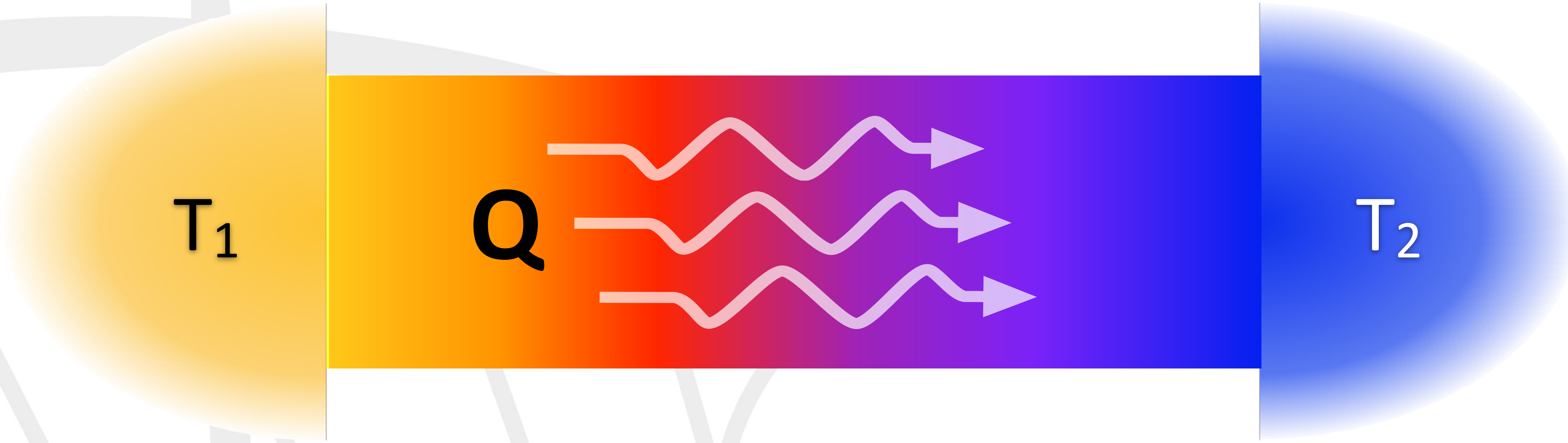
ab initio Green-Kubo simulation of heat transport in liquids, glasses, and strongly anharmonic solids

Stefano Baroni

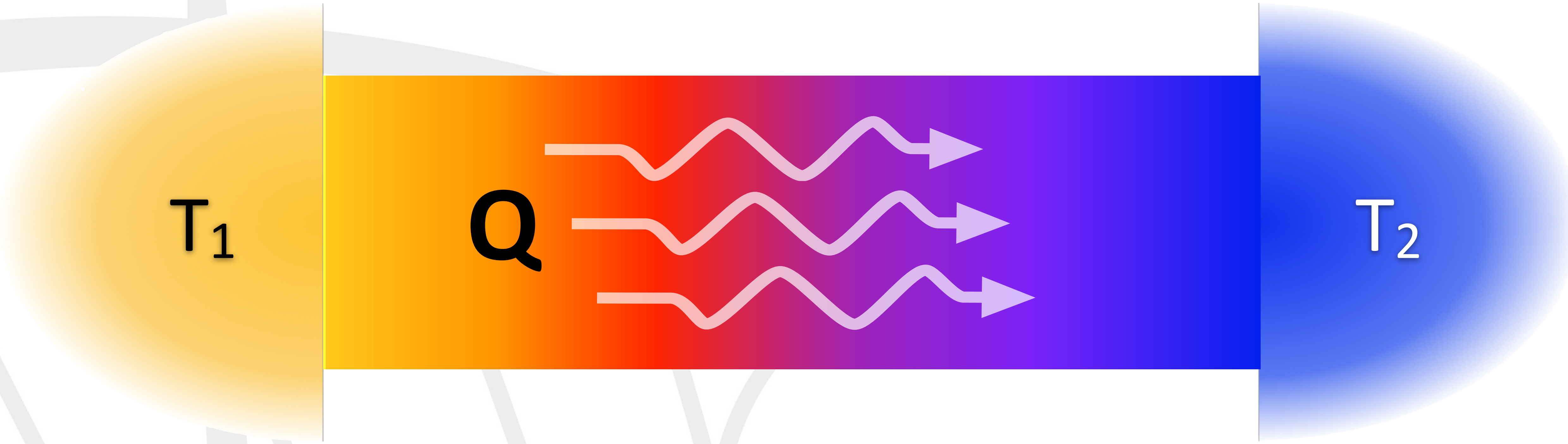
Scuola Internazionale Superiore di Studi Avanzati, Trieste

talk given at the *ICN2 Severo Ochoa International Conference 2018*, Barcelona, February 15-16, 2018

what heat transport is all about

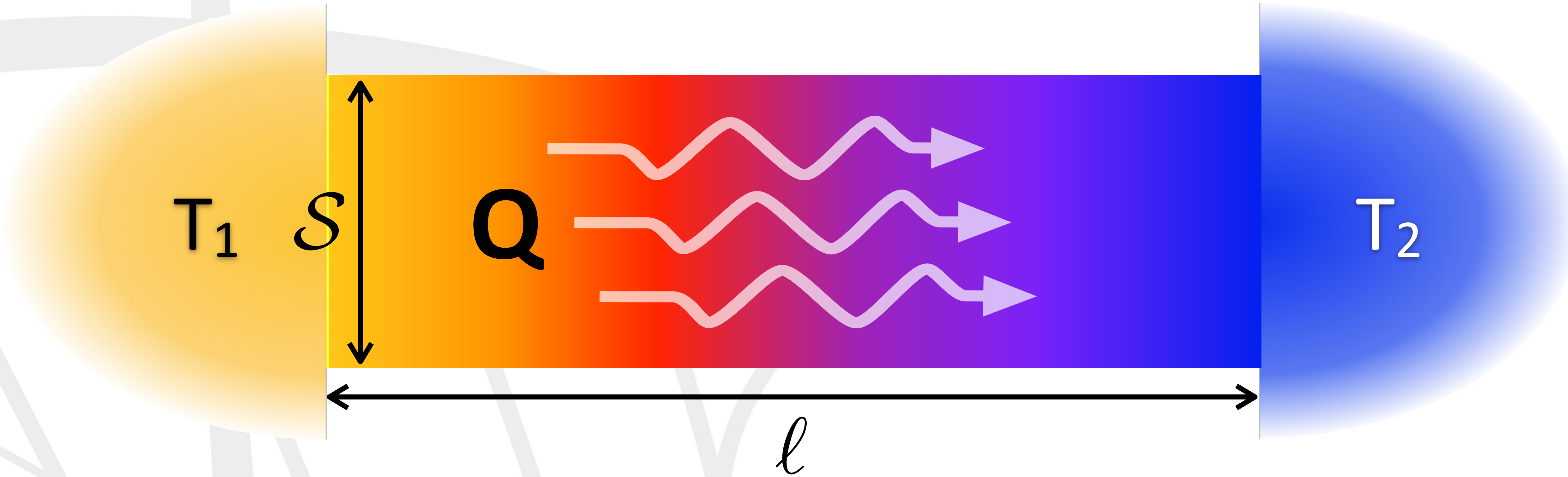


what heat transport is all about



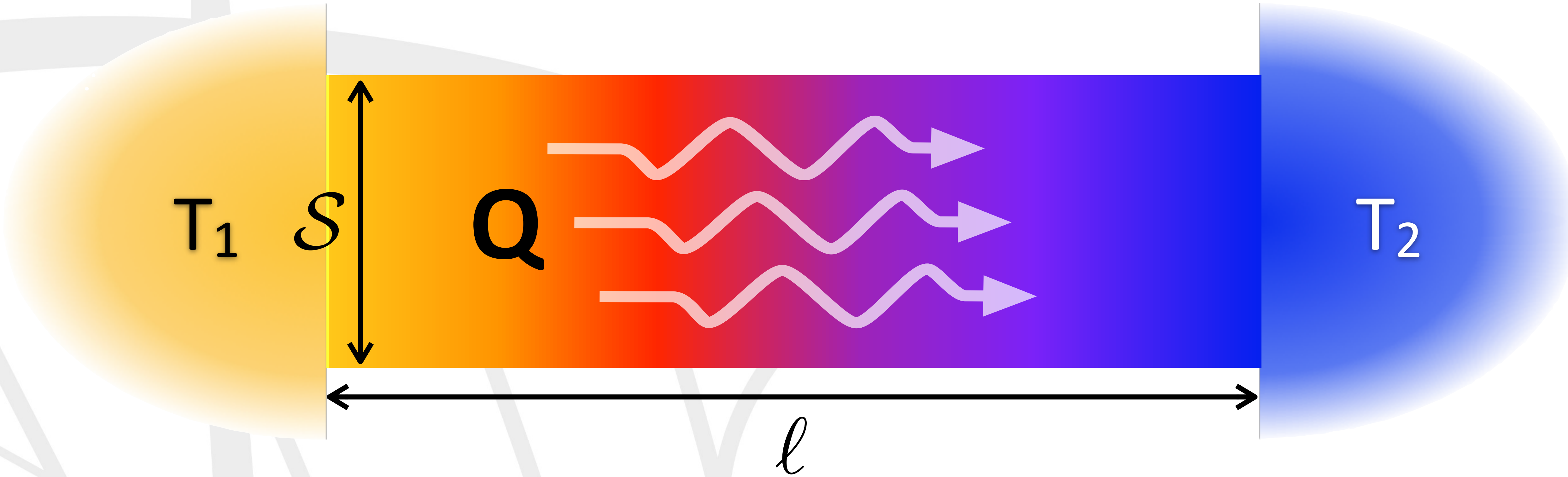
heat flows from the warm to the cool
as time flows from the past to the future

what heat transport is all about



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

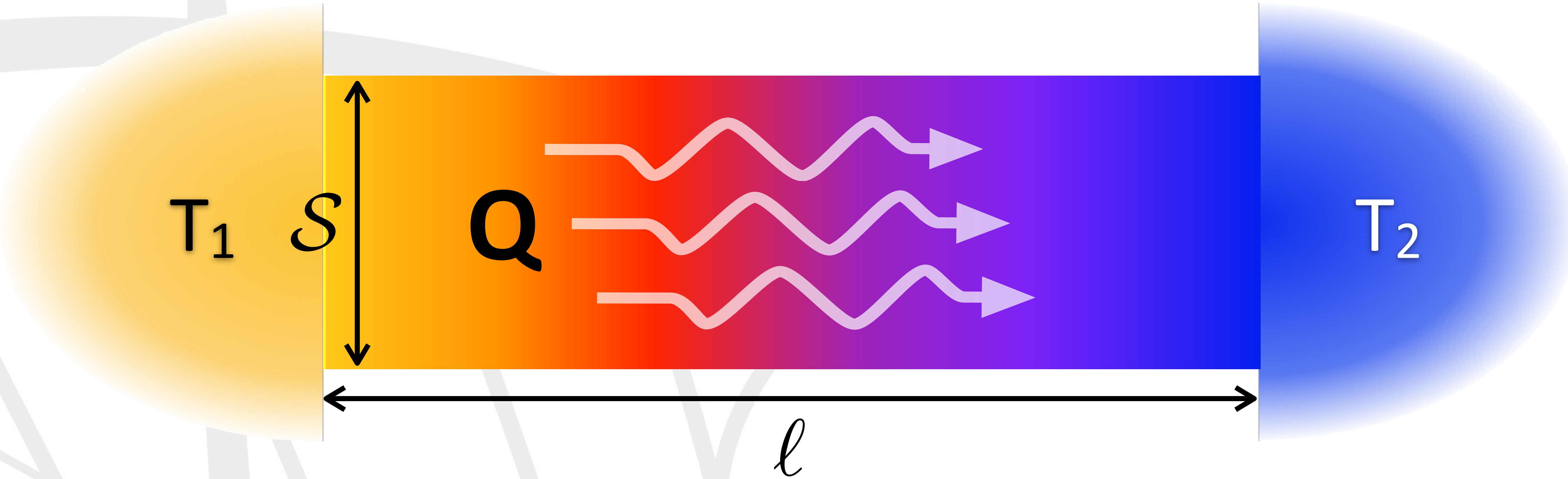
what heat transport is all about



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

$$\mathbf{j}_\mathrm{Q}(\mathbf{r}, \mathrm{t}) = -\kappa \nabla \mathrm{T}(\mathbf{r}, \mathrm{t})$$

what heat transport is all about



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

$$\mathbf{j}_Q(\mathbf{r}, t) = -\kappa\nabla T(\mathbf{r}, t)$$

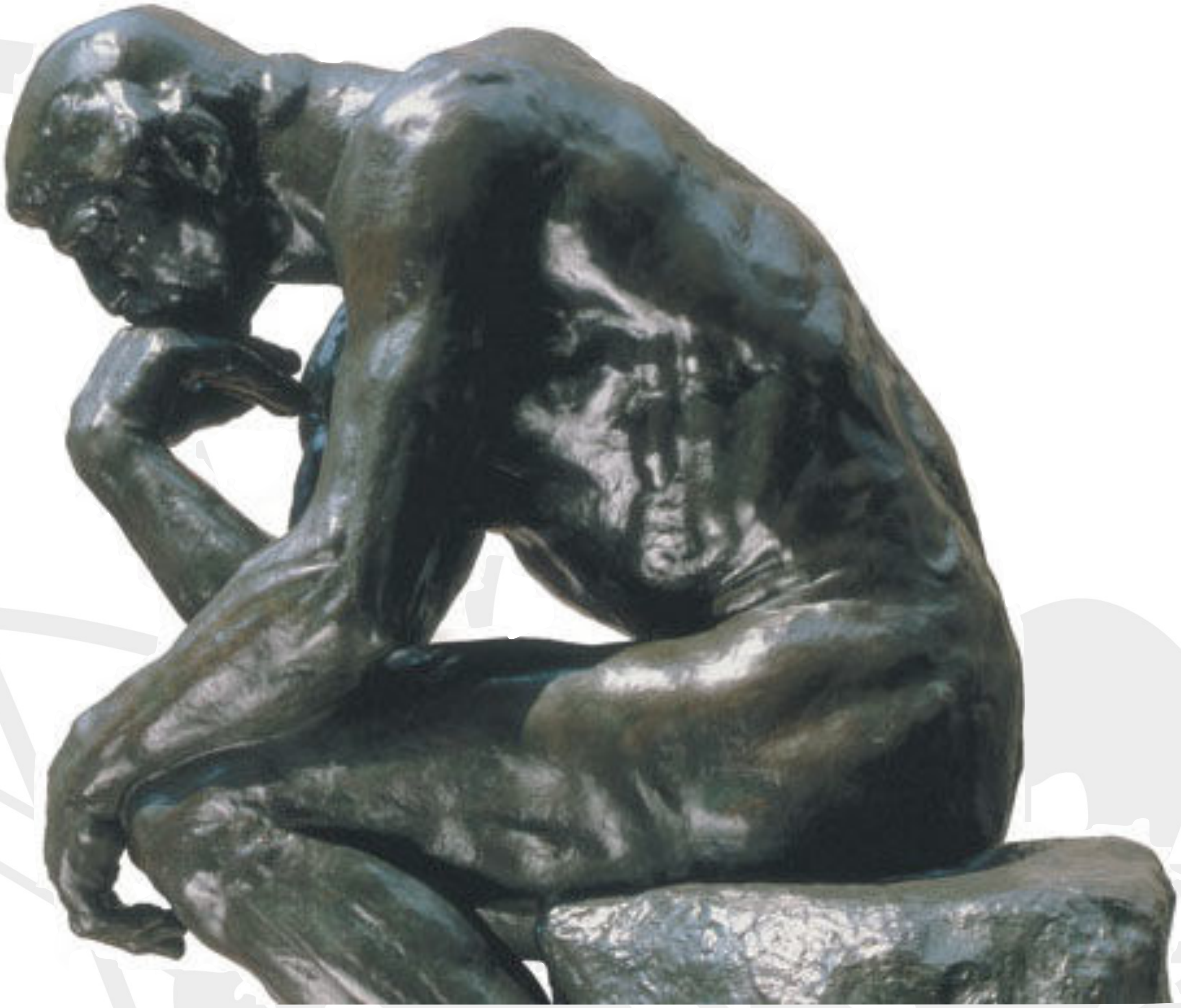
$$\frac{\partial T}{\partial t} = \frac{\kappa}{\rho c_p}\Delta T$$

why should we care?

why should we care?

