Car and Parrinello meet Green and Kubo

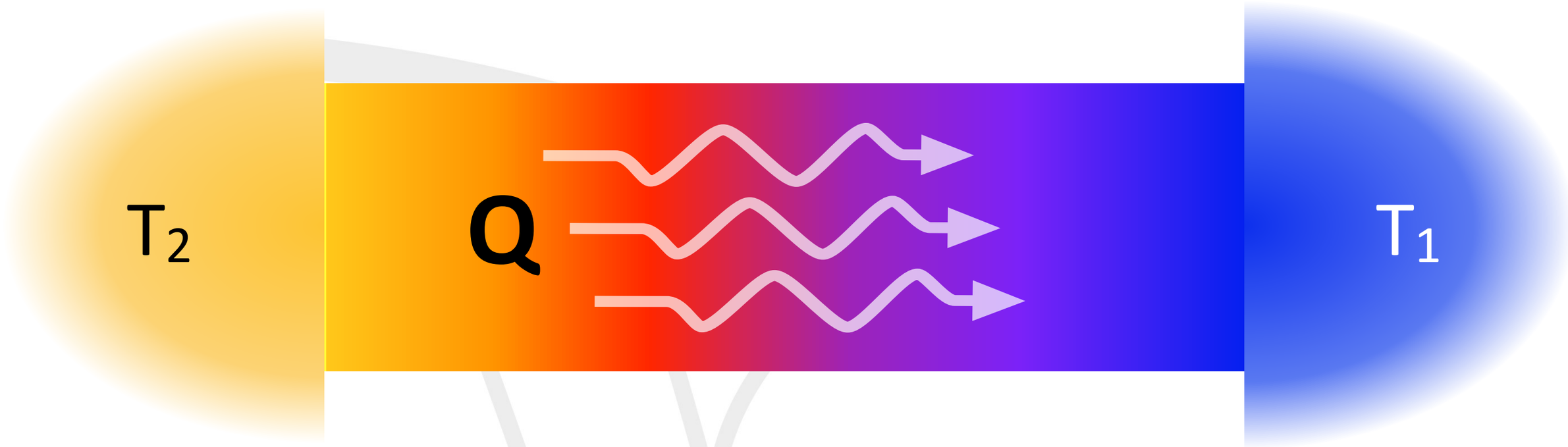
simulating atomic heat transport from equilibrium ab-initio molecular dynamics

Stefano Baroni

Scuola Internazionale Superiore di Studi Avanzati, Trieste

keynote talk given at the *XXIX IUPAP Conference on Computational Physics*, Paris, July 9-13, 2017

what heat transport is all about



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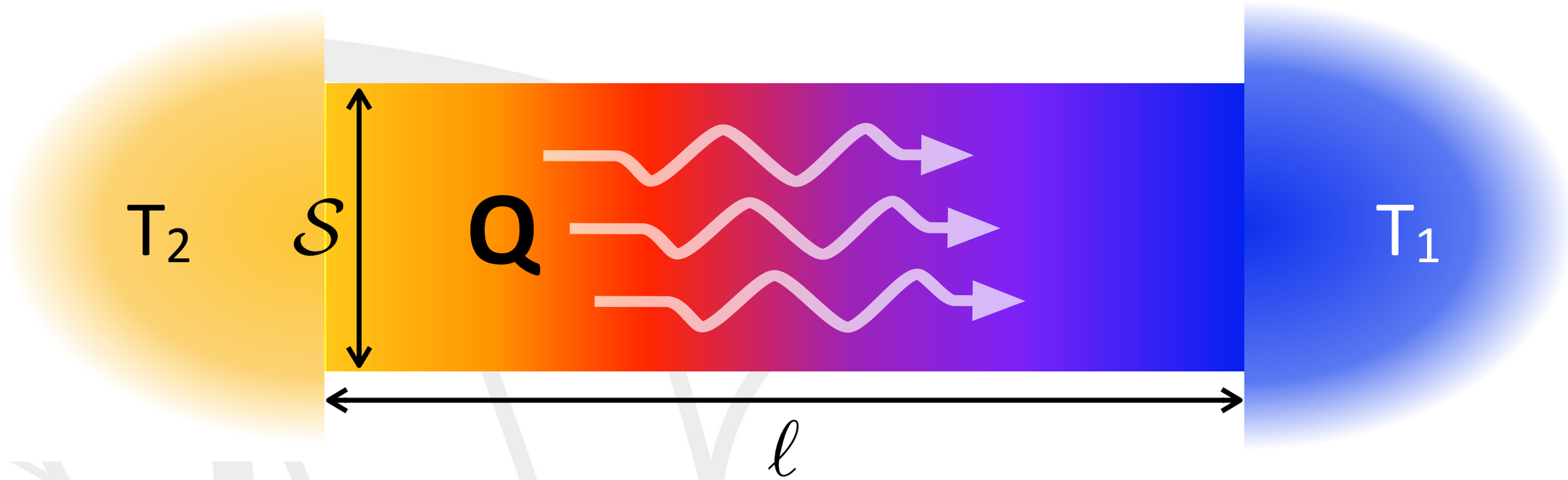

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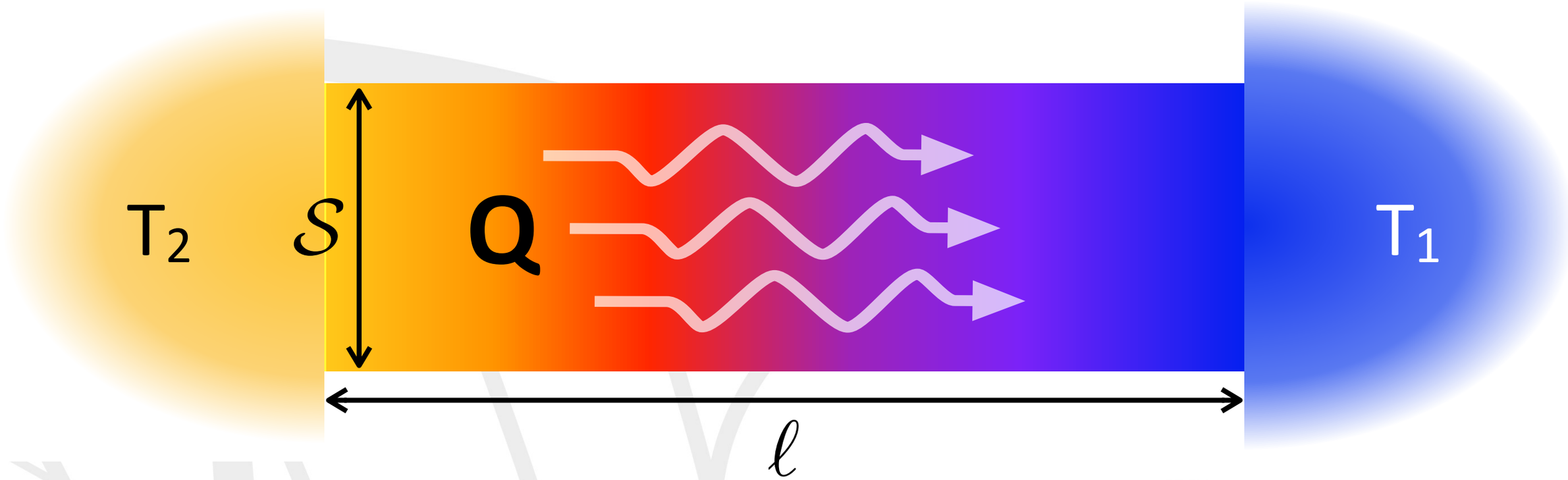

$$\frac{1}{\mathcal{S}}\frac{\mathrm{dQ}}{\mathrm{dt}} = -\kappa\frac{(\mathsf{T}_2 - \mathsf{T}_1)}{\ell}$$

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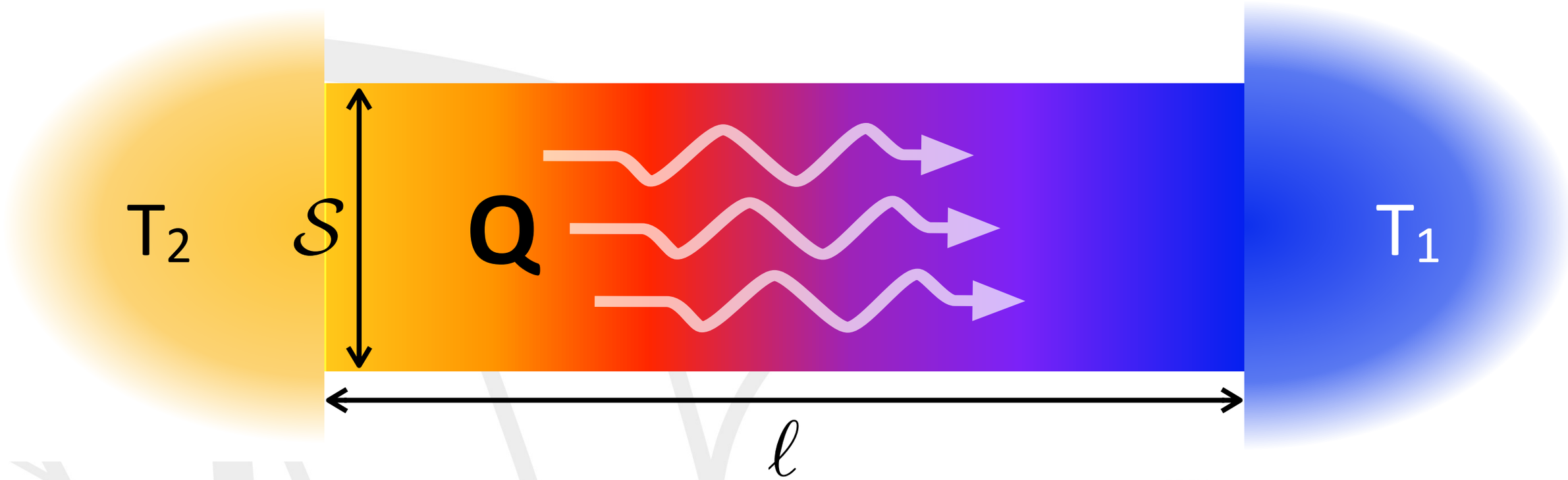

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$$\mathbf{J}_Q = -\kappa\nabla T$$

$$\frac{\partial T}{\partial t} = \frac{\kappa}{\rho c_p}\Delta T$$

why should we care?

why heat transport

- energy saving and heat dissipation
- heat shielding
- energy conversion
- earth and planetary sciences
- …

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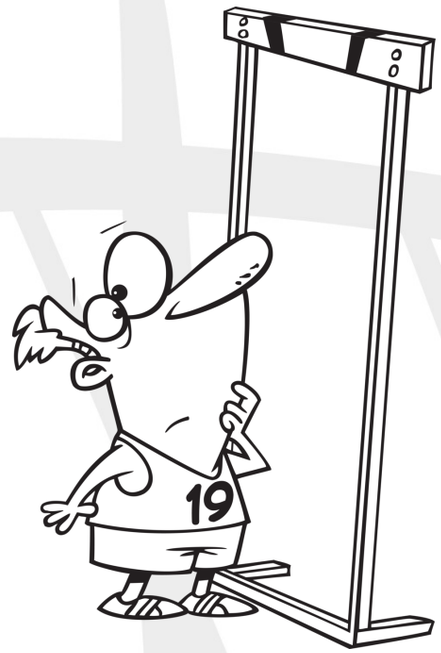
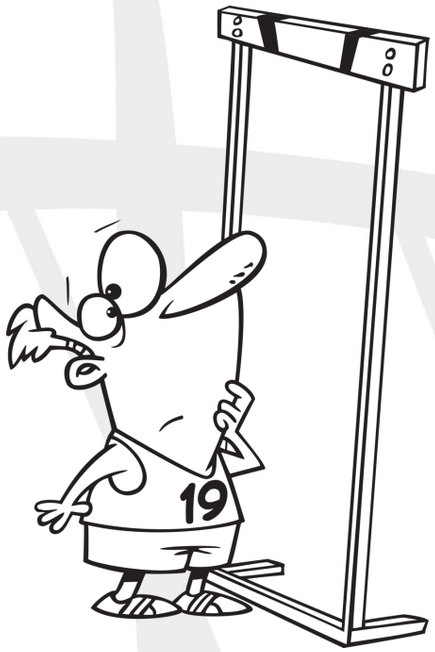
- … sheer curiosity …



the Green-Kubo formalism is not be compatible with ab-initio methods based on electronic-structure theory



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even if it were, coping with statistical noise requires impractically long molecular dynamics simulations

hydrodynamic fluctuations

Extensive, conserved, quantities are characterised by two relations:

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$$\frac{\partial \tilde{a}(\mathbf{k},t)}{\partial t} = -i\mathbf{k} \cdot \tilde{\mathbf{j}}(\mathbf{k},t)$$

the longer the wavelength, the slower the mode

Green-Kubo theory

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$$= \int \mathbf{r}\,\dot{e}(\mathbf{r},t)d\mathbf{r}$$

the classical MD ansatz

$$e(\mathbf{r},\mathrm{t}) = \sum_I \delta\big(\mathbf{r} - \mathbf{R}_I(\mathrm{t})\big)\epsilon_I\big(\mathbf{R}(\mathrm{t}),\mathbf{V}(\mathrm{t})\big)$$

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

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ab initio simulations

Thermal Conductivity of Periclase (MgO) from First Principles

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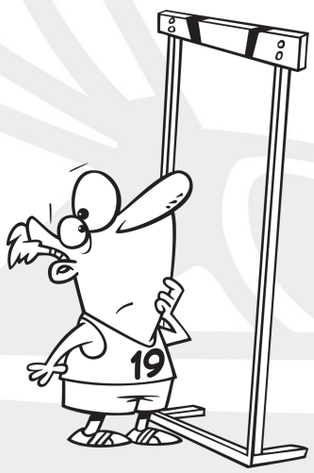
and Department of Geology and Geophysics, Louisiana State University, Baton Rouge, Louisiana 70803, USA

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.



insights from classical mechanics

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

$$= \text{cnst}$$

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insights from classical mechanics

