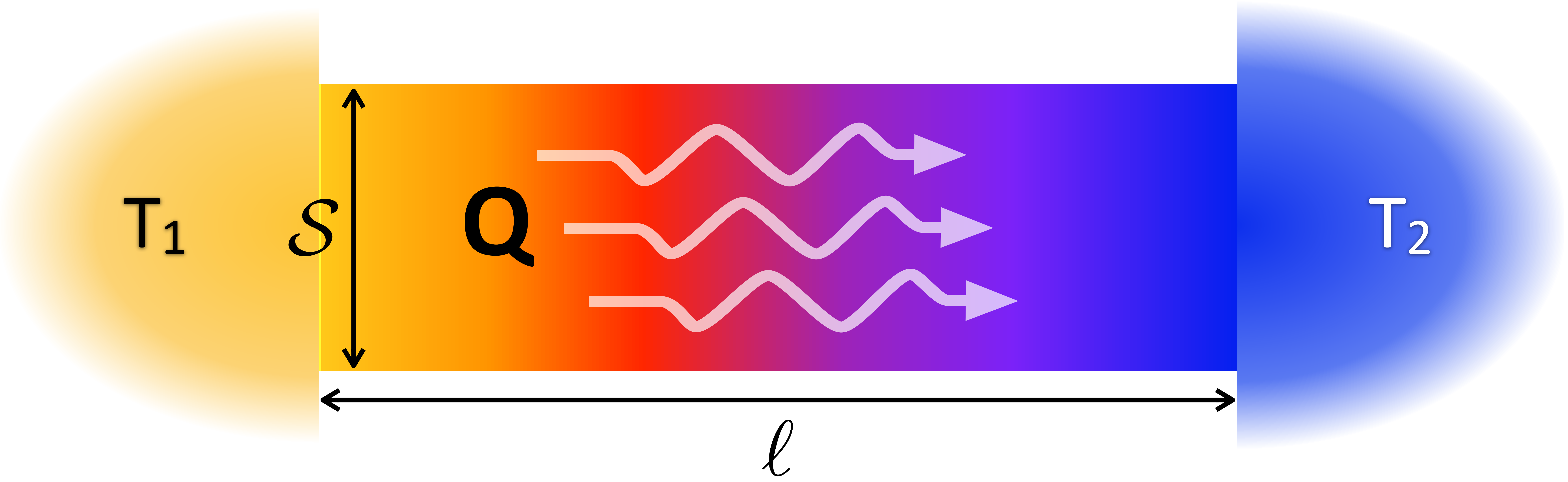


$$\frac{1}{\mathcal{S}}\frac{dQ}{dt} = -\kappa\frac{(T_2 - T_1)}{\ell}$$

what heat transport is all about



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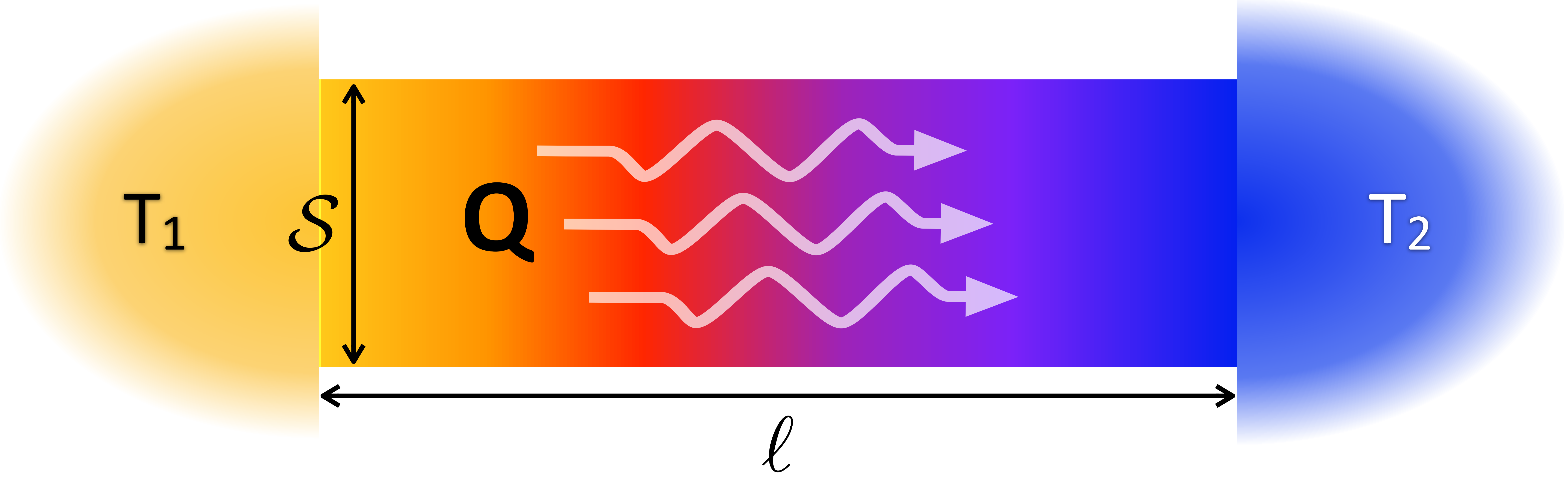

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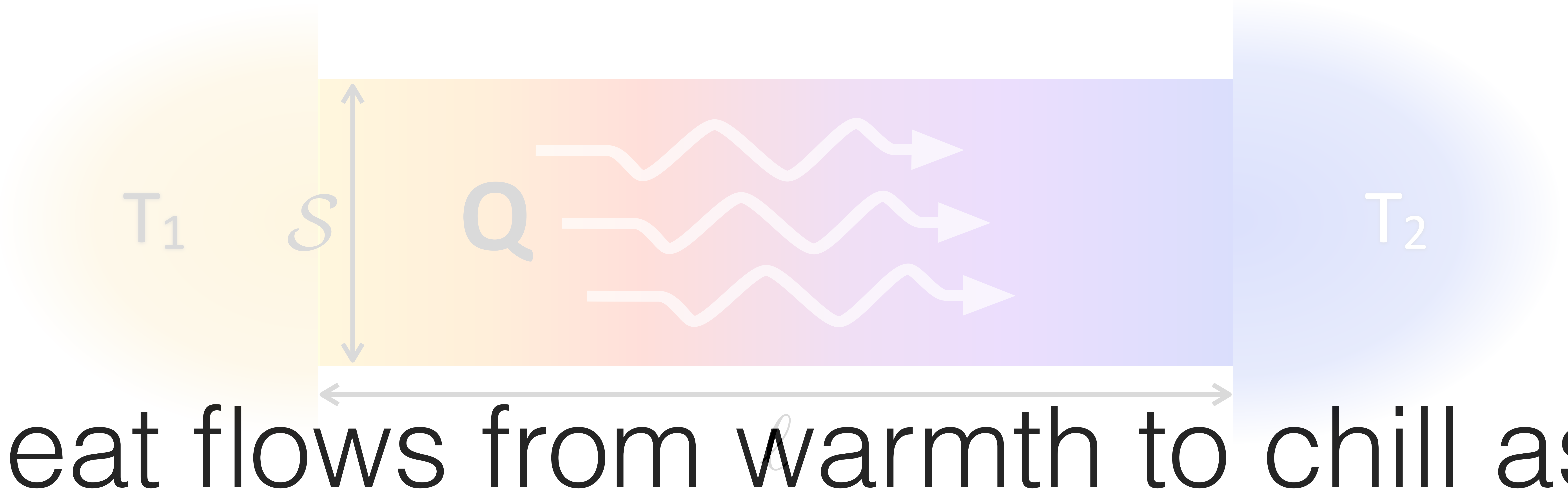

heat flows from warmth to chill as time flows from the past to the future

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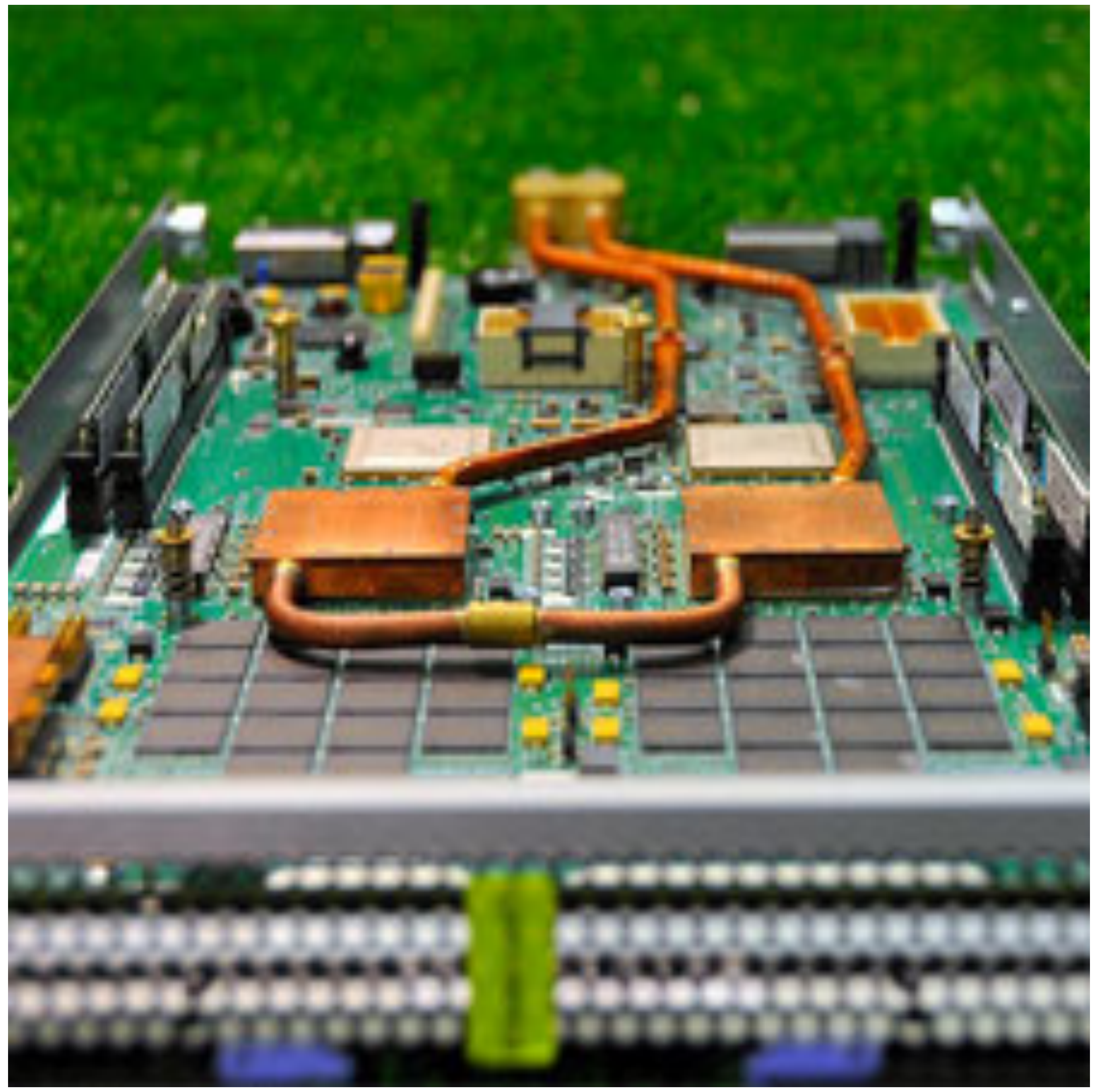
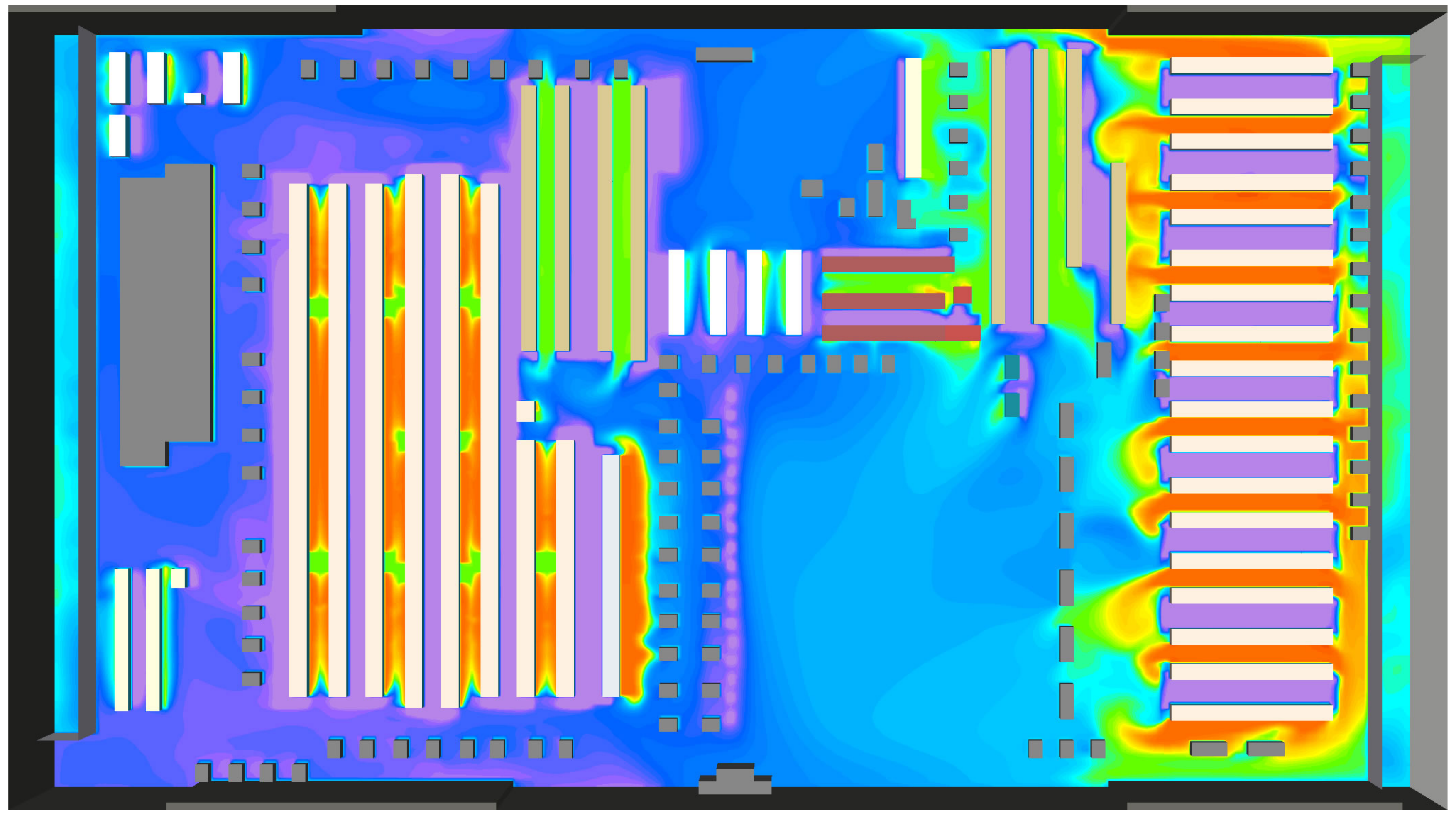
why should we care?

energy saving

heat dissipation





heat shielding

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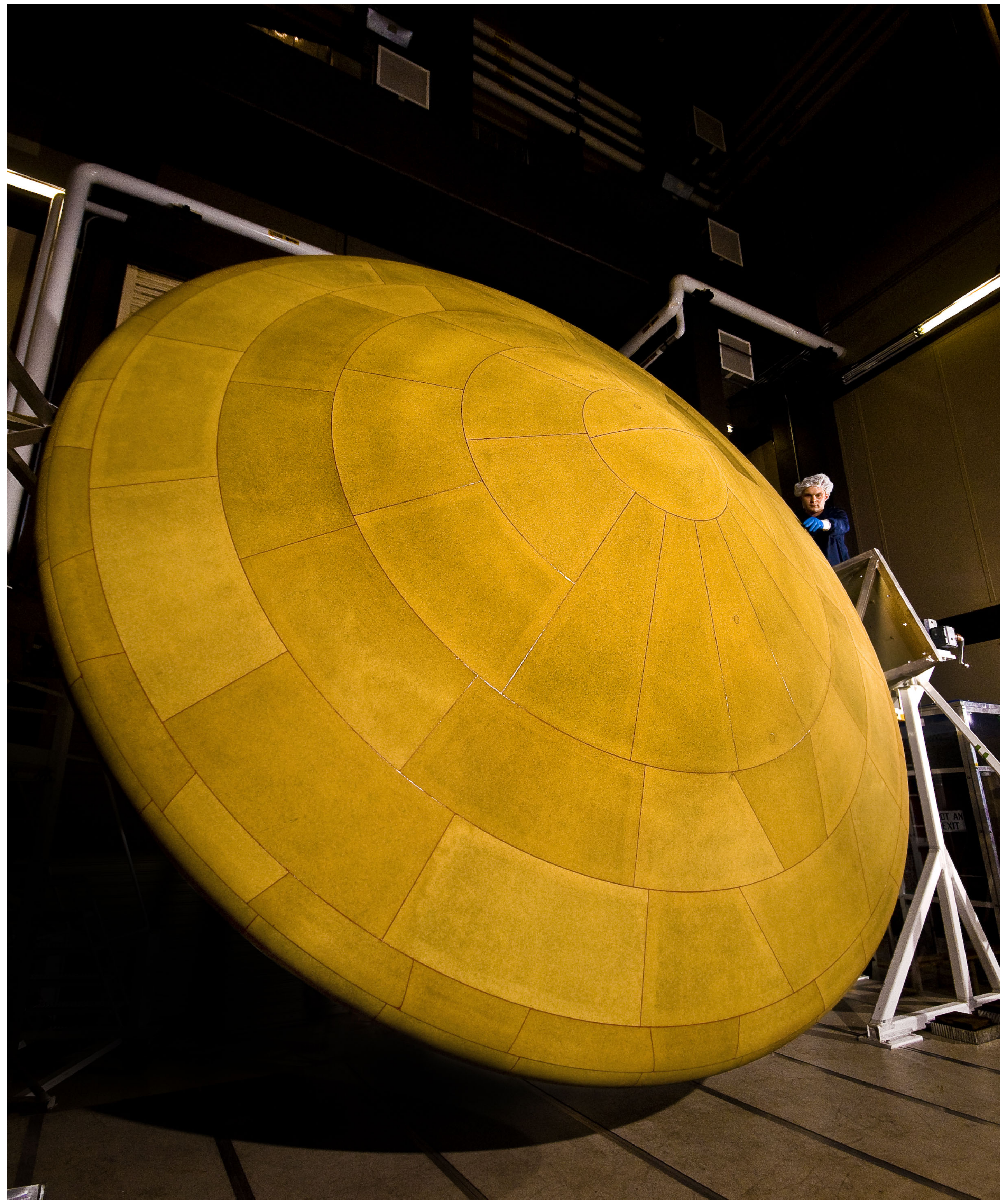
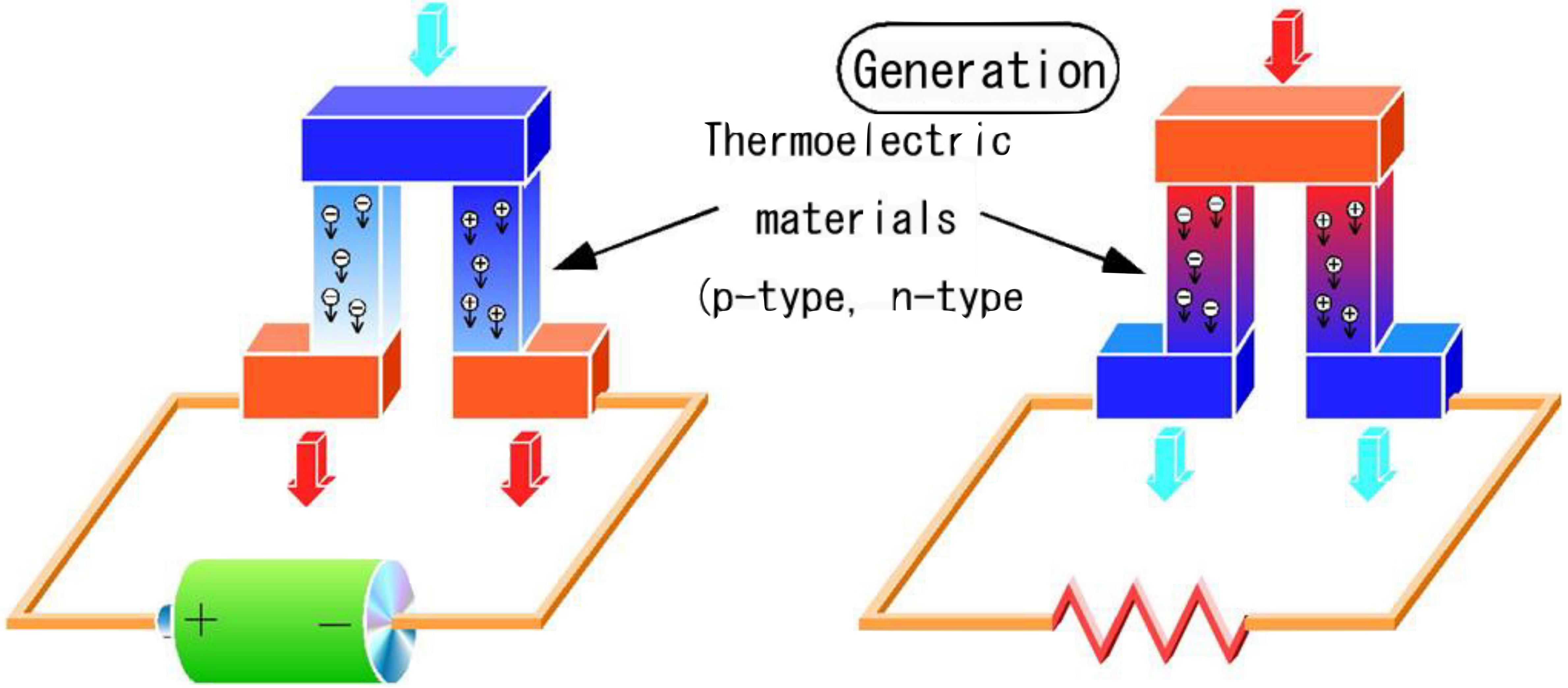
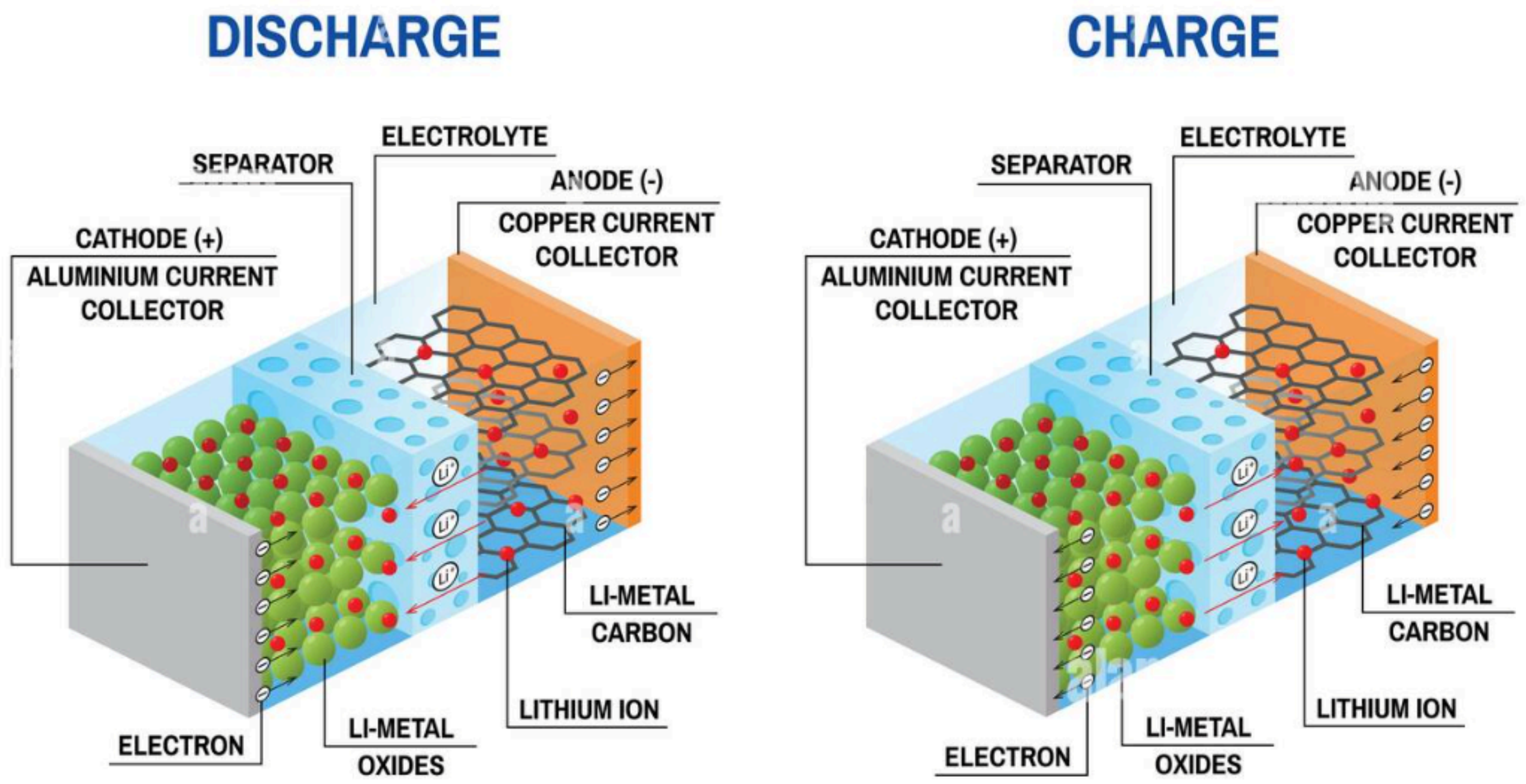
heat shielding