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

why should we care?

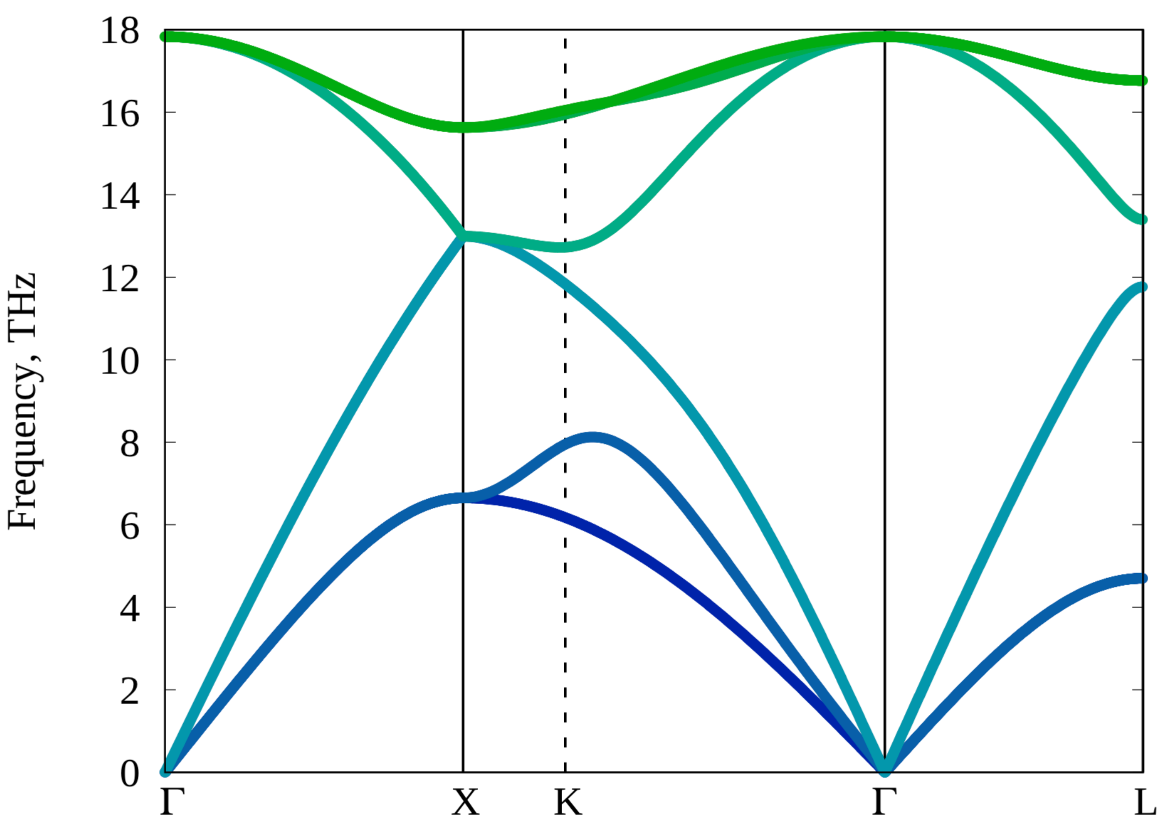


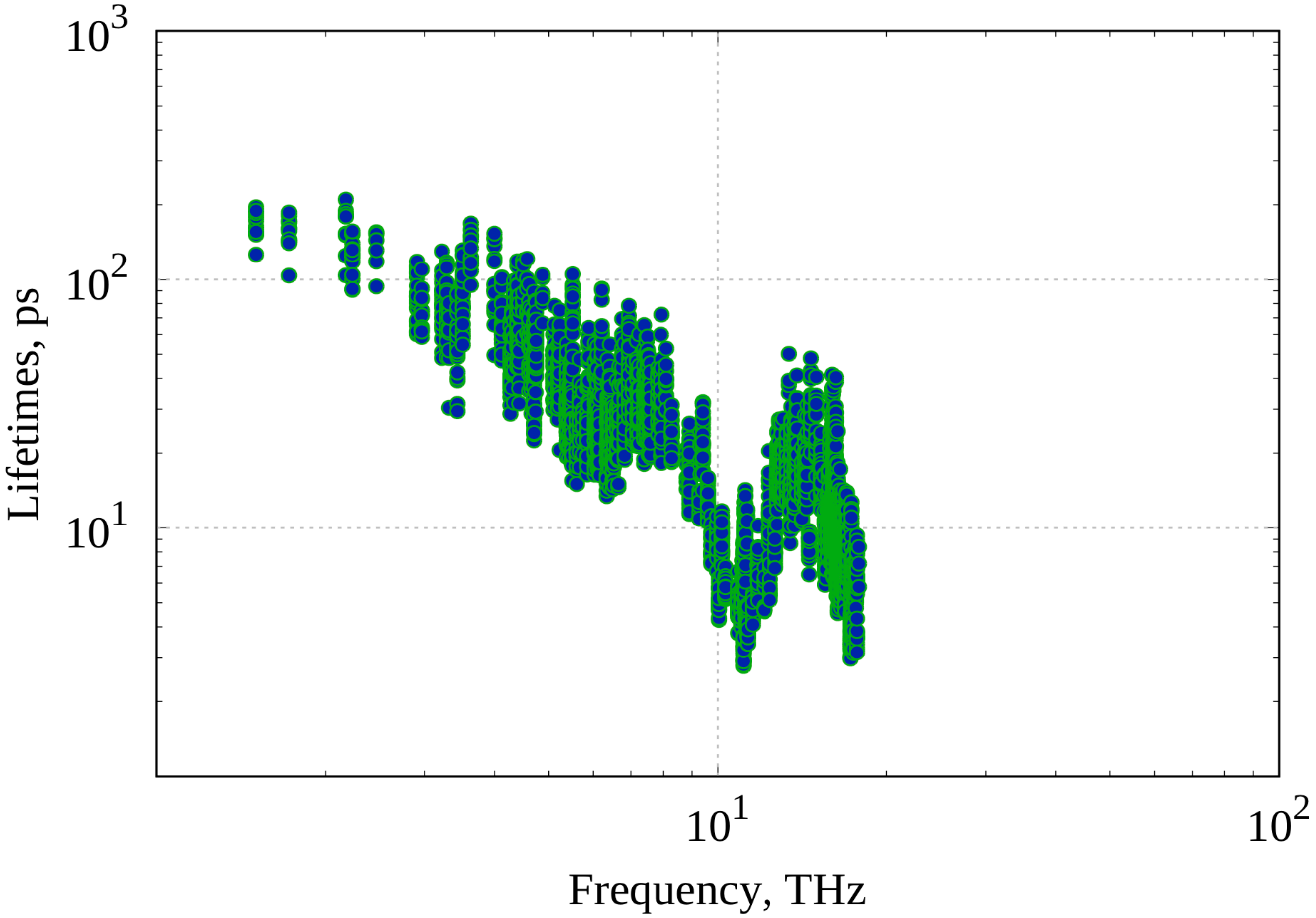
- … because it is important and poorly understood

Boltzmann's Transport Equation

$$\bar{n}_\nu(\mathbf{r},\mathbf{k};t) = \frac{1}{\mathrm{e}^{\frac{\hbar\omega_\nu(\mathbf{k})}{k_B T(\mathbf{r})}} - 1}$$

$$\frac{\partial n_\nu(\mathbf{r},\mathbf{k};t)}{\partial t} + \mathbf{v}_\nu(\mathbf{k}) \cdot \nabla_{\mathbf{r}} n_\nu(\mathbf{r},\mathbf{k};t) = -\frac{1}{V}\sum_{\nu'\mathbf{k}'} \Omega_{\nu\nu'}(\mathbf{k},\mathbf{k}')\big(n_{\nu'}(\mathbf{r},\mathbf{k}';t) - \bar{n}_{\nu'}(\mathbf{r},\mathbf{k}';t)\big)$$





Green-Kubo theory

$$\kappa = \frac{1}{3Vk_BT^2}\int_0^\infty \langle \mathbf{J}_q(t)\cdot\mathbf{J}_q(0)\rangle dt$$

Green-Kubo theory

$$\kappa = \frac{1}{3Vk_BT^2}\int_0^\infty \langle \mathbf{J}_q(t)\cdot\mathbf{J}_q(0)\rangle dt$$

$$\mathbf{J}_q(t) = \int \mathbf{j}_q(\mathbf{r},t)d\mathbf{r}$$

Green-Kubo theory

$$\kappa = \frac{1}{3Vk_BT^2}\int_0^\infty \langle \mathbf{J}_q(t)\cdot\mathbf{J}_q(0)\rangle dt$$

$$\mathbf{J}_q(t) = \int \mathbf{j}_q(\mathbf{r},t)d\mathbf{r}$$

$$\mathbf{j}_q(\mathbf{r},t) = \mathbf{j}_e(\mathbf{r},t) - (p+\langle e\rangle)\,\mathbf{v}(\mathbf{r},t)$$

Green-Kubo theory

$$\kappa = \frac{1}{3Vk_BT^2}\int_0^\infty \langle \mathbf{J}_q(t)\cdot\mathbf{J}_q(0)\rangle dt$$

$$\mathbf{J}_q(t) = \int \mathbf{j}_q(\mathbf{r},t)d\mathbf{r}$$

$$\mathbf{j}_q(\mathbf{r},t) = \mathbf{j}_e(\mathbf{r},t) - \cancel{(p+\langle e\rangle)\,\mathbf{v}(\mathbf{r},t)}$$

Green-Kubo theory

$$\kappa = \frac{1}{3Vk_BT^2}\int_0^\infty \langle \mathbf{J}_q(t)\cdot\mathbf{J}_q(0)\rangle dt$$

$$\mathbf{J}_q(t) = \int \mathbf{j}_q(\mathbf{r},t)d\mathbf{r}$$

$$\mathbf{j}_q(\mathbf{r},t) = \mathbf{j}_e(\mathbf{r},t) - \xcancel{(p+\langle e\rangle)\,\mathbf{v}(\mathbf{r},t)}$$

$$\dot{e}(\mathbf{r},t) + \nabla\cdot\mathbf{j}_e(\mathbf{r},t) = 0$$

Green-Kubo theory

$$\kappa = \frac{1}{3Vk_BT^2}\int_0^\infty \langle \mathbf{J}_q(t)\cdot\mathbf{J}_q(0)\rangle dt$$

$$\begin{aligned}\mathbf{J}_q(t) &= \int \mathbf{j}_q(\mathbf{r},t)d\mathbf{r} \\ &= \int \mathbf{r}\,\dot{e}(\mathbf{r},t)d\mathbf{r}\end{aligned}$$

$$\mathbf{j}_q(\mathbf{r},t) = \mathbf{j}_e(\mathbf{r},t) - (p+\langle e\rangle)\mathbf{v}(\mathbf{r},t)$$

$$\dot{e}(\mathbf{r},t) + \nabla\cdot\mathbf{j}_e(\mathbf{r},t) = 0$$

Green-Kubo theory

$$\kappa = \frac{1}{3Vk_BT^2}\int_0^\infty \langle \mathbf{J}_q(t)\cdot\mathbf{J}_q(0)\rangle dt$$

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

the classical MD ansatz

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

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

the classical MD ansatz

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

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

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

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.