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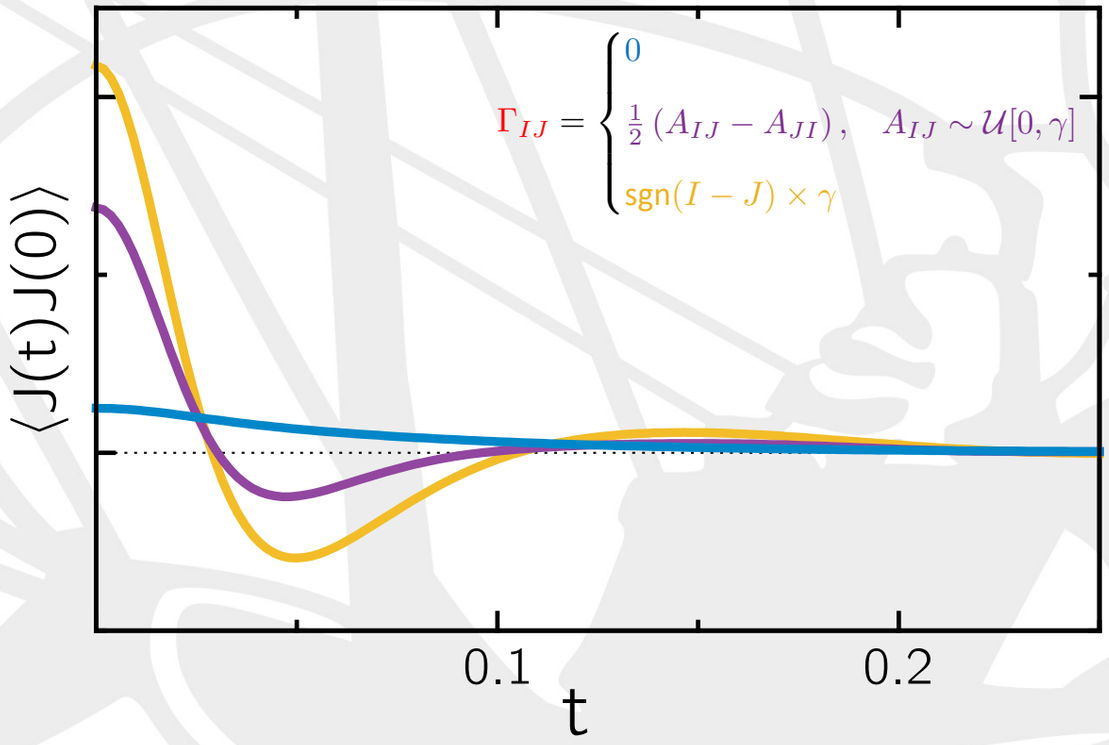

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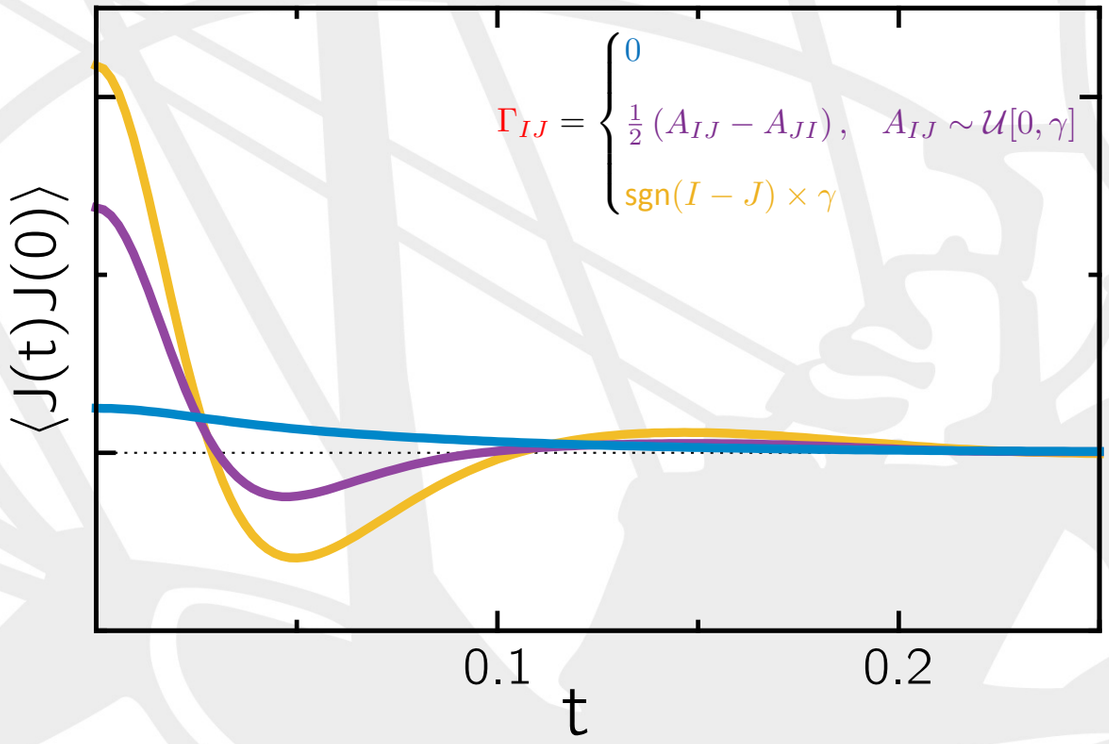

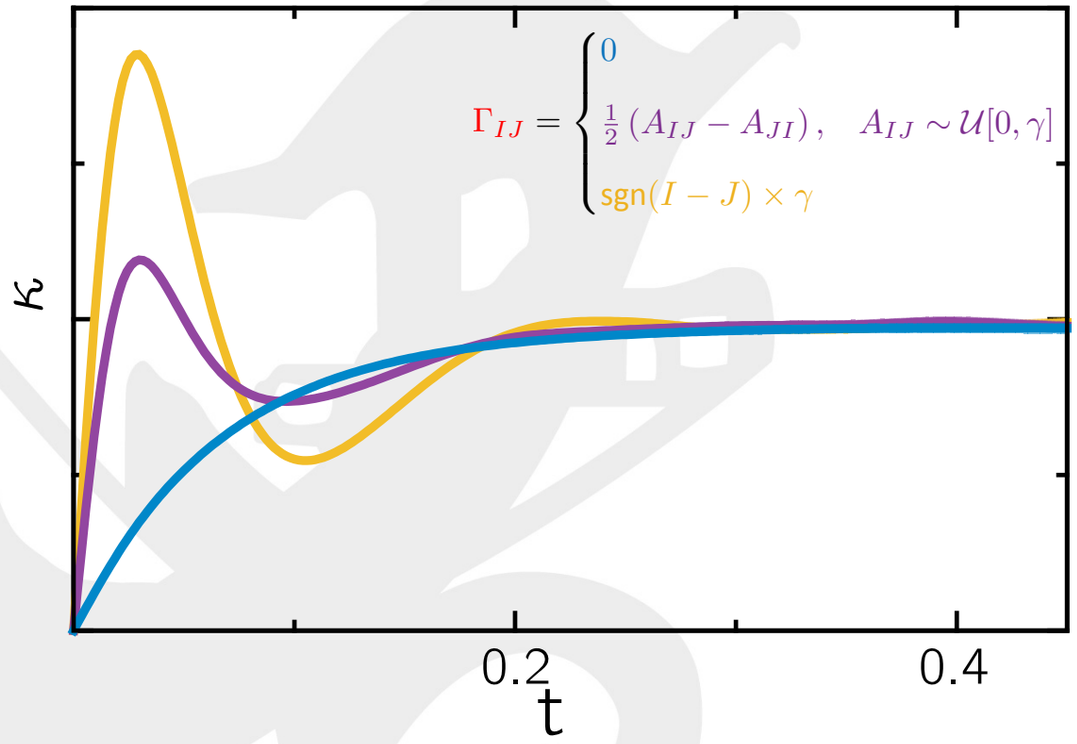

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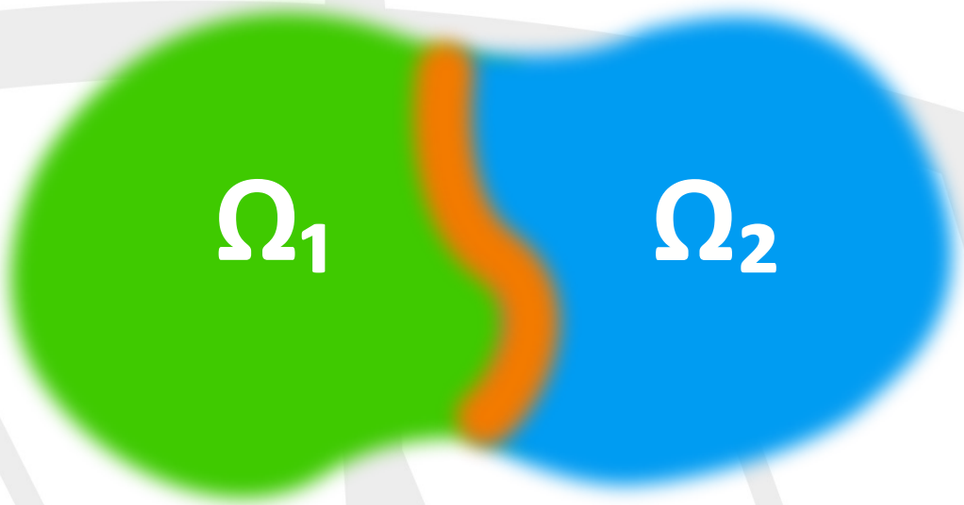
insights from classical mechanics

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

$$\kappa' = \kappa$$

gauge invariance



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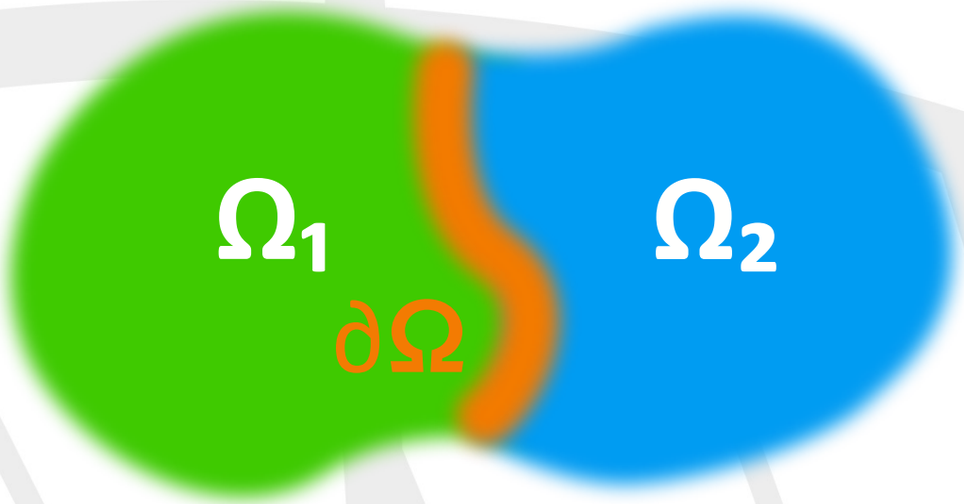

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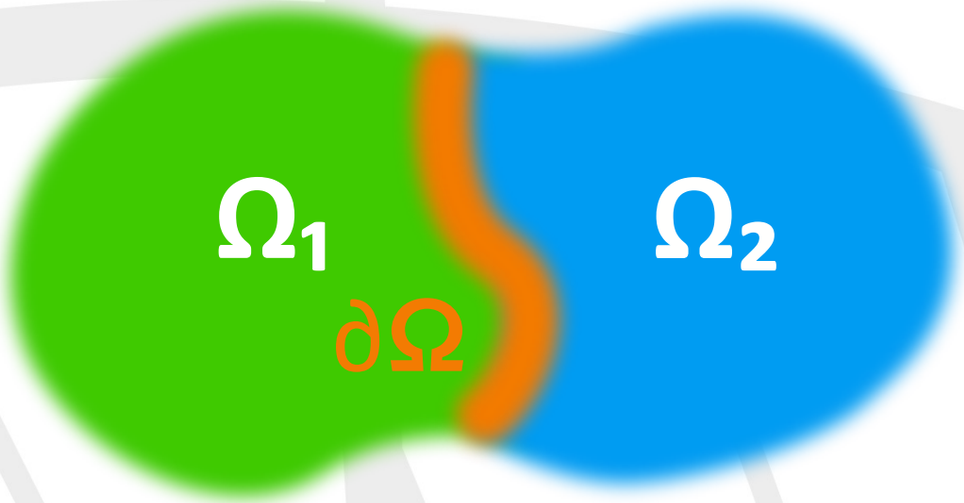

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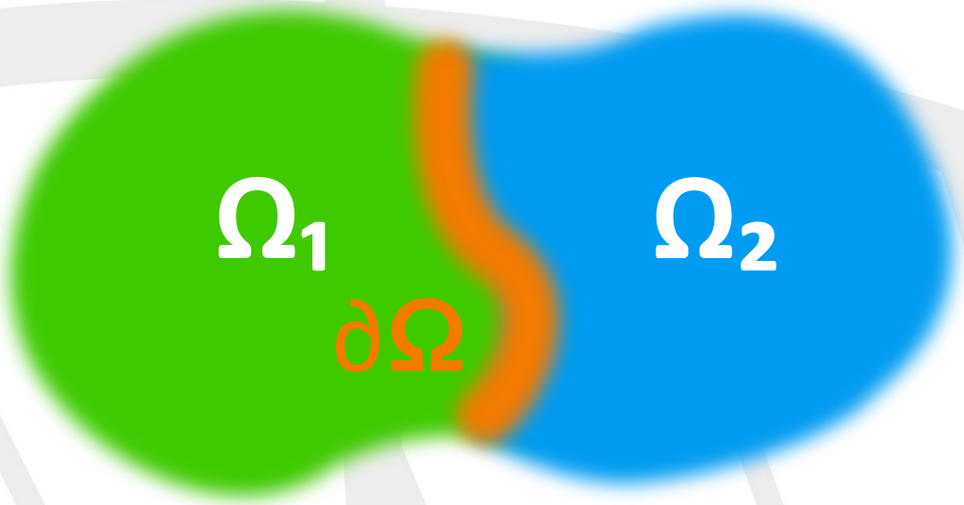

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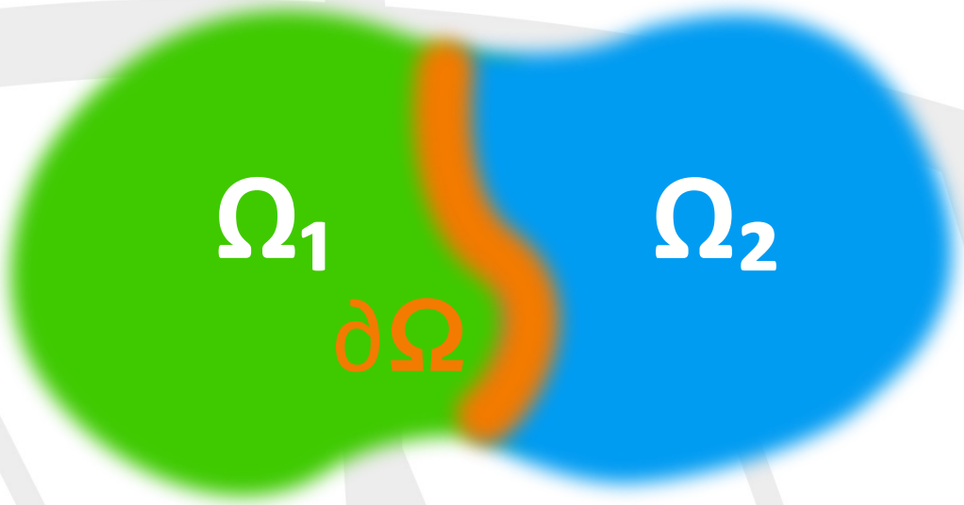