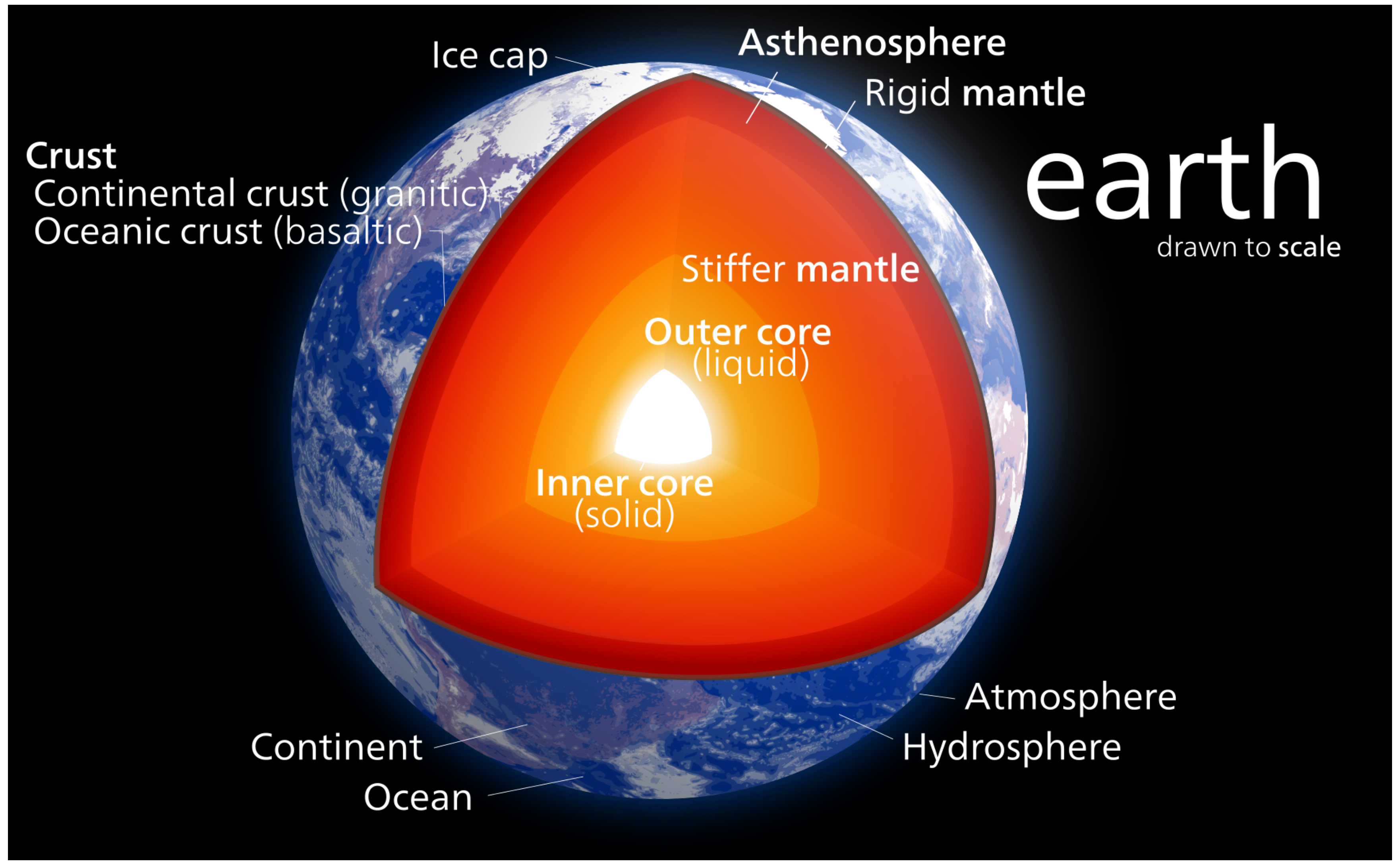


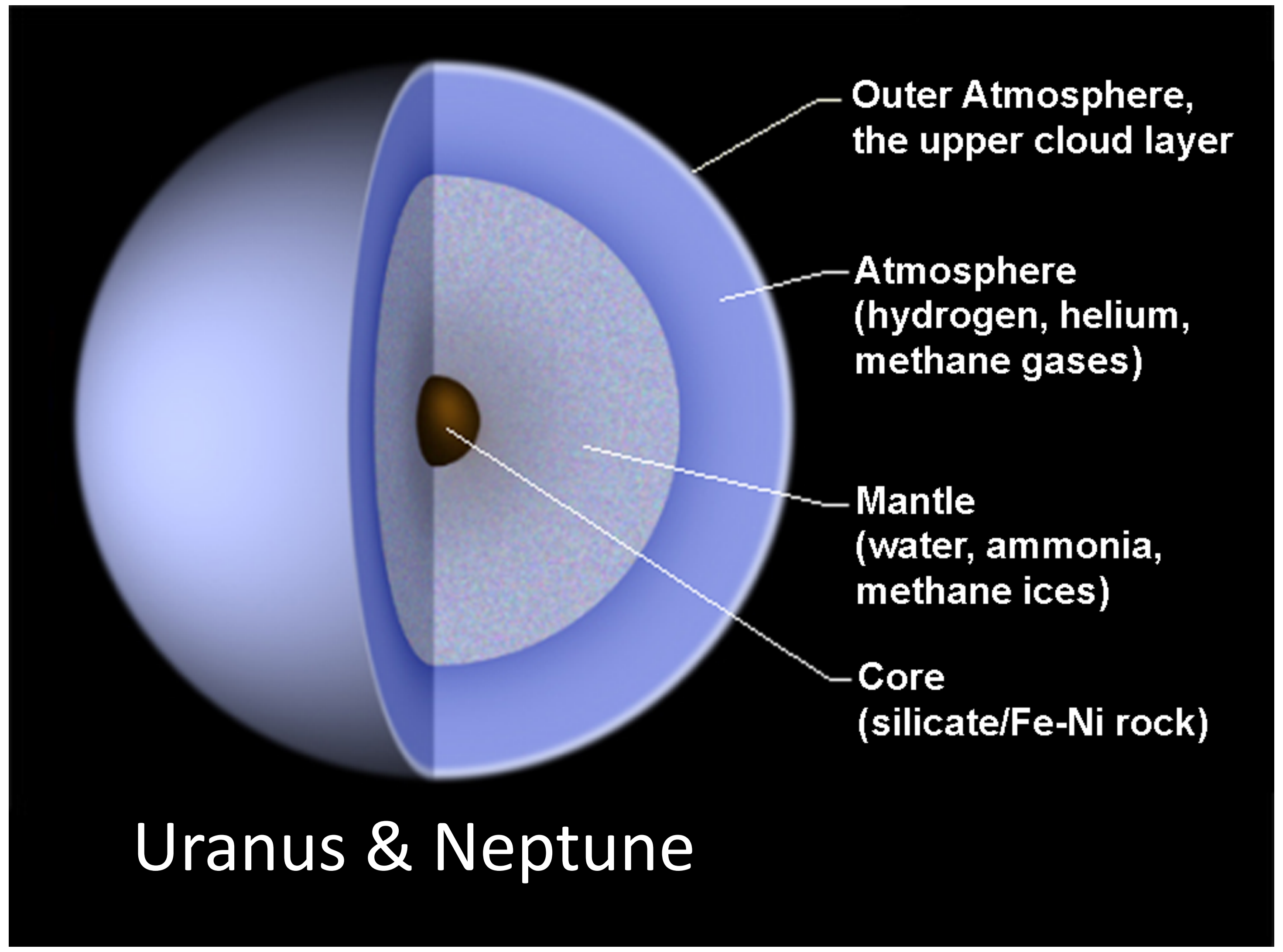
energy conversion & storage

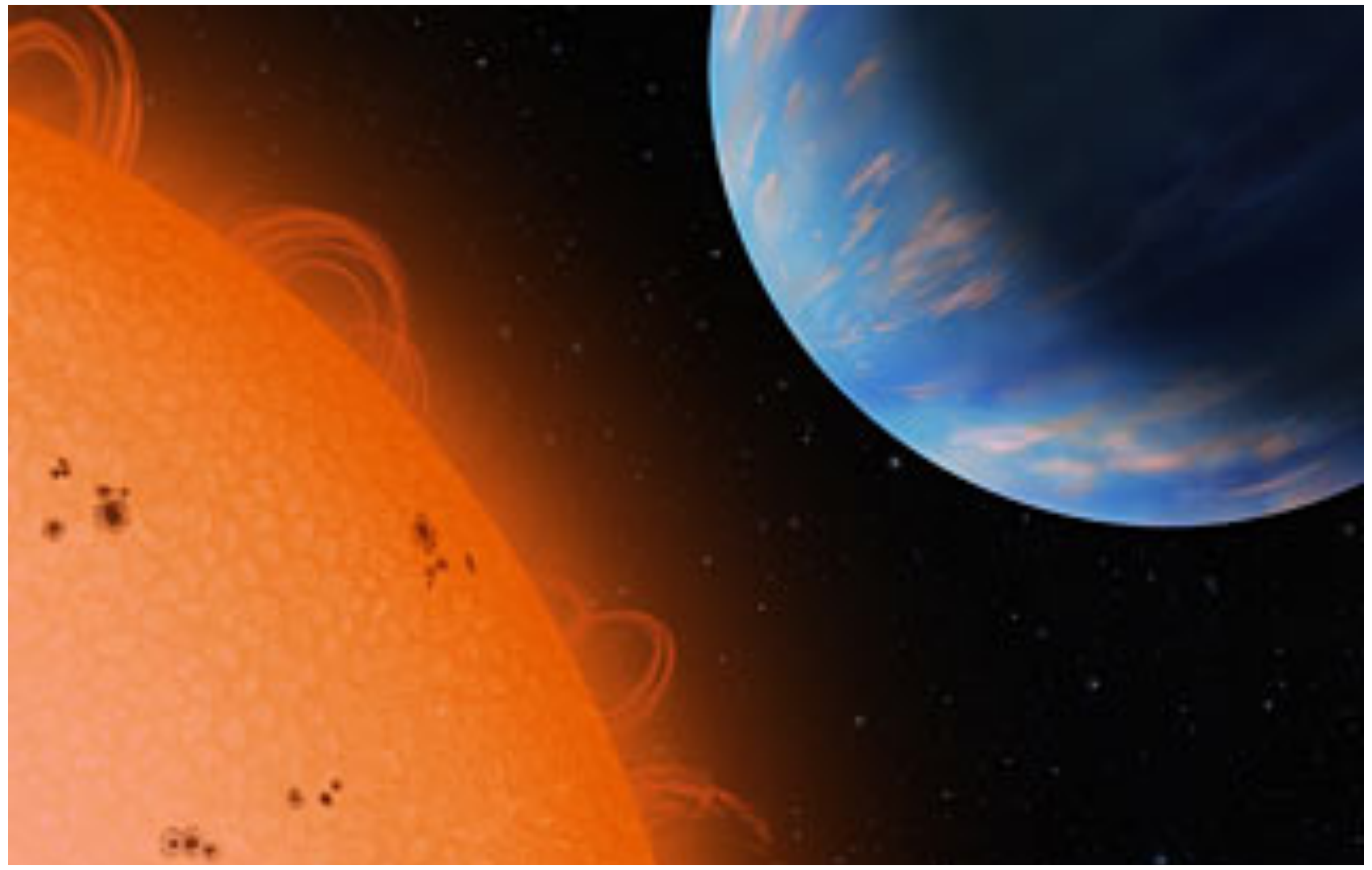


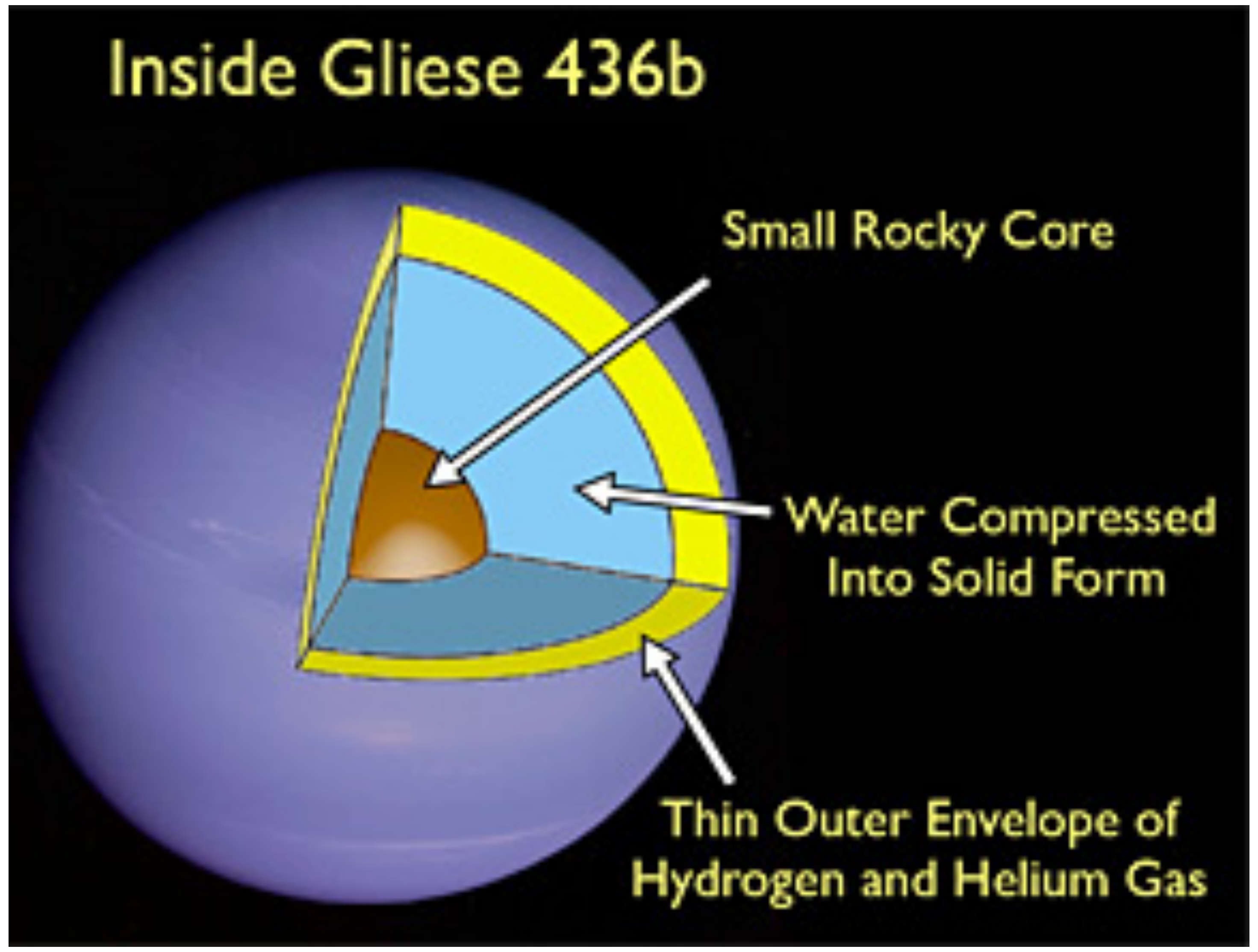


planetary sciences









why should we care?

- energy saving and heat dissipation
- heat shielding
- energy harvesting, scavenging, and storage
- earth and planetary sciences
- …

why should we care?

- … because it is important and still poorly understood *the linear-response theory of transport*

$$\boldsymbol{J} = \lambda \boldsymbol{F}$$

the linear-response theory of transport

$$\boldsymbol{J} = \lambda \boldsymbol{F}$$

charge transport

$$\boldsymbol{J}_{\mathcal{Q}} = \sum_I q_I \boldsymbol{V}_I$$

$$\boldsymbol{F}_{\mathcal{Q}} = -\nabla \phi$$

$\lambda =$ electric conductivity

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energy transport

$$\boldsymbol{J}_{\mathcal{E}} = \sum_I e_I \boldsymbol{V}_I + \frac{1}{2} \sum_{I \neq J} (\boldsymbol{V}_I \cdot \boldsymbol{F}_{IJ})(\boldsymbol{R}_I - \boldsymbol{R}_J)$$
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$$\lambda \propto \int_0^\infty \langle \boldsymbol{J}(t) \boldsymbol{J}(0) \rangle dt \qquad \text{Green-Kubo}$$

the linear-response theory of transport

$$\boldsymbol{J} = \lambda \boldsymbol{F}$$

Green-Kubo

$$\begin{aligned}\lambda &\propto \int_0^\infty \langle \boldsymbol{J}(t)\boldsymbol{J}(0)\rangle dt \\ &= \int \mathrm{P}^\circ(\Gamma_0)\left[\int_0^\infty \boldsymbol{J}(\Gamma_t)\boldsymbol{J}(\Gamma_0)dt\right] d\Gamma_0 \\ &= \lim_{T\to\infty}\int_0^T \left[\frac{1}{T-t}\int_0^{T-t} \boldsymbol{J}(\Gamma_{t+t'})\boldsymbol{J}(\Gamma_{t'})dt'\right] dt\end{aligned}$$

the linear-response theory of transport

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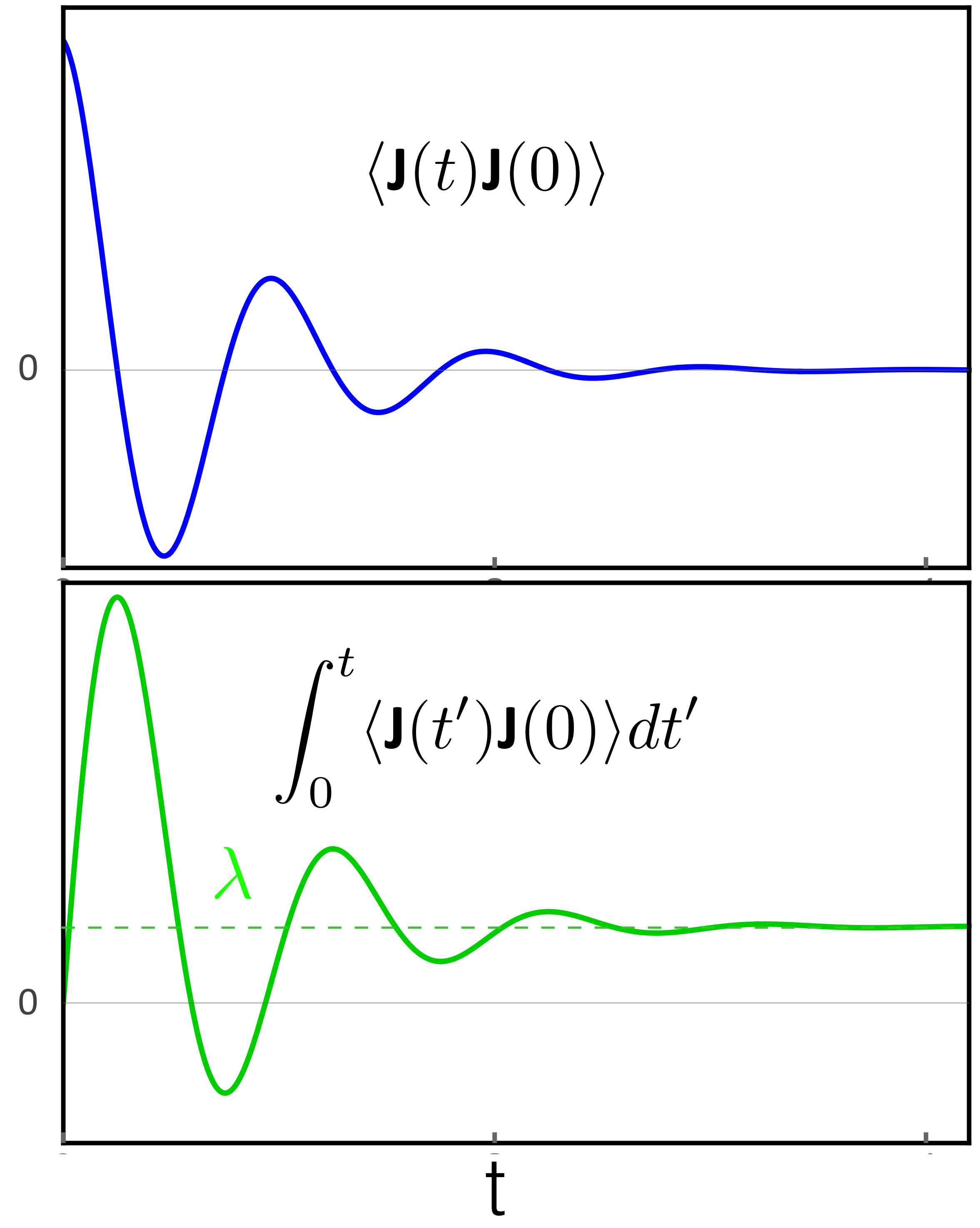
Green-Kubo

$$\lambda \propto \underbrace{\int_0^\infty \langle \boldsymbol{J}(t)\boldsymbol{J}(0)\rangle dt}_{\langle \boldsymbol{J}^2\rangle \tau}$$



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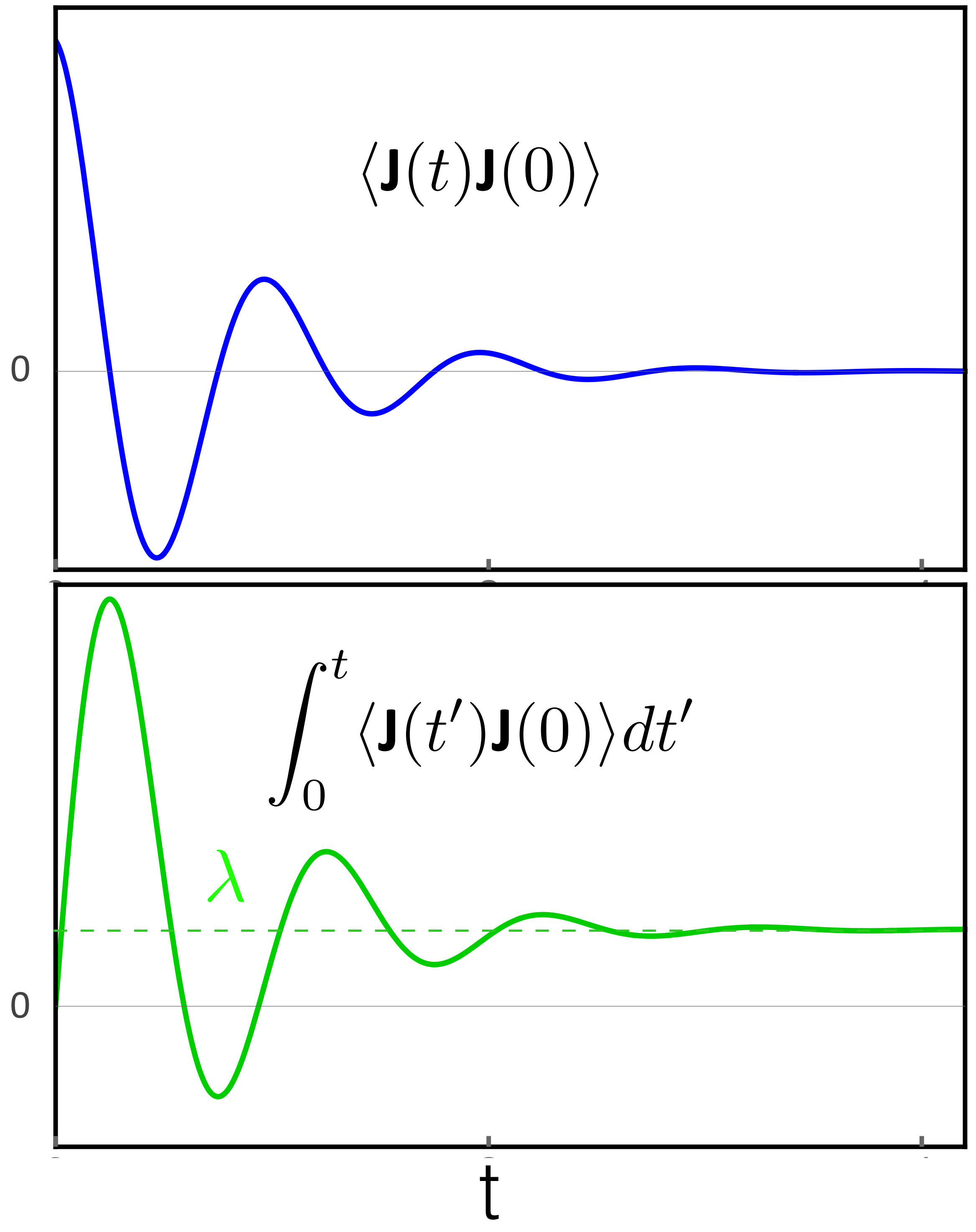
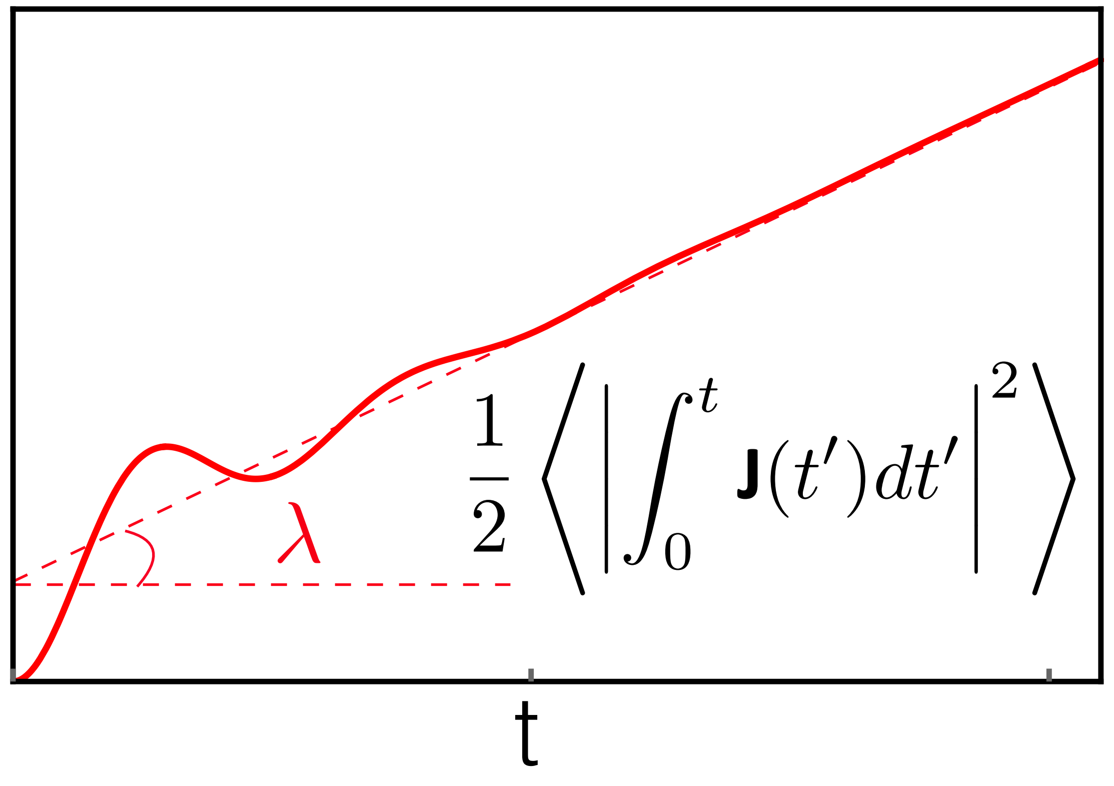
Einstein-Helfand

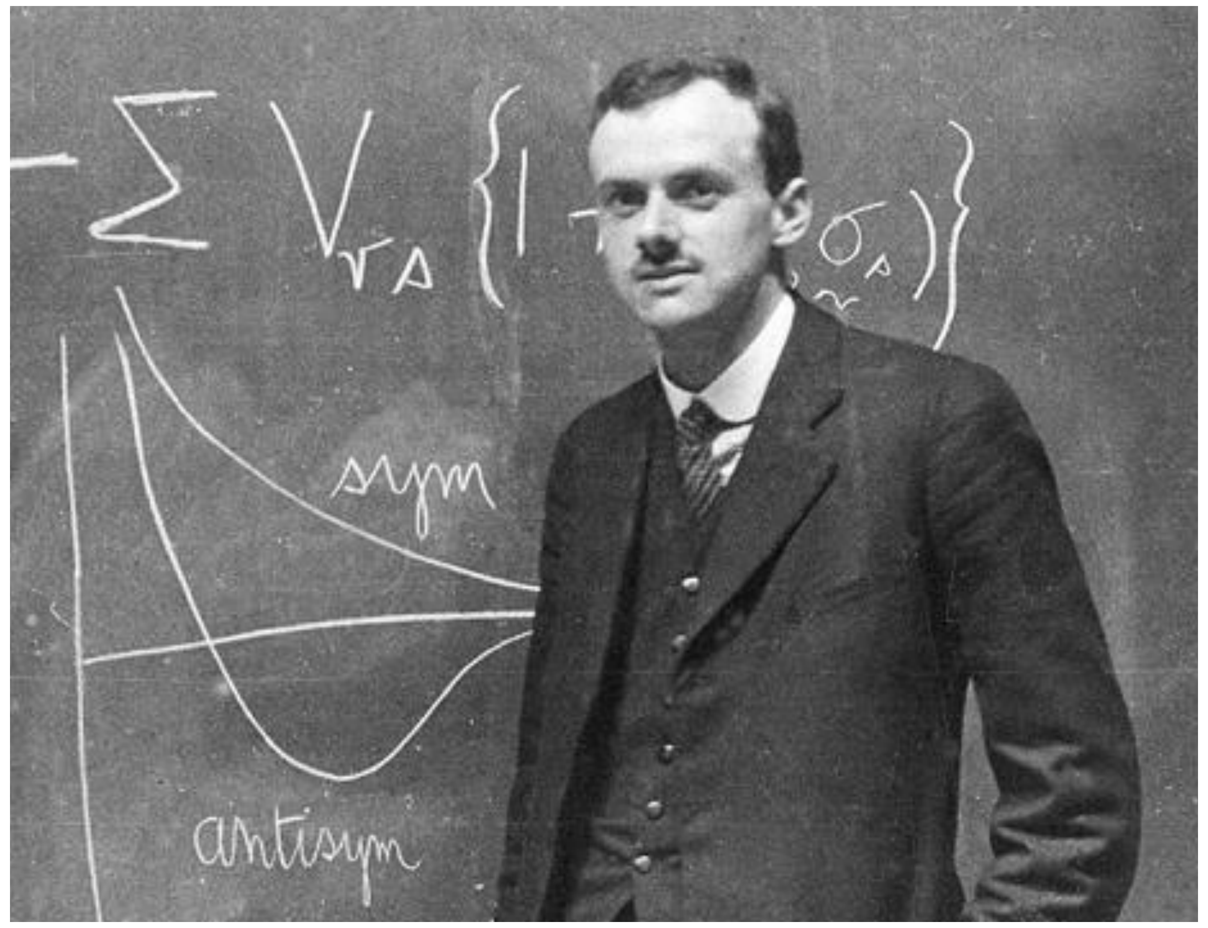
$$\lambda \propto \lim_{t\to\infty} \frac{1}{2t} \mathrm{var}\left[\int_0^t \boldsymbol{J}(t')dt'\right]$$





materials properties from first principles

The underlying physical laws necessary for a large part of physics and all of chemistry are completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble.