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).

insights from classical mechanics

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

$$= \text{cnst}$$

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

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

insights from classical mechanics

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

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

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

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

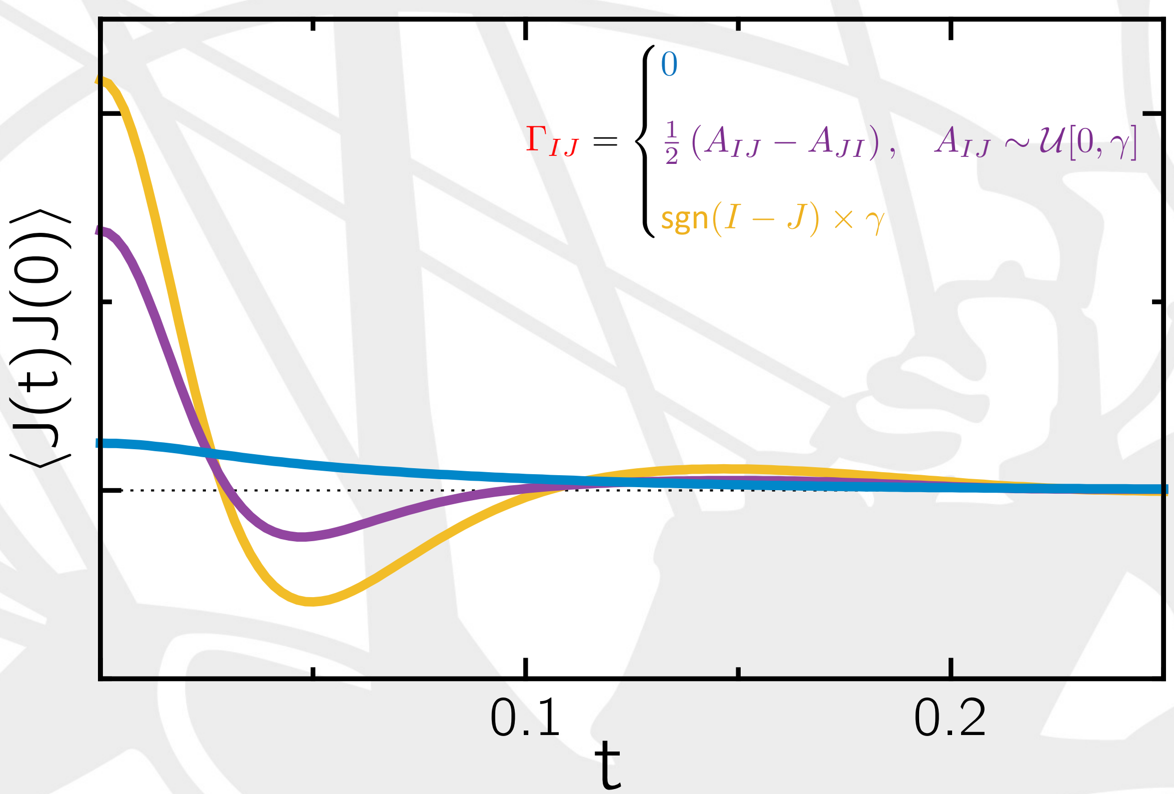
insights from classical mechanics

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

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

insights from classical mechanics

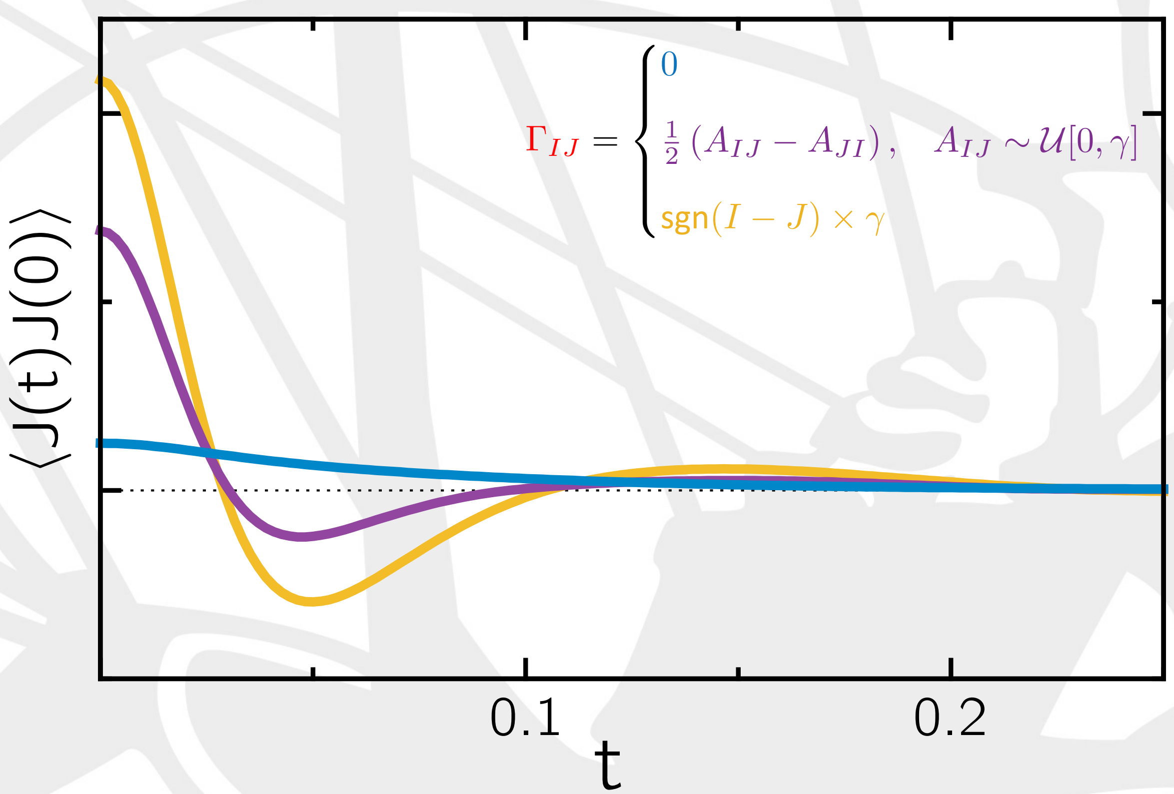
$$\mathbf{J}_e = \sum_I \epsilon_I \mathbf{V}_I + \frac{1}{2}\sum_{I\neq J}(\mathbf{V}_I\cdot\mathbf{F}_{IJ})(\mathbf{R}_I-\mathbf{R}_J)$$
$$+\frac{1}{2}\sum_{I\neq J}\Gamma_{IJ}\left[\mathbf{V}_I v(|\mathbf{R}_I-\mathbf{R}_J|)+(\mathbf{V}_I\cdot\mathbf{F}_{IJ})(\mathbf{R}_I-\mathbf{R}_I)\right]$$

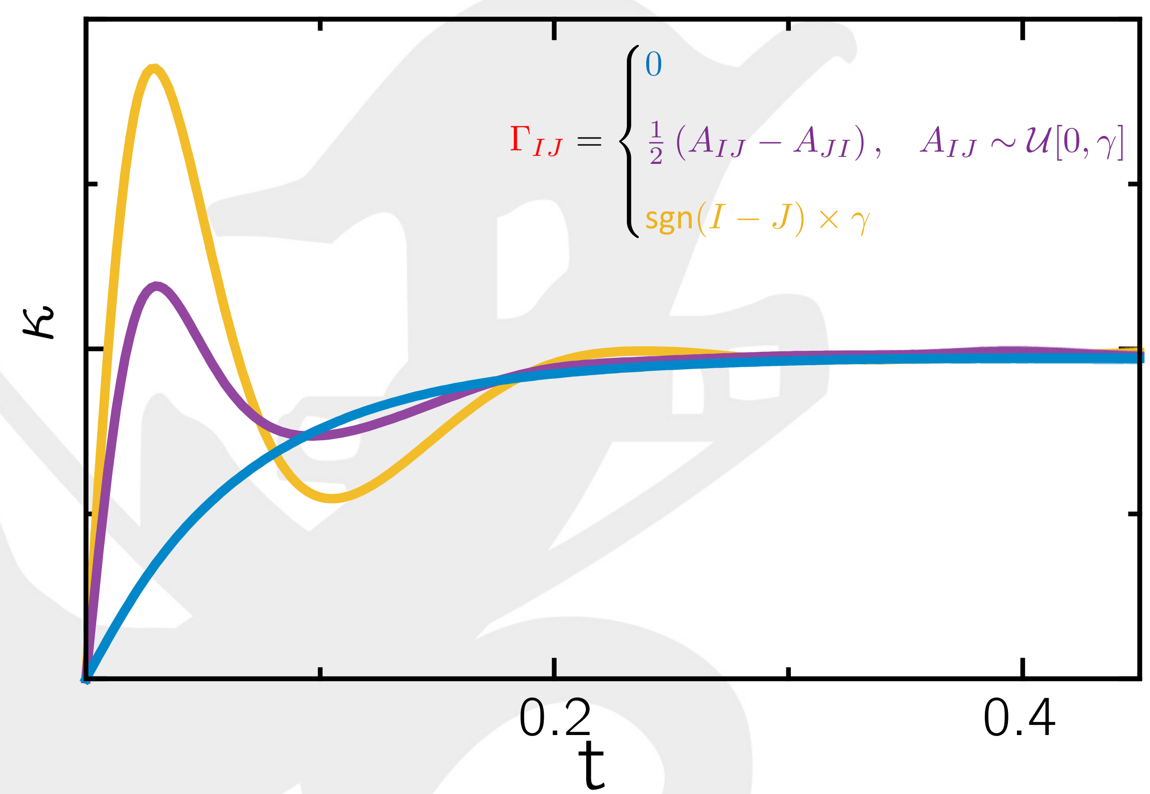


insights from classical mechanics

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

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





insights from classical mechanics

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

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

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

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

$$\int_0^\infty \left\langle \mathbf{J}'(t) \cdot \mathbf{J}'(0) \right\rangle dt = \int_0^\infty \left\langle \mathbf{J}(t) \cdot \mathbf{J}(0) \right\rangle dt + \int_0^\infty \left(\left\langle \dot{\mathbf{P}}(t) \cdot \mathbf{J}(0) \right\rangle + \left\langle \dot{\mathbf{P}}(-t) \cdot \mathbf{J}(0) \right\rangle \right) dt + \int_0^\infty \left\langle \dot{\mathbf{P}}(t) \cdot \dot{\mathbf{P}}(0) \right\rangle dt$$

insights from classical mechanics

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

$$\int_0^\infty \langle \mathbf{J}'(t) \cdot \mathbf{J}'(0) \rangle dt = \int_0^\infty \langle \mathbf{J}(t) \cdot \mathbf{J}(0) \rangle dt$$

$$+ \int_0^\infty \left(\xcancel{\langle \dot{\mathbf{P}}(t) \cdot \mathbf{J}(0) \rangle} + \xcancel{\langle \dot{\mathbf{P}}(-t) \cdot \mathbf{J}(0) \rangle} \right) dt$$

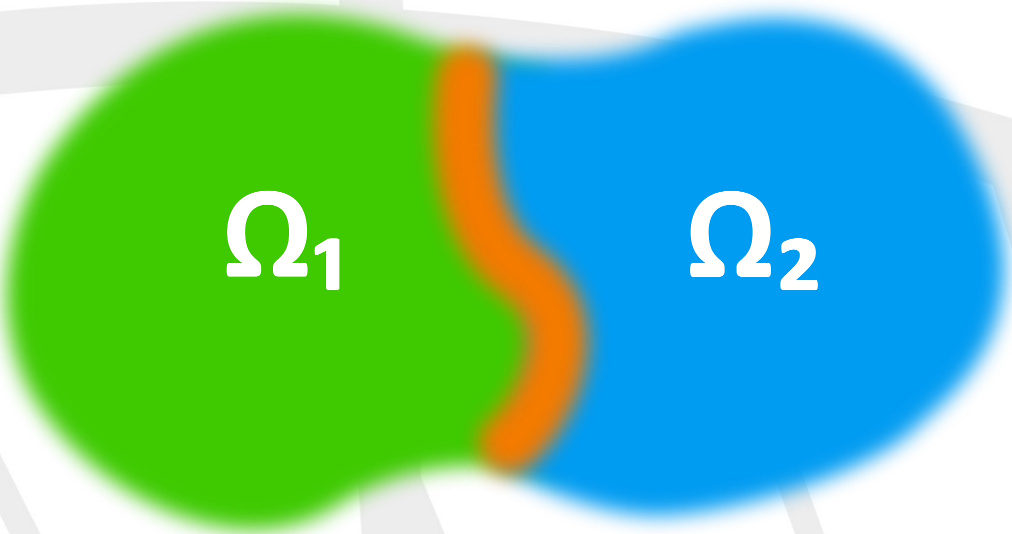
$$+ \int_0^\infty \xcancel{\langle \dot{\mathbf{P}}(t) \cdot \dot{\mathbf{P}}(0) \rangle} dt$$

insights from classical mechanics

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

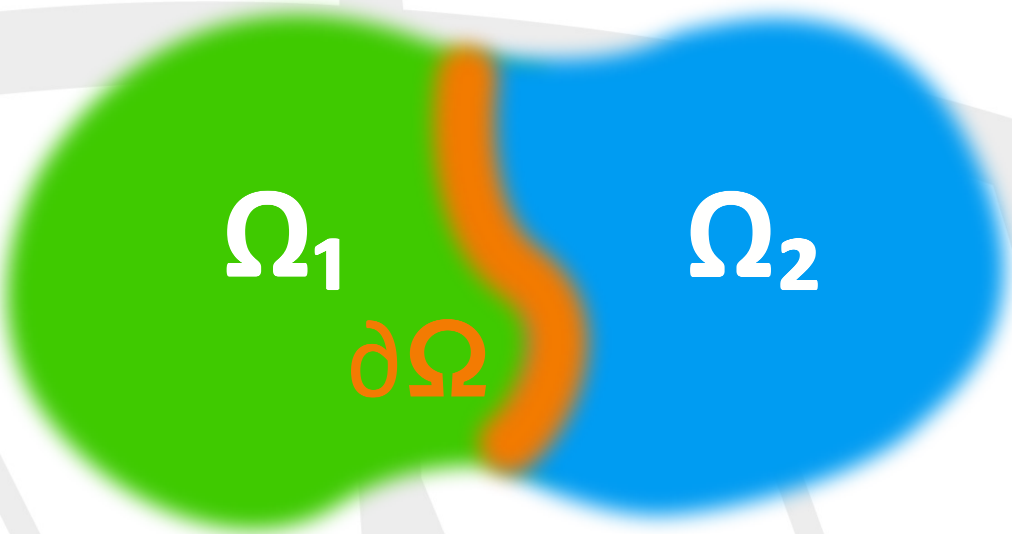
$$\kappa' = \kappa$$

gauge invariance



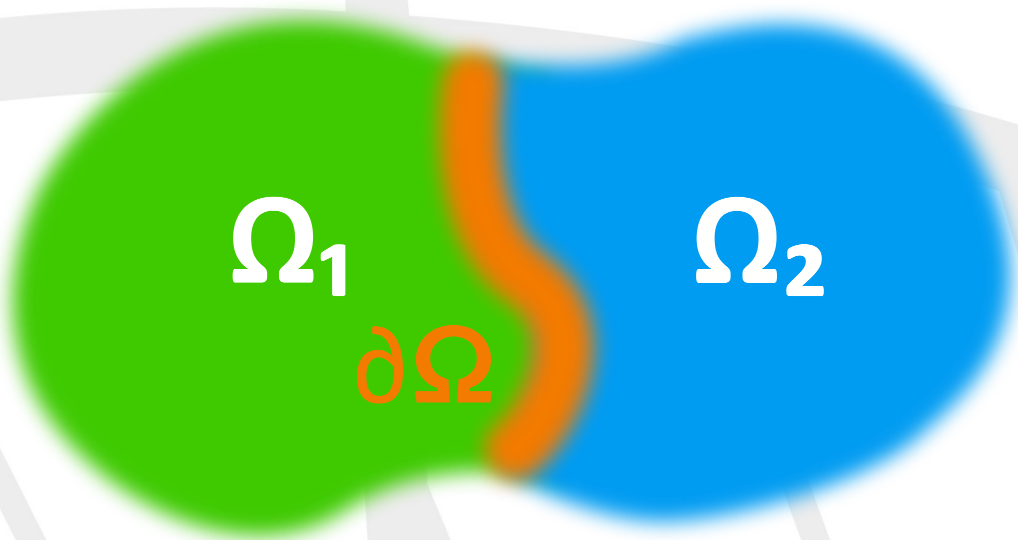
$$E[\Omega_1 \cup \Omega_2] = E[\Omega_1] + E[\Omega_2] + W[\partial\Omega]$$