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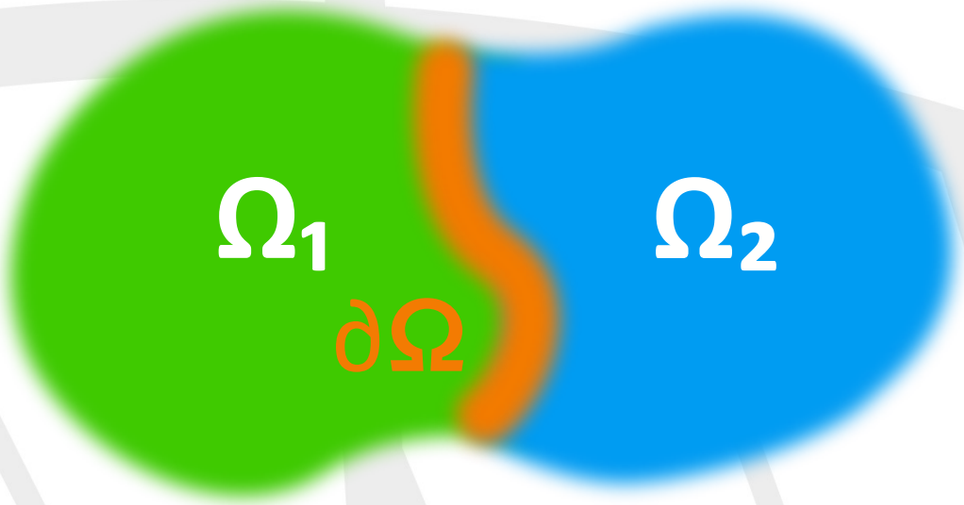

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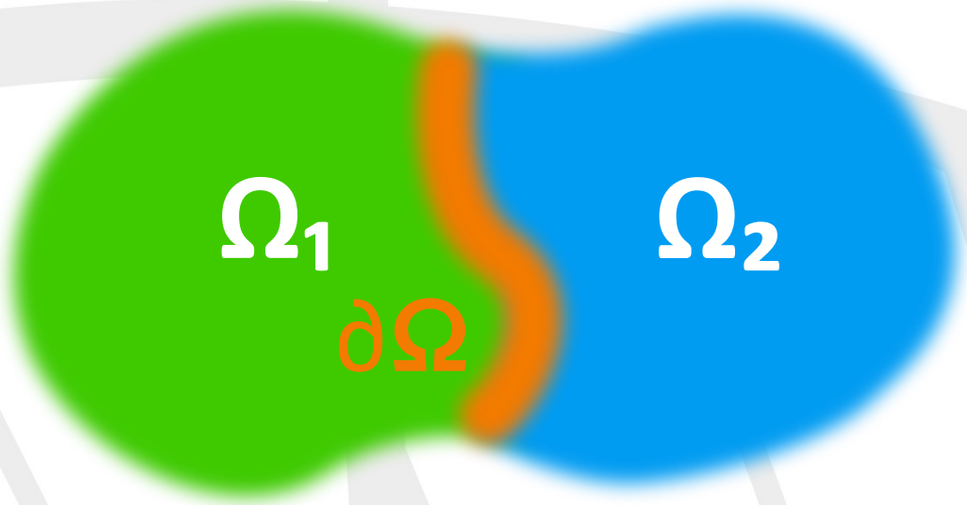

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$$\mathcal{E}[\Omega] = \int_\Omega e(\mathbf{r}) d\mathbf{r}$$

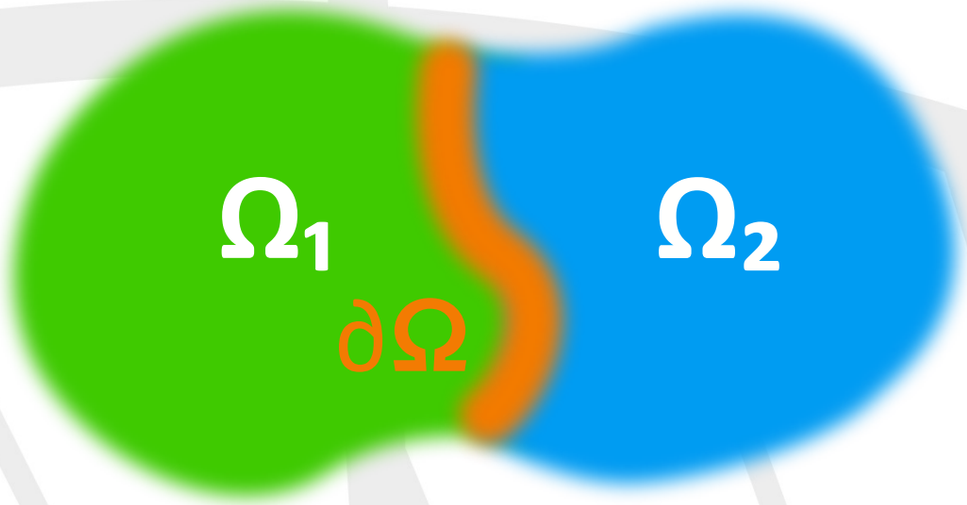
$$\mathcal{E}'[\Omega] = \mathcal{E}[\Omega] + \mathcal{O}[\partial\Omega]$$

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

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

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

gauge invariance



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gauge invariance

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

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gauge invariance

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

The corresponding energy fluxes differ by a total time derivative, and the heat transport coefficients coincide

density-functional theory

$$\mathsf{E}_{DFT} = \frac{1}{2}\sum_{I} M_I \mathsf{V}_I^2 + \frac{\mathsf{e}^2}{2}\sum_{I\neq J}\frac{\mathsf{Z}_I\mathsf{Z}_J}{\mathsf{R}_{IJ}}$$

$$+\sum_{v}\epsilon_v - \frac{1}{2}\mathsf{E}_H + \int\big(\epsilon_{XC}(\mathbf{r}) - \mu_{XC}(\mathbf{r})\big)\rho(\mathbf{r})d\mathbf{r}$$

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$$e_{DFT}(\mathbf{r}) = e_0(\mathbf{r}) + e_{KS}(\mathbf{r}) + e_H(\mathbf{r}) + e_{XC}(\mathbf{r})$$

$$e_0(\mathbf{r}) = \sum_I \delta(\mathbf{r}-\mathbf{R}_I)\left(\frac{1}{2}M_I V_I^2 + w_I\right)$$

$$e_{KS}(\mathbf{r}) = \mathsf{Re}\sum_v \varphi_v^*(\mathbf{r})\left(\hat{H}_{KS}\varphi_v(\mathbf{r})\right)$$

$$e_H(\mathbf{r}) = -\frac{1}{2}\rho(\mathbf{r})v_H(\mathbf{r})$$

$$e_{XC}(\mathbf{r}) = \left(\epsilon_{XC}(\mathbf{r}) - v_{XC}(\mathbf{r})\right)\rho(\mathbf{r})$$

the DFT energy current

$$\mathbf{J}_{DFT} = \int \mathbf{r}\dot{e}_{DFT}(\mathbf{r},t)d\mathbf{r}$$

$$= \mathbf{J}_{KS} + \mathbf{J}_H + \mathbf{J}_0' + \mathbf{J}_0 + \mathbf{J}_{XC}$$

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$$\mathbf{J}_{KS} = \sum_v \left(\langle \varphi_v | \mathbf{r} \hat{H}_{KS} | \dot{\varphi}_v \rangle + \varepsilon_v \langle \dot{\varphi}_v | \mathbf{r} | \varphi_v \rangle \right)$$

$$\mathbf{J}_H = \frac{1}{4\pi} \int \dot{v}_H(\mathbf{r}) \nabla v_H(\mathbf{r}) d\mathbf{r}$$

$$\mathbf{J}_0' = \sum_{v,I} \langle \varphi_v \left| (\mathbf{r} - \mathbf{R}_I) \left(\mathbf{V}_I \cdot \nabla_I \hat{v}_0 \right) \right| \varphi_v \rangle$$

$$\mathbf{J}_0 = \sum_I \left[\mathbf{V}_I e_I^0 + \sum_{L \neq I} (\mathbf{R}_I - \mathbf{R}_L) \left(\mathbf{V}_L \cdot \nabla_L w_I \right) \right]$$

$$\mathbf{J}_{XC} = \begin{cases} 0 & \text{(LDA)} \\ -\int \rho(\mathbf{r}) \dot{\rho}(\mathbf{r}) \partial \epsilon_{GGA}(\mathbf{r}) d\mathbf{r} & \text{(GGA)} \end{cases}$$

the DFT energy current

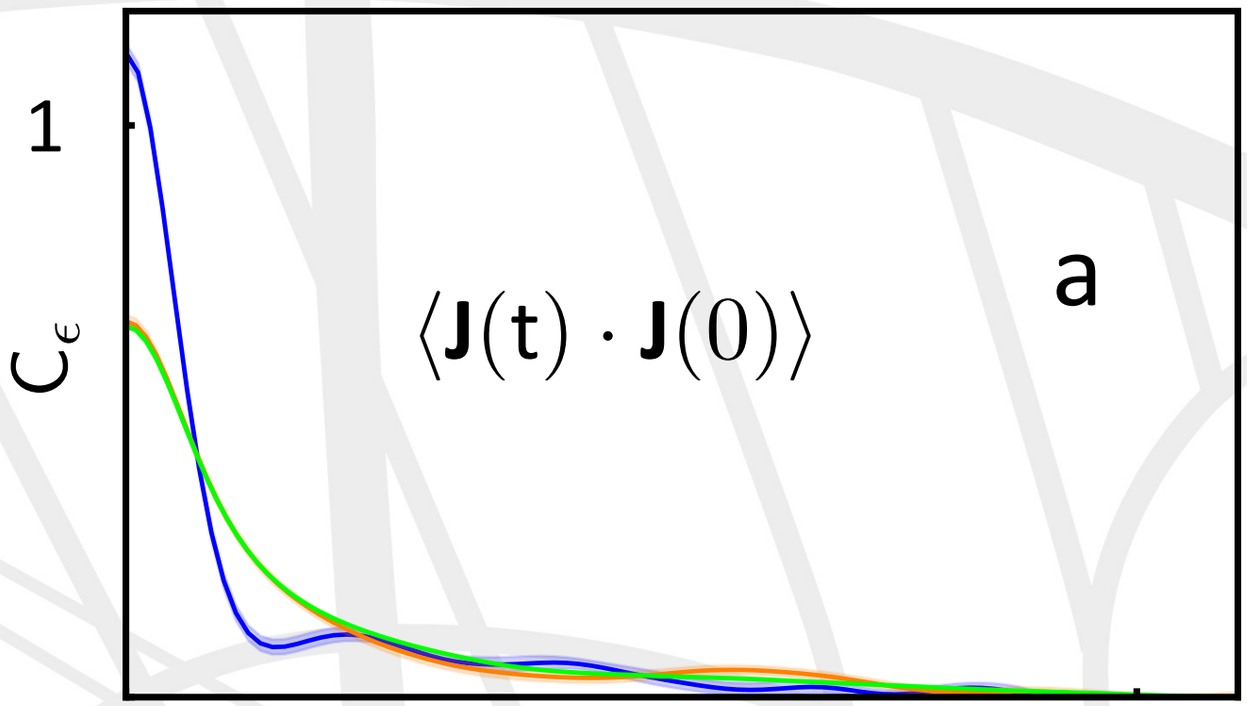
$$\mathbf{J}_{DFT} = \int \mathbf{r}\dot{e}_{DFT}(\mathbf{r},t)d\mathbf{r}$$

$$= \mathbf{J}_{KS} + \mathbf{J}_H + \mathbf{J}'_0 + \mathbf{J}_0 + \mathbf{J}_{XC}$$

$$\mathbf{J}_{KS} = \sum_v \left(\langle \varphi_v | \mathbf{r} \hat{H}_{KS} | \dot{\varphi}_v \rangle + \varepsilon_v \langle \dot{\varphi}_v | \mathbf{r} | \varphi_v \rangle \right)$$

- $|\dot{\varphi}_v\rangle$ and $\hat{H}_{KS}|\dot{\varphi}_v\rangle$ orthogonal to the occupied-state manifold
- $\hat{P}_c \mathbf{r} |\varphi_v\rangle$ computed from standard DFPT