P.A.M. Dirac, 1929

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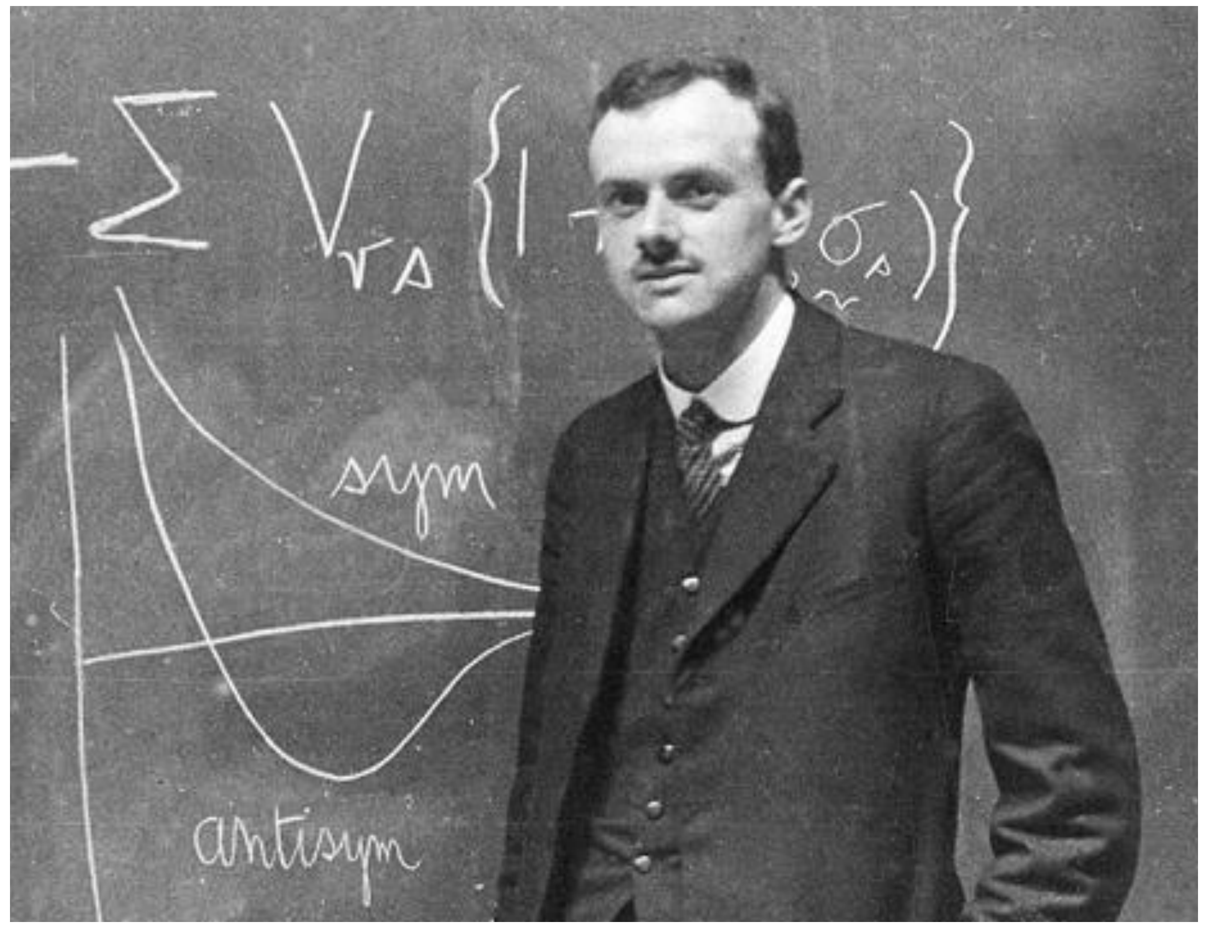

P.A.M. Dirac, 1929

Dirac's challenge has been answered in [our] field [… using] new physical models [… and] computers.

M.L. Cohen, 2015

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*
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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.

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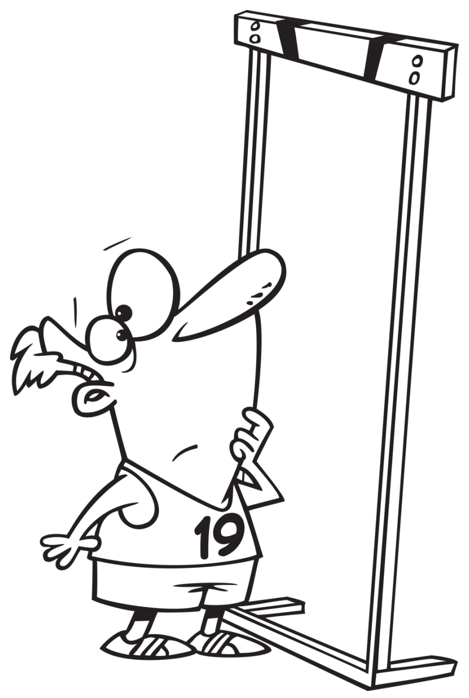
how come?



how come?

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

insights from classical mechanics

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

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

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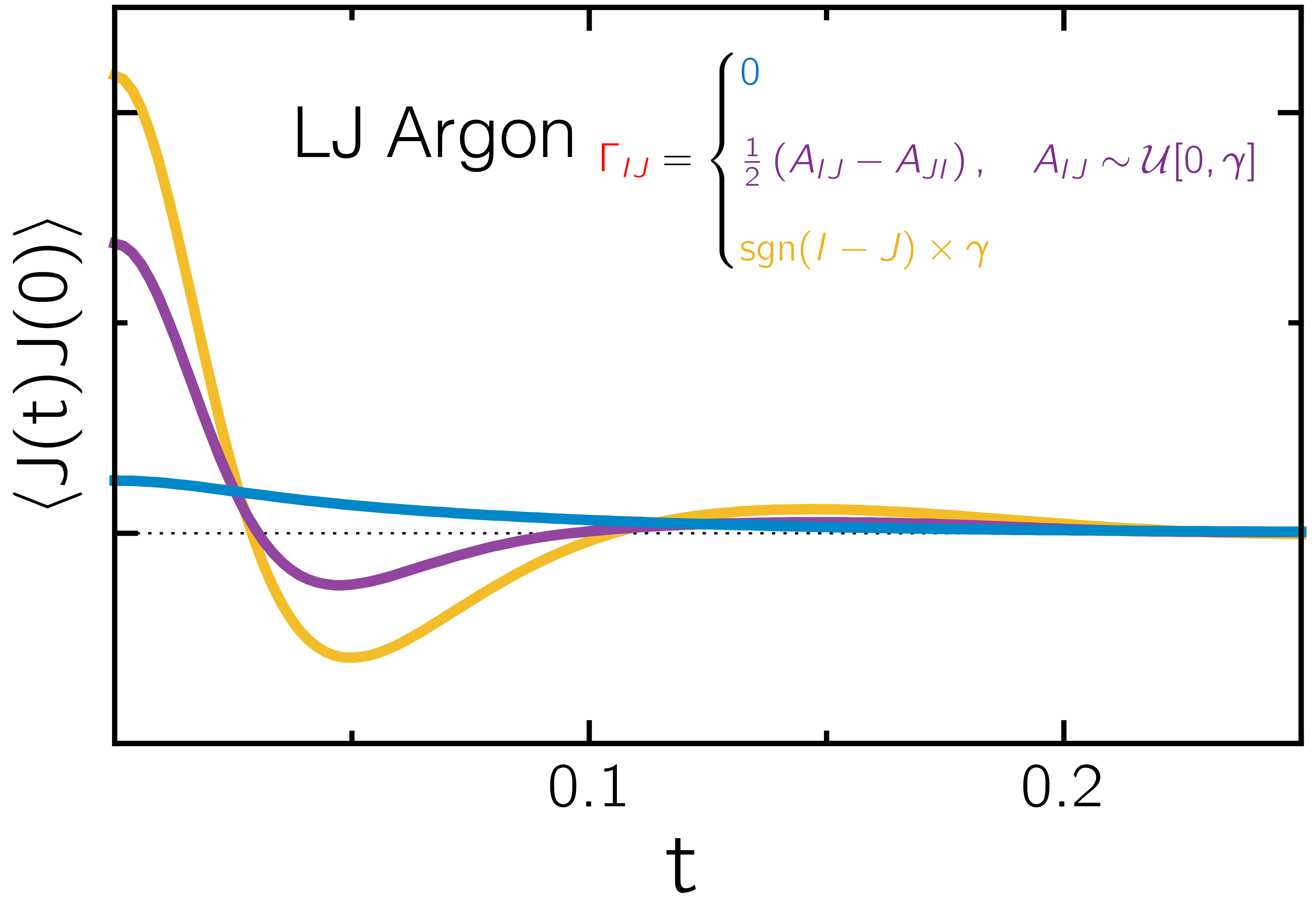

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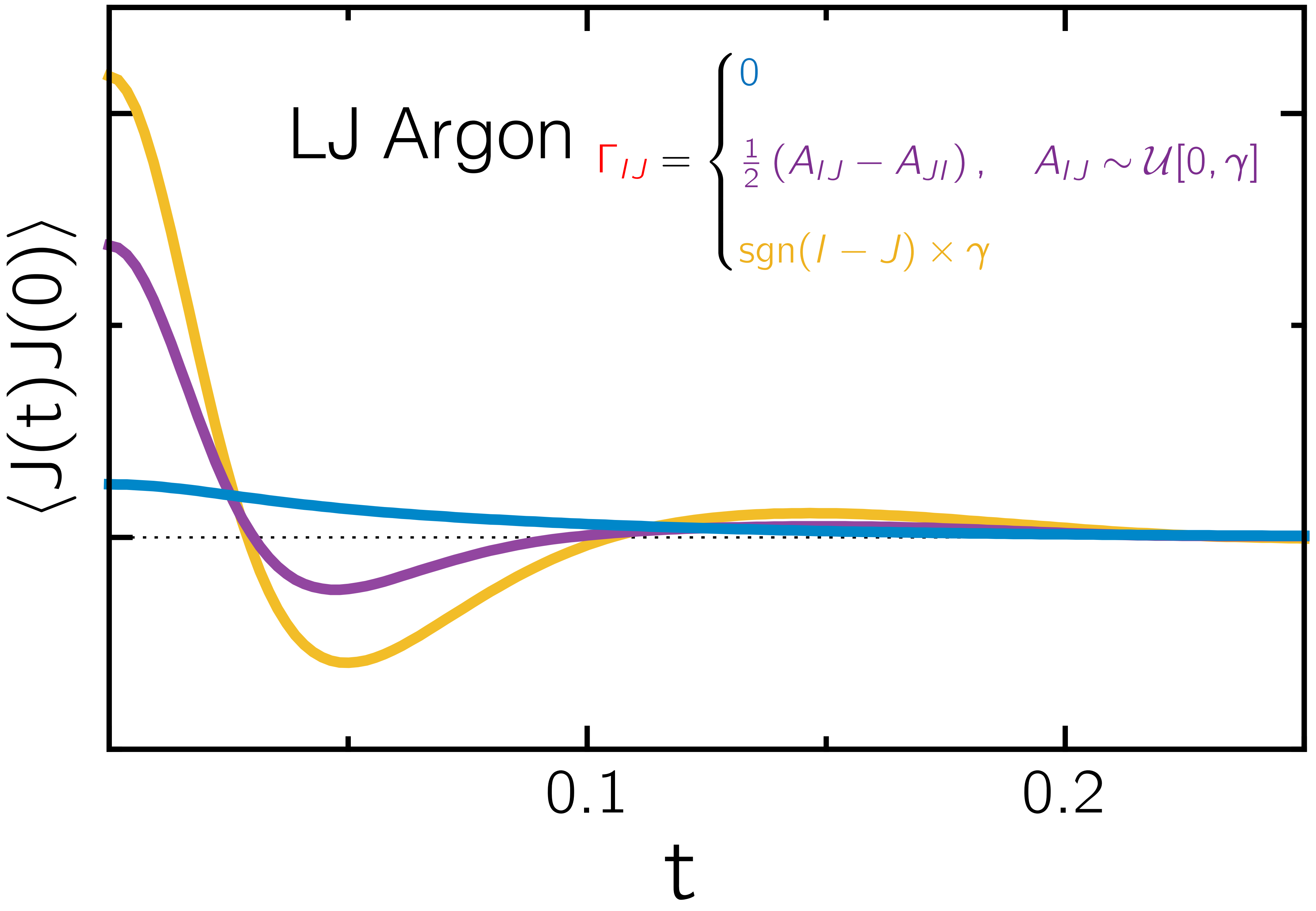

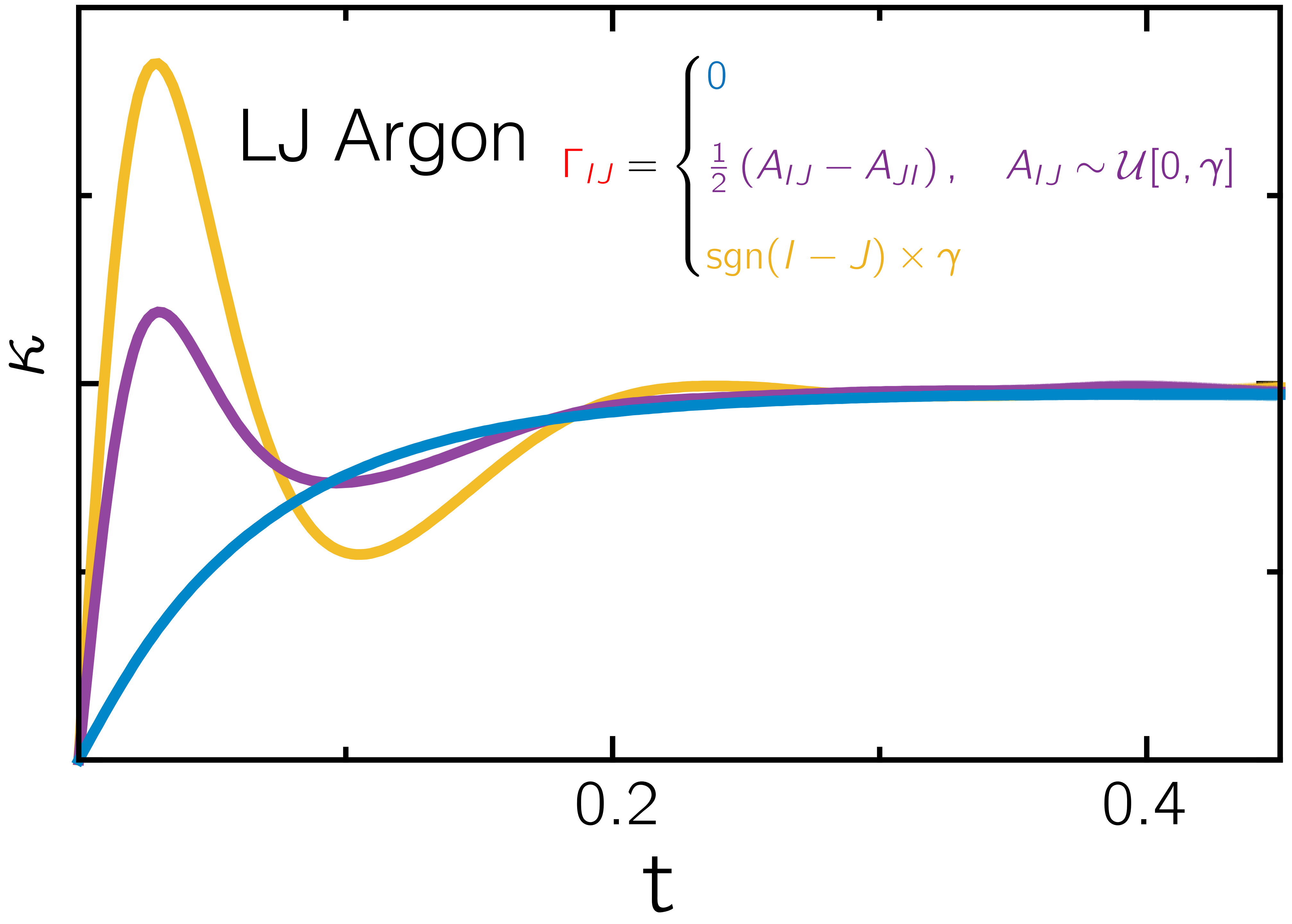

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$$\dot{\mathbf{P}} = \frac{\mathrm{d}}{\mathrm{dt}} \frac{1}{4} \sum_{I \neq J} \Gamma_{IJ}\, v(|\mathbf{R}_I - \mathbf{R}_J|)(\mathbf{R}_I - \mathbf{R}_I)$$

insights from classical mechanics

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

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

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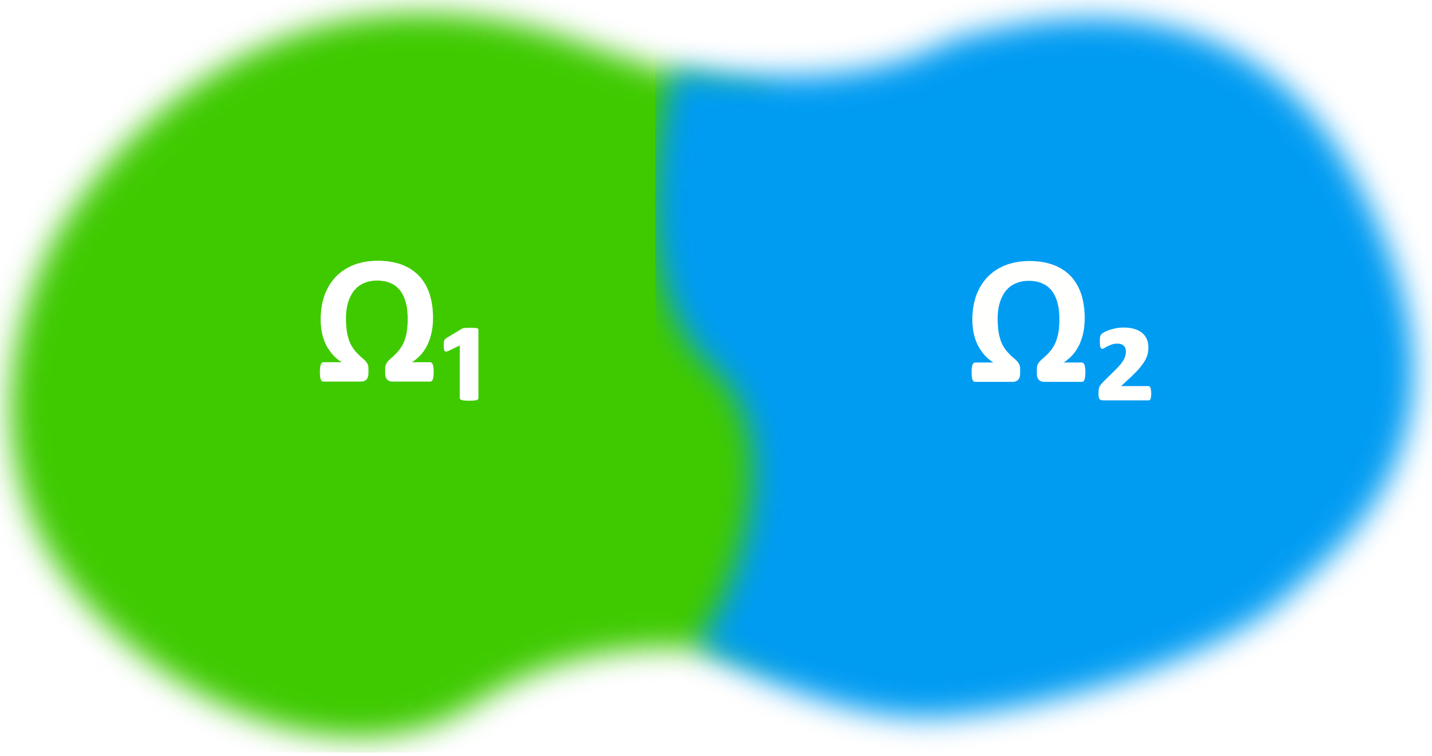
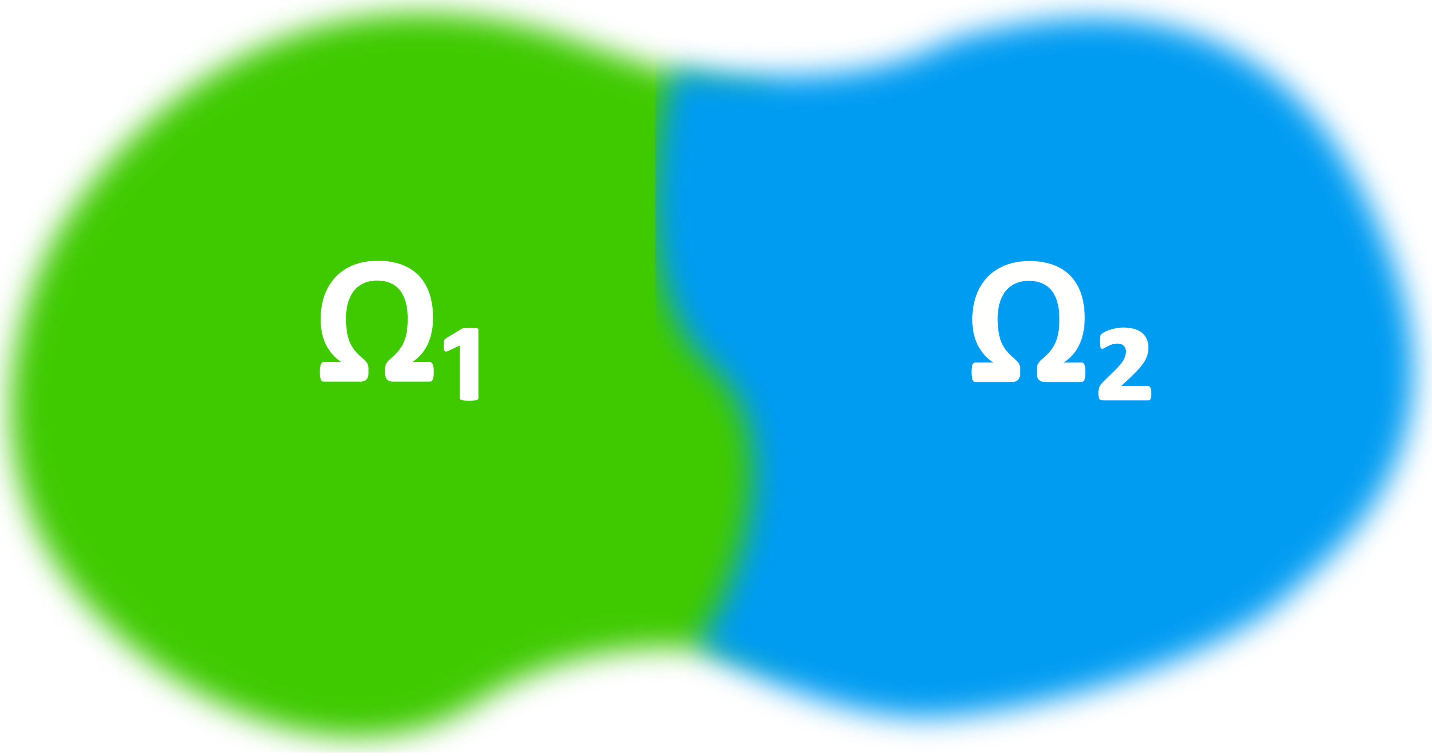
gauge invariance of transport coefficients