gauge invariance



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

gauge invariance

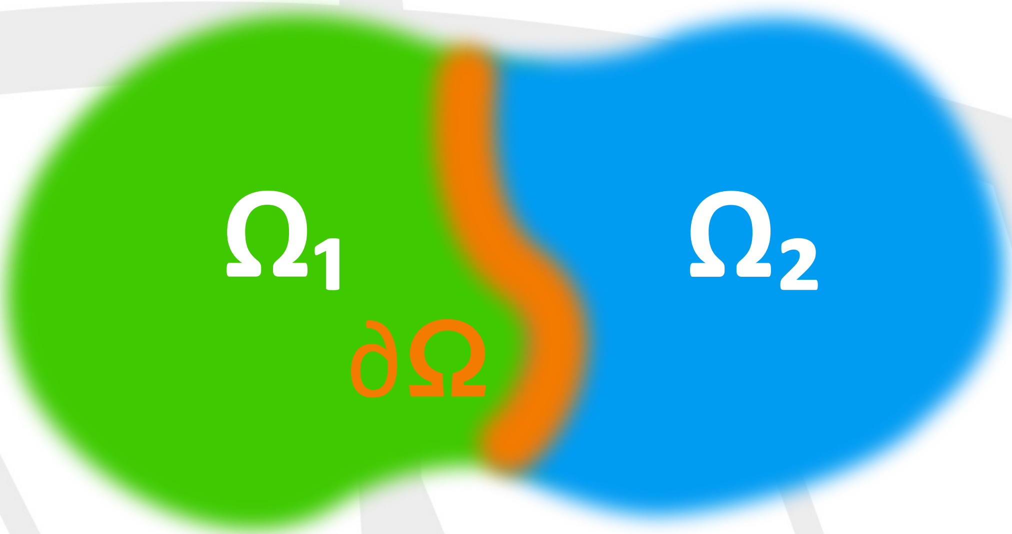


$$\mathsf{E}[\Omega_1 \cup \Omega_2] = \mathsf{E}[\Omega_1] + \mathsf{E}[\Omega_2] + \mathsf{W}[\partial\Omega]$$

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

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

gauge invariance



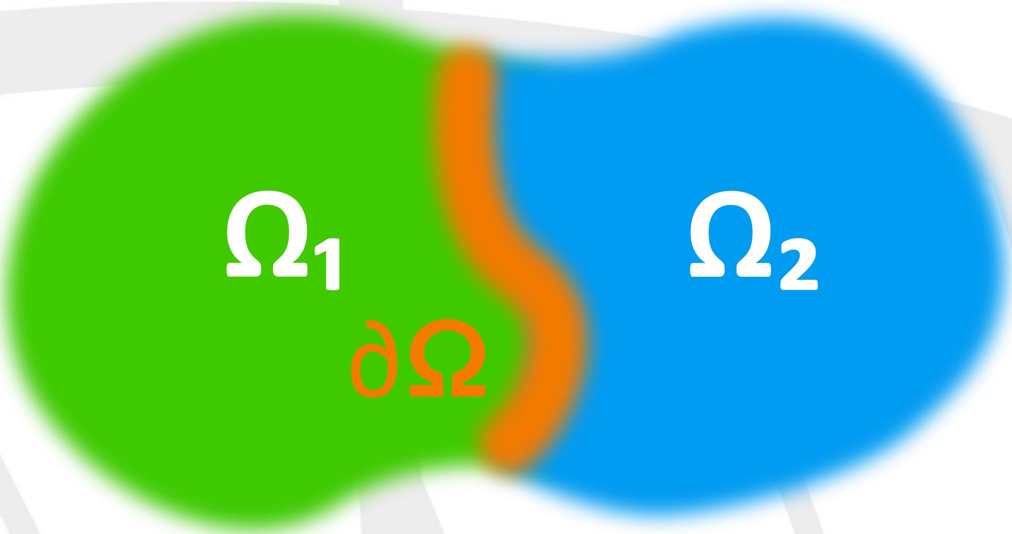
$$\mathsf{E}[\Omega_1 \cup \Omega_2] = \mathsf{E}[\Omega_1] + \mathsf{E}[\Omega_2] + \mathsf{W}[\partial\Omega]$$

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

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

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

gauge invariance



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

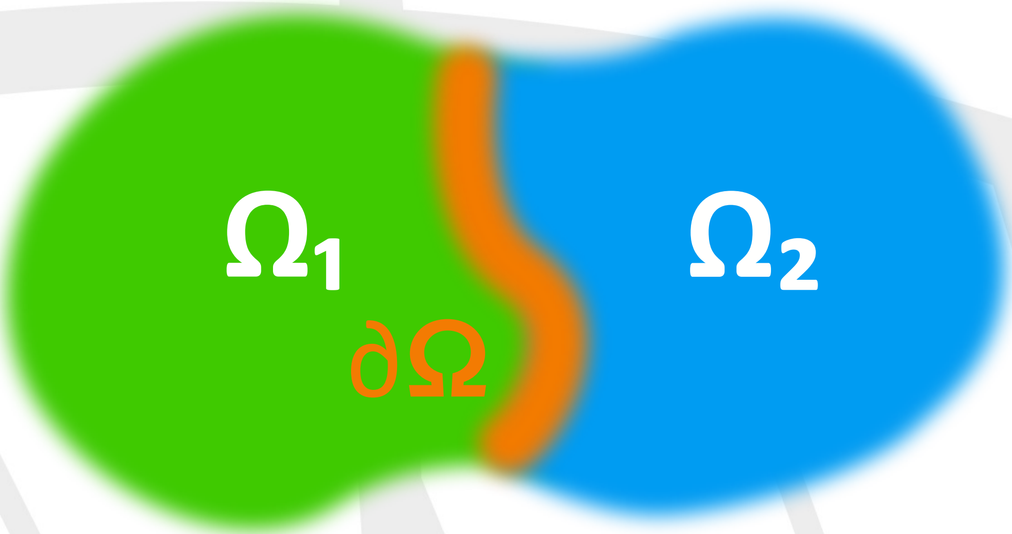
$$\stackrel{?}{=} \mathcal{E}[\Omega_1] + \mathcal{E}[\Omega_2]$$

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

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

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

gauge invariance



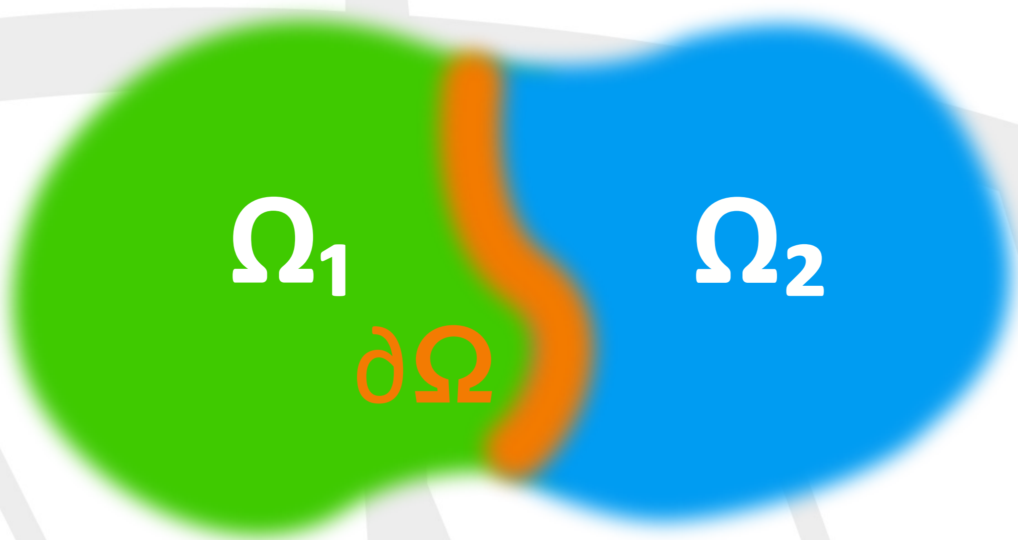
$$\mathsf{E}[\Omega_1 \cup \Omega_2] = \mathsf{E}[\Omega_1] + \mathsf{E}[\Omega_2] + \mathsf{W}[\partial\Omega]$$
$$\stackrel{?}{=} \mathcal{E}[\Omega_1] + \mathcal{E}[\Omega_2]$$
$$\mathcal{E}[\Omega] = \int_\Omega e(\mathbf{r}) d\mathbf{r}$$

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

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

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

gauge invariance



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

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

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

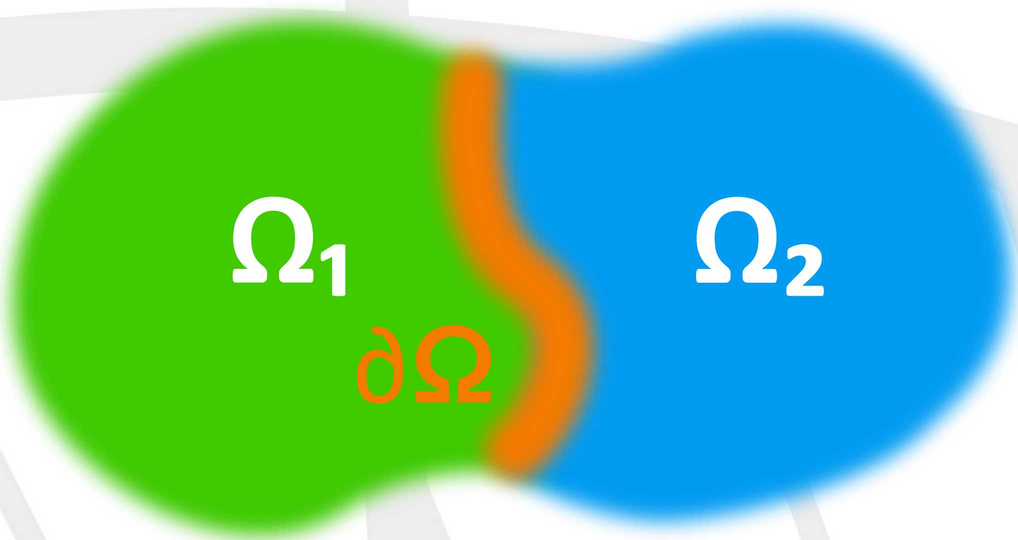
$$\mathcal{E}'[\Omega] = \mathcal{E}[\Omega] + \mathcal{O}[\partial\Omega]$$

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

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

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

gauge invariance



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

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

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

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

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

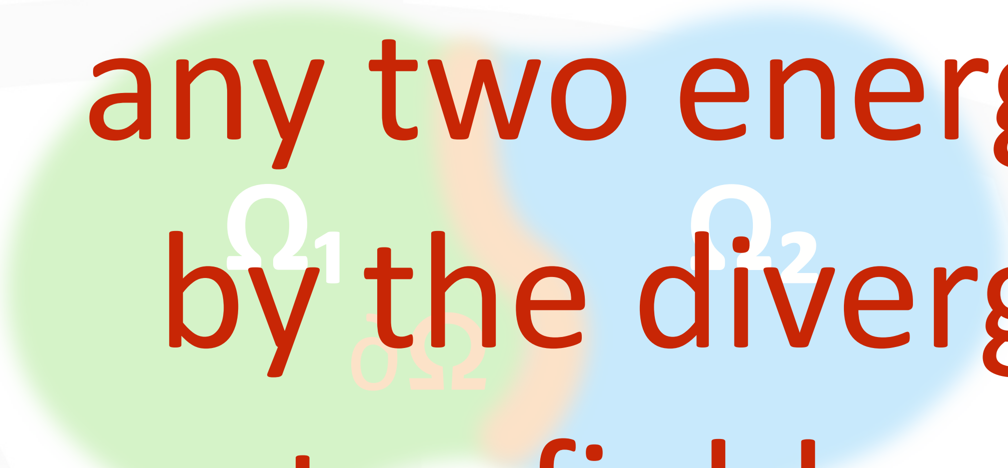
$$\dot{e}'(\mathbf{r},t) = -\nabla \cdot \big(\mathbf{j}(\mathbf{r},t) + \dot{\mathbf{p}}(\mathbf{r},t)\big)$$

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

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

gauge invariance

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



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

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

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

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

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

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

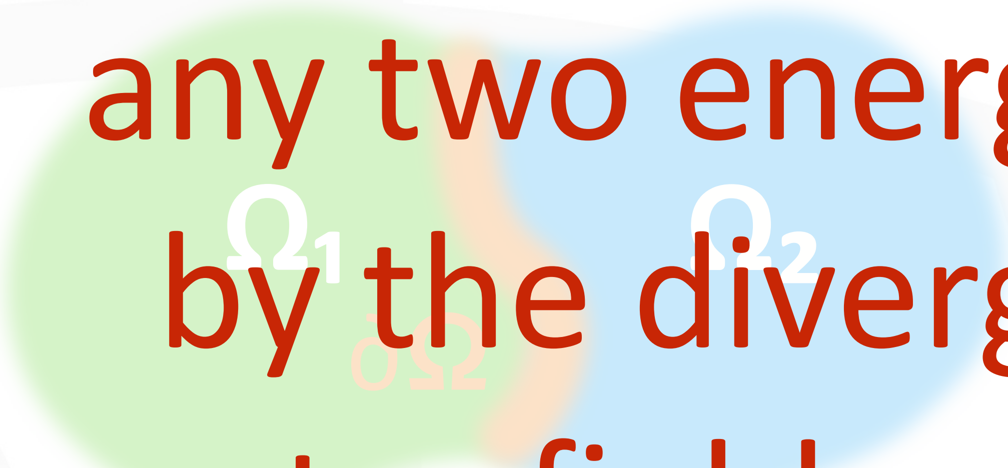
$$\mathbf{j}'(\mathbf{r},t) = \mathbf{j}(\mathbf{r},t) + \dot{\mathbf{p}}(\mathbf{r},t)$$