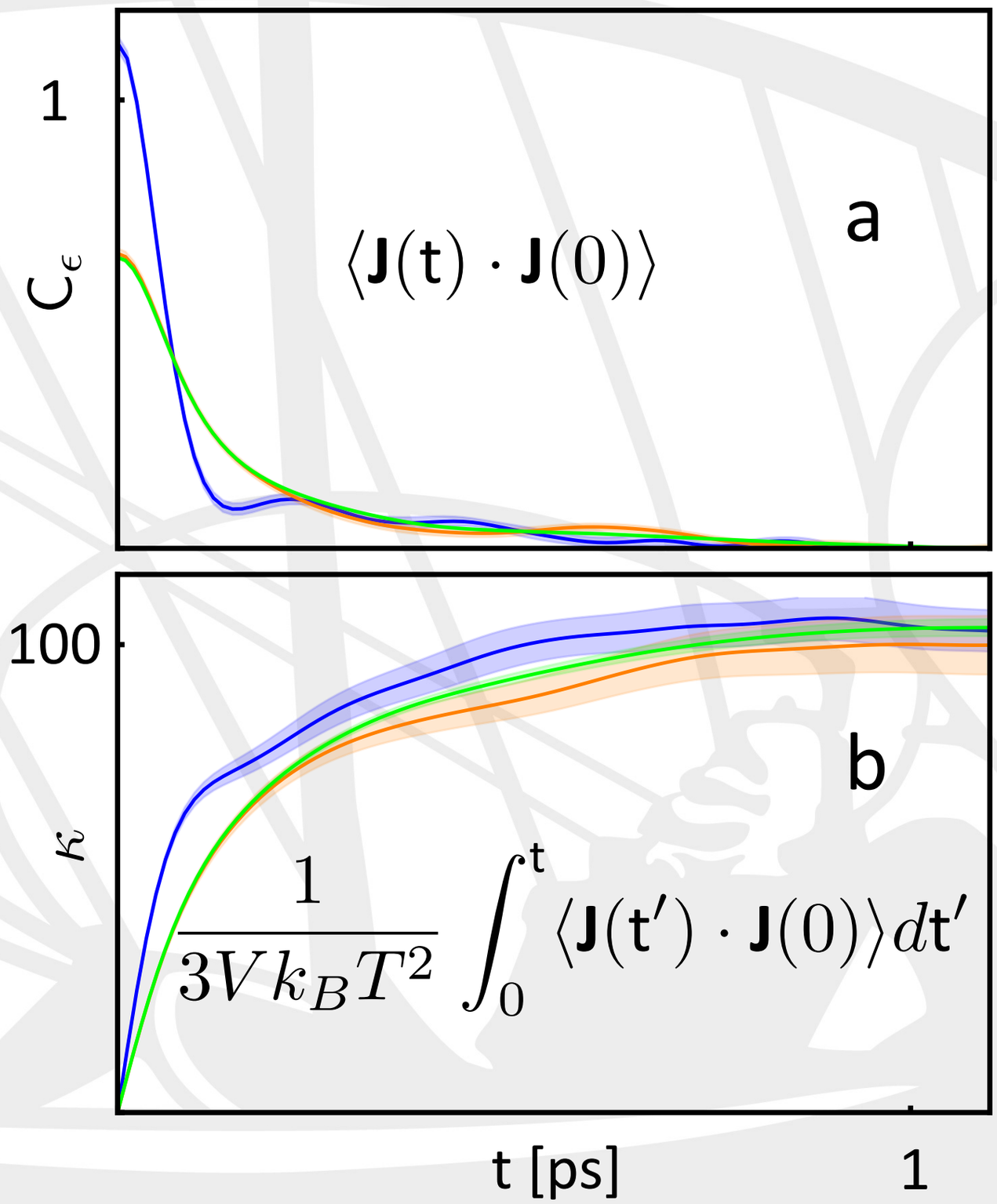
a benchmark



108 “LDA Ar” atoms
@bp density, T= 250 K

100 ps CP trajectory
100 ps classical FF trajectory
1 ns classical FF trajectory

a benchmark



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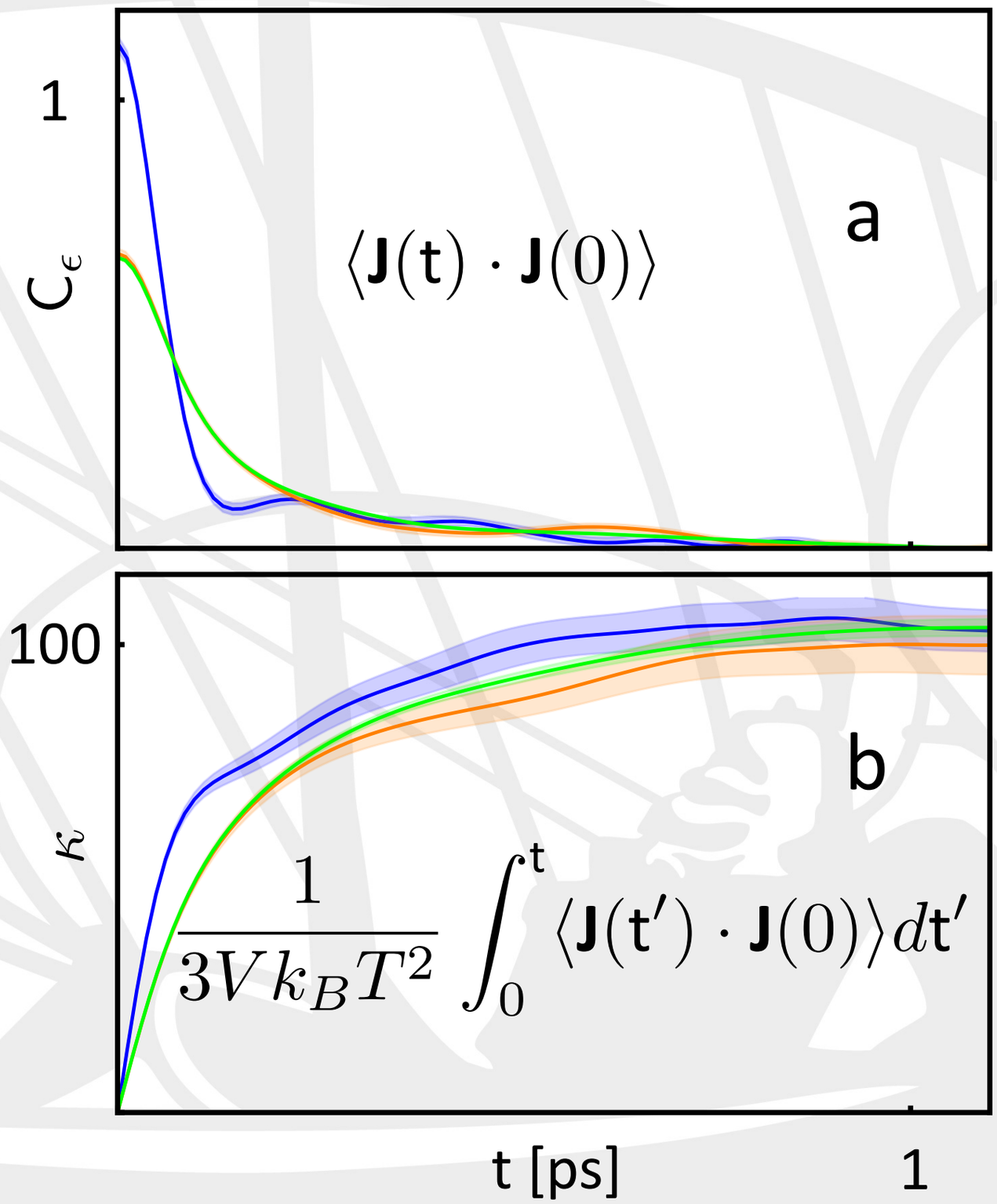

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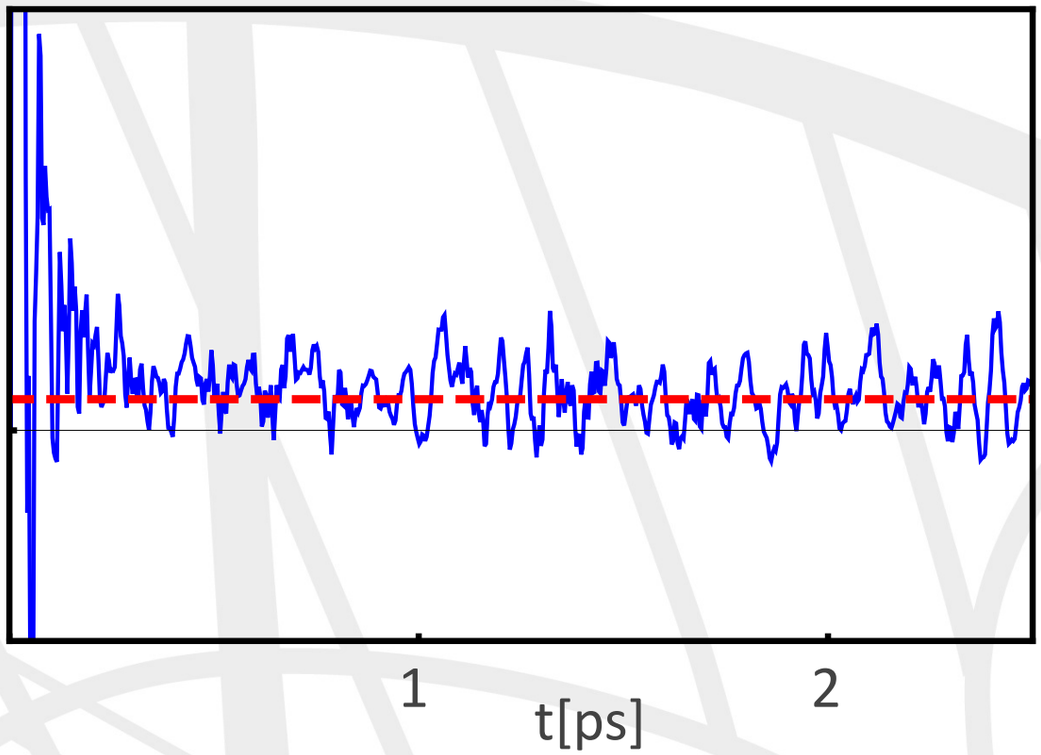
100 ps CP trajectory
100 ps classical FF trajectory
1 ns classical FF trajectory

same behavior at T=400 K

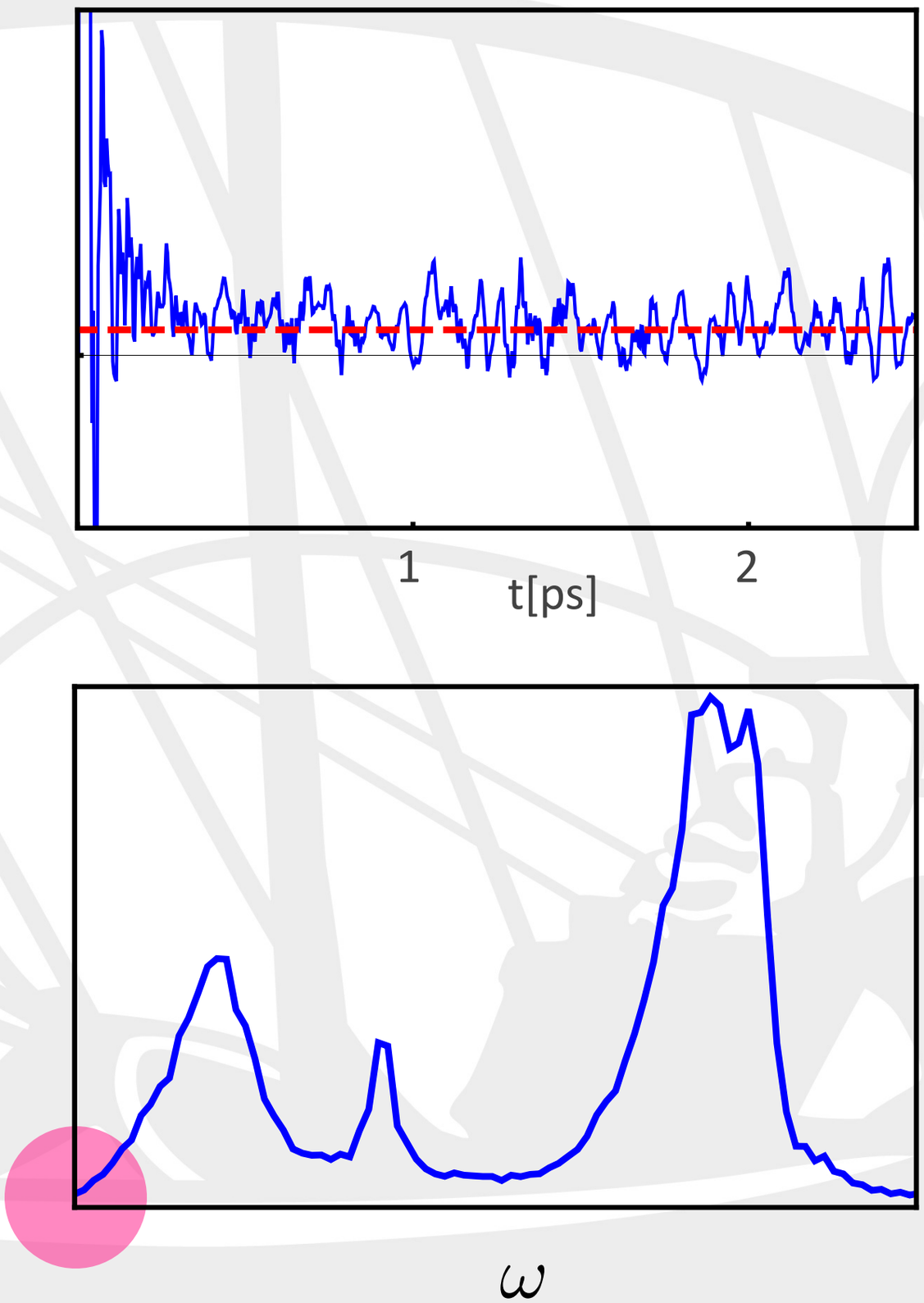
liquid (heavy) water



64 molecules, T=385 K
expt density @ac

$$\frac{1}{3Vk_BT^2}\int_0^{\mathrm{t}}\langle \mathbf{J}(\mathrm{t}')\cdot\mathbf{J}(0)\rangle d\mathrm{t}'$$

liquid (heavy) water



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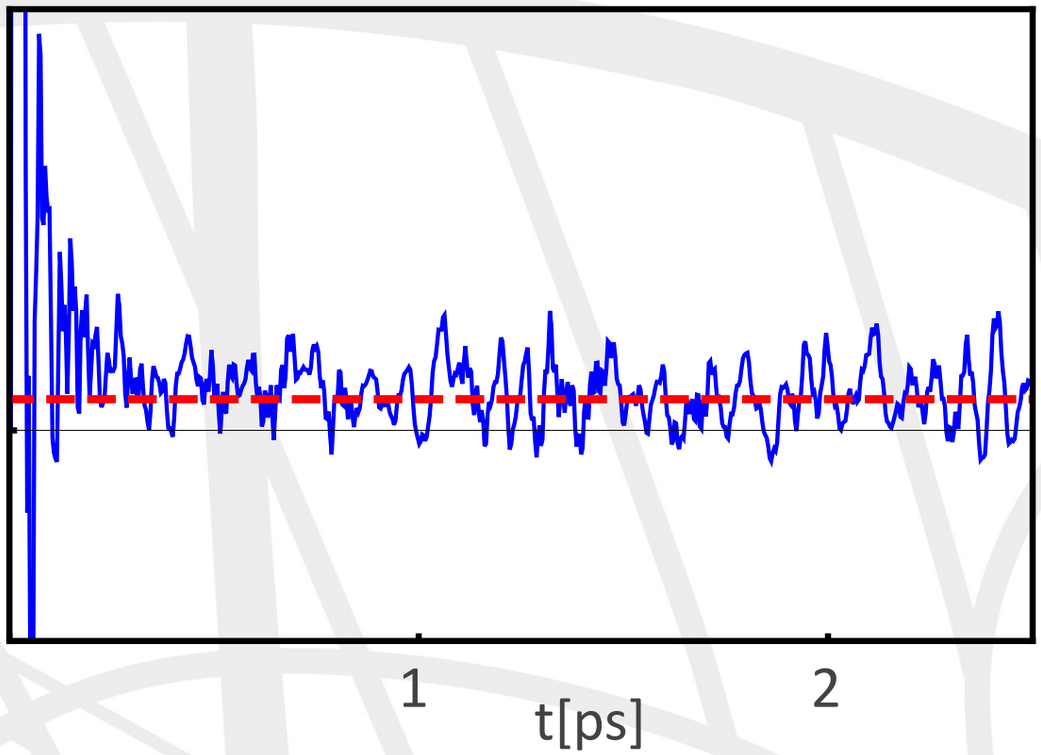
$$\frac{1}{3Vk_BT^2}\int_0^{\mathrm{t}}\langle \mathbf{J}(\mathrm{t}')\cdot\mathbf{J}(0)\rangle d\mathrm{t}'$$

$$S(\omega)=\int_{-\infty}^{\infty}\langle \mathbf{J}(\mathrm{t})\cdot\mathbf{J}(0)\rangle\ \mathrm{e}^{i\omega\mathrm{t}}d\mathrm{t}$$

liquid (heavy) water



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Einstein's relation

$$\frac{\mathrm{t}}{3Vk_BT^2}\int_0^{\mathrm{t}}\langle \mathbf{J}(\mathrm{t}')\cdot\mathbf{J}(0)\rangle d\mathrm{t}' \approx \frac{1}{6Vk_BT^2}\left\langle\left|\int_0^{\mathrm{t}}\mathbf{J}(\mathrm{t}')d\mathrm{t}'\right|^2\right\rangle$$