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

gauge invariance of transport coefficients



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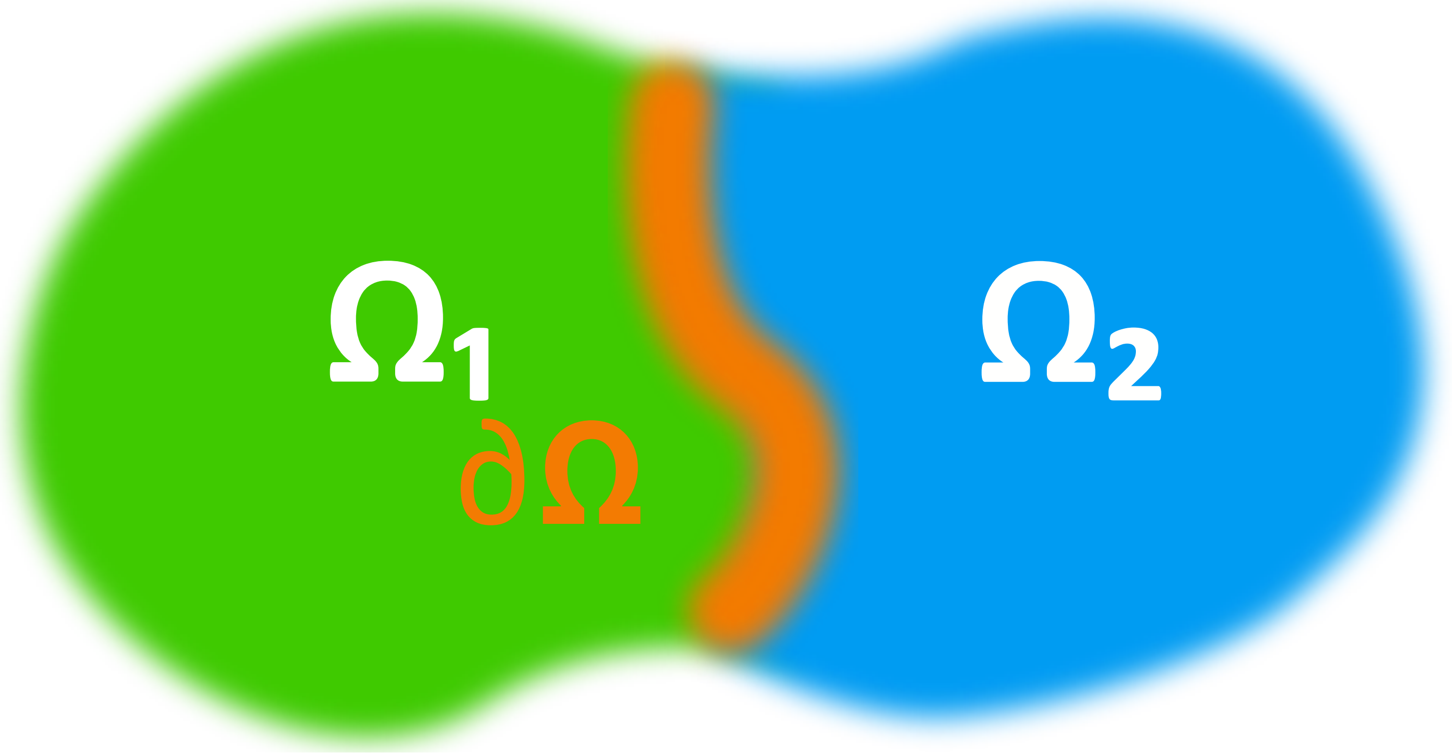
extensivity

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

gauge invariance of transport coefficients



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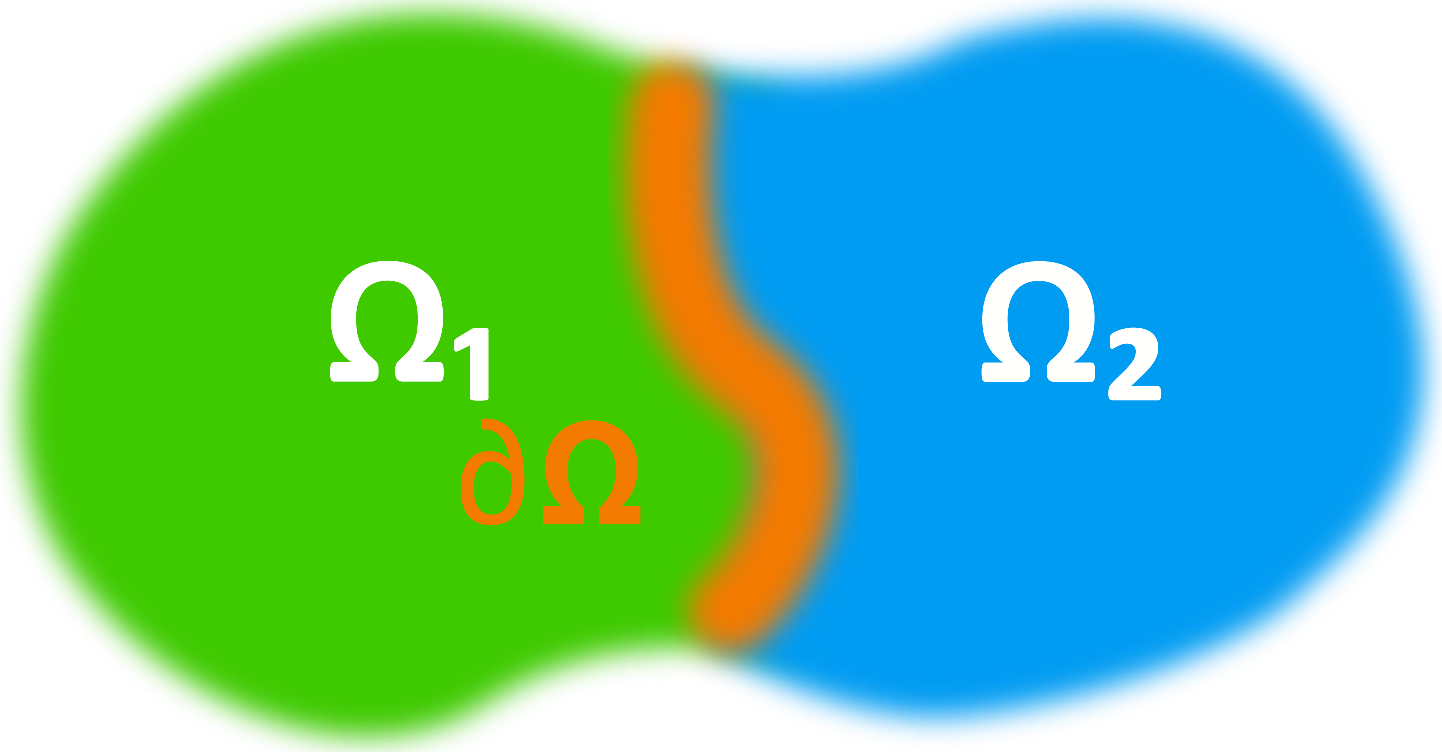

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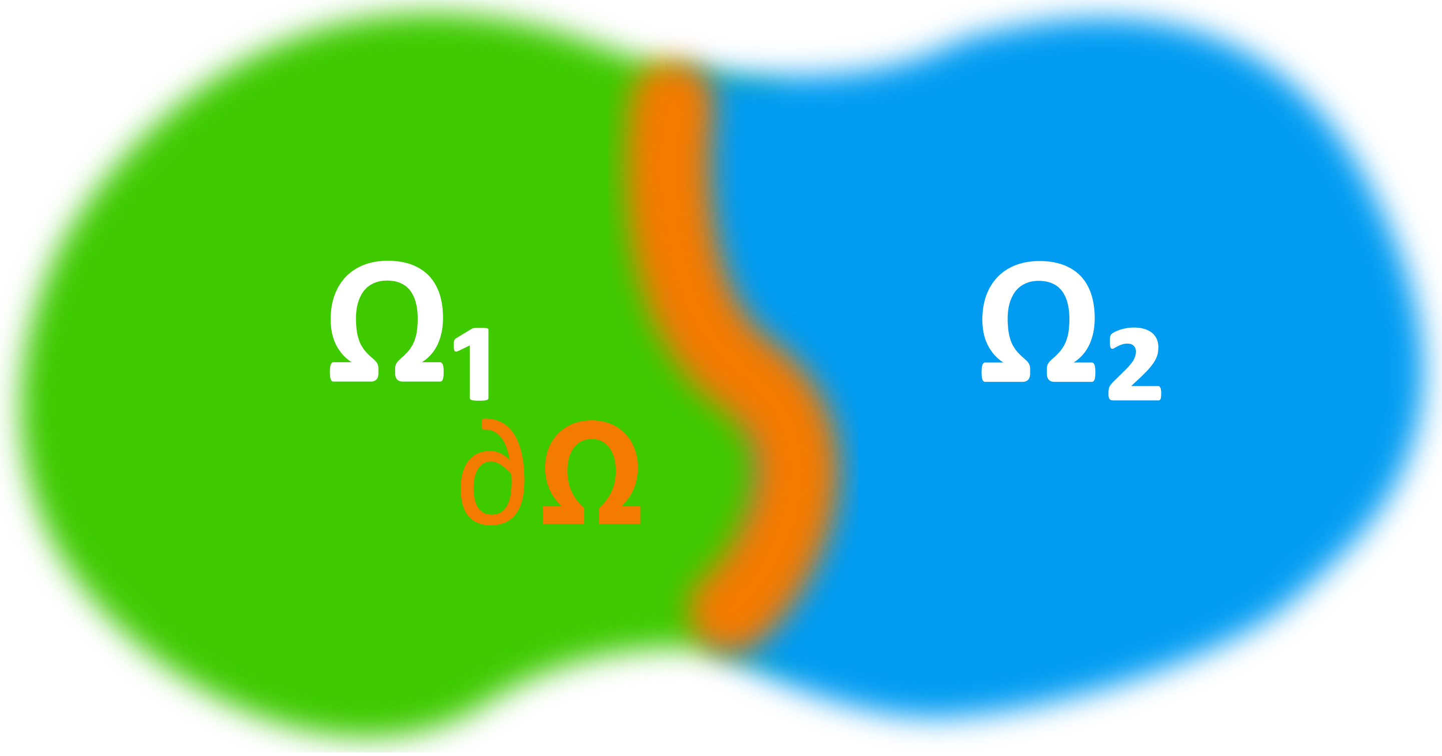

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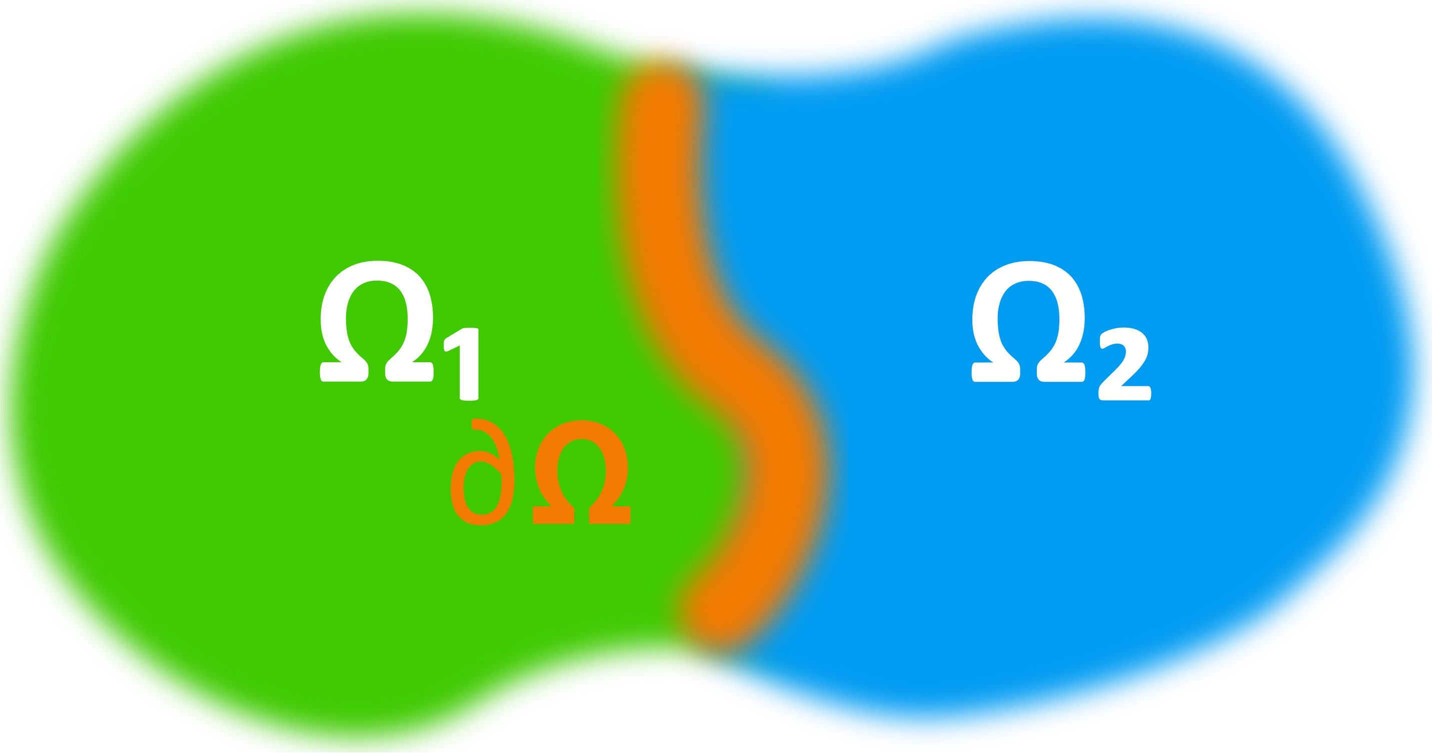
thermodynamic invariance

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

gauge invariance of transport coefficients



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

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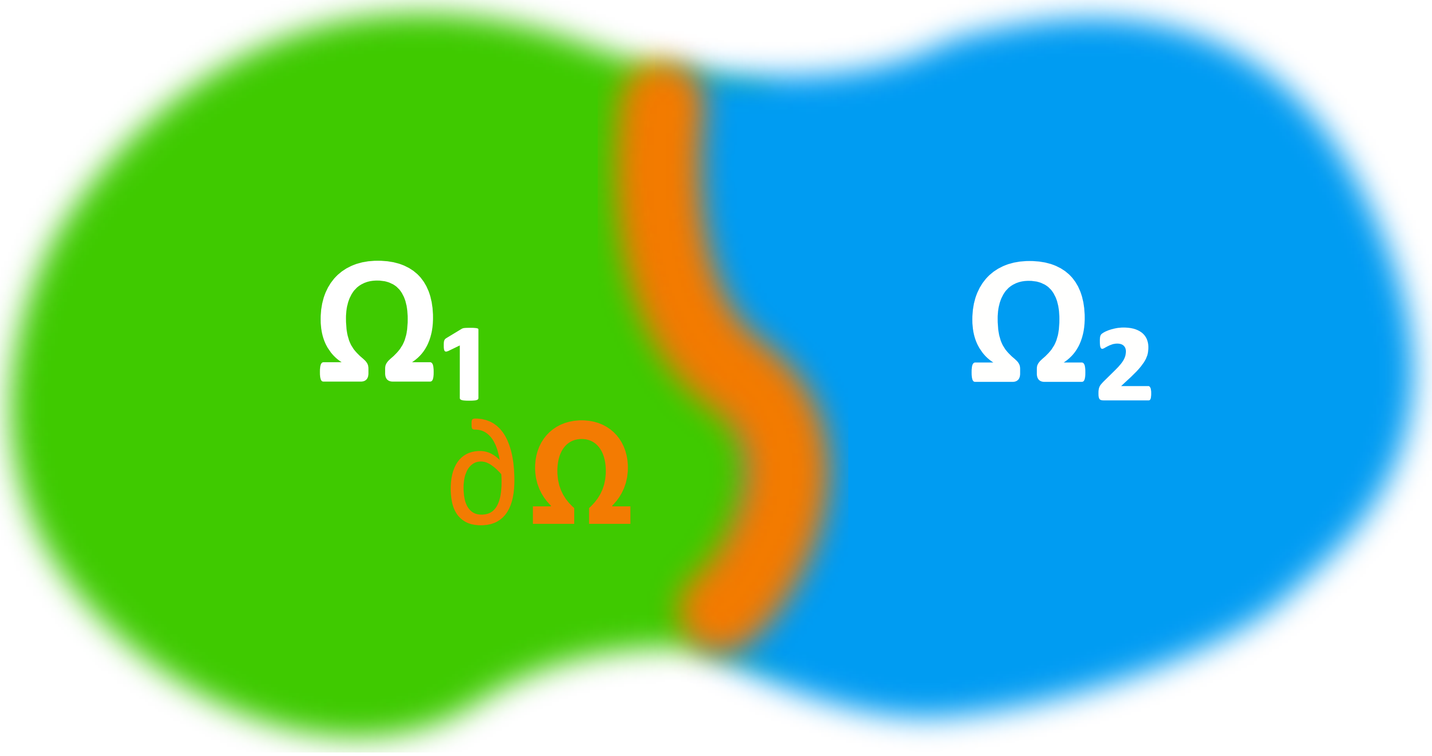
gauge invariance of transport coefficients



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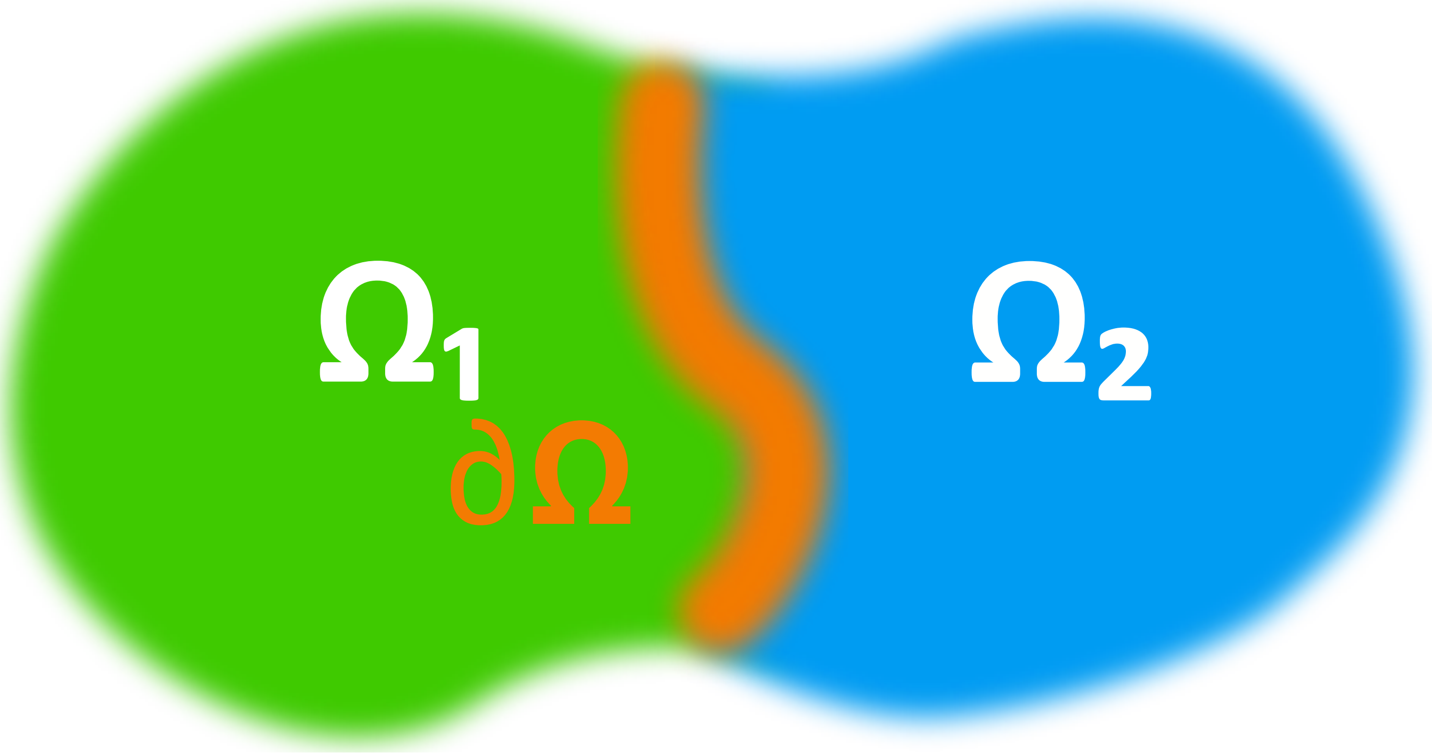

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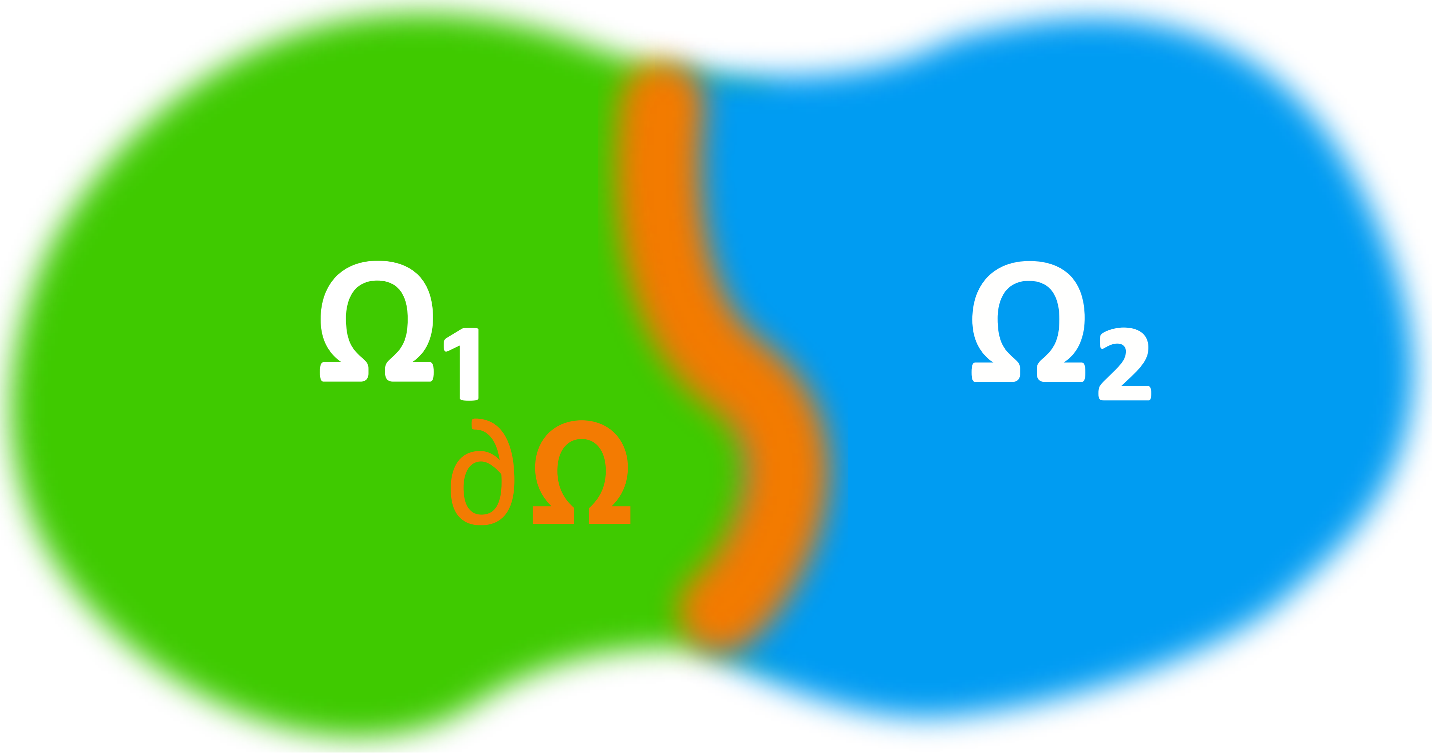

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conservation

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

gauge invariance of transport coefficients

any two conserved densities that differ by the divergence of a (bounded) vector field are physically equivalent

the corresponding conserved fluxes differ by a total time derivative, and the transport coefficients coincide

nature physics
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Microscopic theory and quantum simulation of atomic heat transport

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

Topology, oxidation states, and charge transport in ionic conductors

Paolo Pegolo

Scuola Internazionale Superiore di Studi Avanzati - SISSA - Trieste, Italy

Mixed-Gen Season 3 – Session 2: Theory and numerical simulation of transport processes in condensed matter

gauge invariance of heat transport

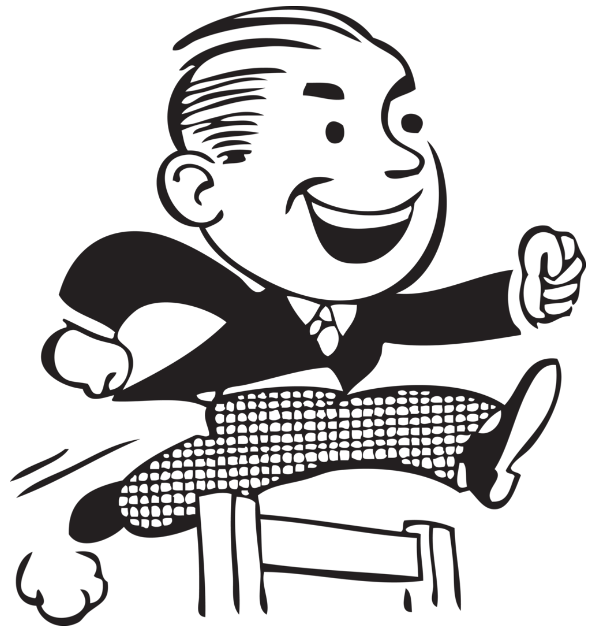
PRL **104,** 208501 (2010) PHYSICAL REVIEW LETTERS week ending 21 MAY 2010

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.