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

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



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

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

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

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

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

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

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

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

density-functional theory

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

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

the DFT energy density

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

$$+ \sum_v \epsilon_v - \frac{1}{2}\mathsf{E}_H + \int \left(\epsilon_{XC}(\mathbf{r}) - \mu_{XC}(\mathbf{r})\right)\rho(\mathbf{r})d\mathbf{r}$$

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

the DFT energy density

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

$$+ \sum_v \epsilon_v - \frac{1}{2}\mathsf{E}_H + \int \left(\epsilon_{XC}(\mathbf{r}) - \mu_{XC}(\mathbf{r})\right)\rho(\mathbf{r})d\mathbf{r}$$

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

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

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

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

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

the DFT energy current

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

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

the DFT energy current

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

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

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

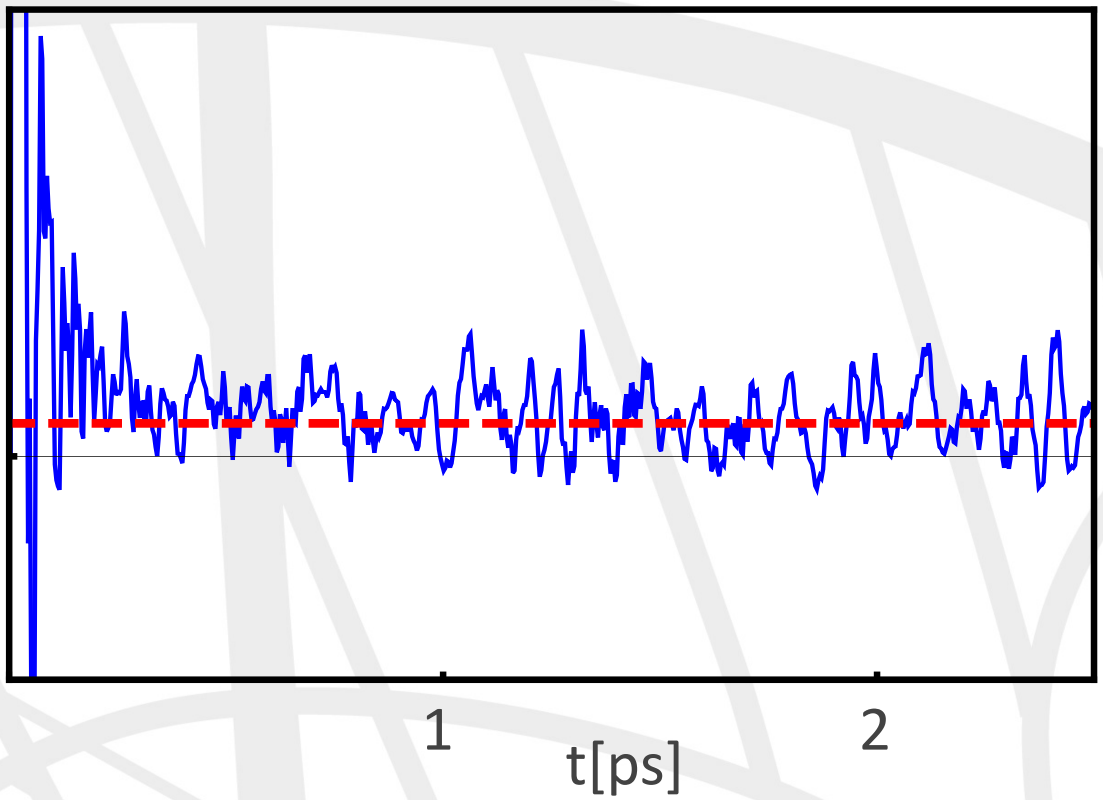
$$\mathbf{J}_H = \frac{1}{4\pi} \int \dot{v}_H(\mathbf{r}) \nabla v_H(\mathbf{r}) d\mathbf{r}$$

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

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

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

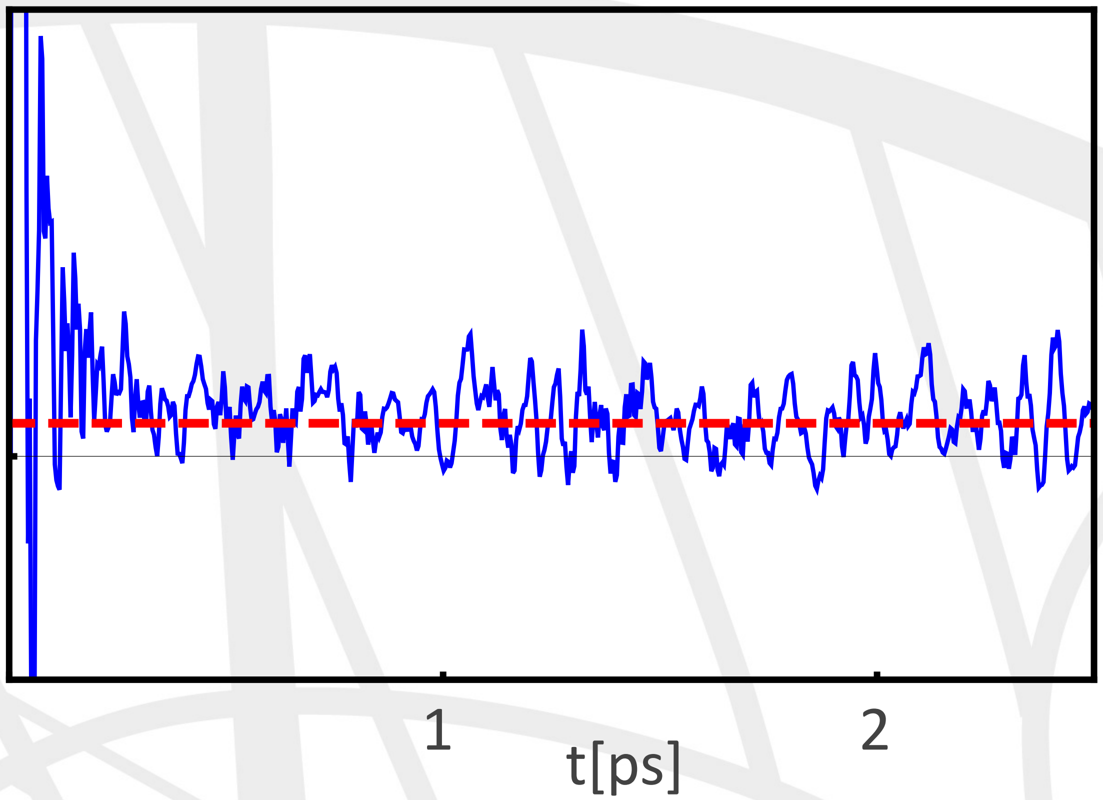
liquid water



64 molecules, T=385 K
expt density @ac

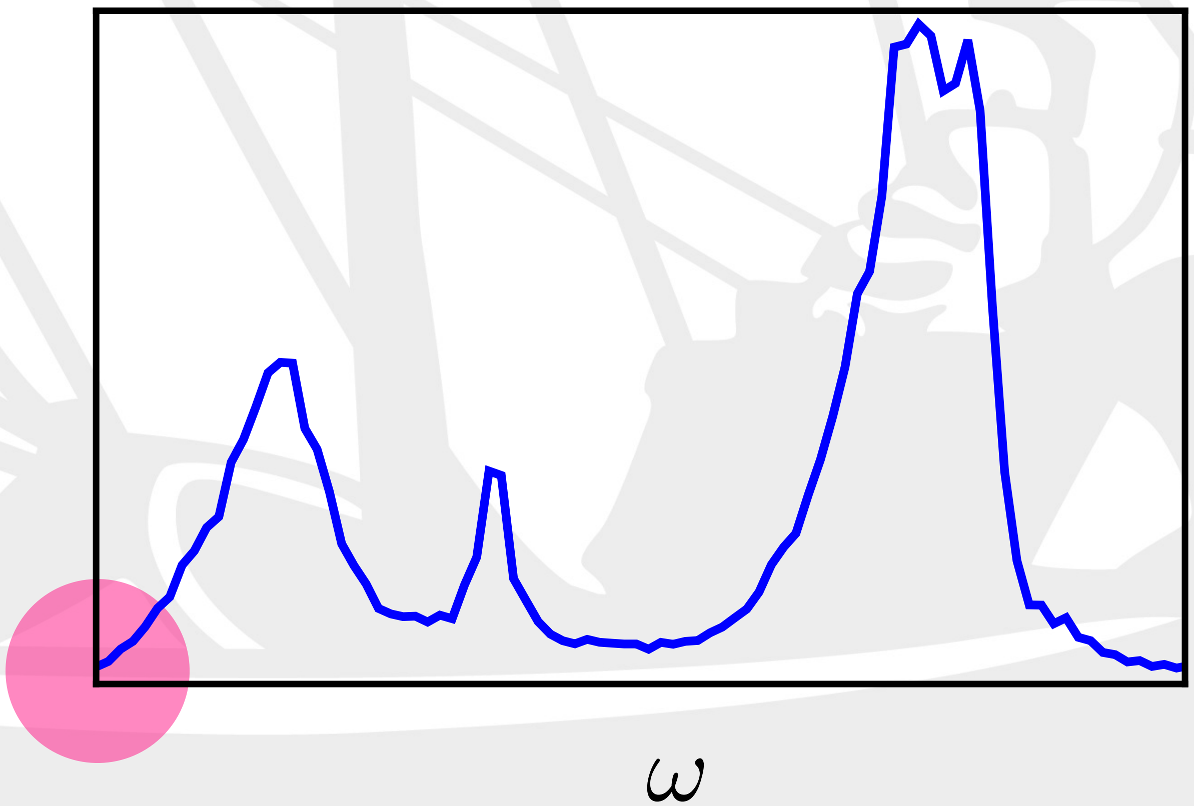
$$\frac{1}{3Vk_BT^2}\int_0^{\mathsf{t}}\langle \mathbf{J}(\mathsf{t}')\cdot\mathbf{J}(0)\rangle d\mathsf{t}'$$