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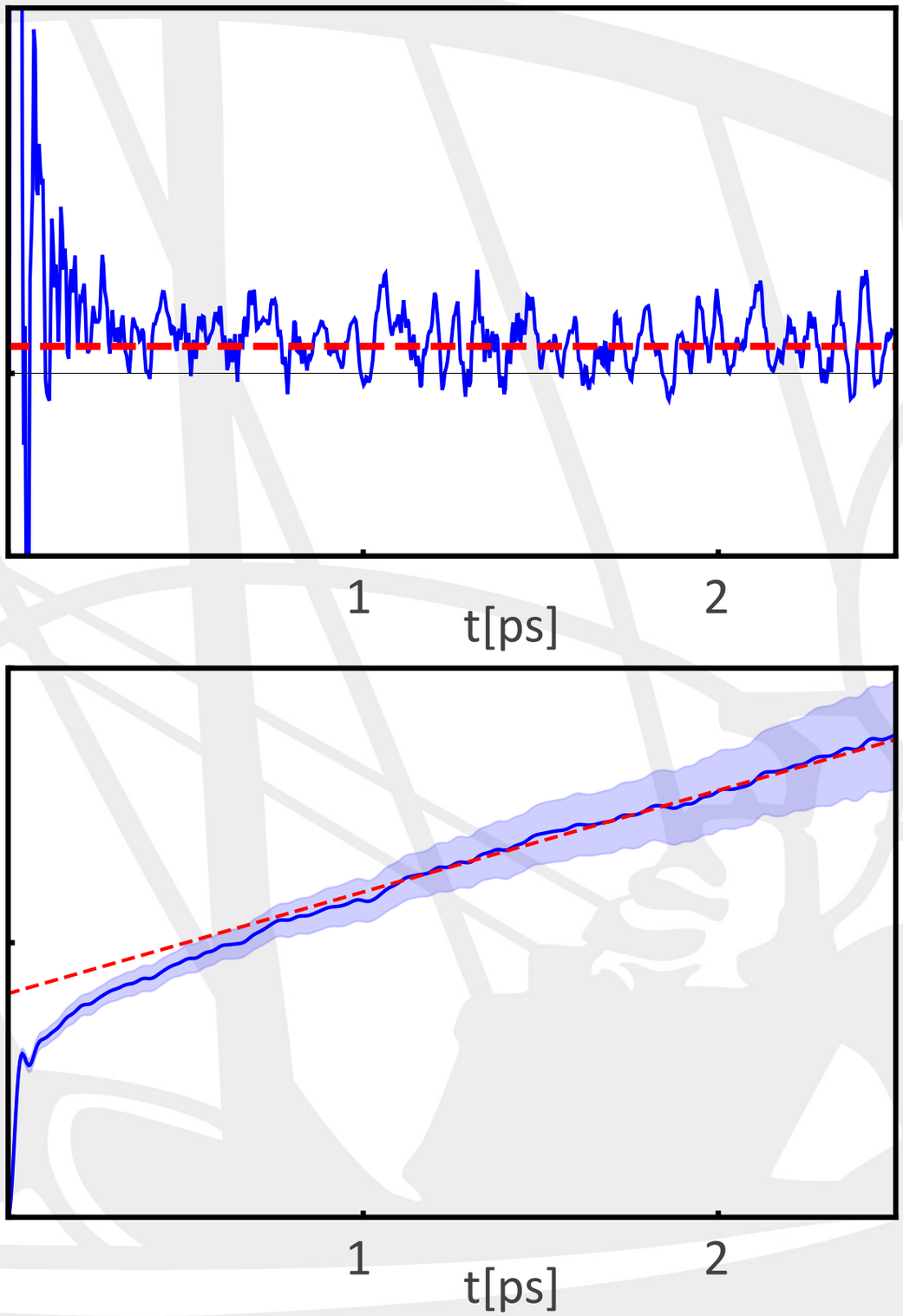

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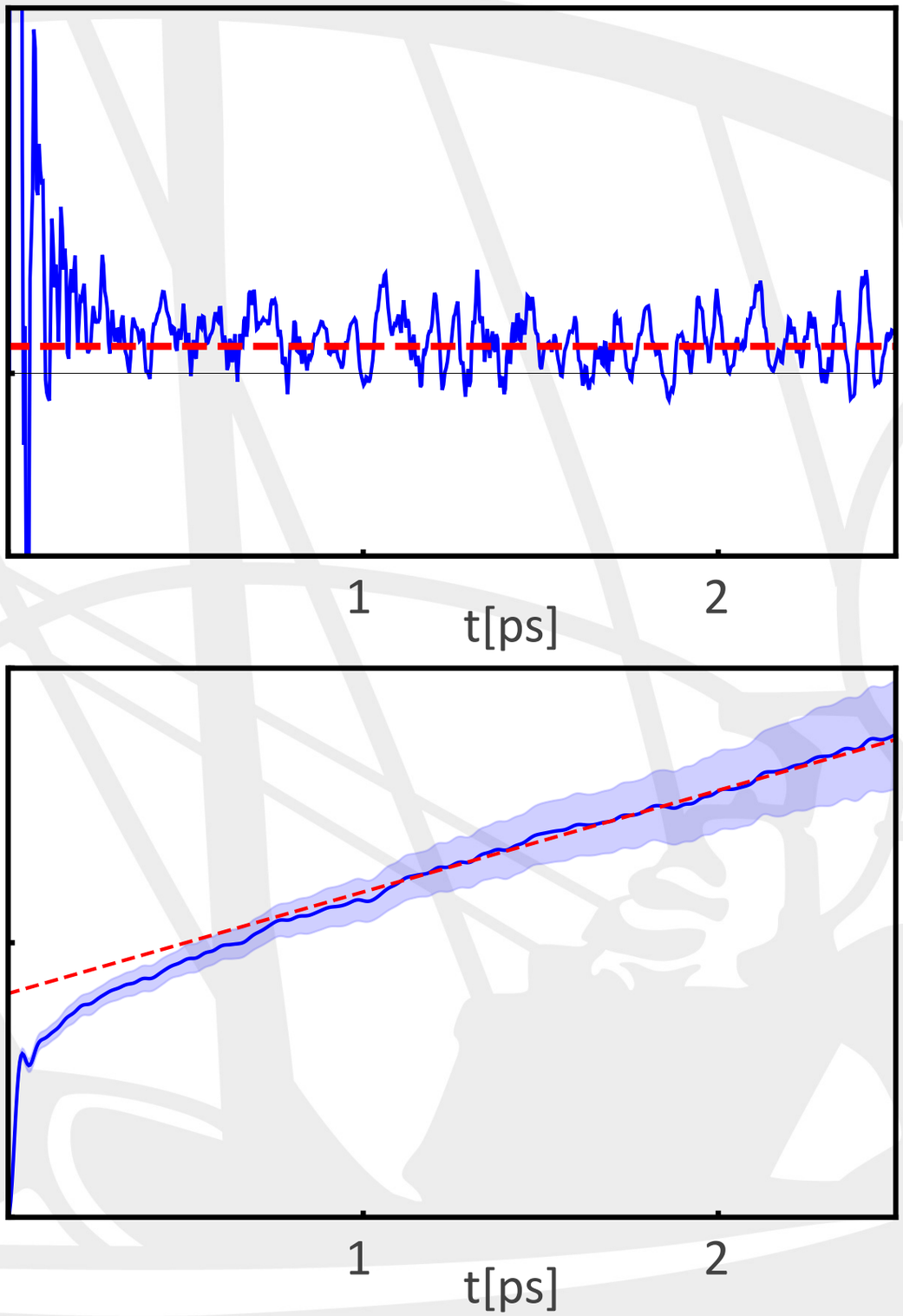

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$\kappa_{\mathrm{DFT}} = 0.74 \pm 0.12$ W/(mK)

$\kappa_{\mathrm{expt}} = 0.60$

$$\frac{1}{6Vk_BT^2}\left\langle\left|\int_0^{\mathrm{t}}\mathbf{J}(\mathrm{t}')d\mathrm{t}'\right|^2\right\rangle$$

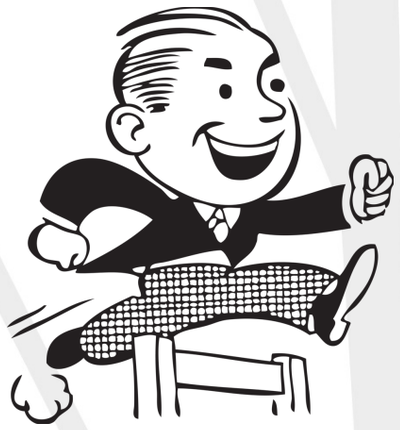
hurdles towards an ab initio Green Kubo theory

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.

hurdles towards an ab initio Green Kubo theory



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

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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).

squeezing more juice from a time series

$$\kappa \propto 2\int_0^\infty C(t)dt \qquad\qquad C(t) = \langle J(t)J(0)\rangle$$

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$$= S(\omega = 0)$$

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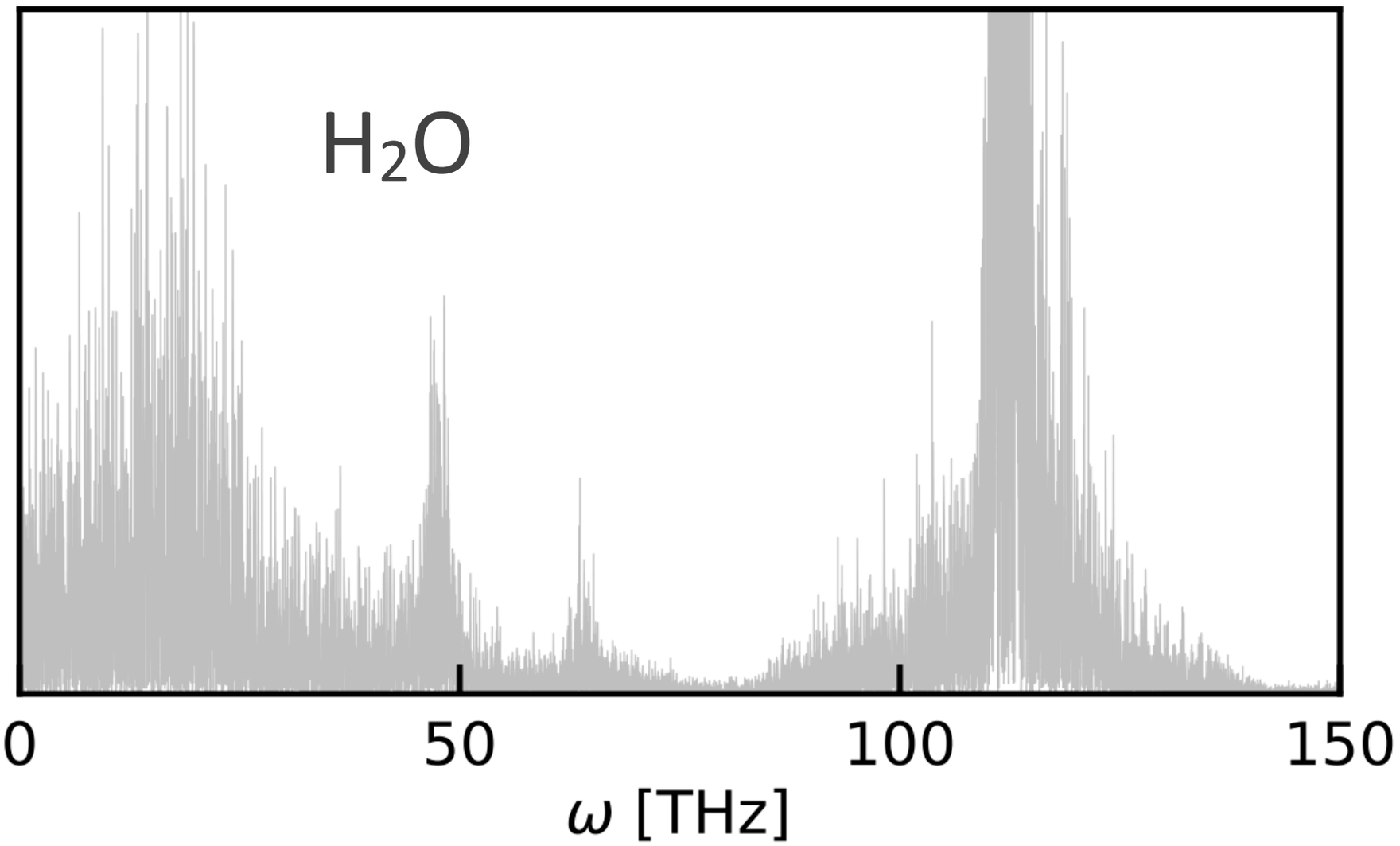
$$C(n\epsilon) \sim \hat{C}(n)$$
$$\hat{C}(n) = \frac{1}{N}\sum_{m=0}^{N-n-1} J(n+m)J(m)$$

$$S\left(k\frac{2\pi}{N\epsilon}\right) \sim \hat{S}(k)$$
$$\hat{S}(k) = \frac{\epsilon}{N}\left|\tilde{J}(k)\right|^2$$

squeezing more juice from a time series

$$\hat{S}(k) = \frac{\epsilon}{N} \left| \tilde{J}(k) \right|^2$$
$$= \frac{1}{2} S(\omega_k) \times \chi^2_2$$