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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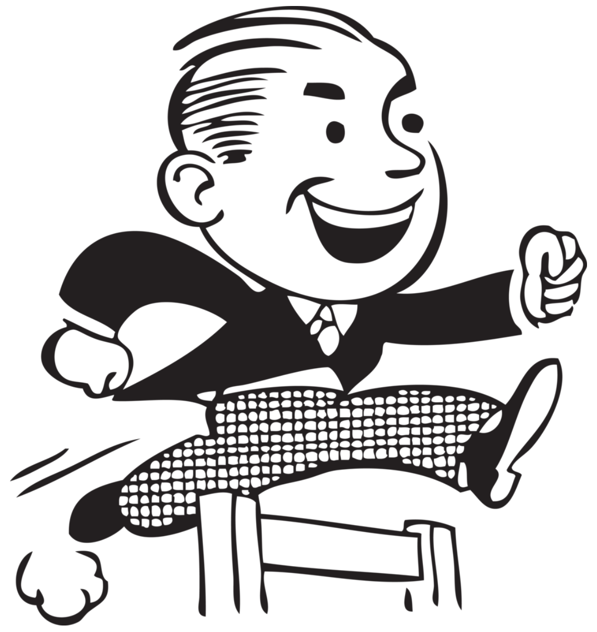

PRL **118,** 175901 (2017) PHYSICAL REVIEW LETTERS week ending 28 APRIL 2017

***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).

spectral analysis

$$\boldsymbol{J} = \int_V \boldsymbol{j}(\boldsymbol{r}) d\boldsymbol{r}$$

$$= \sum_i \int_{V_i} \boldsymbol{j}(\boldsymbol{r}) d\boldsymbol{r}$$

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if $\langle \boldsymbol{j}(\boldsymbol{r})\boldsymbol{j}(\boldsymbol{r}')\rangle$ is short-range, $\int_{V_i} \boldsymbol{j}(\boldsymbol{r}) d\boldsymbol{r}$ and $\int_{V_j} \boldsymbol{j}(\boldsymbol{r}) d\boldsymbol{r}$ for $i \neq j$ are independent stochastic variables and, by the central-limit theorem,

$\boldsymbol{J}(t)$ is a Gaussian process

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stationarity implies:

$$\langle \tilde{J}_T(\omega) \tilde{J}_T(-\omega') \rangle \sim \frac{1}{T} \quad \text{for} \quad \omega \neq \omega'$$

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$$\lambda = \int_0^\infty \langle \boldsymbol{J}(t)\boldsymbol{J}(0)\rangle dt$$

$S(\omega)$

$$= \frac{1}{2}\int_{-\infty}^{\infty} \langle \boldsymbol{J}(t)\boldsymbol{J}(0)\rangle e^{i\omega t} dt \Big|_{\omega=0}$$

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sample spectrum
aka "*periodogram*"

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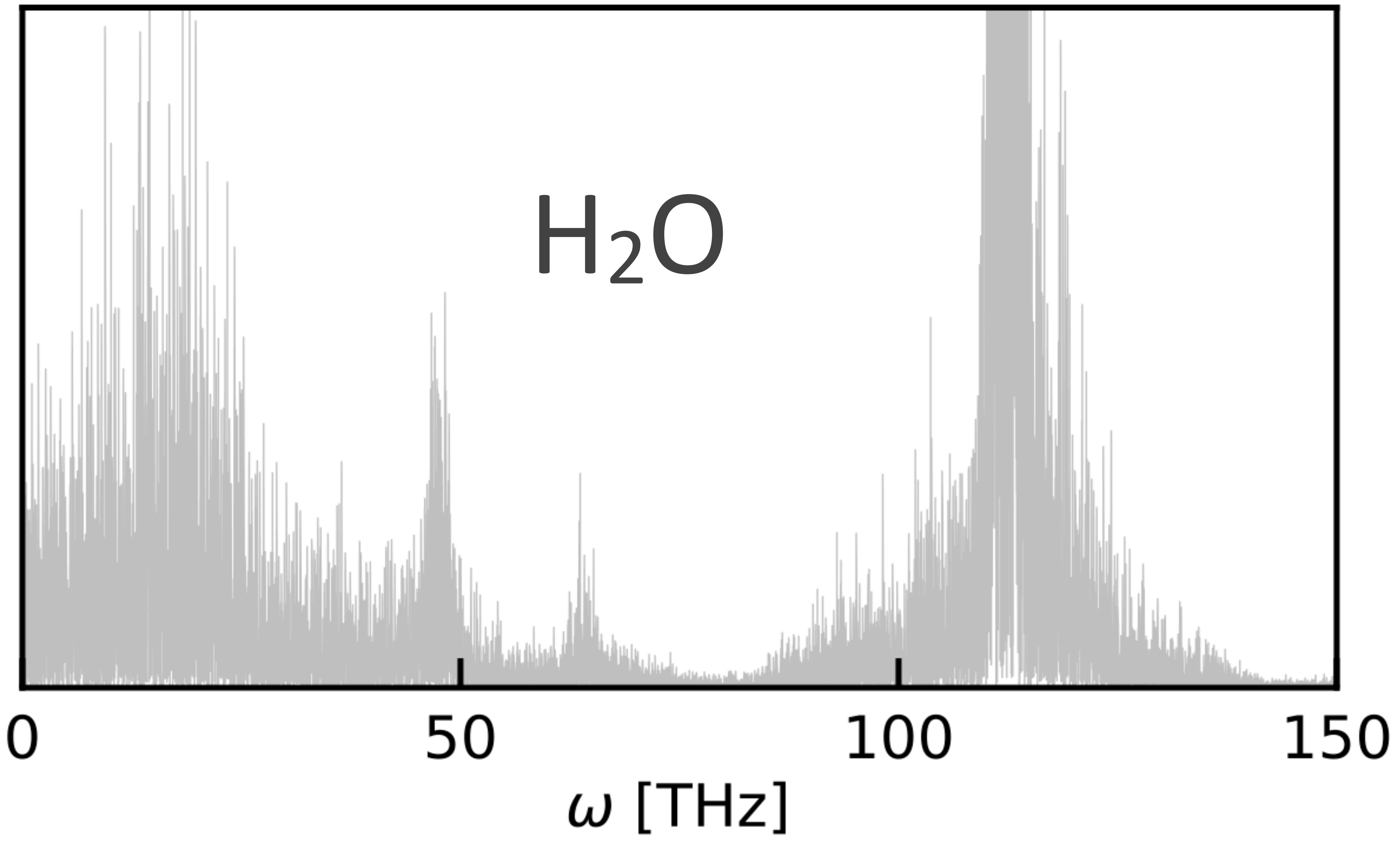

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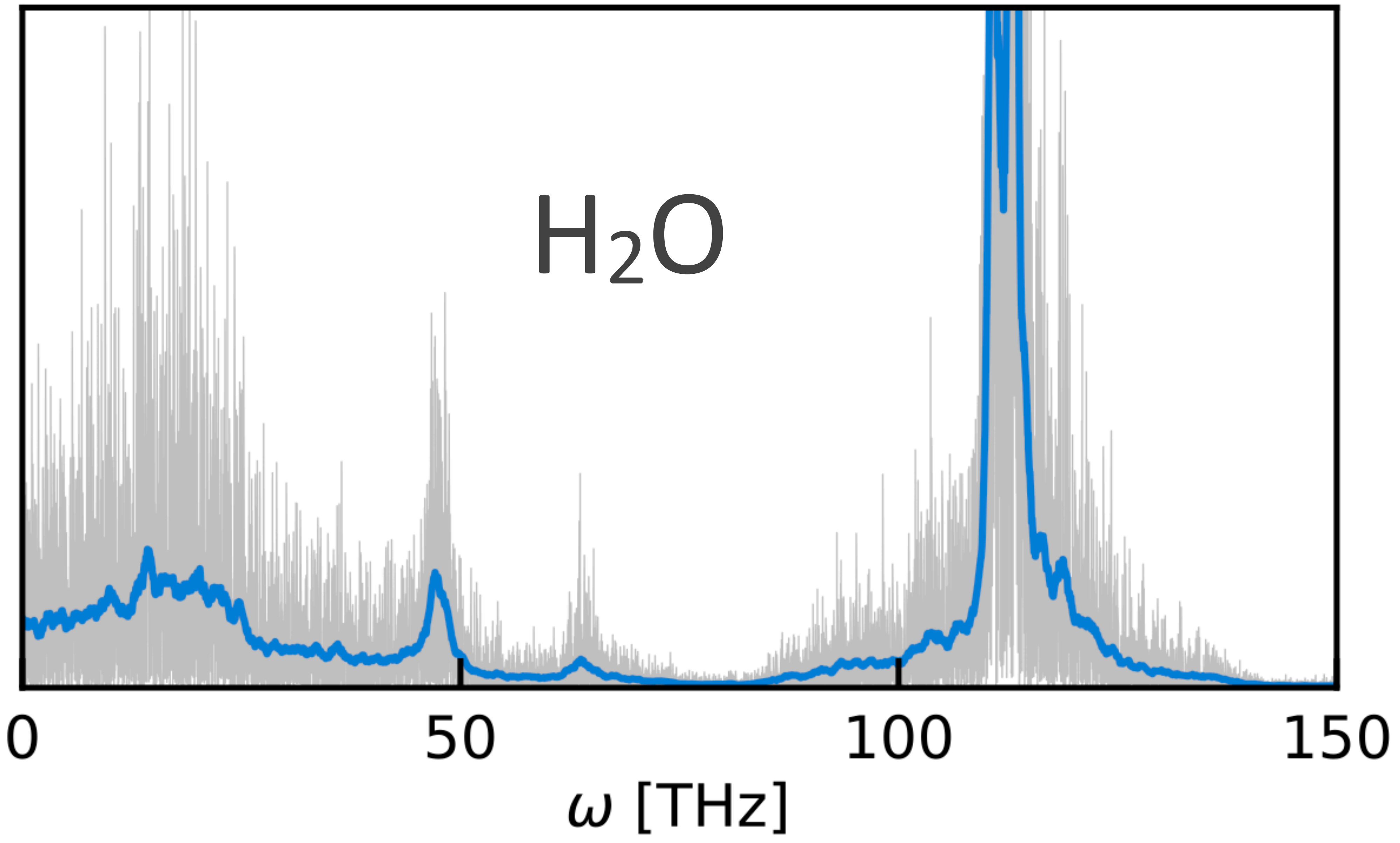

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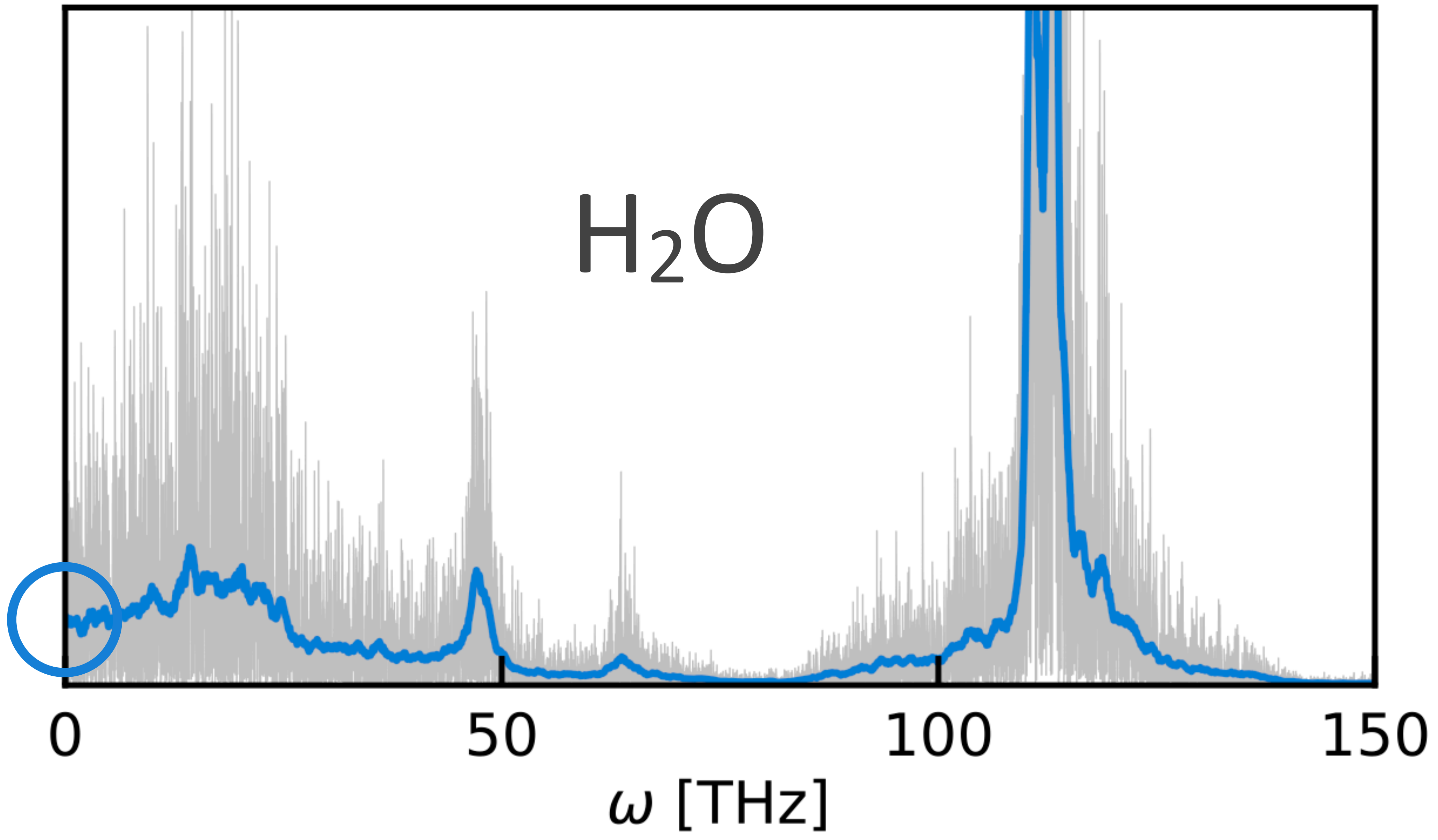

separating flour from bran

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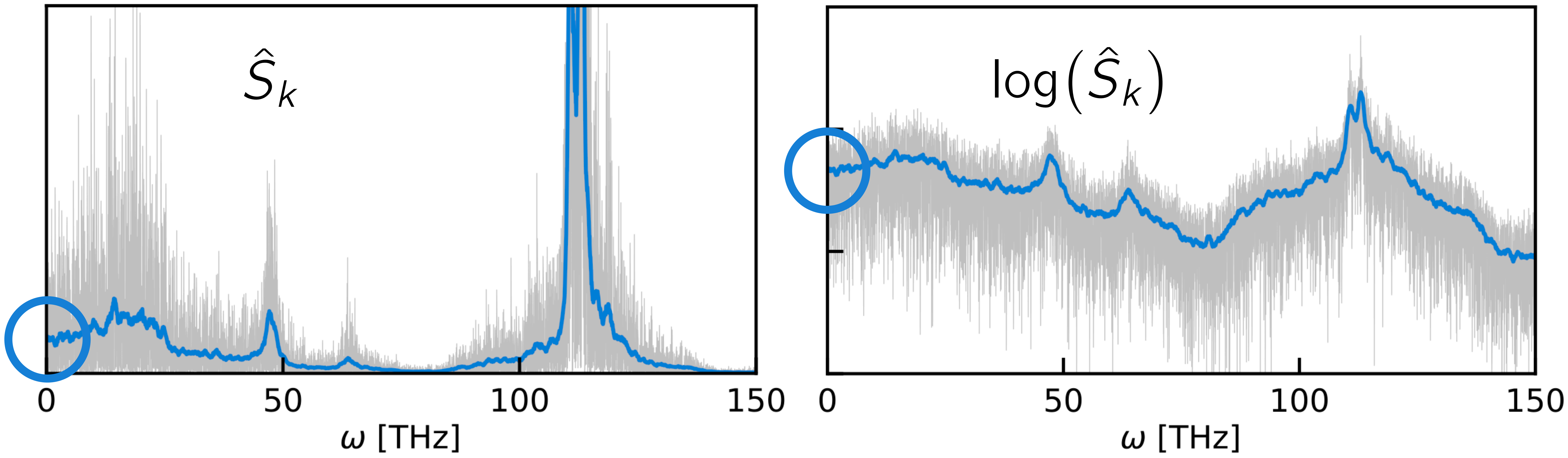

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separating flour from bran

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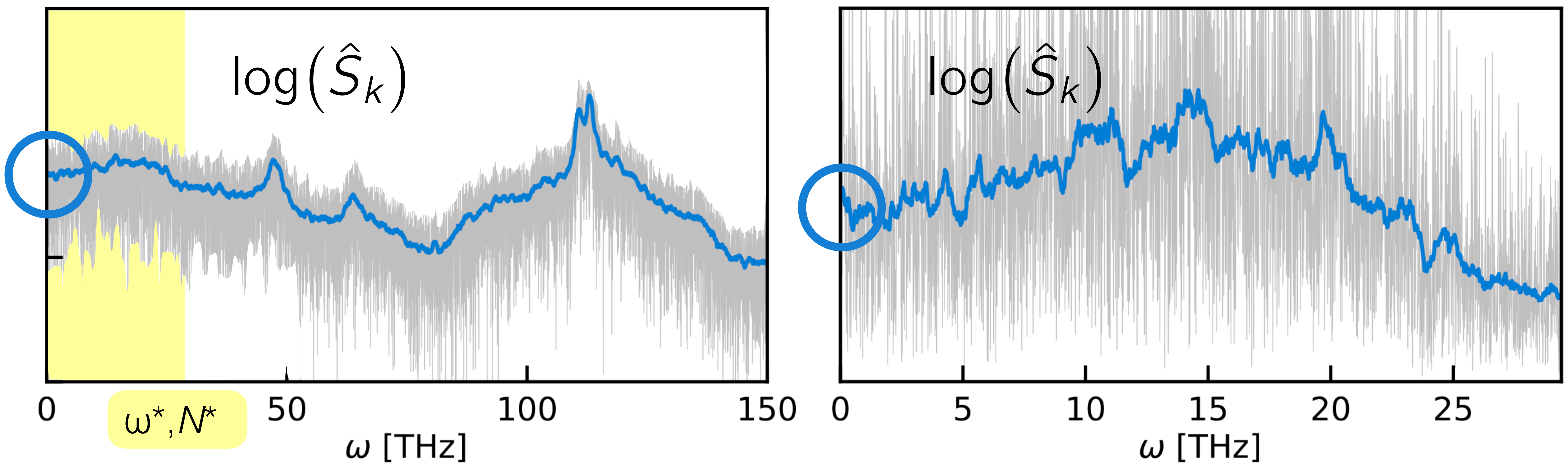

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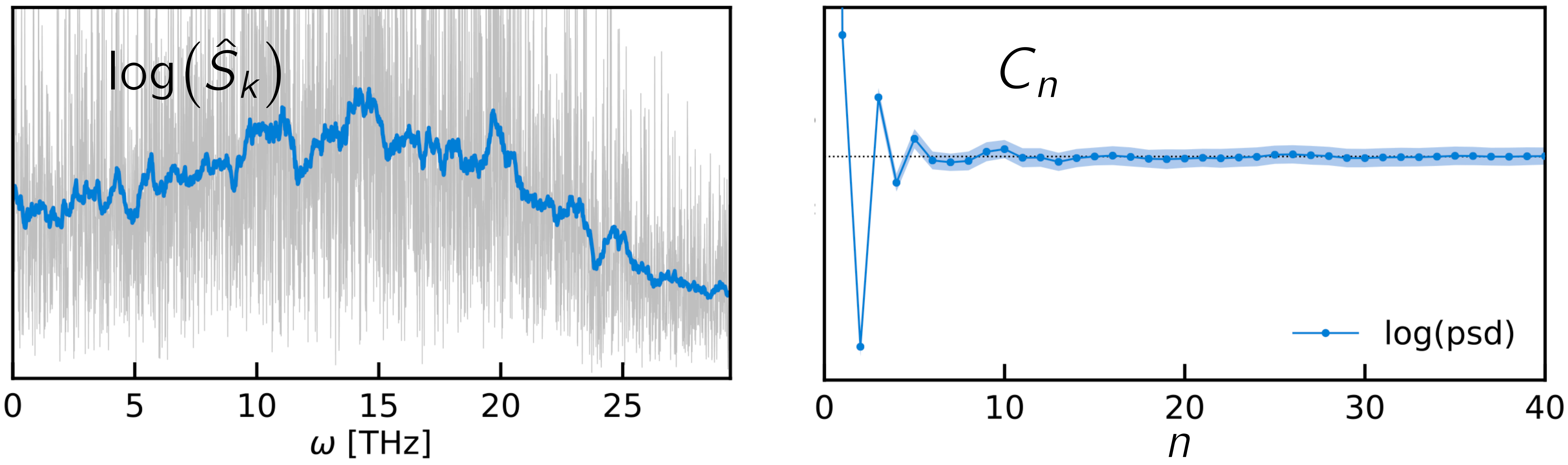

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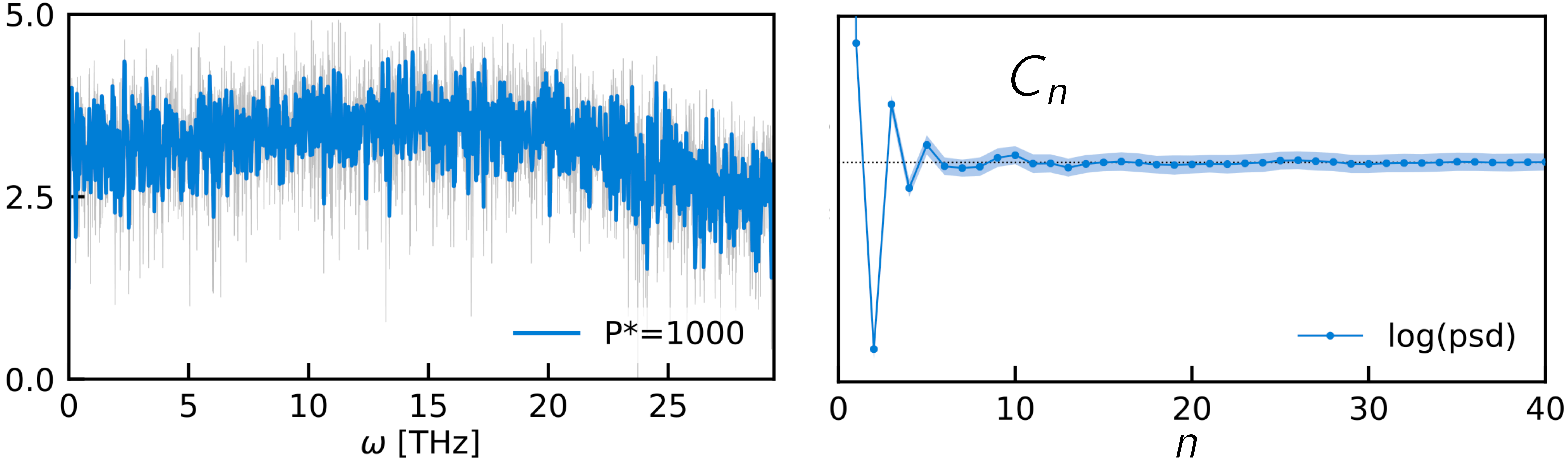

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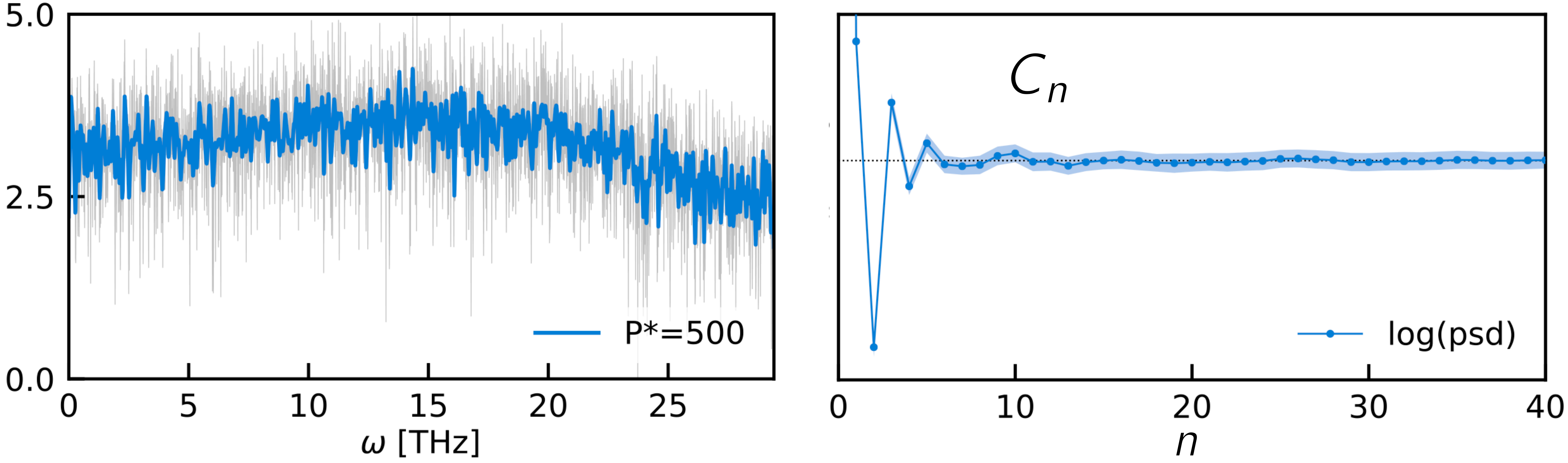

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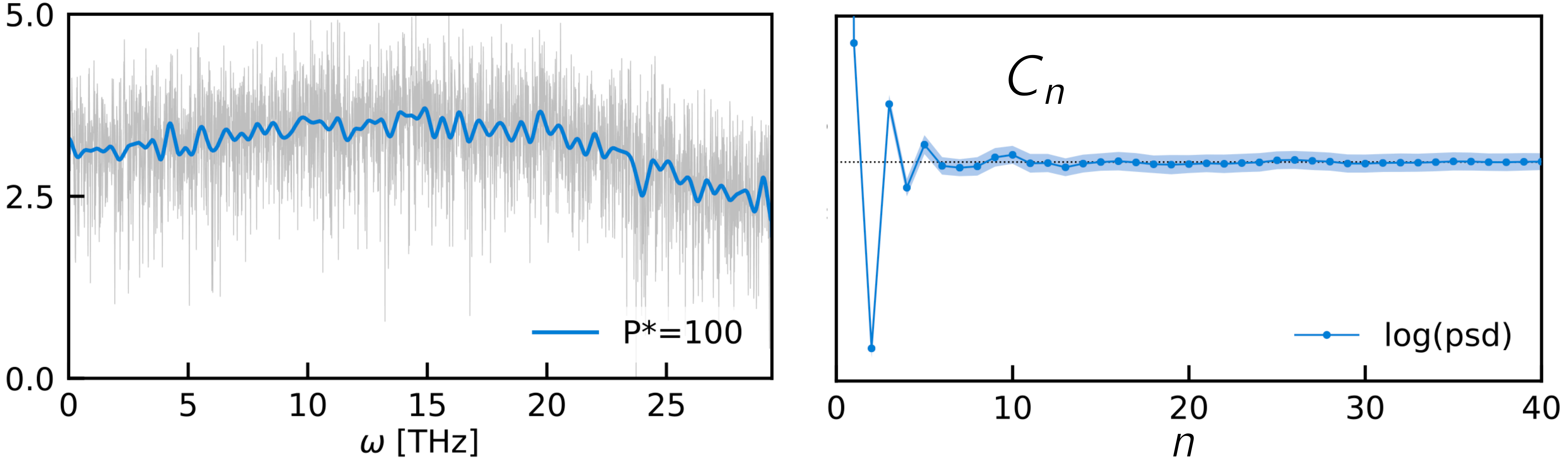

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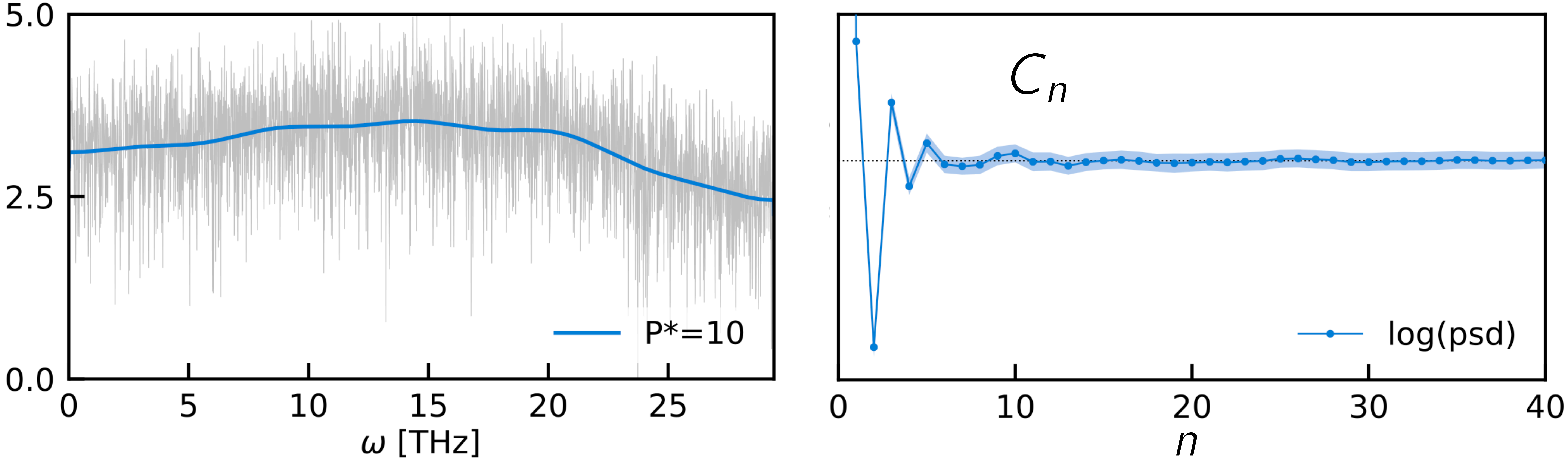

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separating flour from bran

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

constants independent of the time series being sampled

determining the optimal number of cepstral coefficients

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Optimal model, maximum of:

$$\mathcal{P}(\mathrm{M|D}) = \frac{\mathcal{L}(\mathrm{D|M})P(\mathrm{M})}{P(\mathrm{D})}$$

determining the optimal number of cepstral coefficients

cepstral analysis amounts to assuming that the logarithm of the power spectrum can be modelled by a smooth Fourier series:

Model: $\{P, C_0, C_1, \cdots C_{P-1}\}$; Data: $\{\hat{C}_0, \hat{C}_1, \cdots \hat{C}_{N/2}\}$.