liquid water



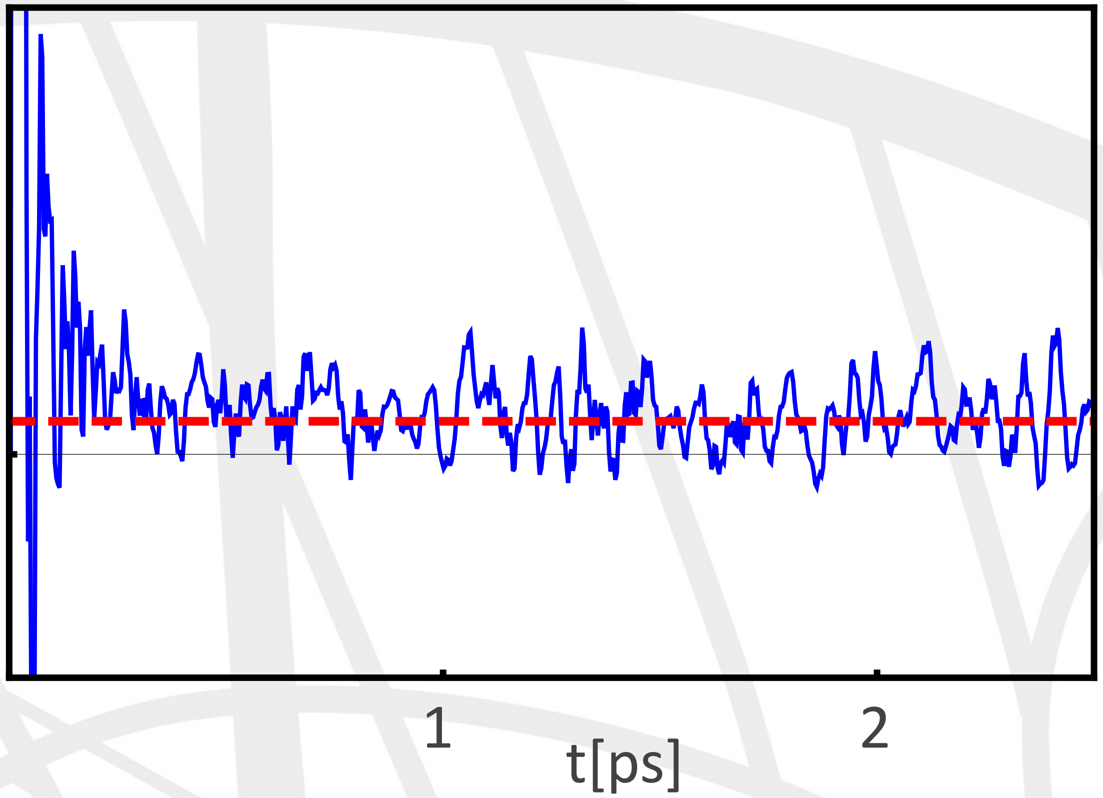
64 molecules, T=385 K
expt density @ac

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



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

liquid water



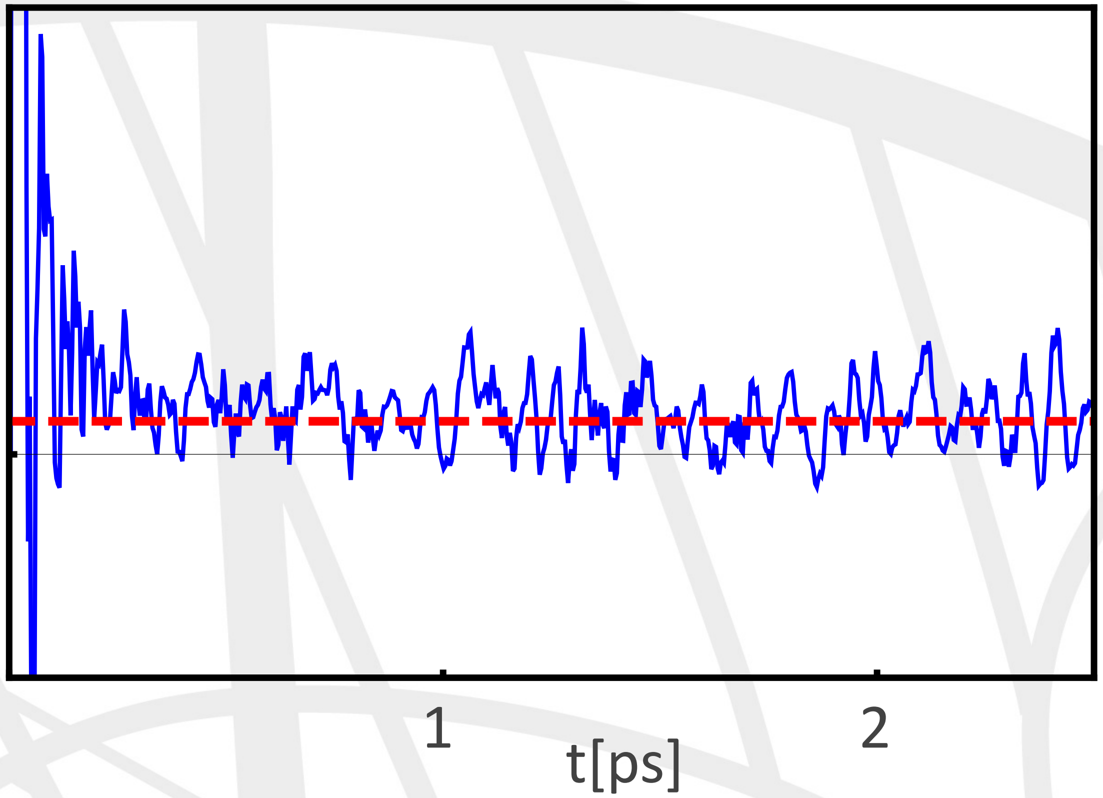
64 molecules, T=385 K
expt density @ac

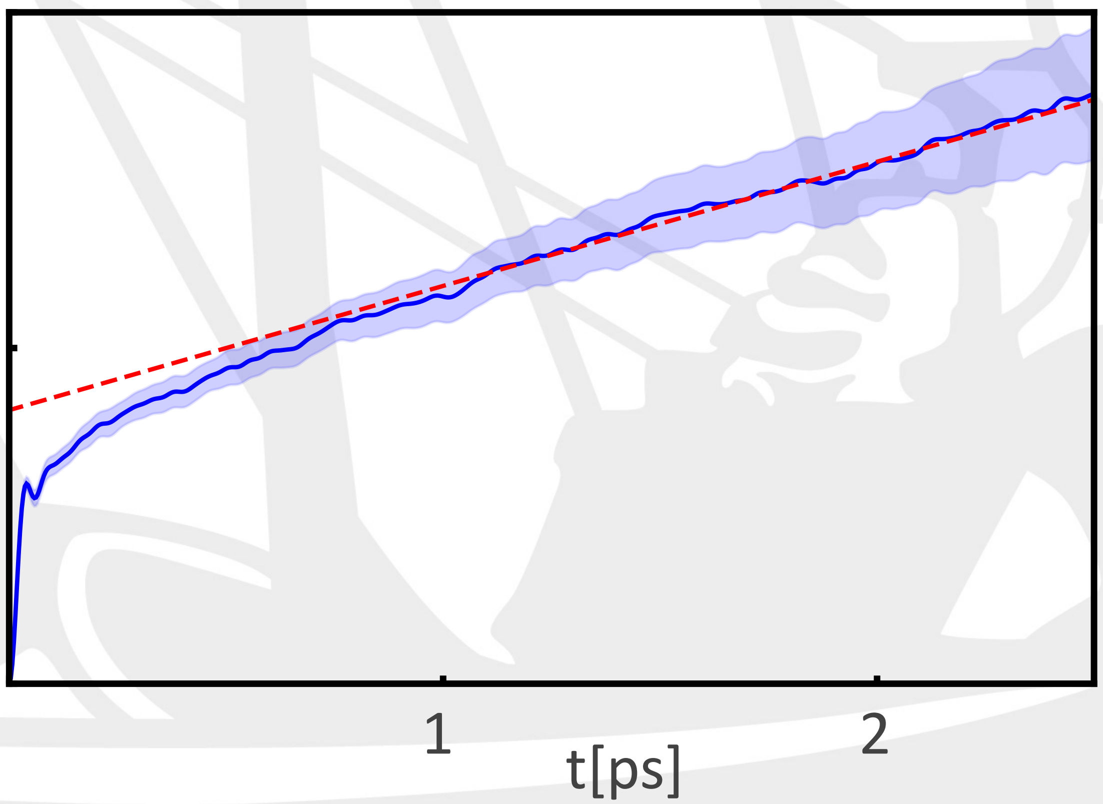
$$\frac{1}{3Vk_BT^2}\int_0^{t}\langle \mathbf{J}(t')\cdot\mathbf{J}(0)\rangle dt'$$

Einstein's relation

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

liquid water



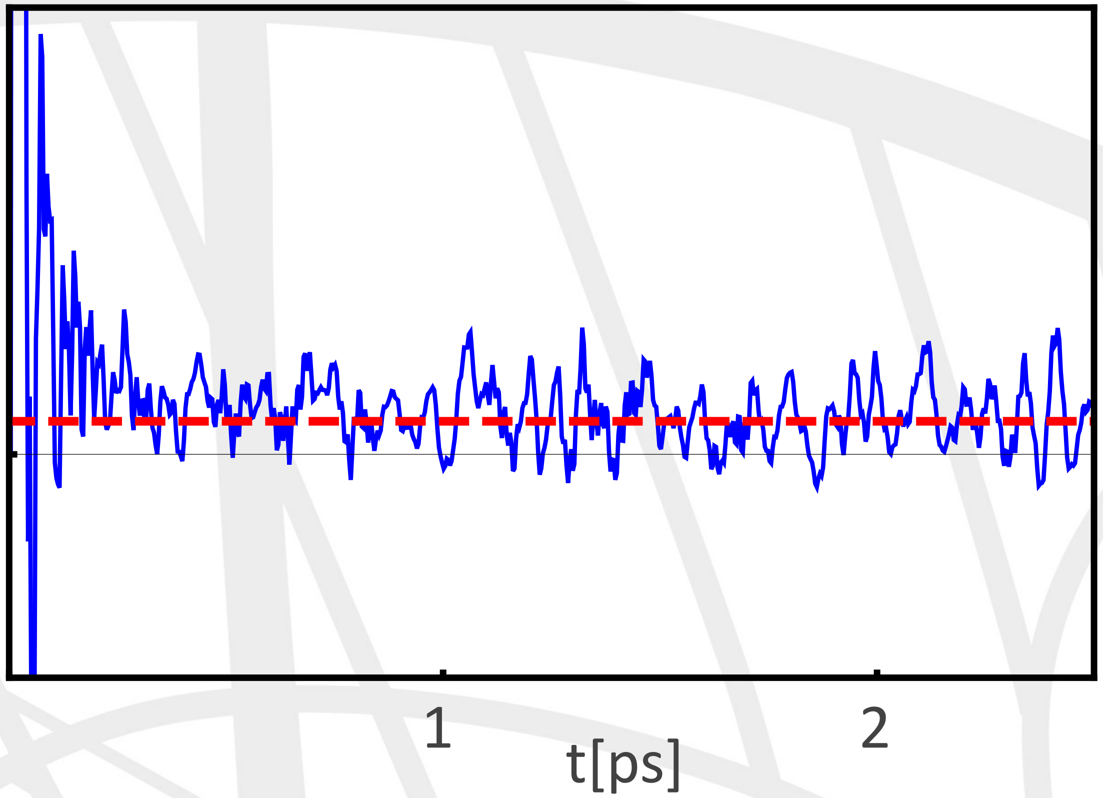


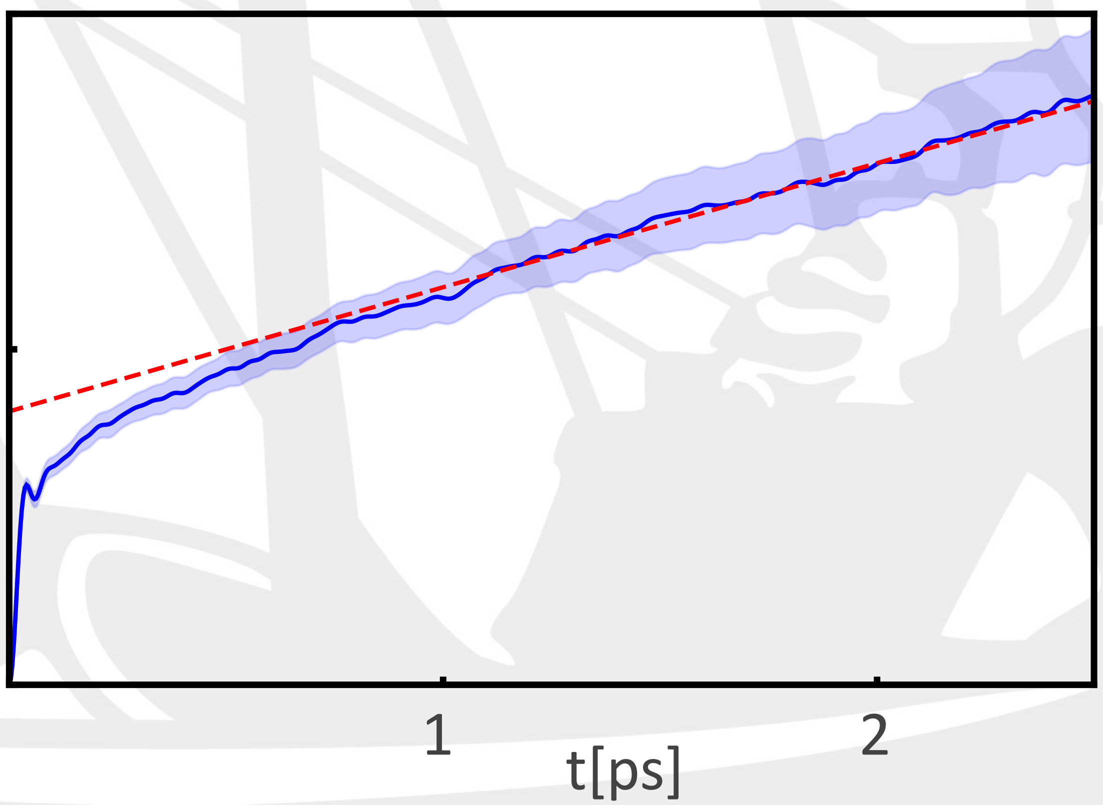
64 molecules, T=385 K
expt density @ac

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

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

liquid water





64 molecules, T=385 K
expt density @ac

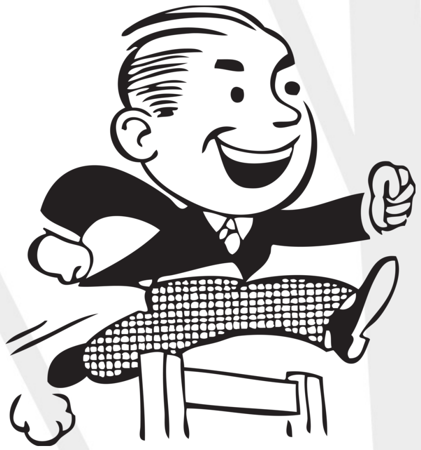
$$\frac{1}{3Vk_BT^2}\int_0^{\mathsf{t}}\langle \mathbf{J}(\mathsf{t}')\cdot\mathbf{J}(0)\rangle dt'$$

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

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

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

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).