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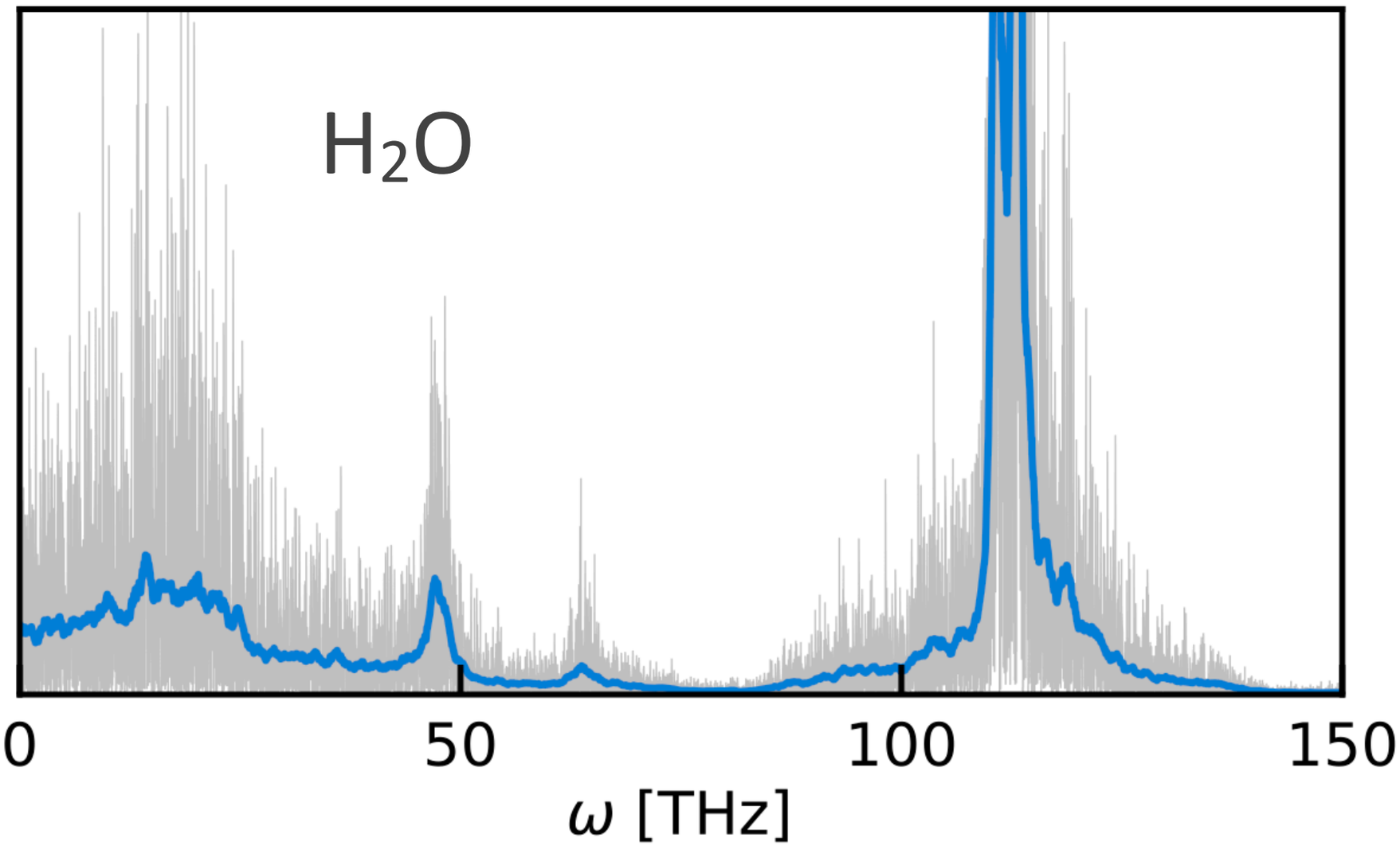

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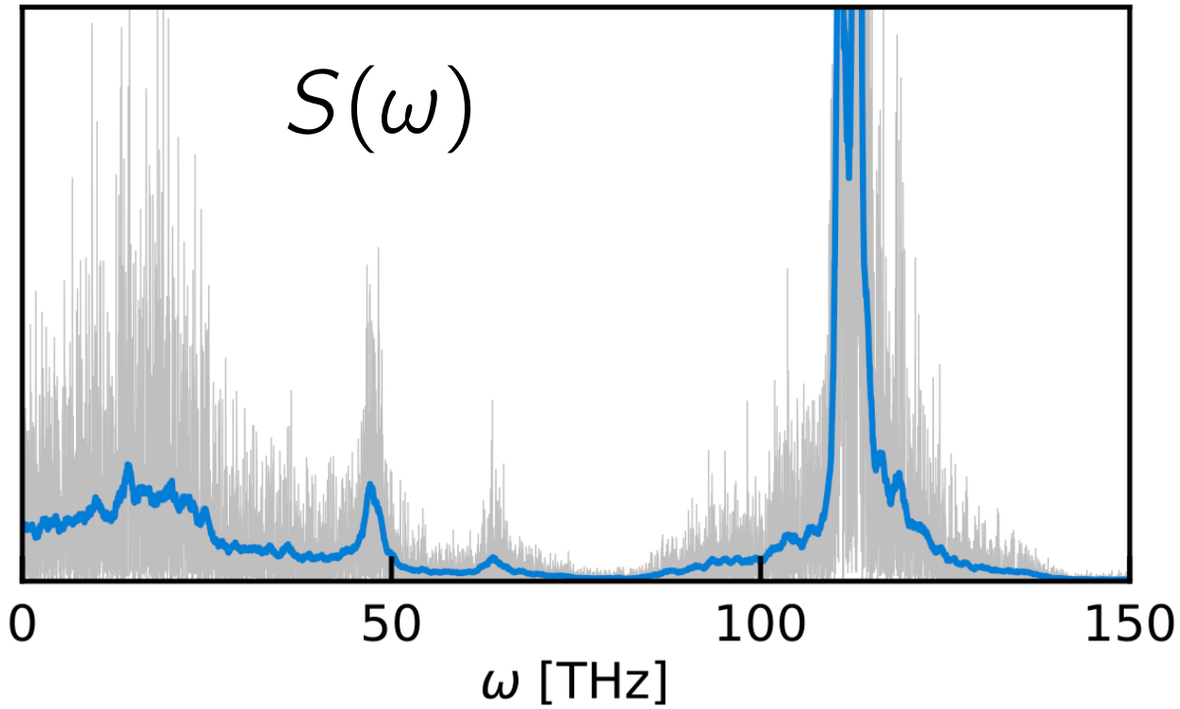
$$\hat{S}(k) = S(\omega_k)\hat{\xi}_k$$



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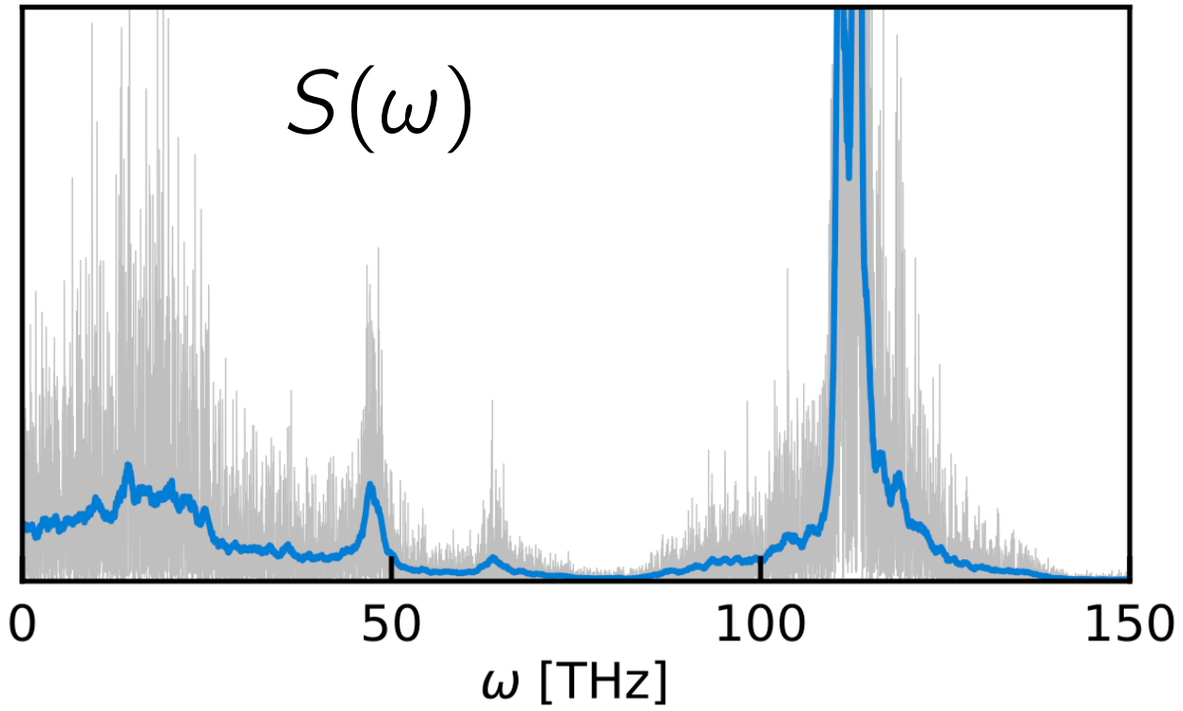
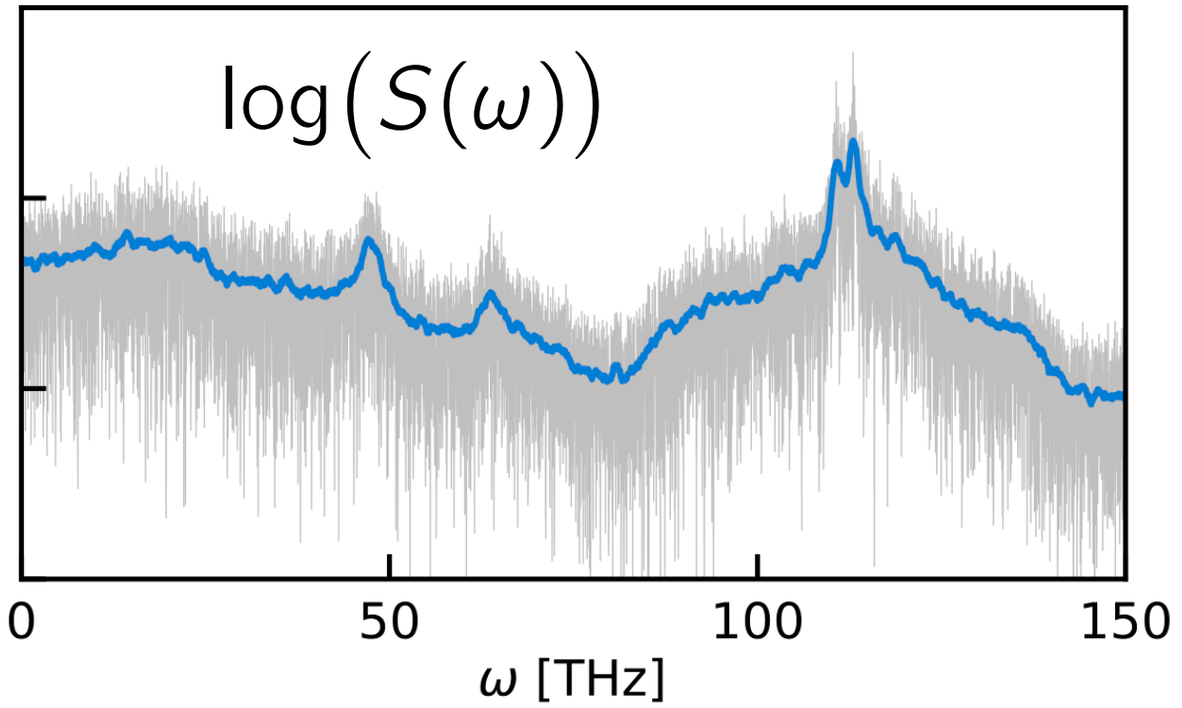
$$\hat{S}(k) = S(\omega_k)\hat{\xi}_k$$

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





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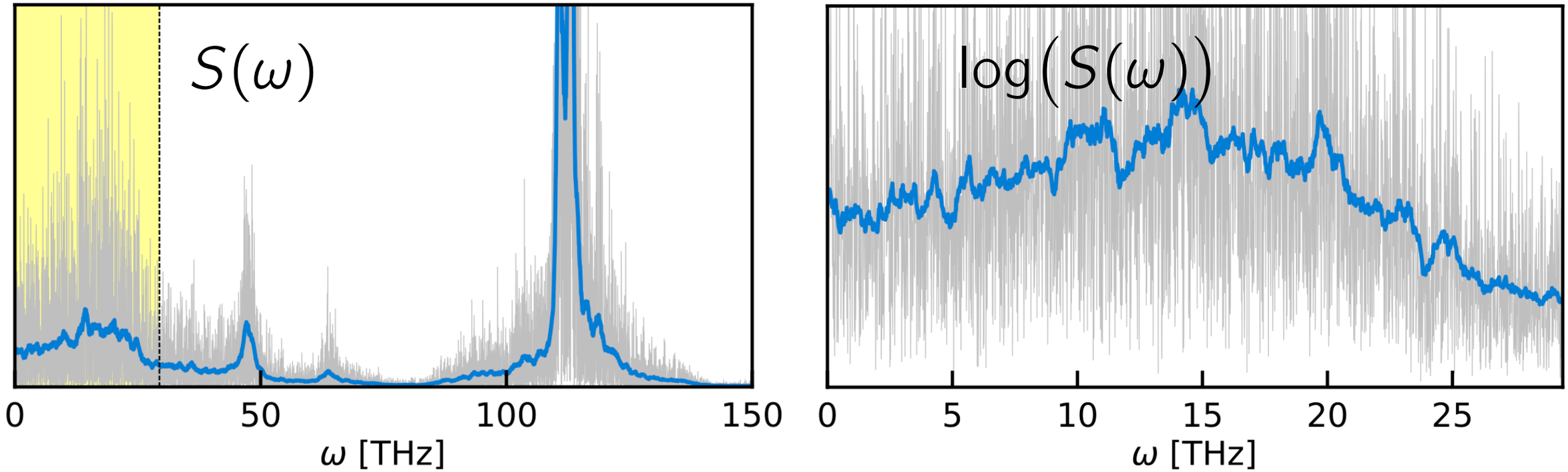