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Optimal model, maximum of:

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$$-2\log(\mathcal{L}) \sim \frac{N}{\sigma^2}\left[\frac{1}{2}\left(C_0 + \lambda - \hat{C}_0\right)^2 + \sum_{n=1}^{P-1}\left(C_n - \hat{C}_n\right)^2 + \sum_{n=P}^{\frac{N}{2}} \hat{C}_n^2\right]$$

$$P(M) \propto \mathrm{e}^{-\alpha P}$$

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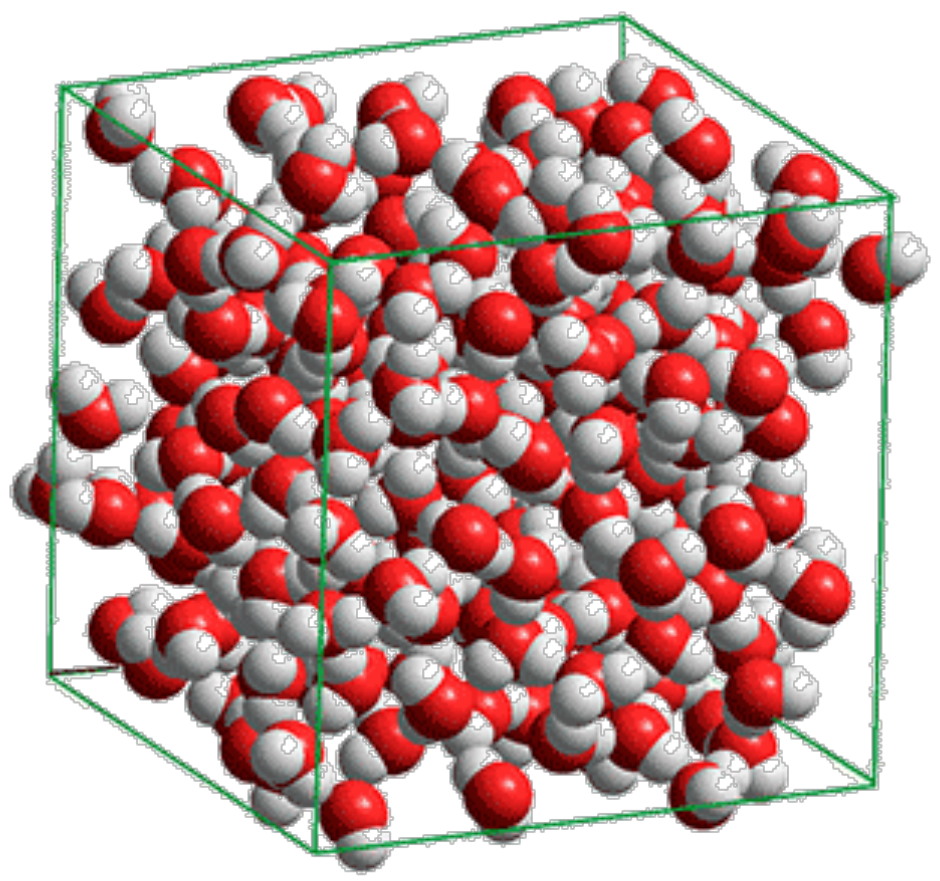
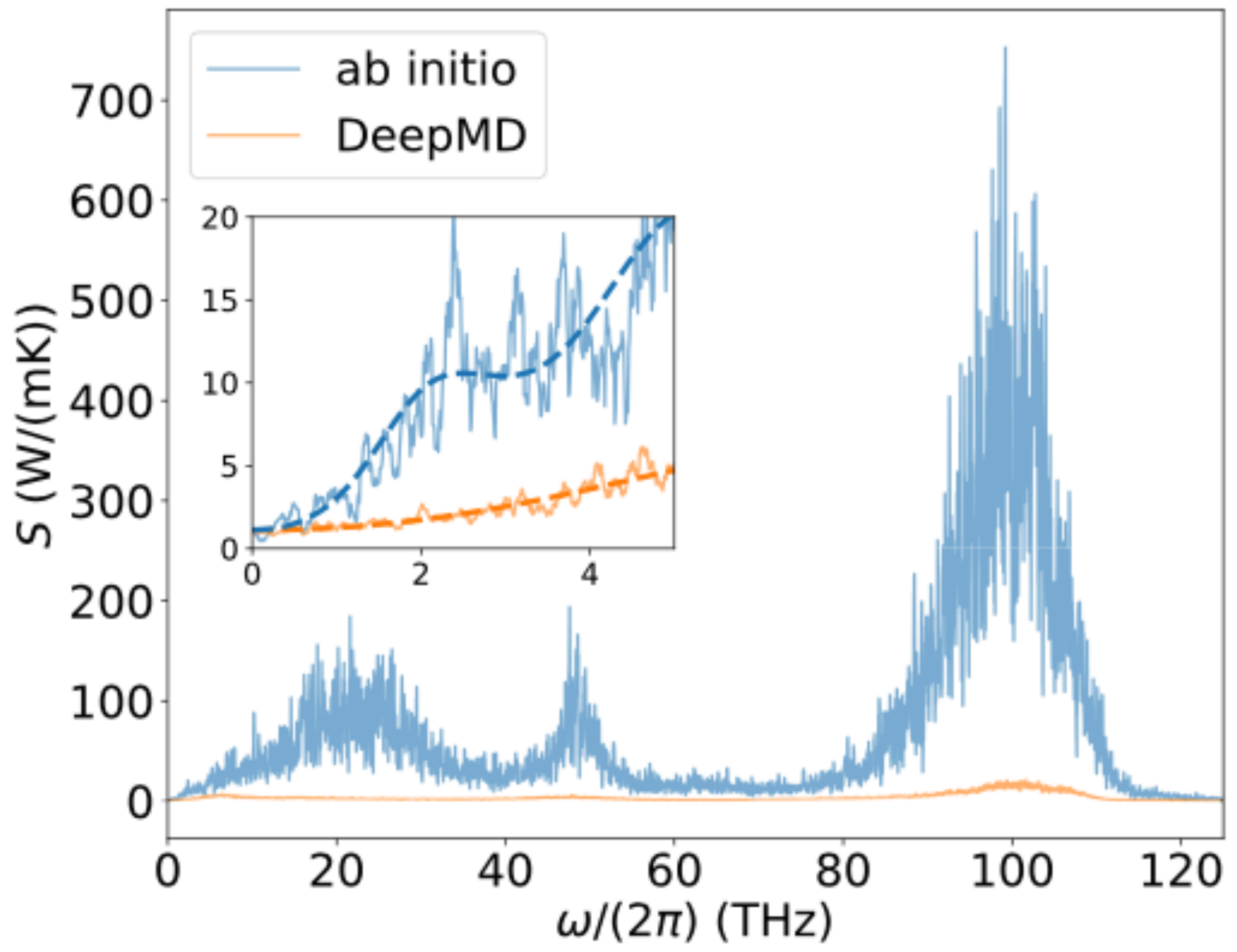
AIC: $\alpha = 2$

thermal conductivity of liquid water from DFT





PHYSICAL REVIEW B **104**, 224202 (2021)

Heat transport in liquid water from first-principles and deep neural network simulations

Davide Tisi,[1] Linfeng Zhang,[2] Riccardo Bertossa,[1] Han Wang,[3] Roberto Car,[2,4] and Stefano Baroni[1,5]

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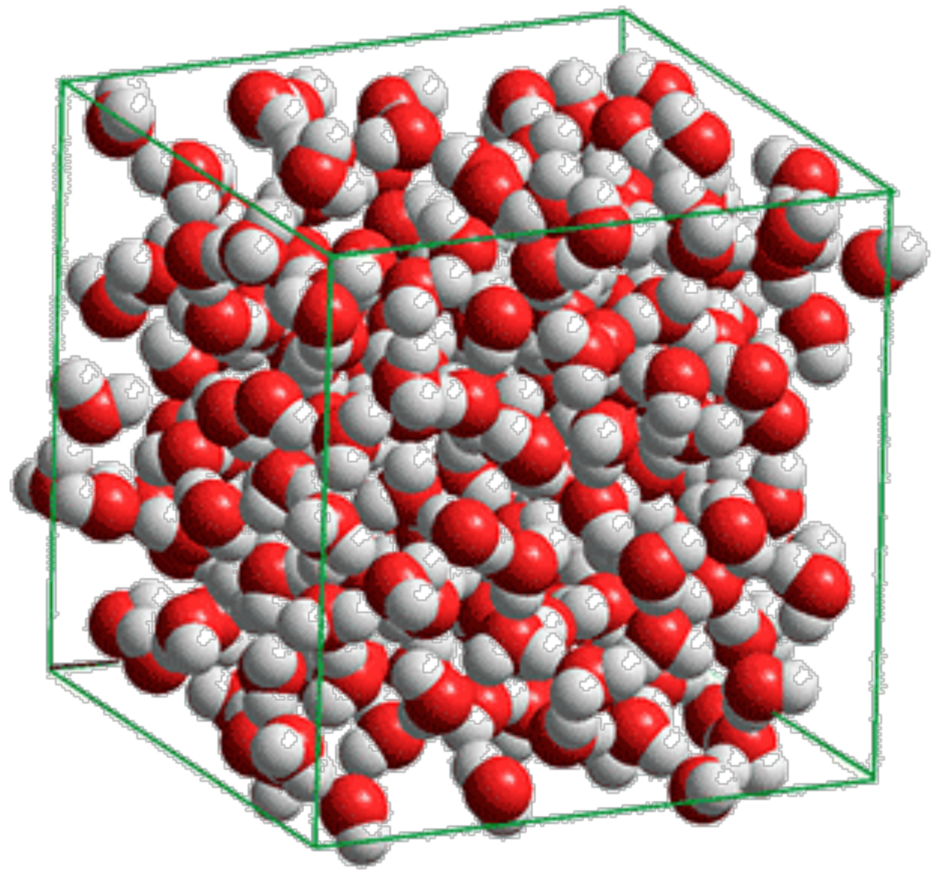

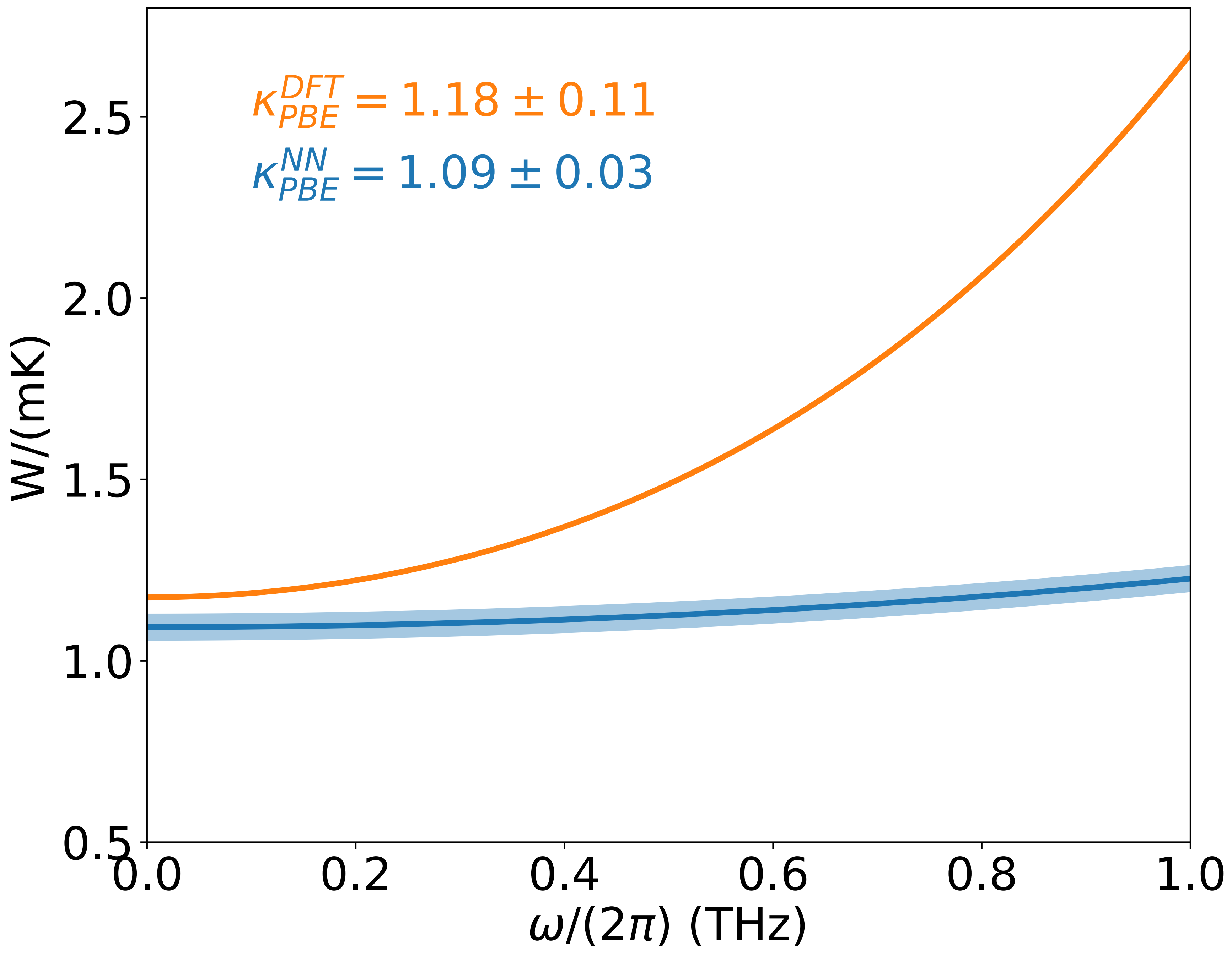

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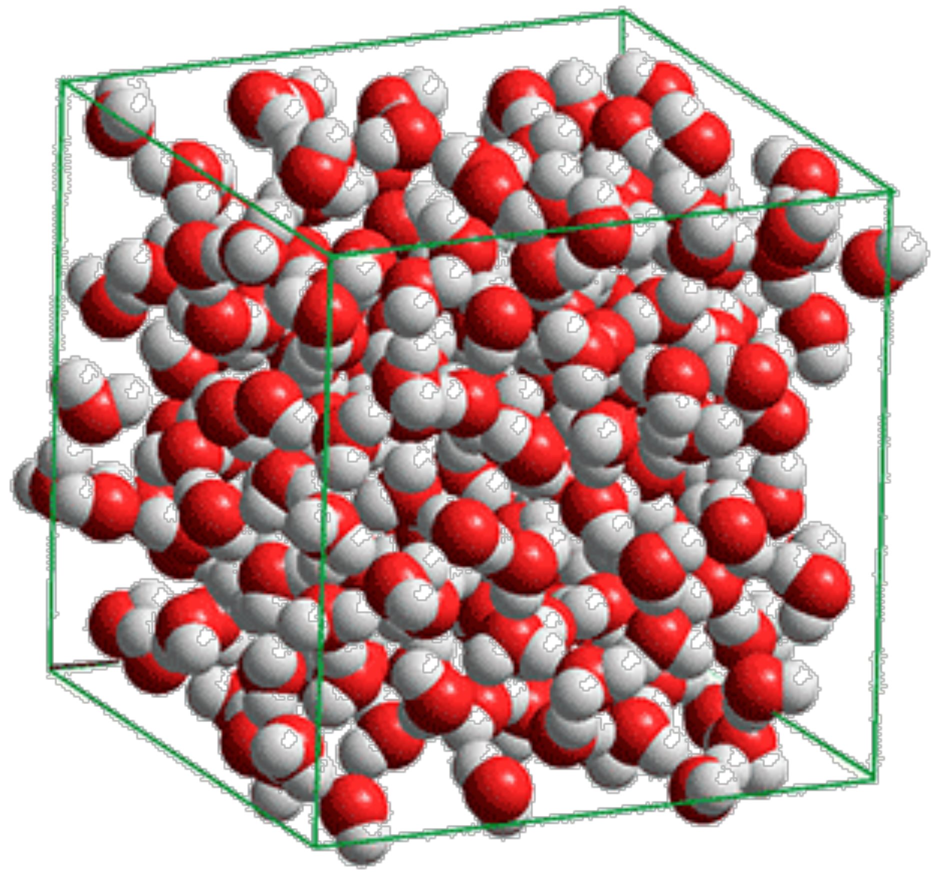

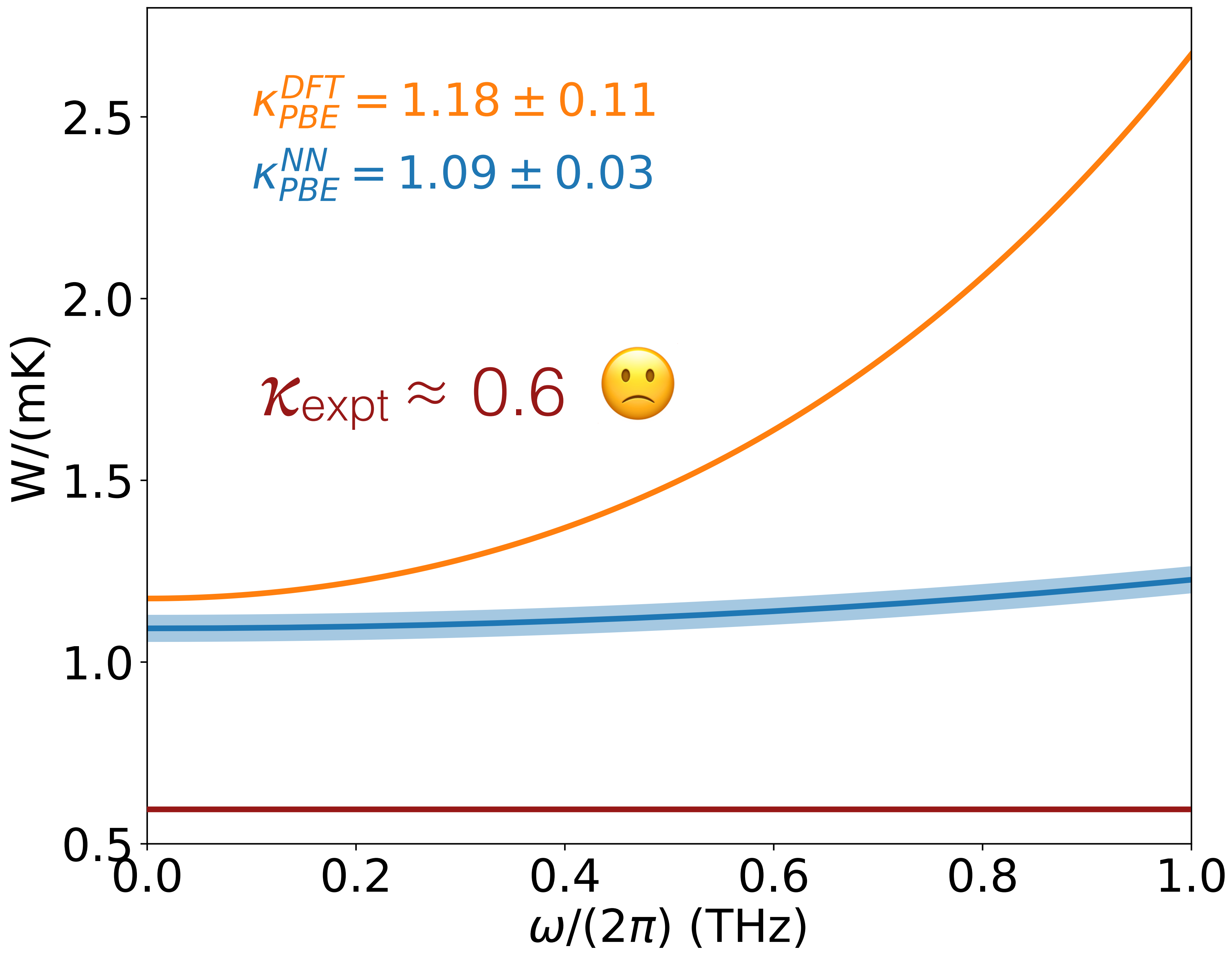

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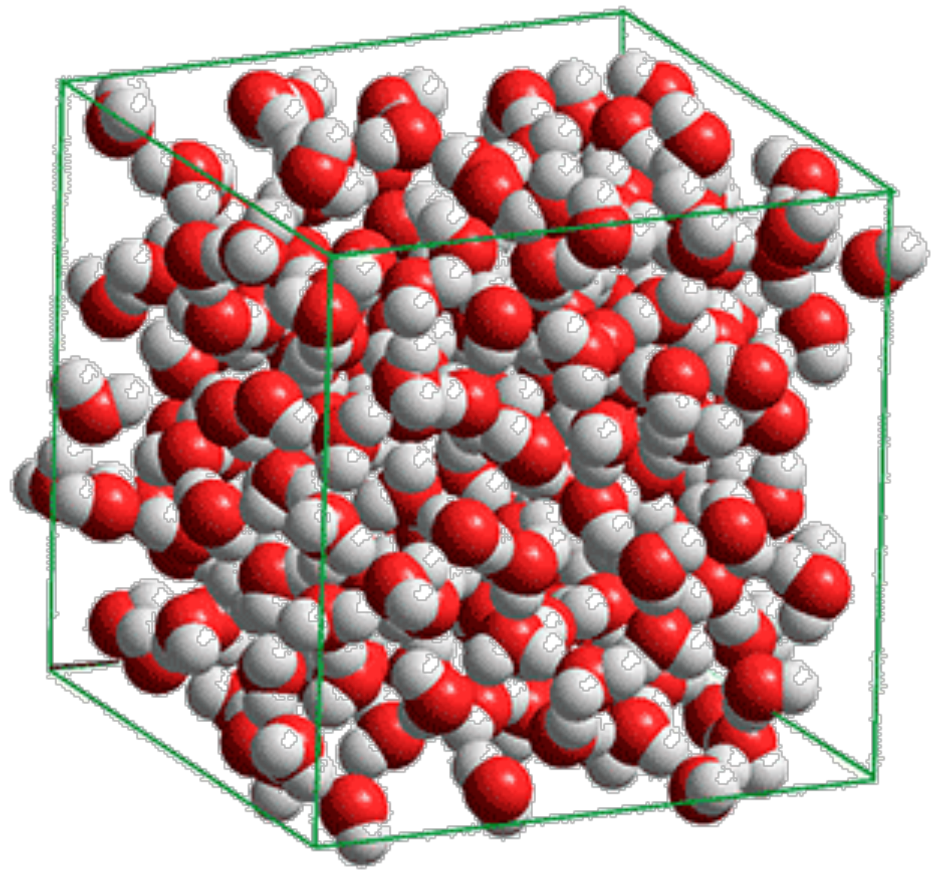