separating wheat from chaff

$$\kappa \propto \int_0^\infty C(t)dt$$

$$C(t) = \langle J(t)J(0)\rangle$$

separating wheat from chaff

$$\kappa \propto \int_0^\infty C(t)dt$$

$$C(t) = \langle J(t)J(0) \rangle$$

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

$$S(\omega) = \int_{-\infty}^{\infty} C(t)\mathrm{e}^{-i\omega t}dt$$

separating wheat from chaff

$$\kappa \propto \int_0^\infty C(t)dt$$

$$C(t) = \langle J(t)J(0)\rangle$$

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

$$S(\omega) = \int_{-\infty}^{\infty} C(t)\mathrm{e}^{-i\omega t}dt$$

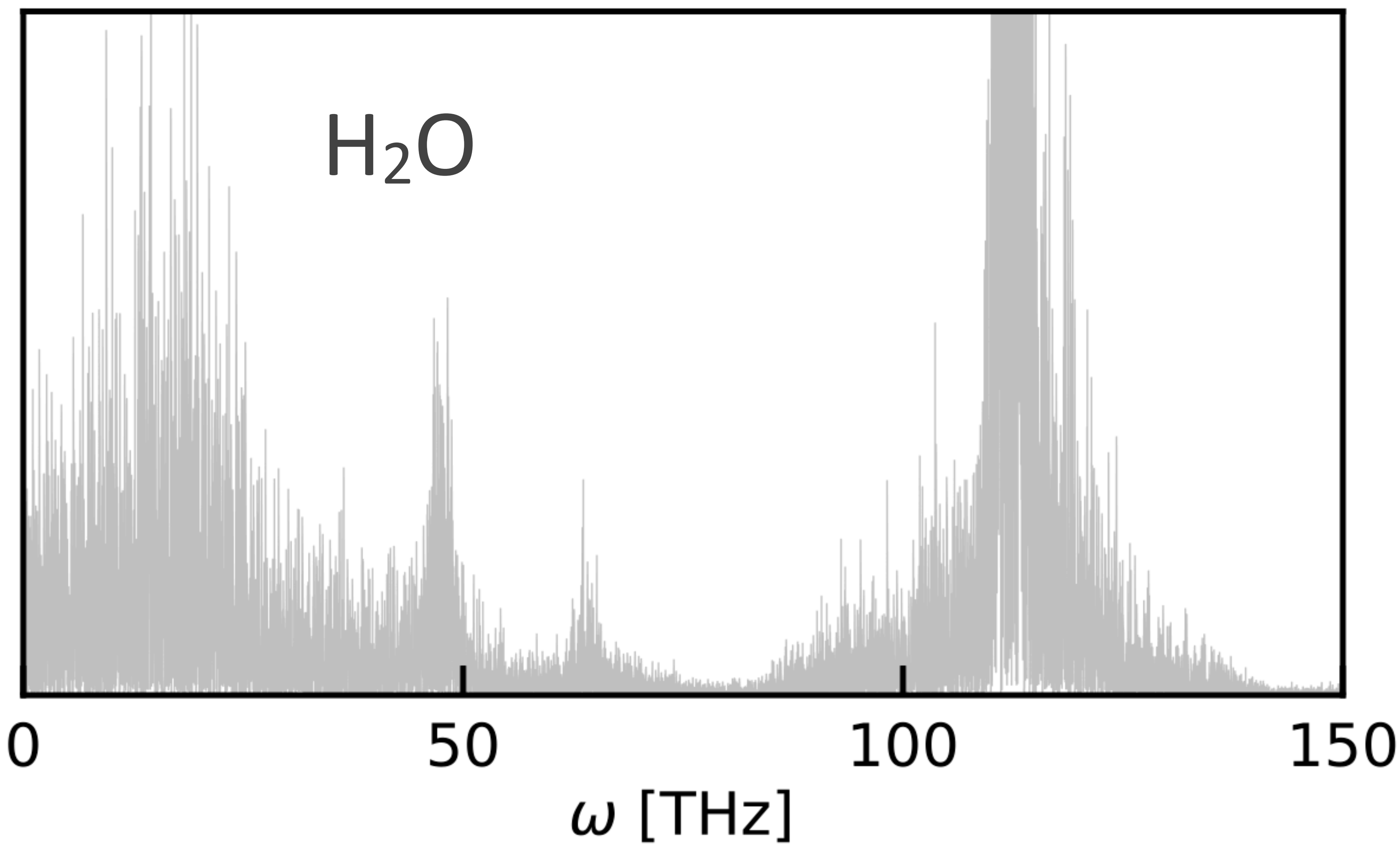
the Wiener-Khintchin theorem

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

$$\tilde{J}_k = \sum_{m=0}^{N-1} J_n \mathrm{e}^{-i\frac{2\pi nk}{N}}$$

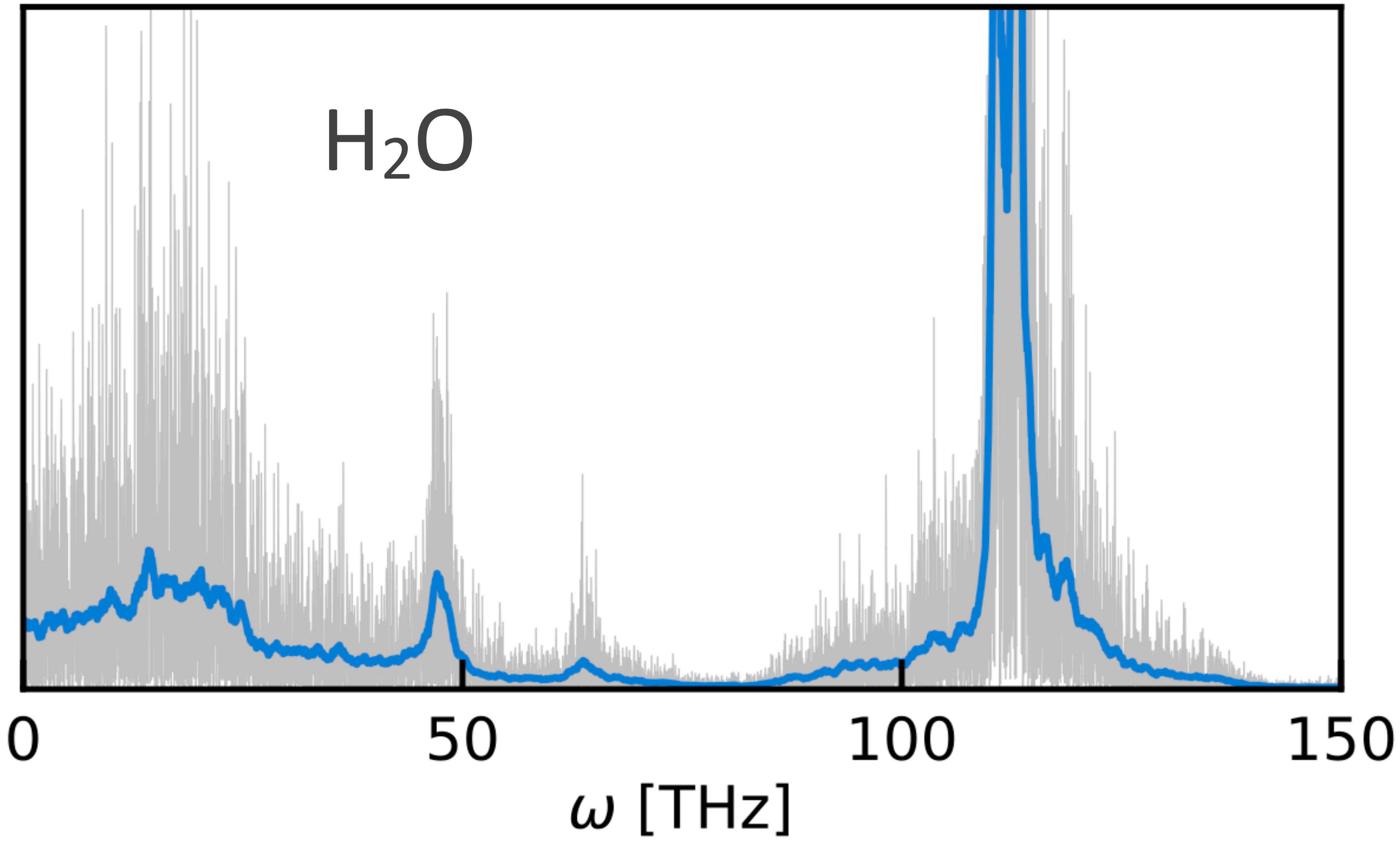
separating wheat from chaff

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



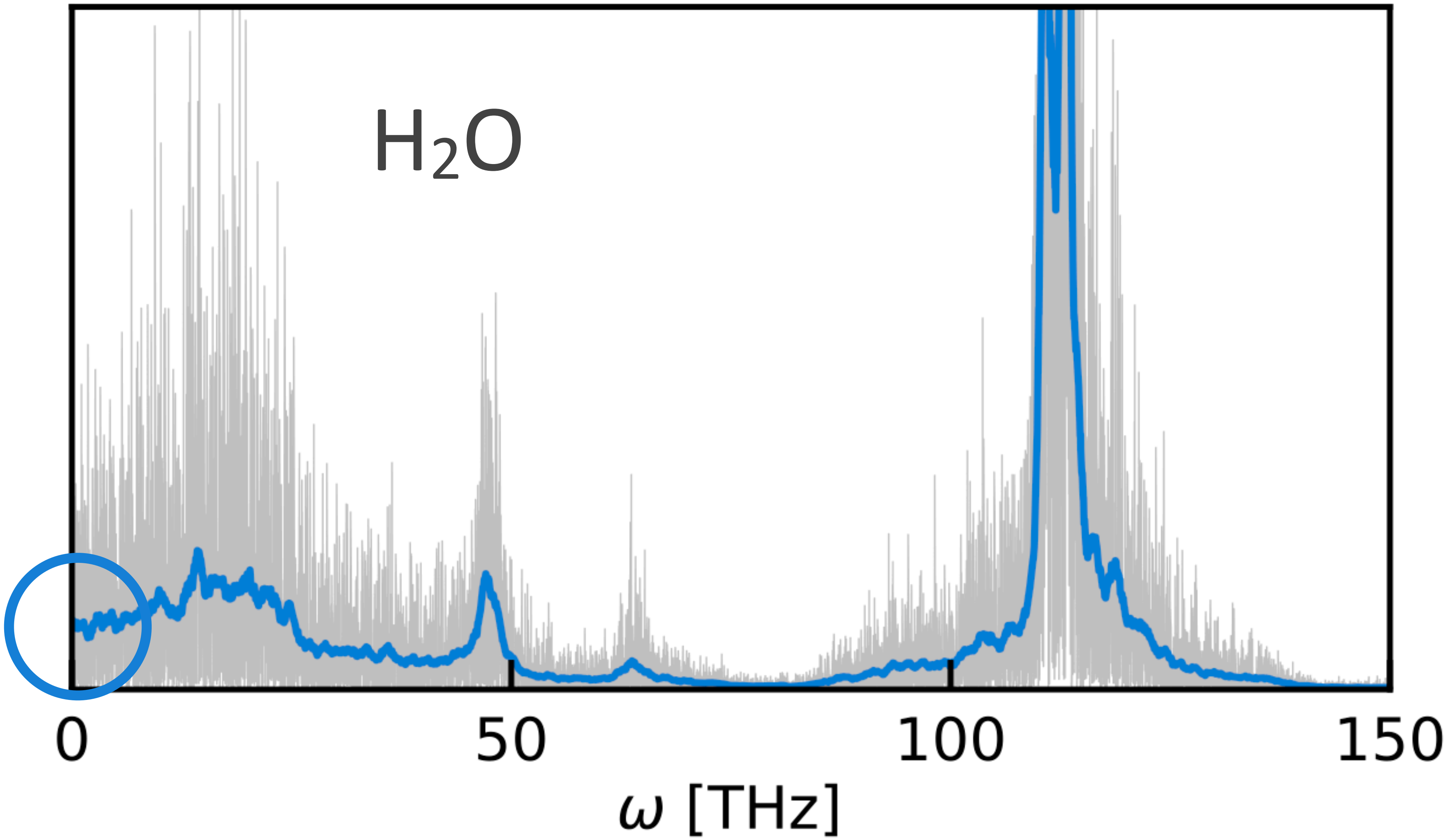
separating wheat from chaff

$$\hat{S}(k) = \frac{\epsilon}{N}\left|\tilde{J}(k)\right|^2$$
$$= \frac{1}{2}S(\omega_k) \times \chi_2^2$$



separating wheat from chaff

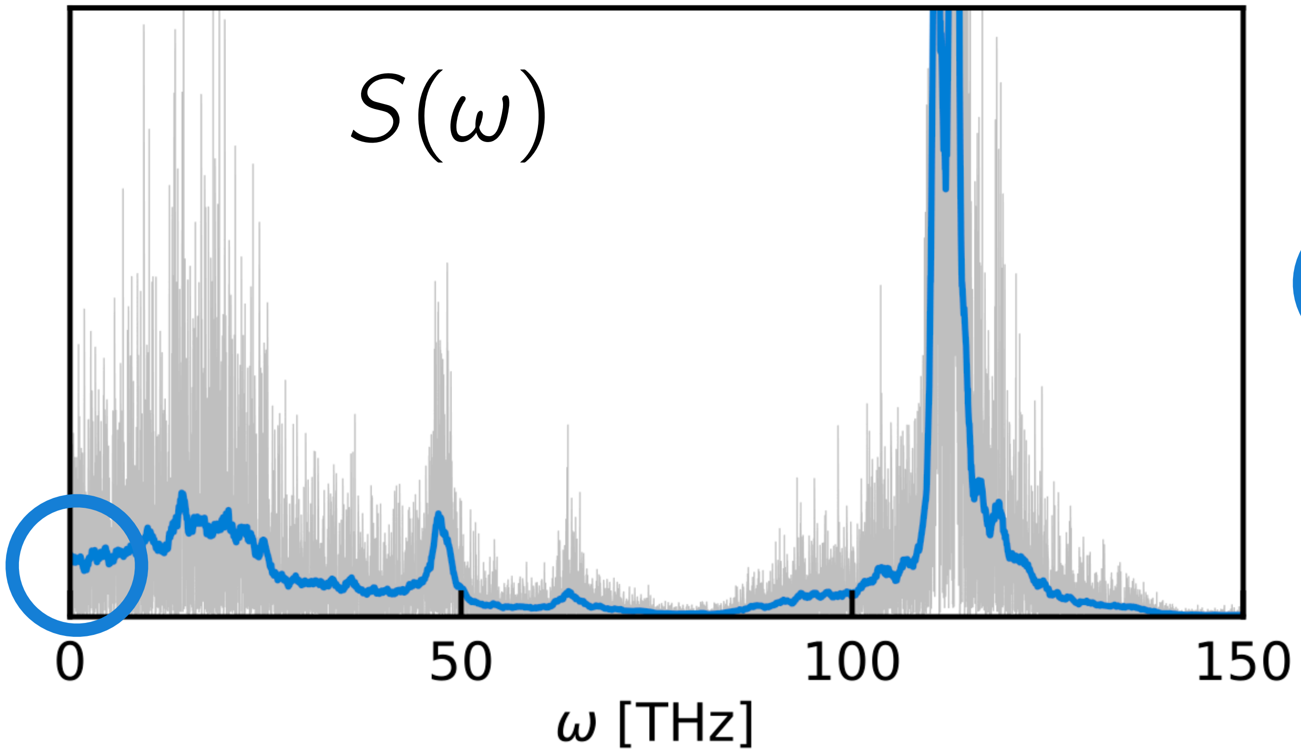
$$\hat{S}(k) = \frac{\epsilon}{N}\left|\tilde{J}(k)\right|^2 = \frac{1}{2}S(\omega_k) \times \chi_2^2$$