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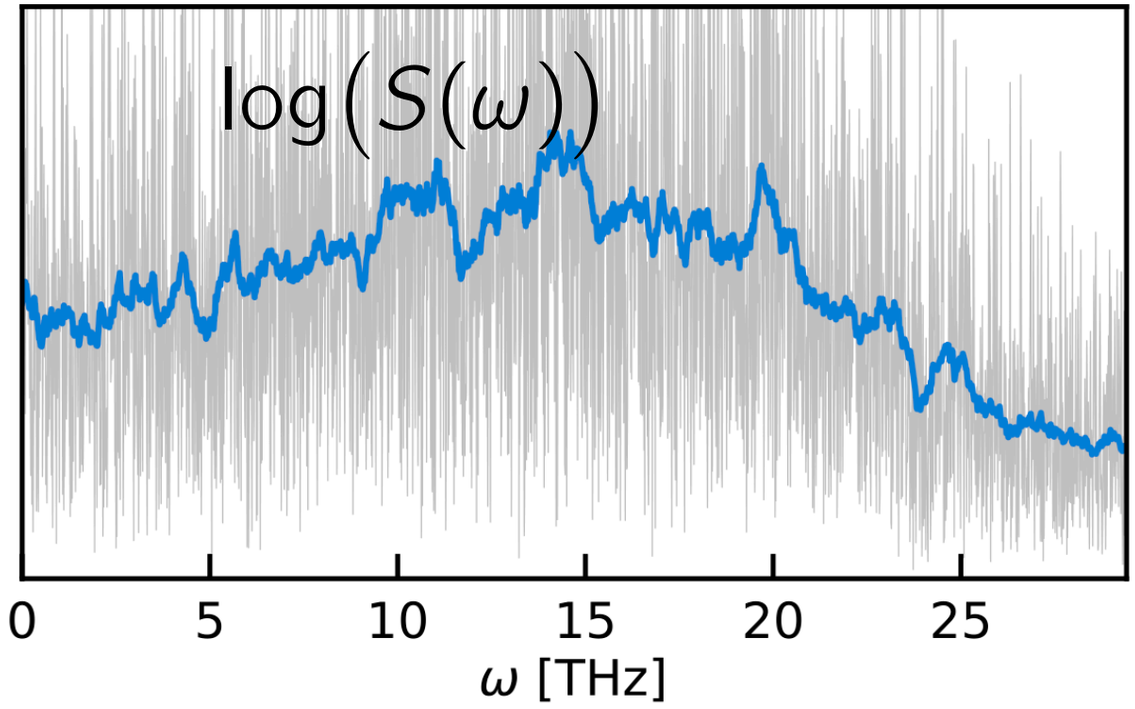

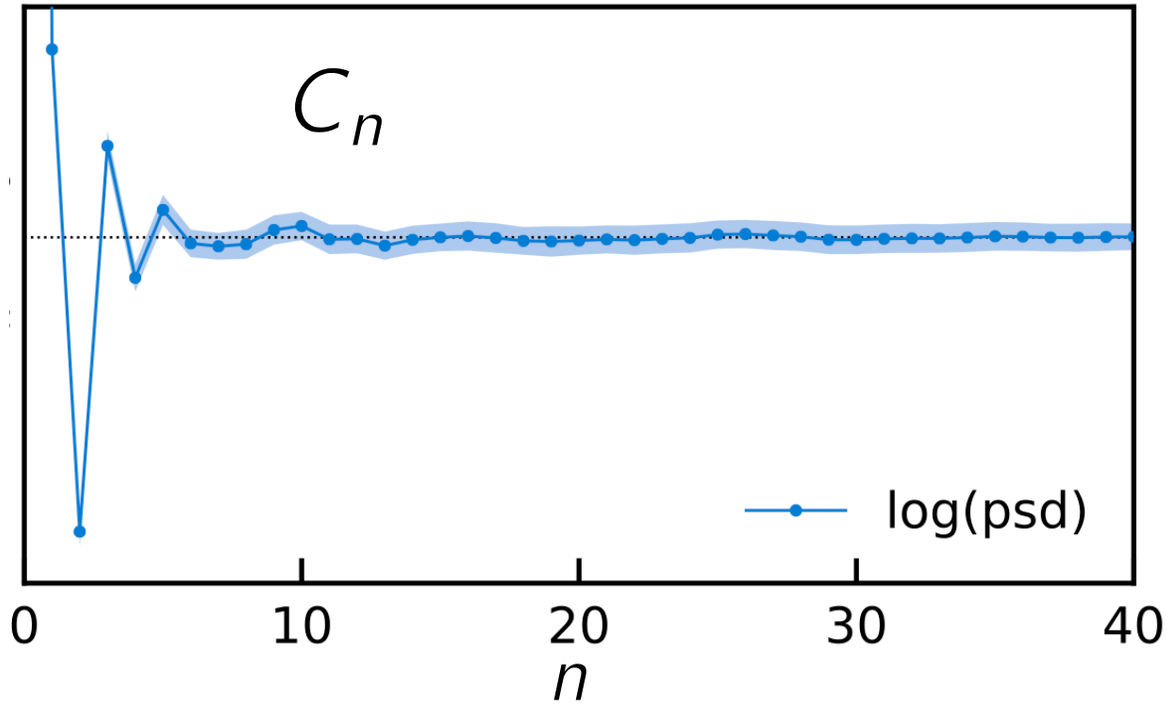

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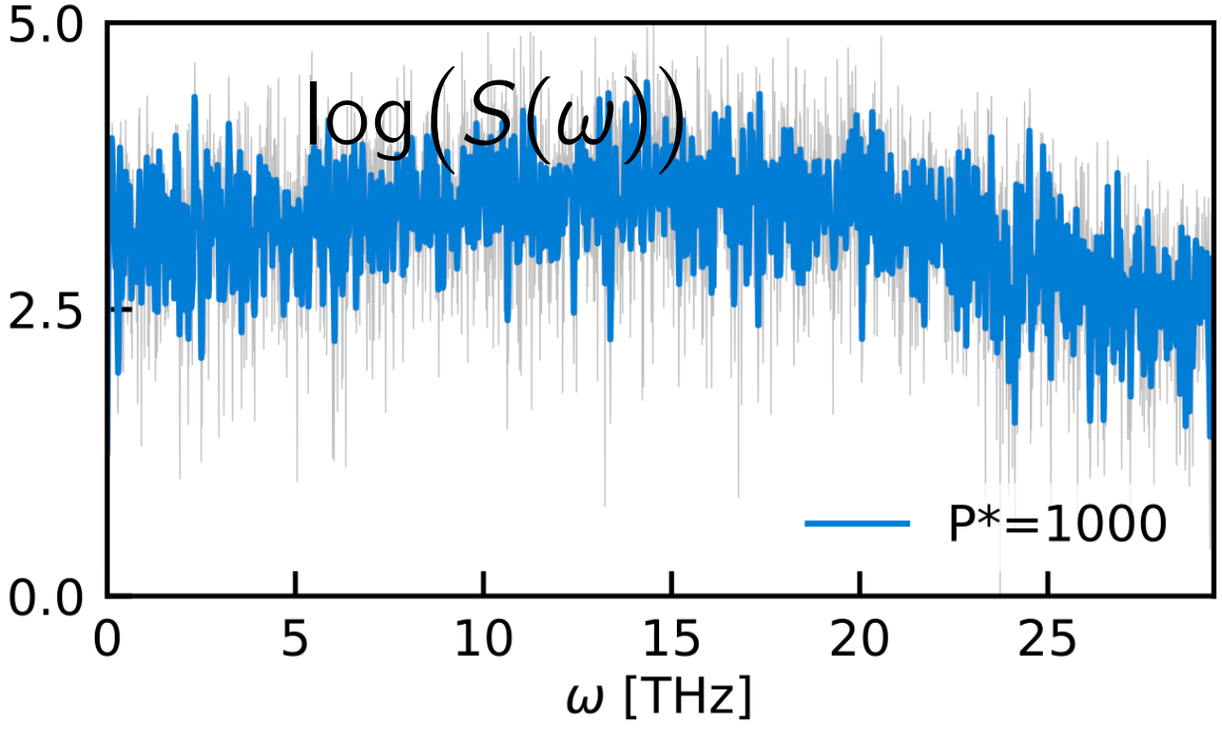

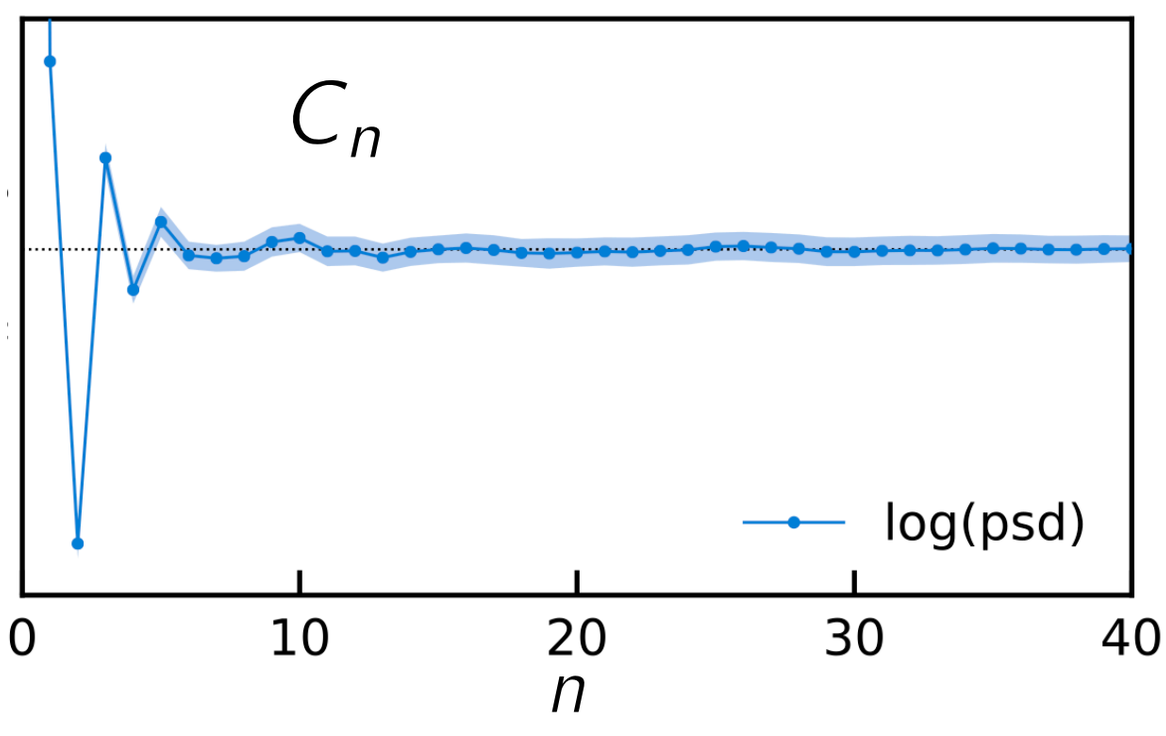

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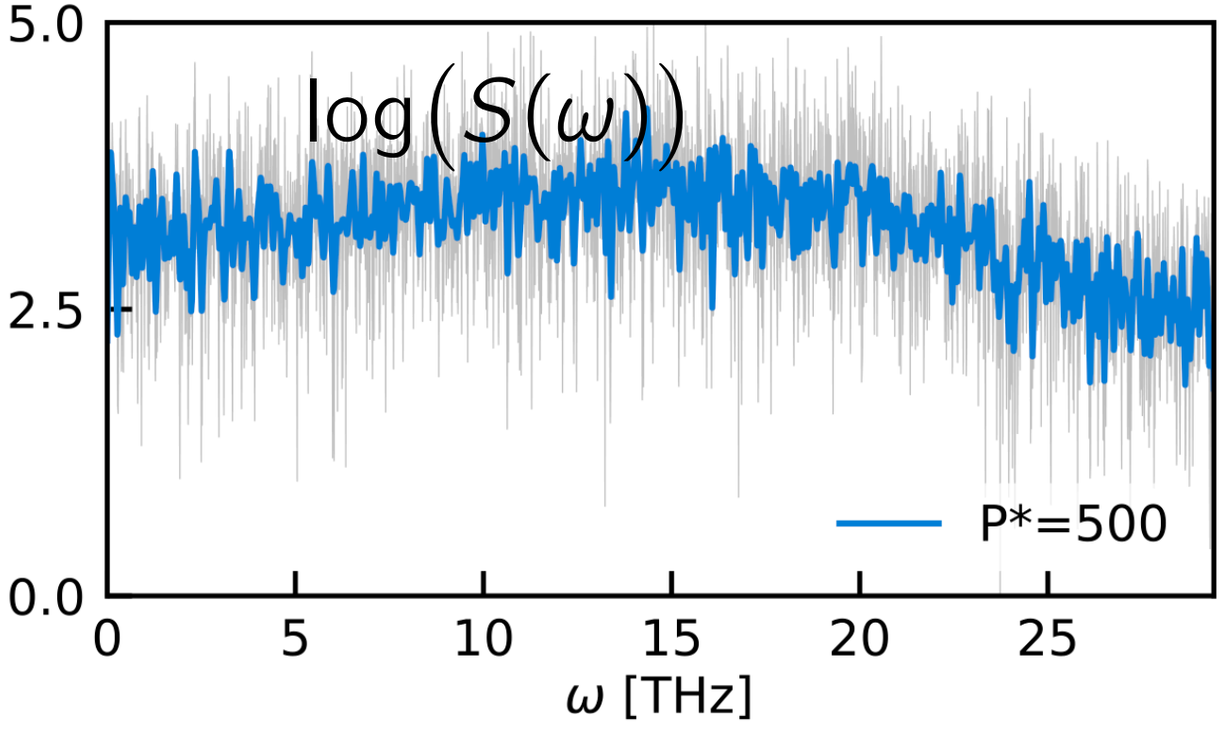