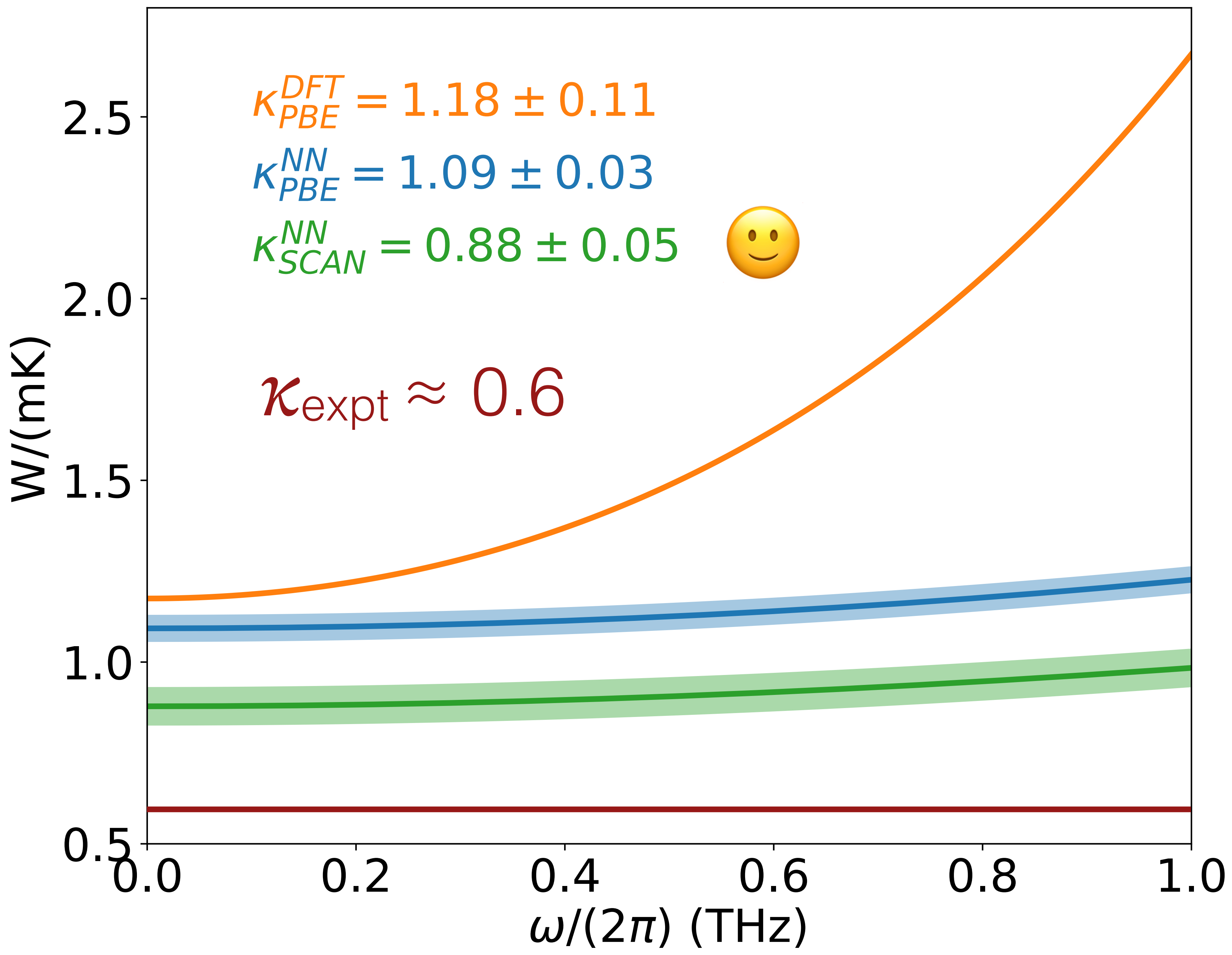

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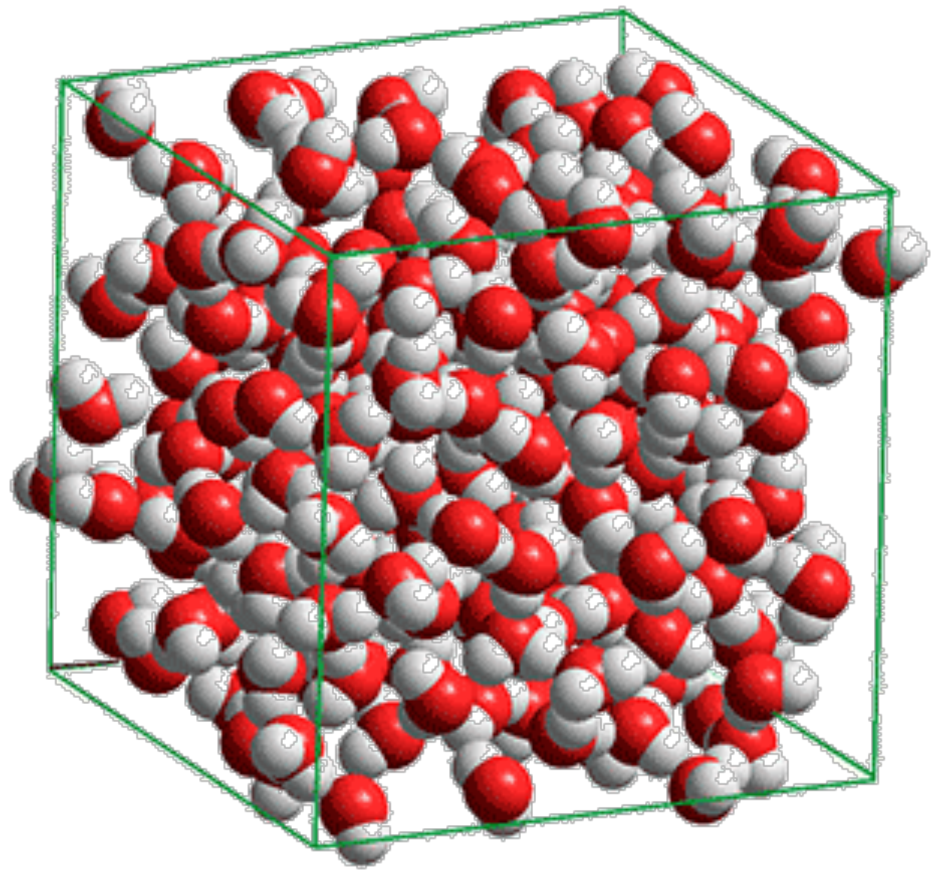

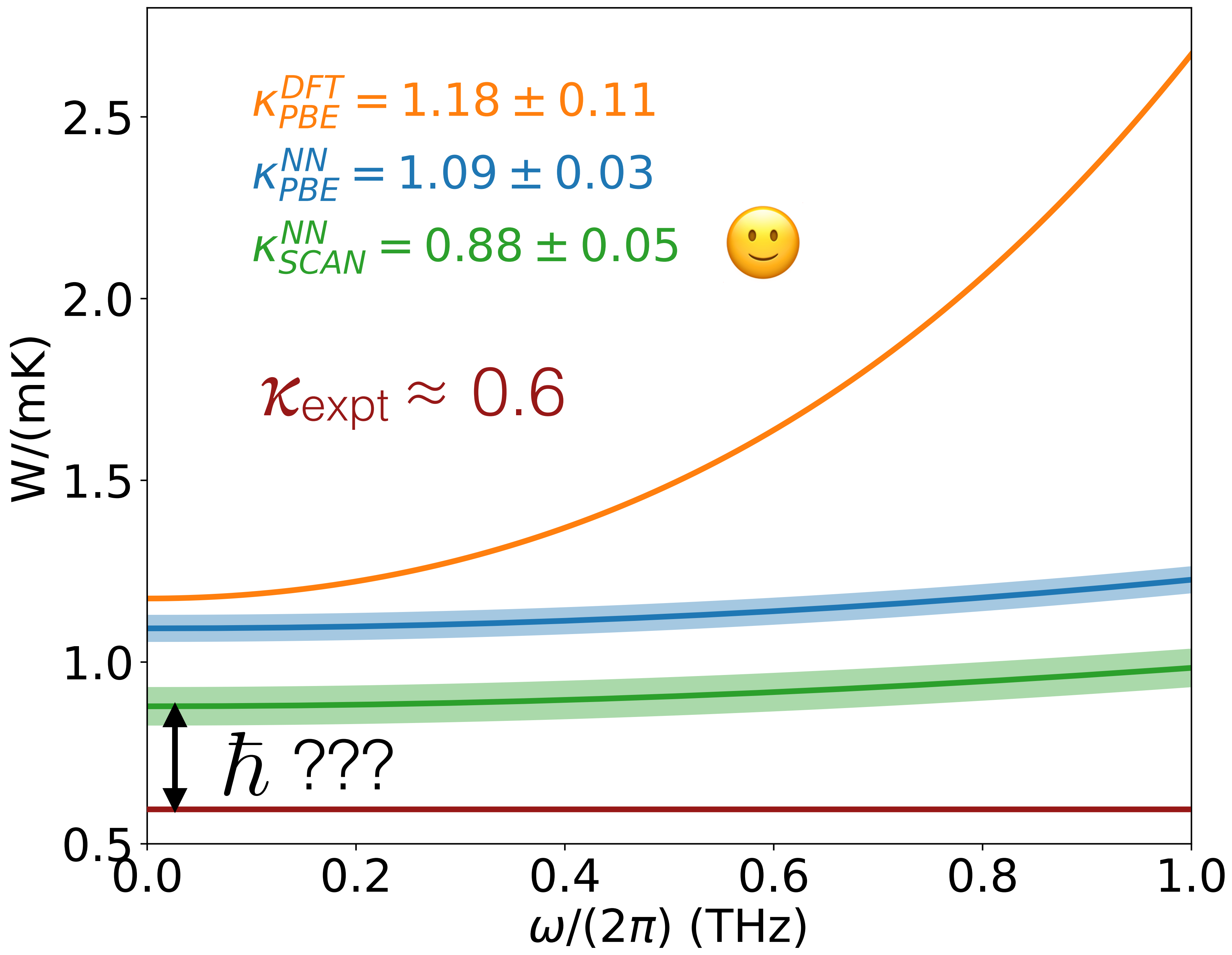

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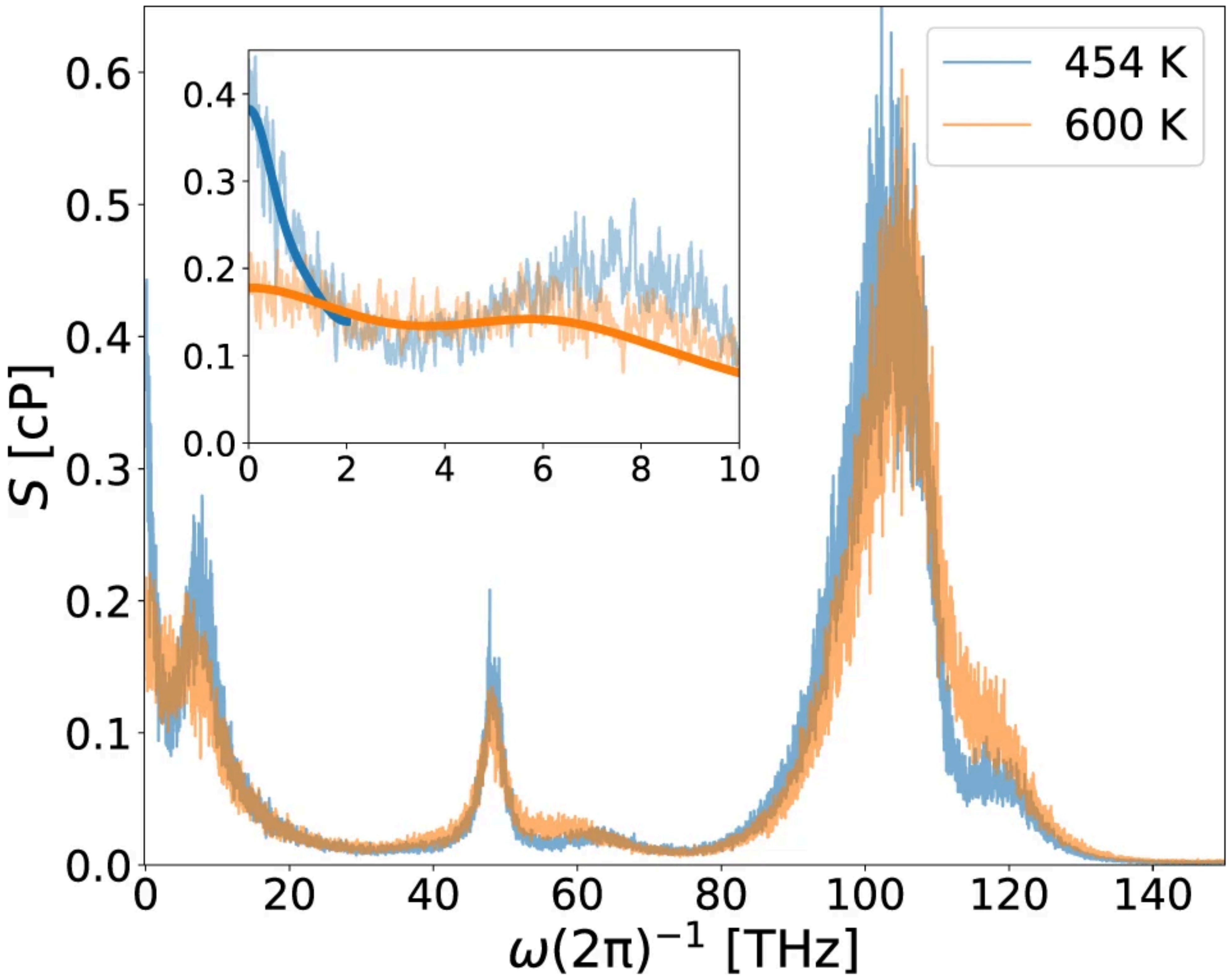
ab initio shear viscosity in water



npj | computational materials

Viscosity in water from first-principles and deep-neural-network simulations

Cesare Malosso, Linfeng Zhang, Roberto Car, Stefano Baroni & Davide Tisi

npj Computational Materials **8**, Article number: 139 (2022) | Cite this article

checking normality

$$\eta = \frac{V}{k_B T} \int_0^\infty \langle \sigma_s(t) \sigma_s(0) \rangle dt$$

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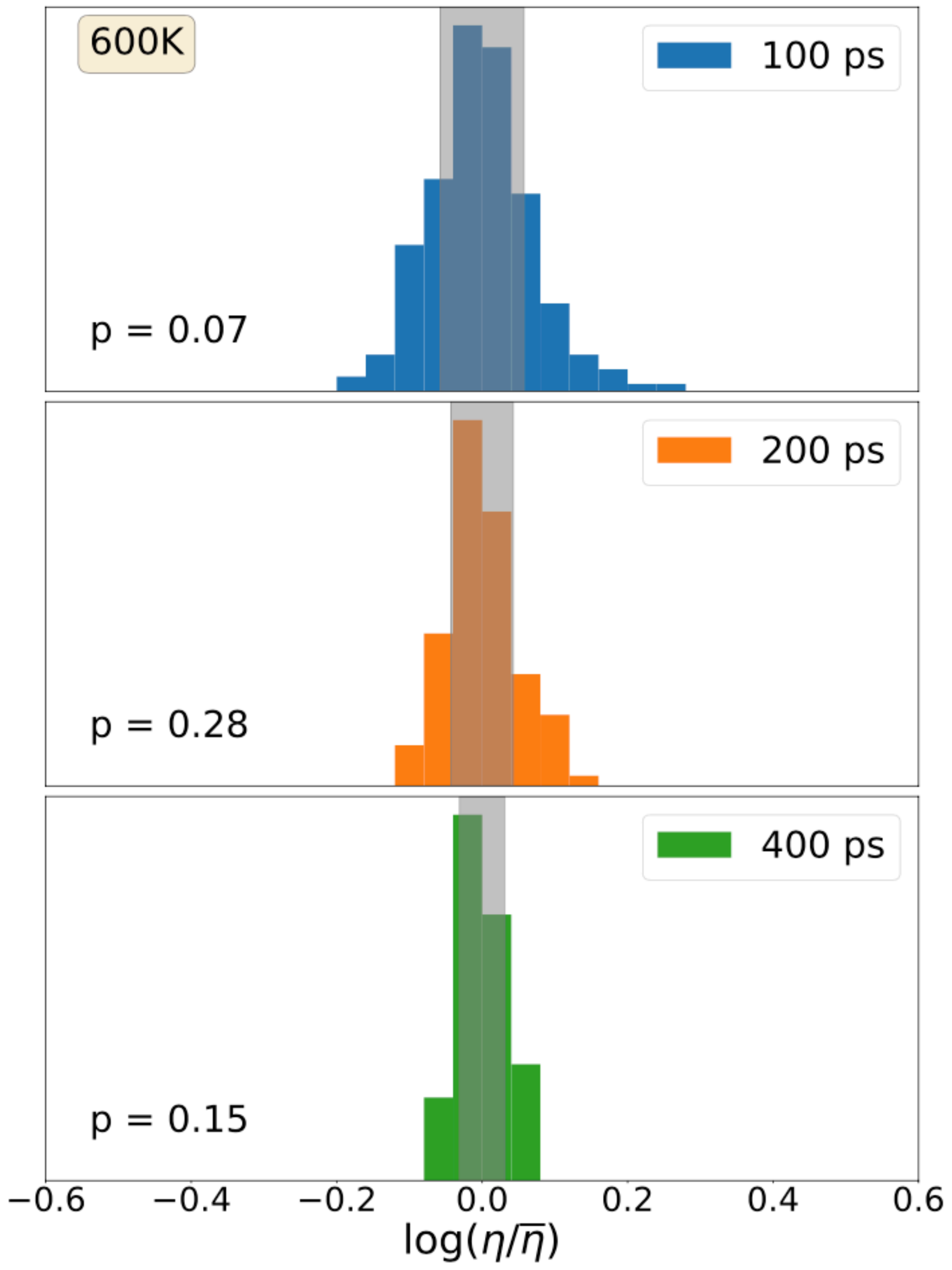
viscosity of water computed for different temperatures
and using trajectory segments of different lengths



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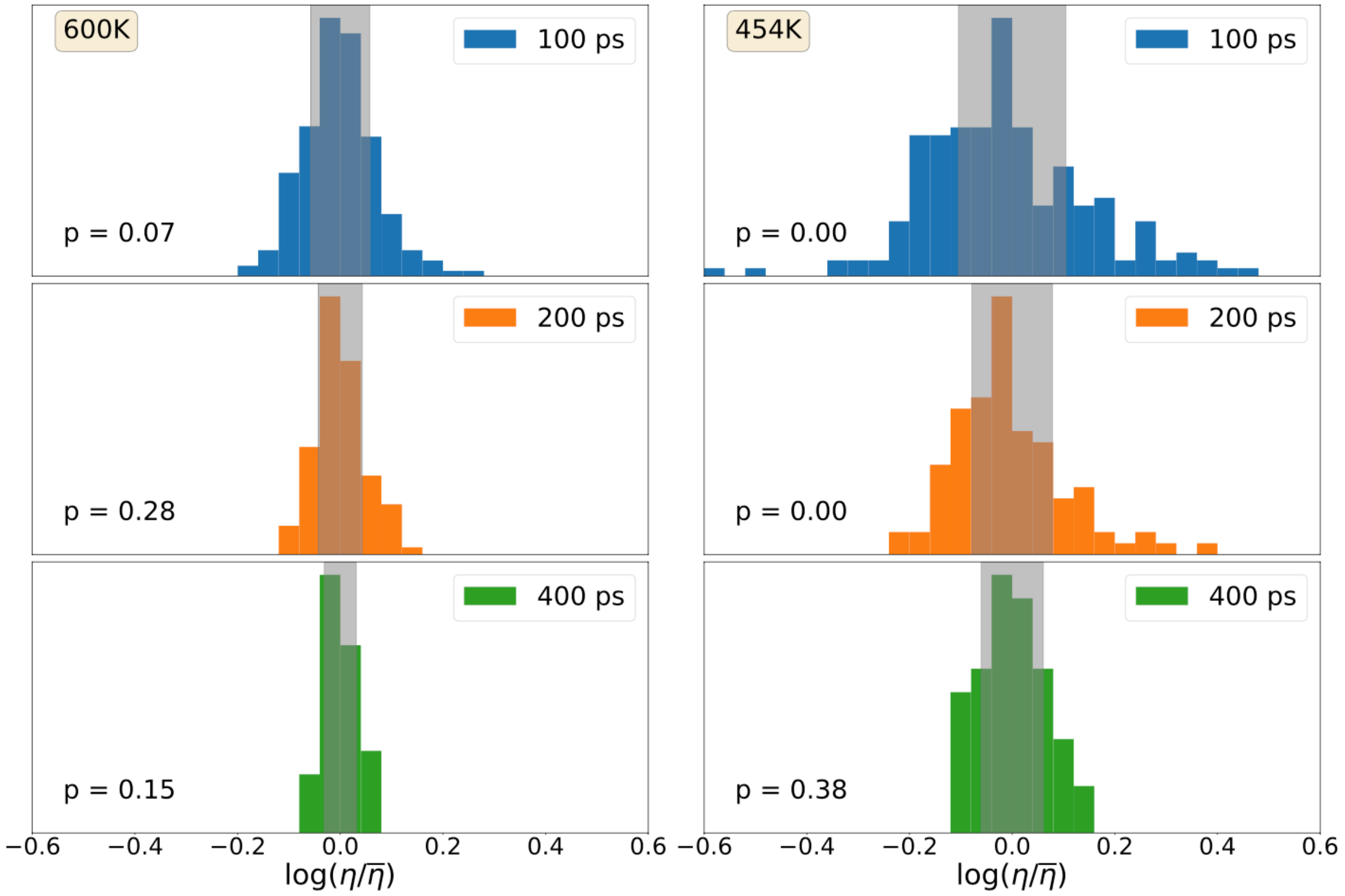

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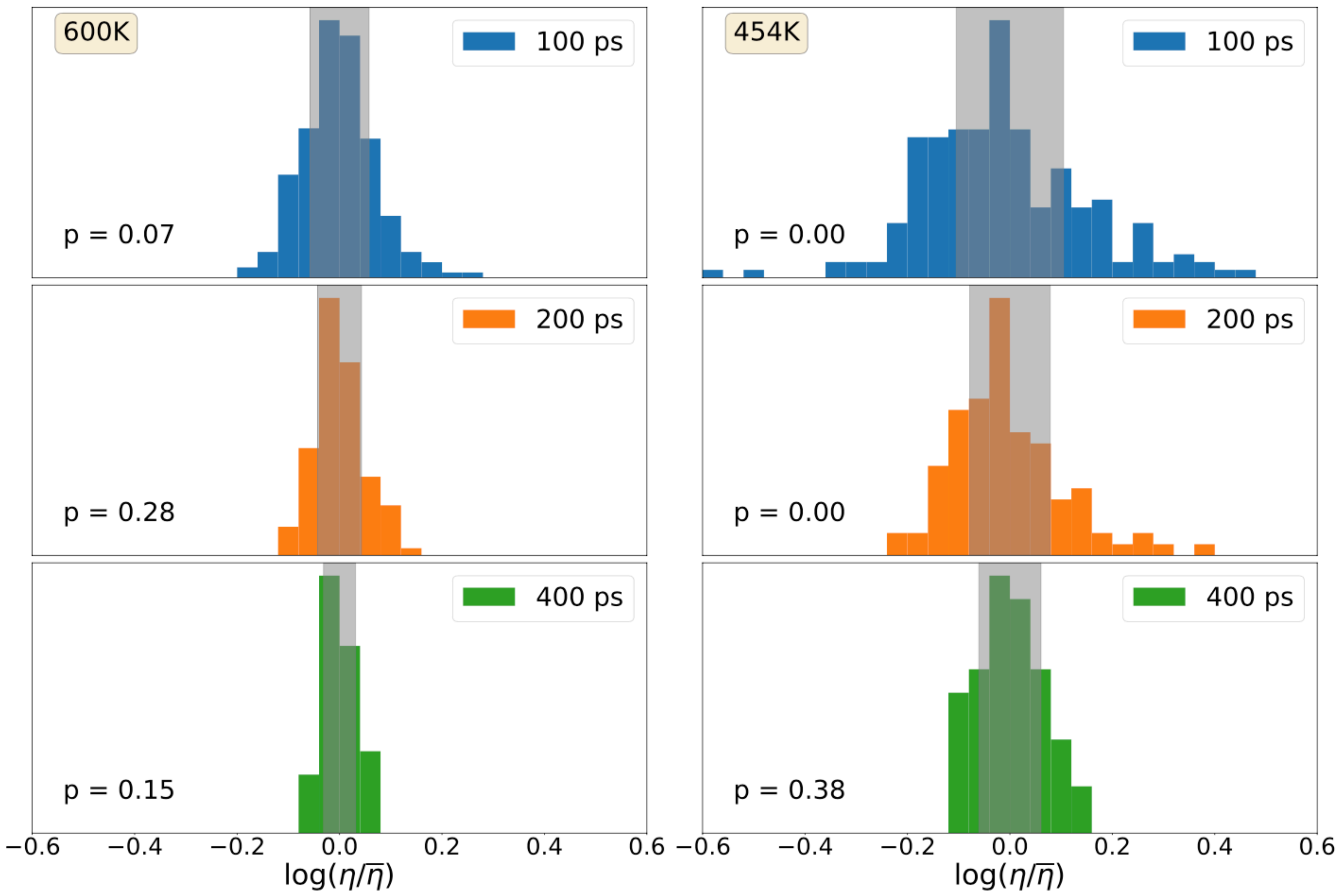

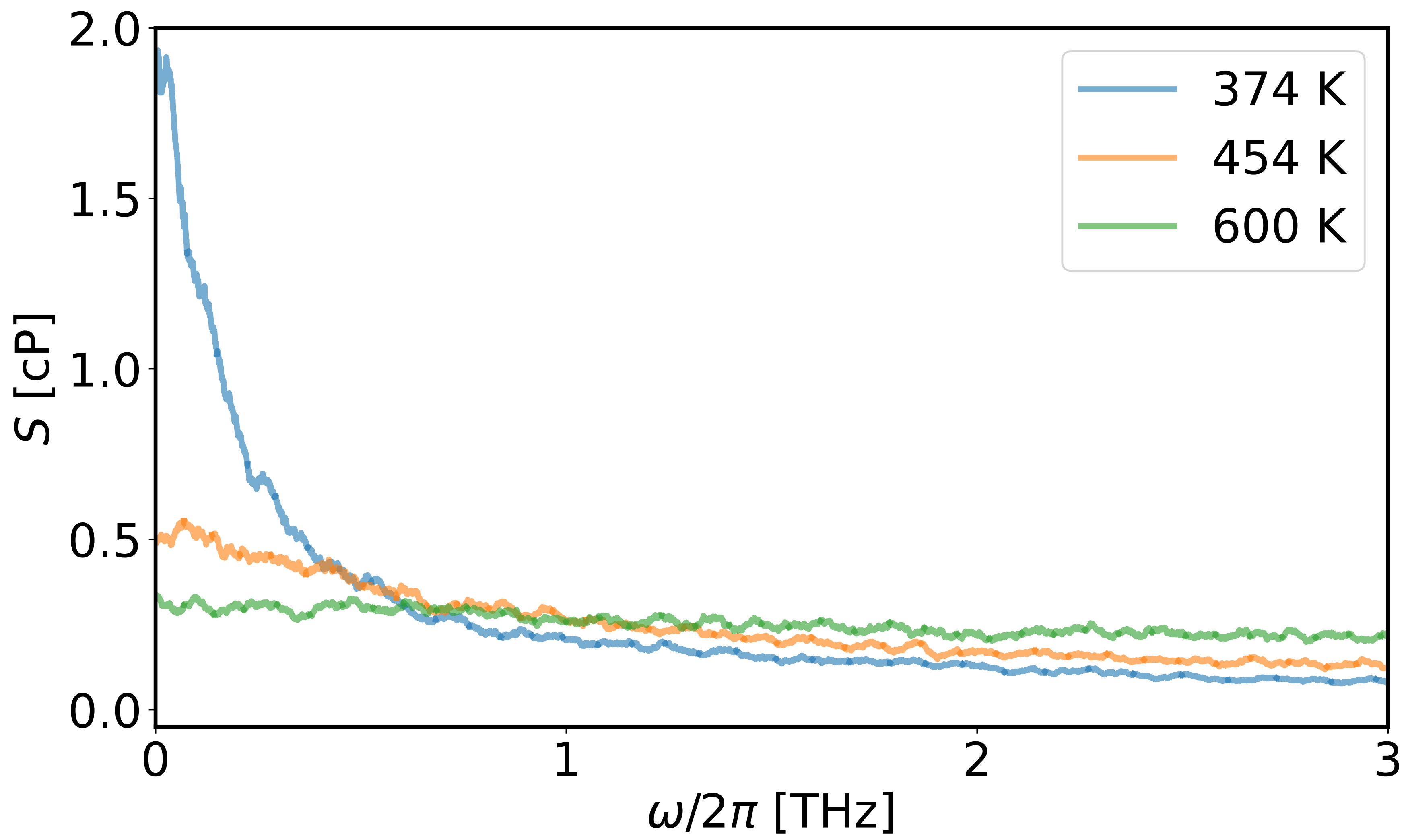

the cepstral cavobulary

The Quefrency Alanysis of Time Series for Echoes: Cepstrum, Pseudo-Autocovariance, Cross-Cepstrum and Saphe Cracking

Bruce P. Bogert, M. J. R. Healy, John W. Tukey†*
Bell Telephone Laboratories and Princeton University

Proceedings of the Symposium on Time Series Analysis (M. Rosenblatt, Ed) Chapter 15, 209-243. New York: Wiley, 1963.

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spectrum	....	cepstrum
frequency	....	quefrency
analysis	....	alansys
period	....	repiod
filtering	....	liftering
phase	....	saphe

SporTran: a code to estimate transport coefficients from current time series

Riccardo Bertossa[1], Loris Ercole[3,1], Stefano Baroni[1,2]
[1]SISSA, Italy, [2]CNR-IOM, Italy, [3]EPFL, Switzerland

github.com/sissaschoool/sportran

ELSEVIER
Computer Physics Communications
Volume 280, November 2022, 108470

SporTran: A code to estimate transport coefficients from the cepstral analysis of (multivariate) current time series ☆, ☆☆

https://doi.org/10.1016/j.cpc.2022.108470

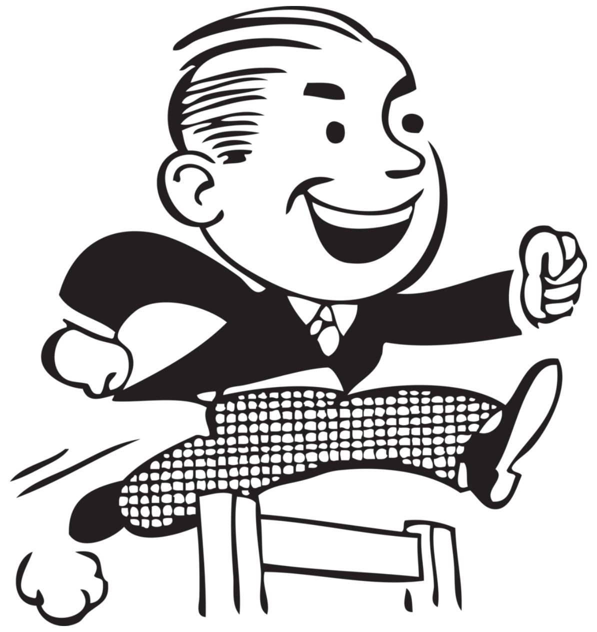
hurdles toward an ab initio Green-Kubo theory

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.

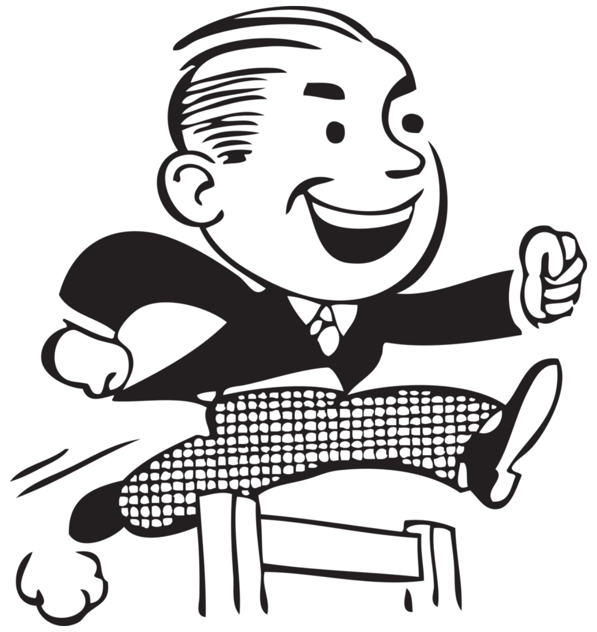


PRL **118,** 175901 (2017) PHYSICAL REVIEW LETTERS week ending 28 APRIL 2017

***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).



heat transport from lattice dynamics

$$\mathbf{J} = \sum_n \left(\dot{\mathbf{R}}_n e_n + \mathbf{R}_n \dot{e}_n \right)$$

heat transport from lattice dynamics

$$\mathbf{R}_n = \mathbf{R}_n^\circ + \mathbf{u}_n$$

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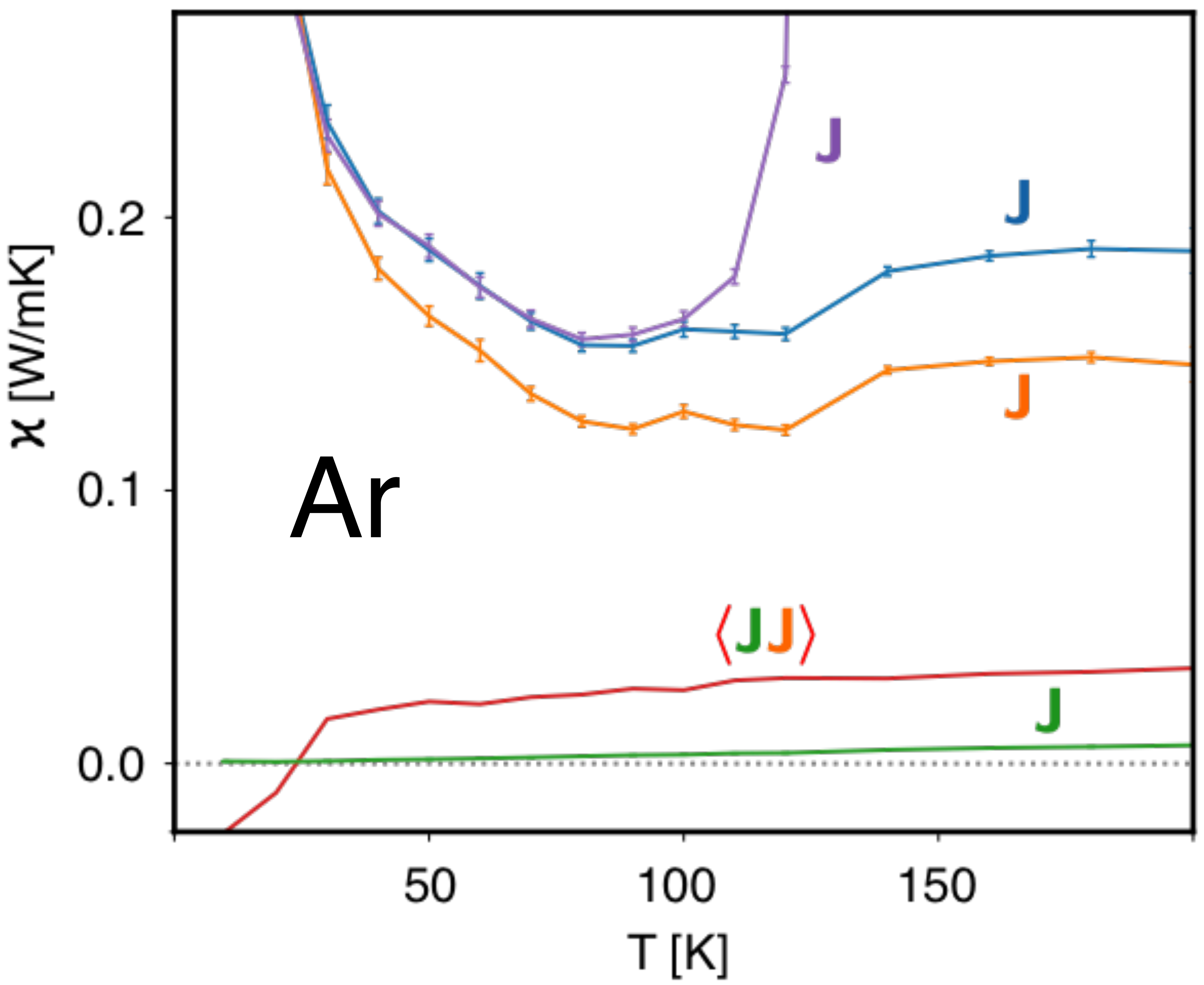

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$$= \sum_n \mathbf{R}_n^\circ \dot{e}_n + \frac{d}{dt} \sum_n \mathbf{u}_n e_n$$

$$\Phi_{i\beta}^{j\gamma} = \left. \frac{\partial^2 E}{\partial u_{i\beta} \partial u_{j\gamma}} \right|_{\mathrm{u}=0}$$

$$J_\alpha = \frac{1}{2} \sum_{ij\beta\gamma} \left(R_{i\alpha}^\circ - R_{j\alpha}^\circ \right) \Phi_{i\beta}^{j\gamma} u_{i\beta} \dot{u}_{j\gamma},$$

heat transport from lattice dynamics

$$J_\alpha = \frac{1}{2} \sum_{ij\beta\gamma} \left(R^\circ_{i\alpha} - R^\circ_{j\alpha} \right) \Phi^{j\gamma}_{i\beta} u_{i\beta} \dot{u}_{j\gamma},$$

$$\kappa \propto \int_0^\infty dt \int du_\circ d\dot{u}_\circ \underbrace{J(u_t \dot{u}_t) J(u_\circ \dot{u}_\circ)}_{\text{4-th order polynomial}} \underbrace{\mathrm{e}^{-\beta H(u_\circ \dot{u}_\circ)}}_{\text{Gaussian}}$$

heat transport from lattice dynamics

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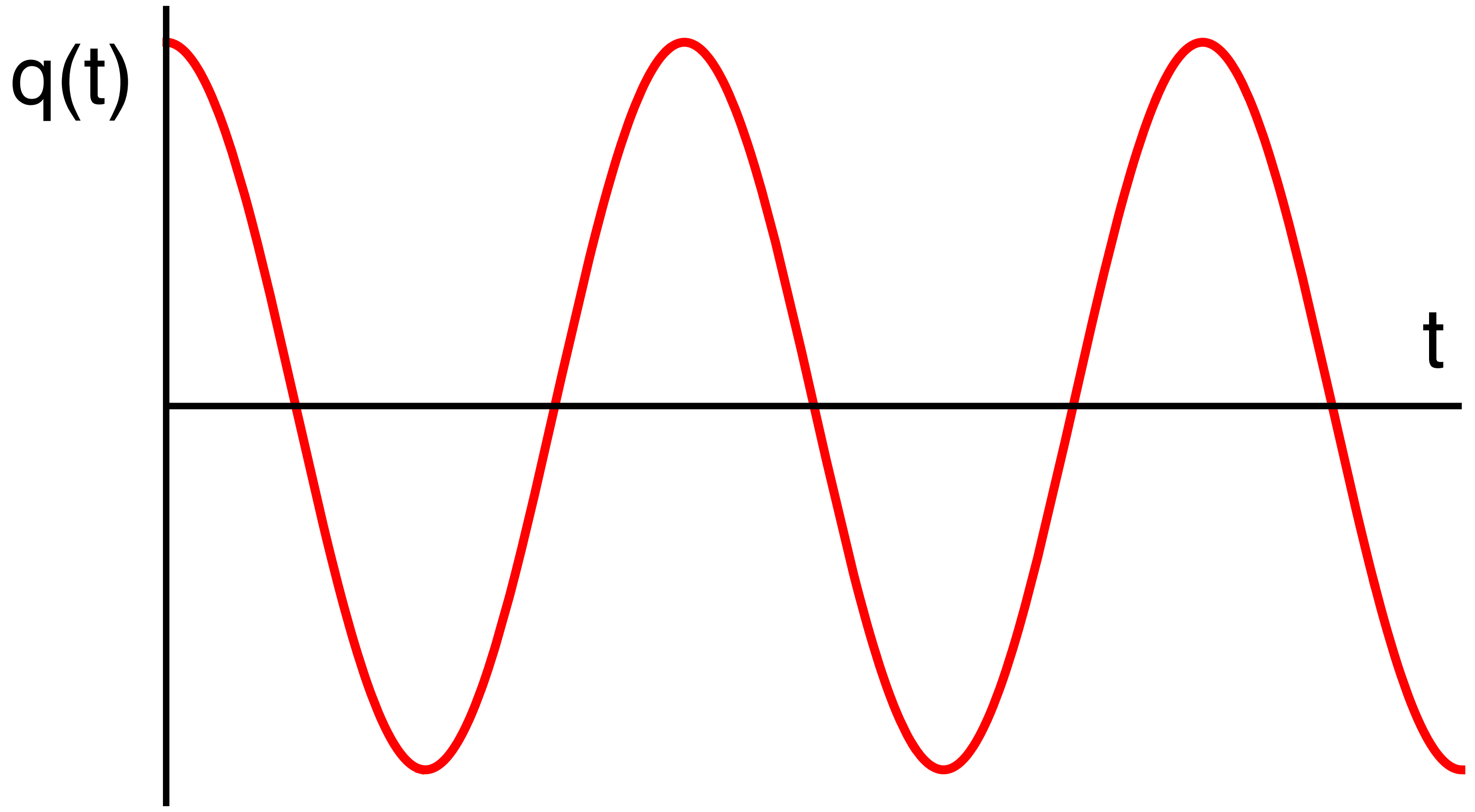

⟶ $\kappa = \infty$

heat transport from lattice dynamics

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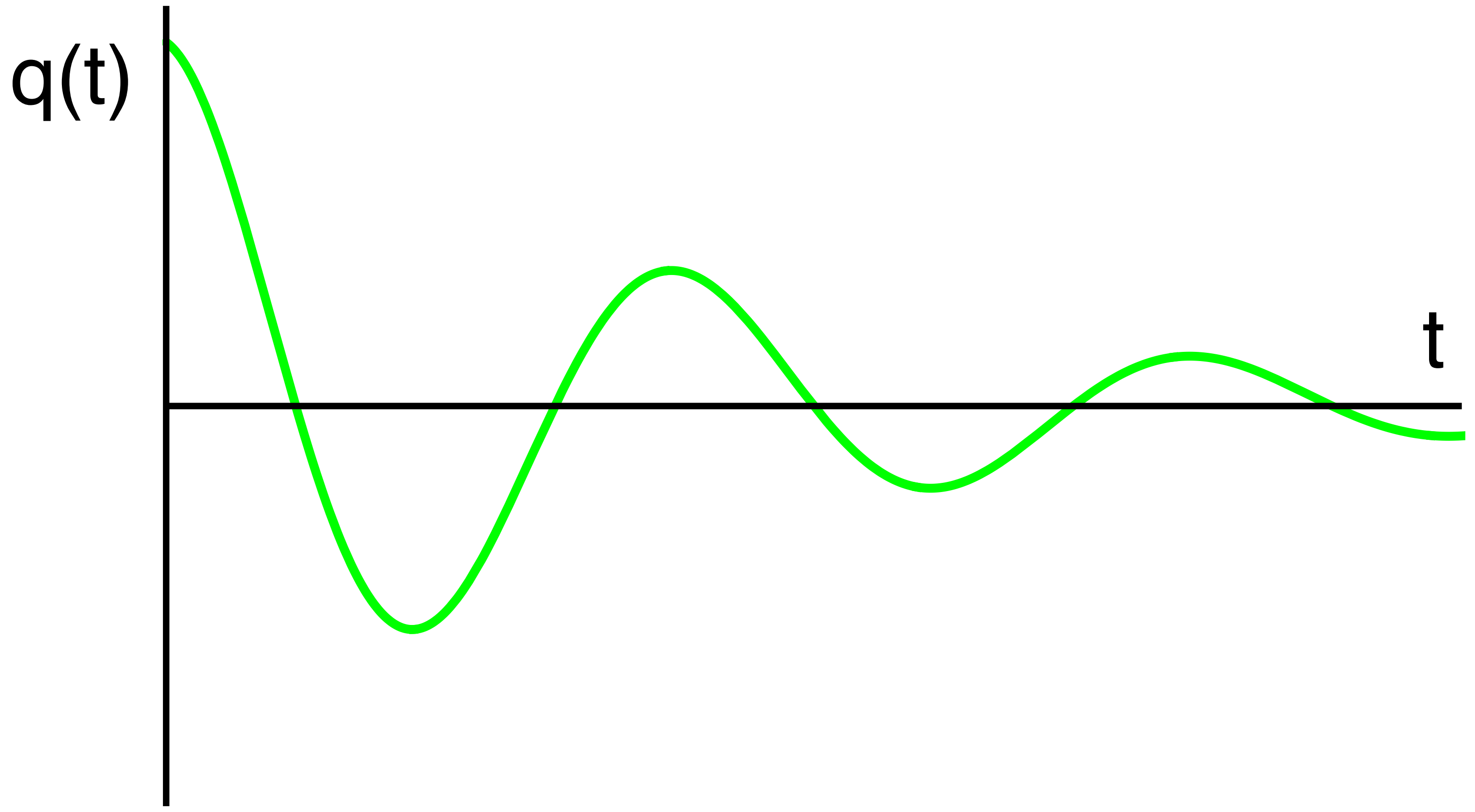

$\omega \mapsto \omega + i\gamma$

$\kappa < \infty$

heat transport from lattice dynamics

$$J_\alpha = \frac{1}{2}\sum_{ij\beta\gamma}\left(R^\circ_{i\alpha} - R^\circ_{j\alpha}\right)\Phi^{j\gamma}_{i\beta} u_{i\beta}\dot{u}_{j\gamma}$$

$$= \sum_{nm} v^\alpha_{nm}\sqrt{\omega_n\omega_m}\xi_n\pi_m$$

$$v^\alpha_{nm} = \frac{1}{2\sqrt{\omega_n\omega_m}}\sum_{ij\beta\gamma}\frac{R^\circ_{i\alpha} - R^\circ_{j\alpha}}{\sqrt{M_i M_j}}\Phi^{j\gamma}_{i\beta} e^{i\beta}_n e^{j\gamma}_m$$

$$\kappa = \frac{1}{V}\sum_{nm} c_{nm}\left(v_{nm}\right)^2 \tau^\circ_{nm}$$

$$\tau^\circ_{nm} = \frac{\gamma_n + \gamma_m}{(\gamma_n + \gamma_m)^2 + (\omega_n - \omega_m)^2}$$

$$c_{nm} = \frac{\hbar\omega_m\omega_n}{T}\frac{n(\omega_n) - n(\omega_m)}{\omega_m - \omega_n} \approx k_B\left(\frac{\hbar\omega}{k_B T}\right)^2 \frac{1}{\left(e^{\frac{\hbar\omega}{k_B T}} - 1\right)^2}$$

heat transport from lattice dynamics

$$J_\alpha = \frac{1}{2}\sum_{ij\beta\gamma}\left(R^\circ_{i\alpha} - R^\circ_{j\alpha}\right)\Phi^{j\gamma}_{i\beta} u_{i\beta}\dot{u}_{j\gamma},$$

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In a periodic system

$$v_{nn'} = \delta_{\nu\nu'}\delta_{\mathbf{q}\mathbf{q}'}$$

L. Isaeva, G. Barbalinardo, D. Donadio, and S. Baroni, Nature Commun. in press (2019), https://arxiv.org/abs/1904.02255

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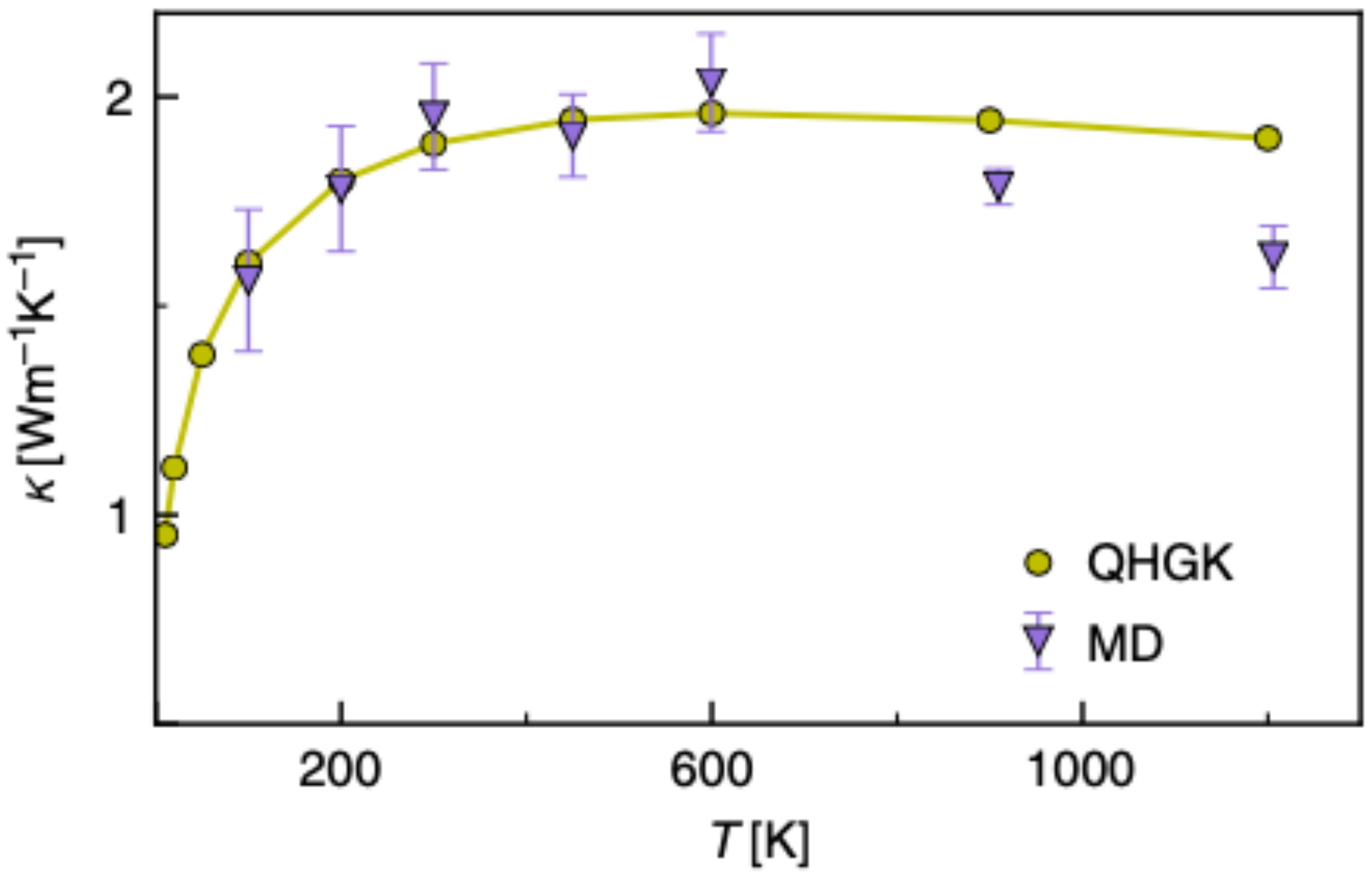
BTE

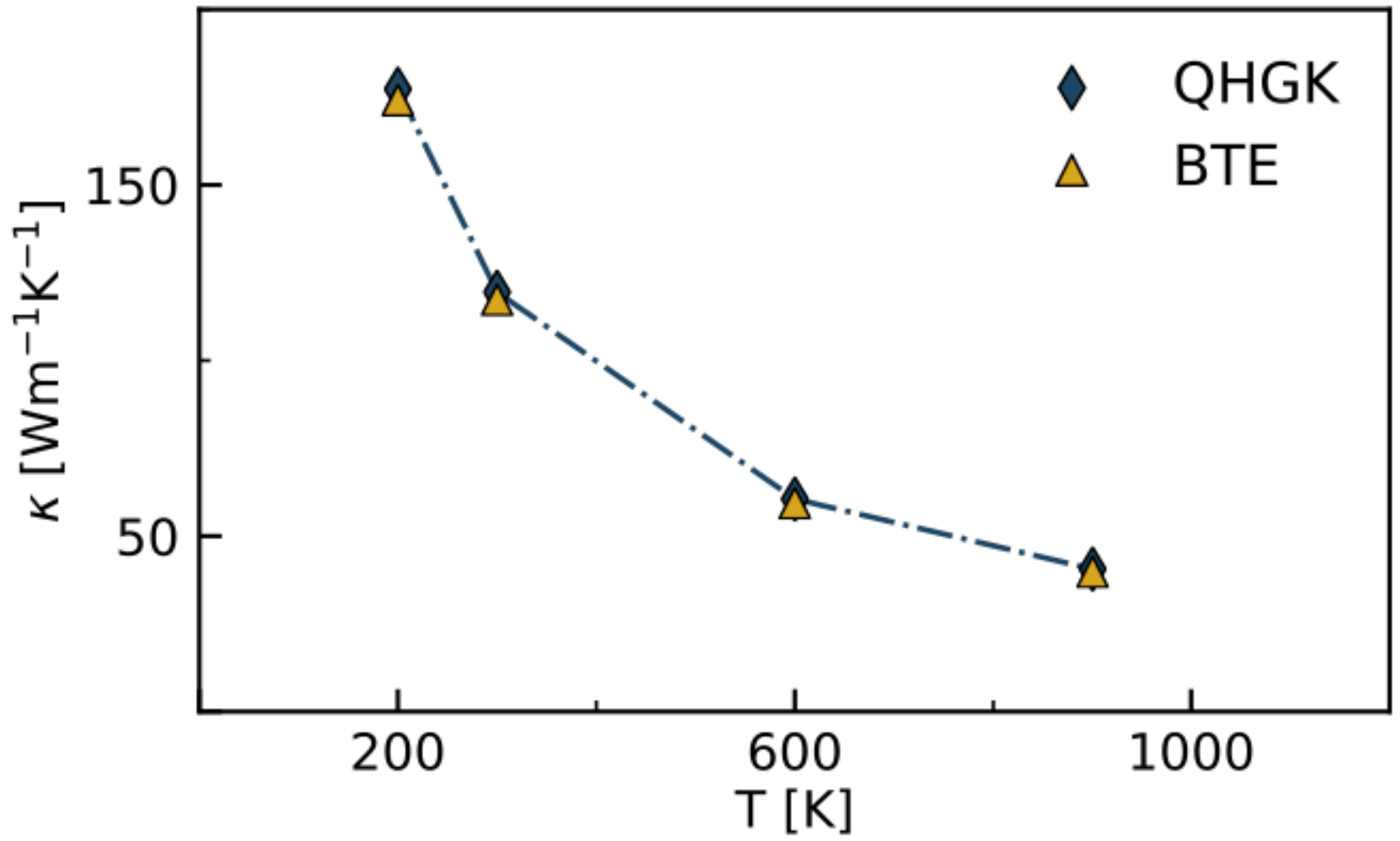
L. Isaeva, G. Barbalinardo, D. Donadio, and S. Baroni, Nature Commun. in press (2019), https://arxiv.org/abs/1904.02255

heat transport in c- and a-Si

a-Si



c-Si



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ARTICLE

https://doi.org/10.1038/s41467-019-11572-4 OPEN

Modeling heat transport in crystals and glasses from a unified lattice-dynamical approach

Leyla Isaeva[1], Giuseppe Barbalinardo[2], Davide Donadio[2] & Stefano Baroni[1,3]

From Green-Kubo to the full Boltzmann kinetic approach to heat transport in crystals and glasses

Alfredo Fiorentino[1], Stefano Baroni[1,2]

[1] SISSA, Trieste, Italy, [2] CNR-IOM, Trieste, Italy

SISSA

conclusions

- conserved currents are intrinsically ill-defined at the atomic scale
- conservation and extensiveness make transport coefficients independent of the specific microscopic representation of the conserved densities and currents
- this *gauge invariance* of transport coefficients makes it possible to compute thermal transport coefficients from DFT using equilibrium AIMD and the Green-Kubo formalism
- cepstral analysis of the current time series generated by (AI) MD substantially shorten the length of simulations needed to achieve a given target accuracy
- gauge invariance can be leveraged to unify the Green-Kubo and lattice Boltzmann approaches to heat transport in crystalline and amorphous solids

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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

these slides soon available at
http://talks.baroni.me