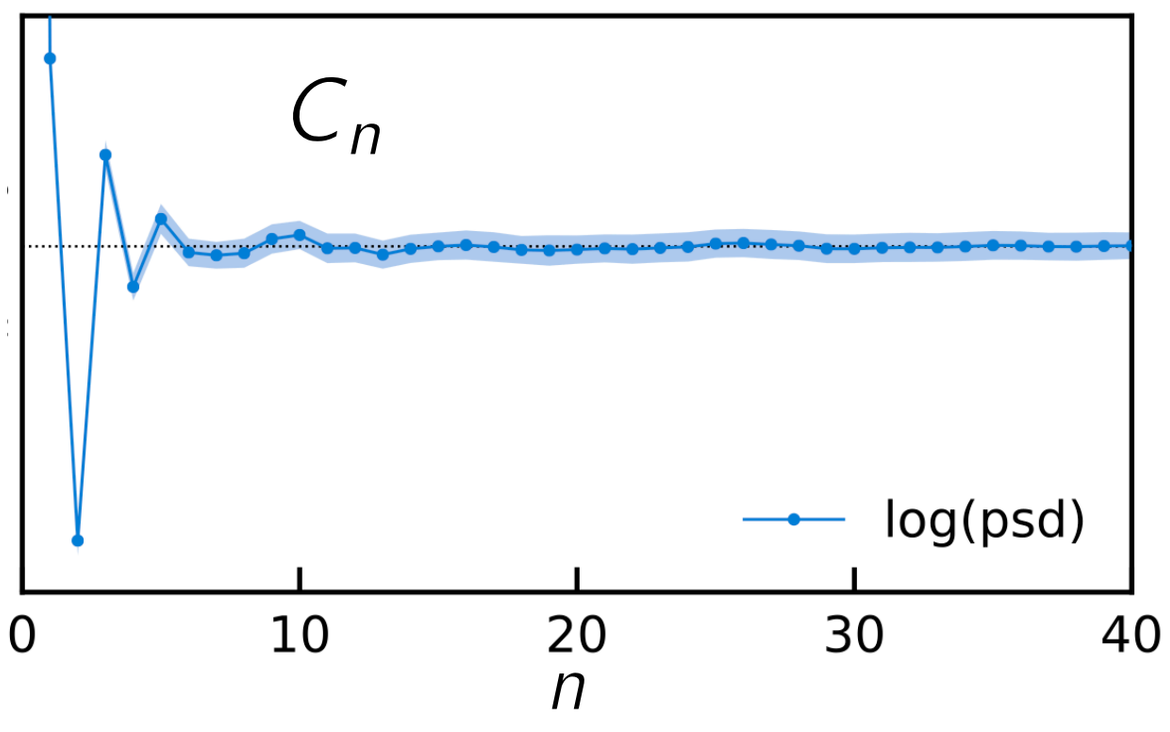

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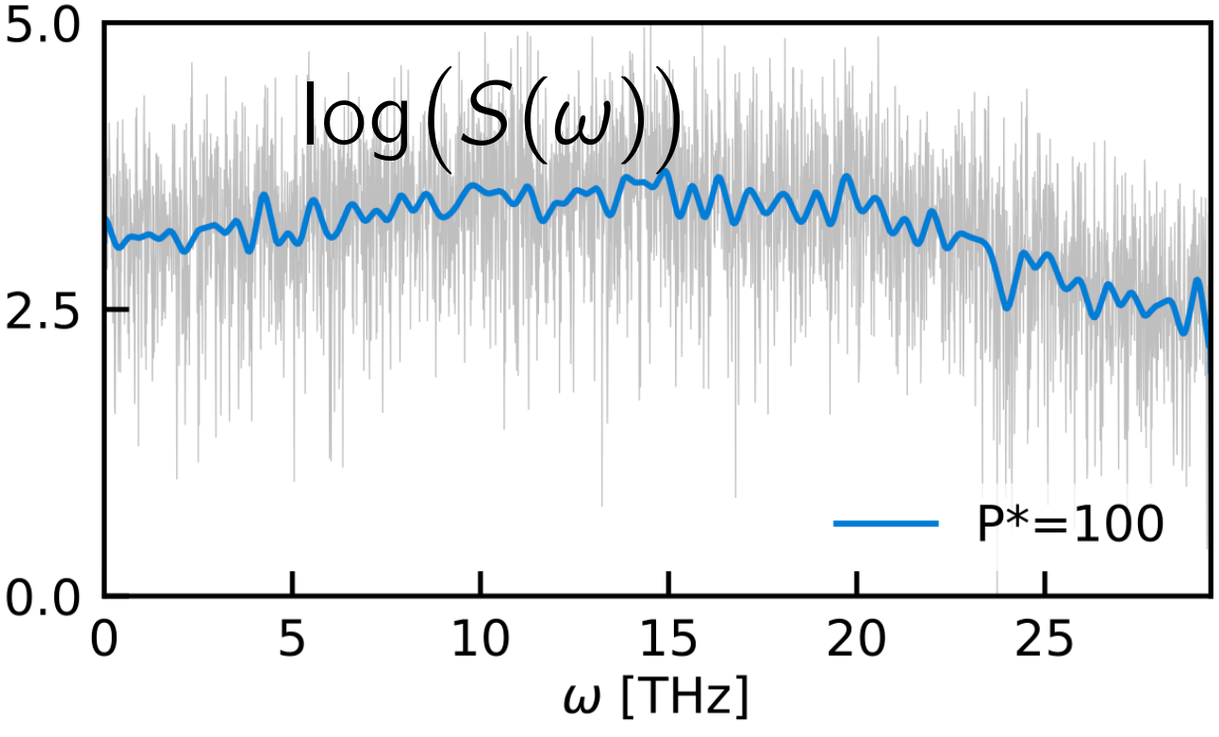

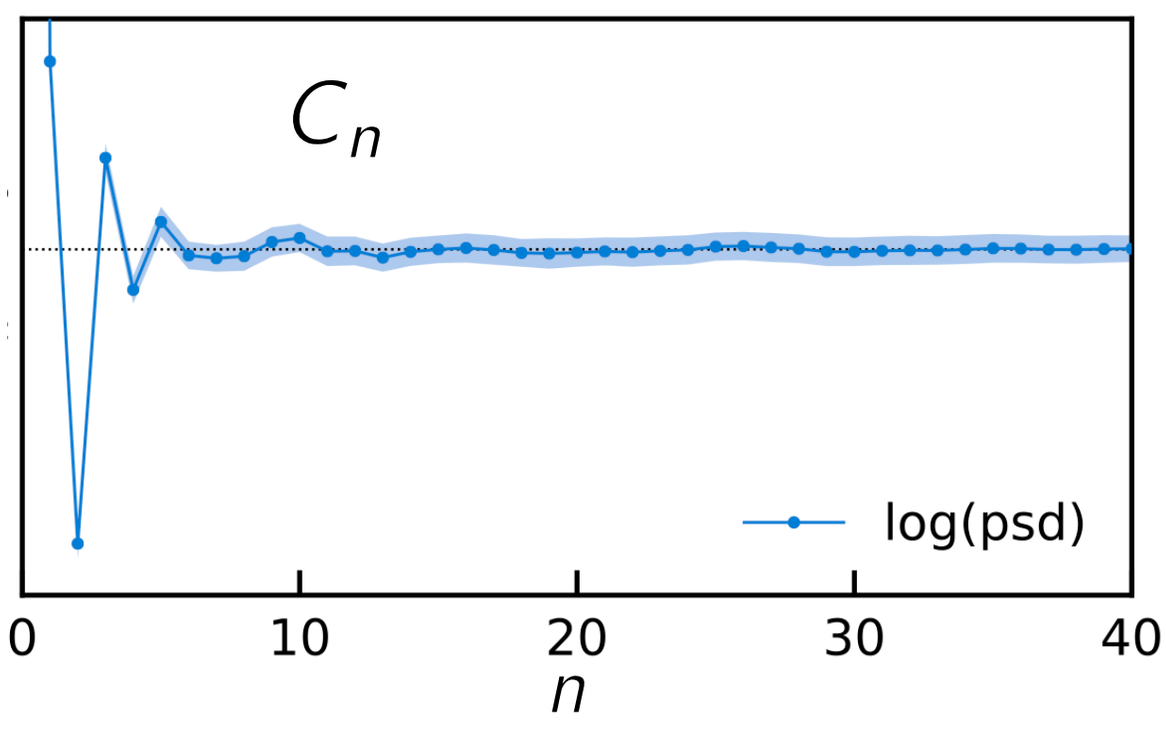

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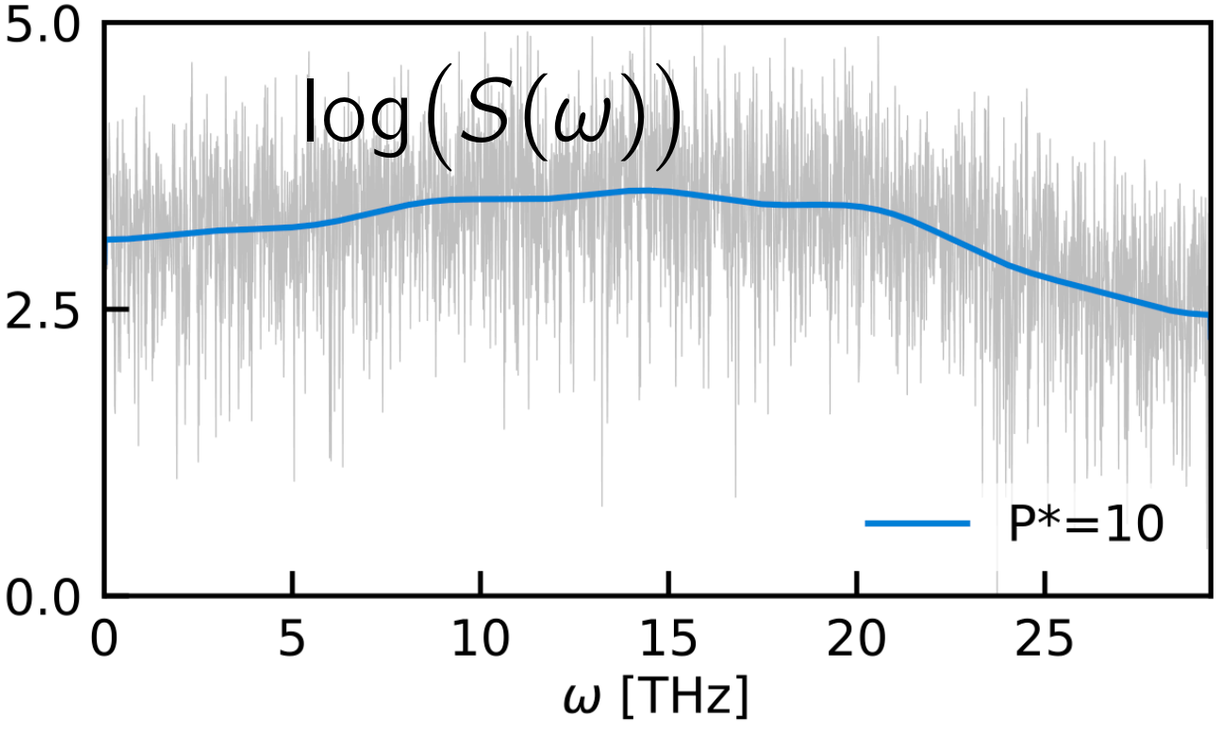

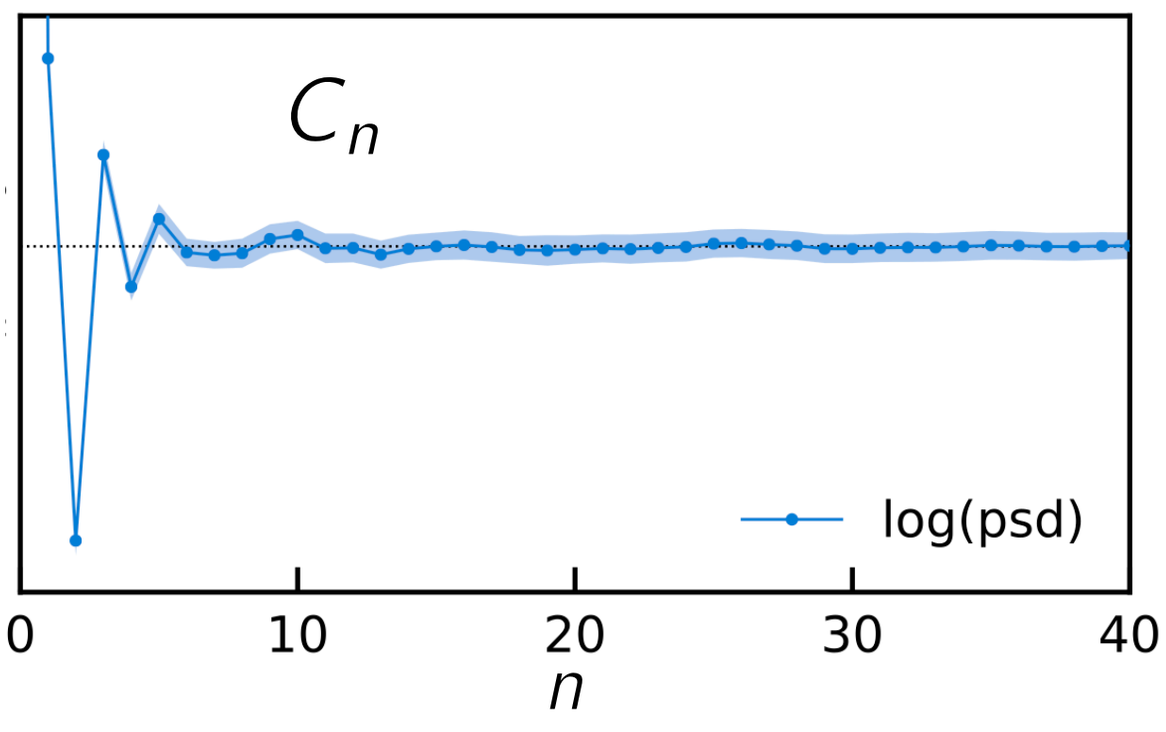

squeezing more juice from a time series

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

$$\frac{\Delta\kappa}{\kappa} = \begin{cases} \text{Ar} & (100\ \text{ps}) & 10\ \% \\ \text{H}_2\text{O} & (100\ \text{ps}) & 5\ \% \\ \text{a-SiO}_2 & (100\ \text{ps}) & 12\ \% \\ \text{c-MgO} & (500\ \text{ps}) & 15\ \% \end{cases}$$

hurdles towards 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).

summary

- heat currents are intrinsically ill-defined at the atomic scale;
- energy conservation and extensivity make heat-transport coefficients independent of such an indeterminacy;
- this *gauge invariance* of thermal transport makes it possible to compute thermal transport coefficients from DFT using equilibrium AIMD and the Green-Kubo formalism;
- The statistical theory of time series can be leveraged to significantly improve the accuracy of the transport coefficients estimated from MD.

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Microscopic theory and quantum simulation of atomic heat transport

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

J Low Temp Phys (2016) 185:79–86
DOI 10.1007/s10909-016-1617-6

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Gauge Invariance of Thermal Transport Coefficients

Loris Ercole[1] · Aris Marcolongo[2] · Paolo Umari[3] · Stefano Baroni[1]

arXiv:1706.01381v1 [cond-mat.stat-mech] 5 Jun 2017

Heat transport coefficients from optimally short molecular dynamics simulations

Loris Ercole[1], Aris Marcolongo[2], and Stefano Baroni[1]

these slides shortly at http://talks.baroni.me