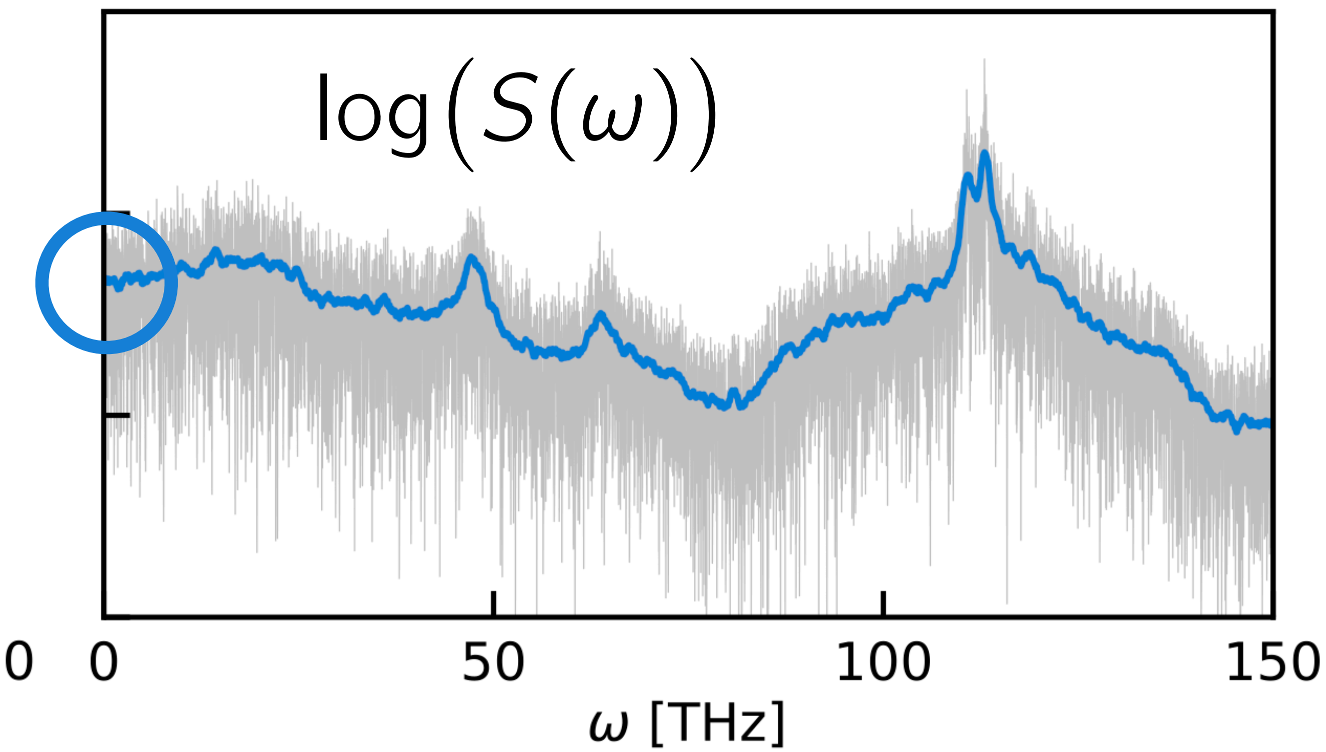


separating wheat from chaff

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

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

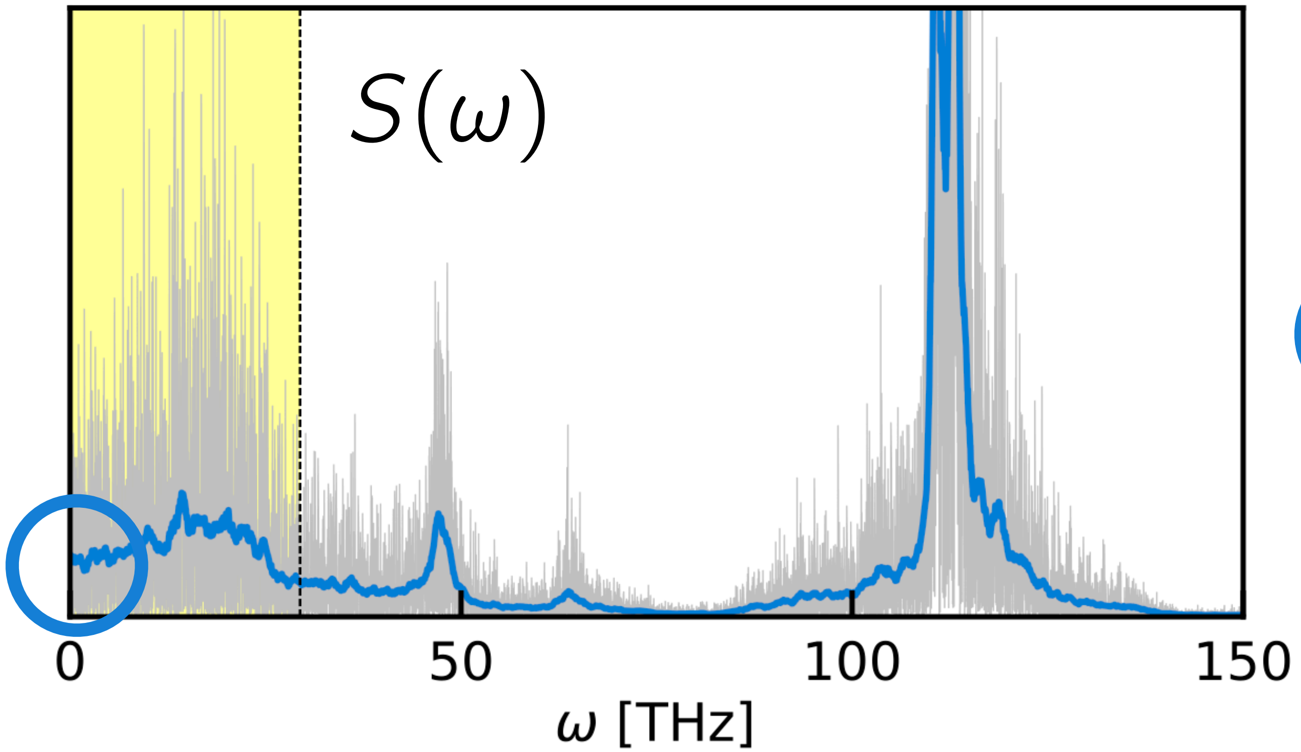


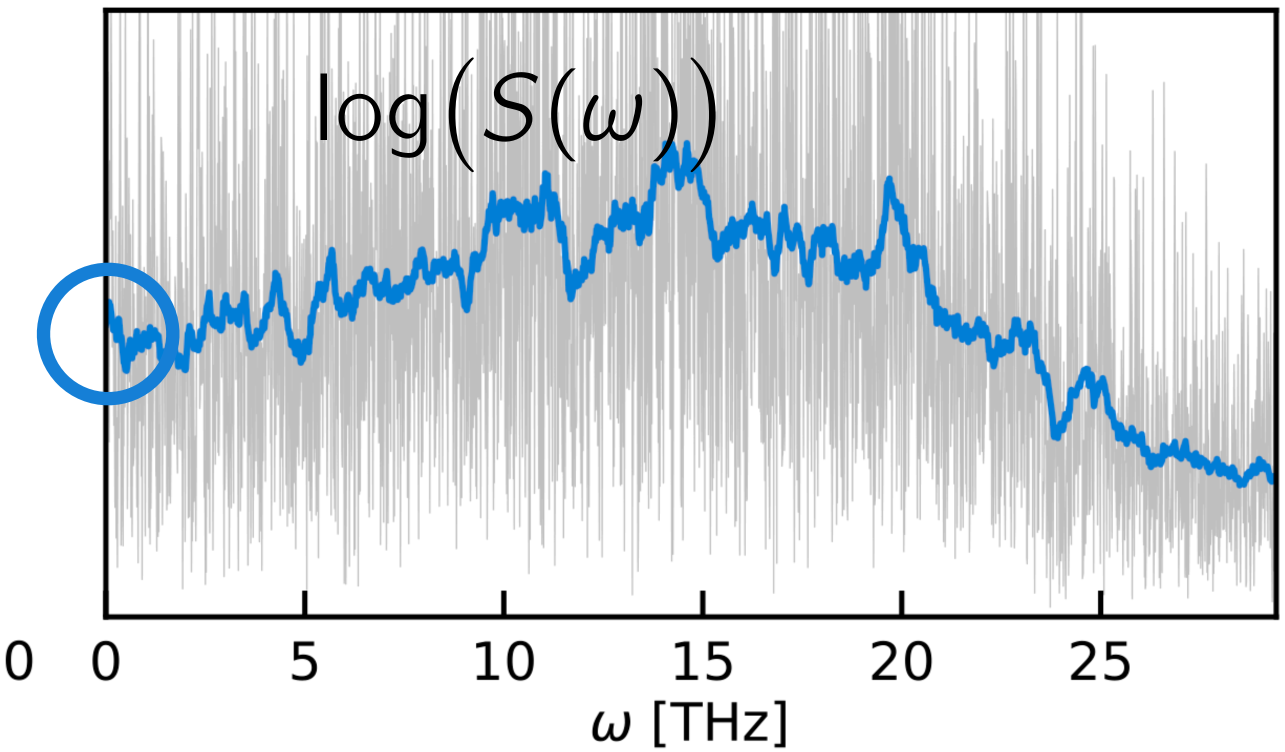


separating wheat from chaff

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

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

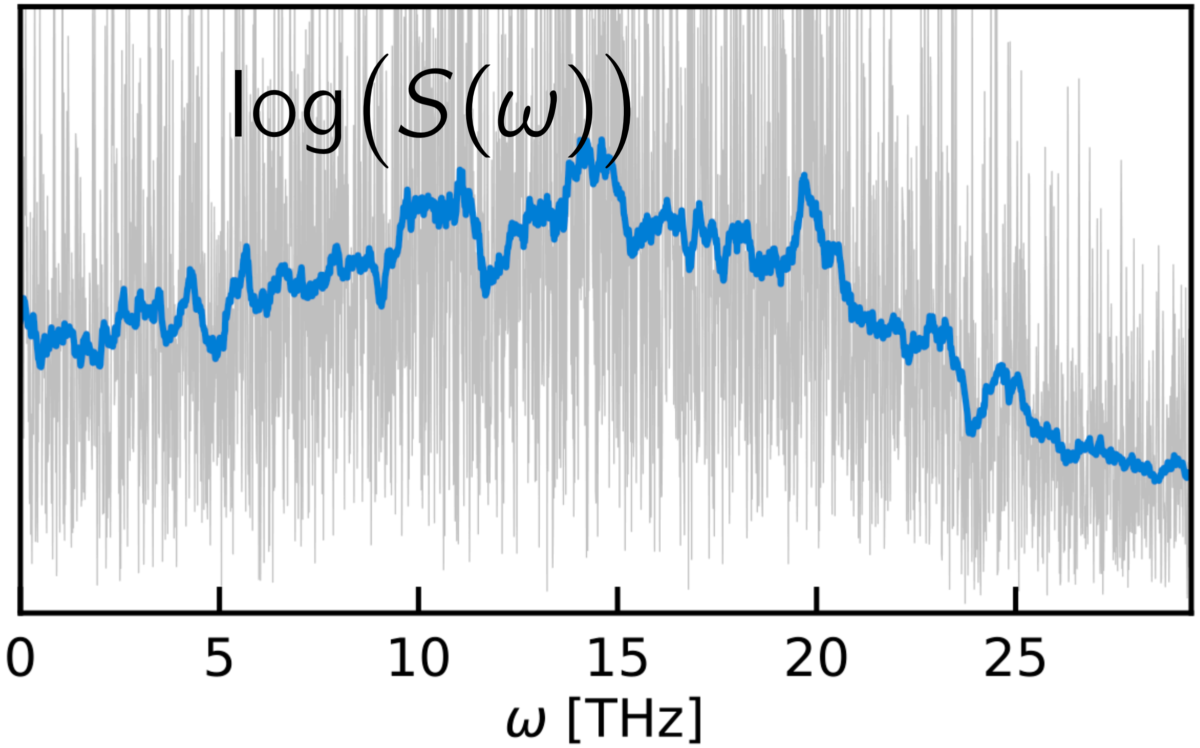


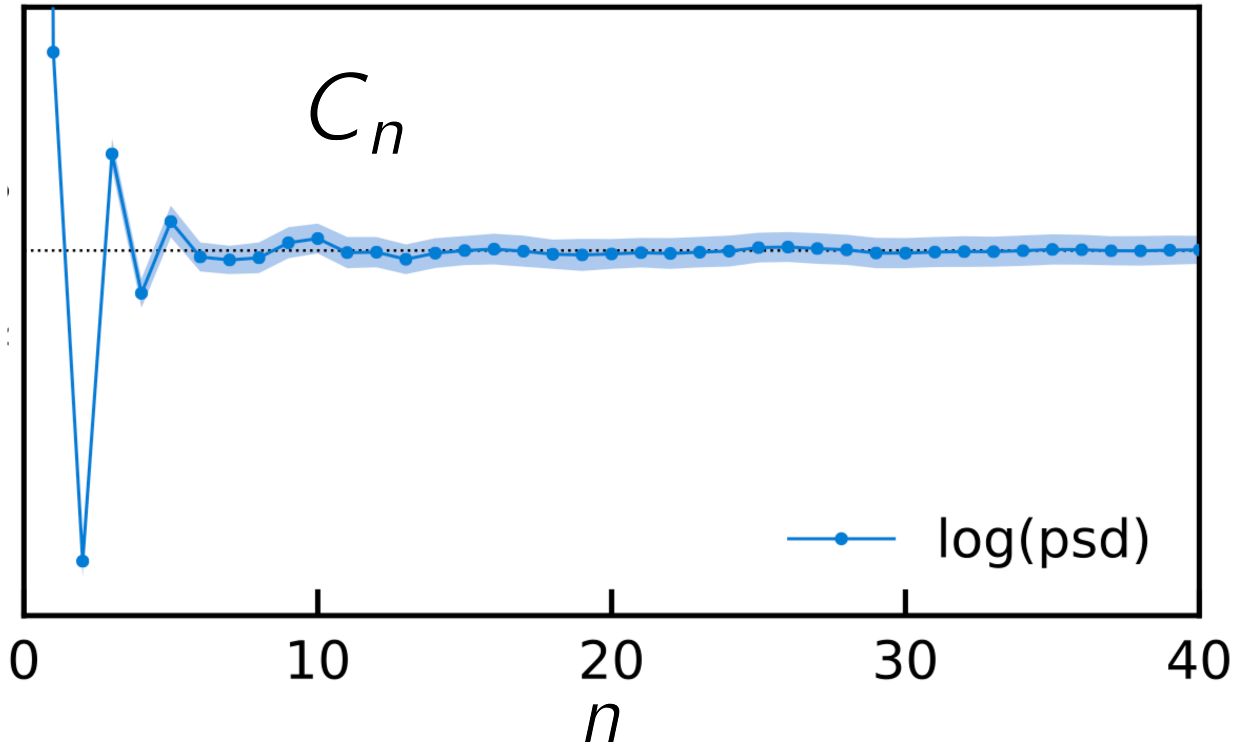


separating wheat from chaff

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

$$\frac{1}{N}\sum_{k=0}^{N-1} \log\left(\hat{S}(k)\right) e^{-i\frac{2\pi k n}{N}} = C_n + \text{white noise}$$

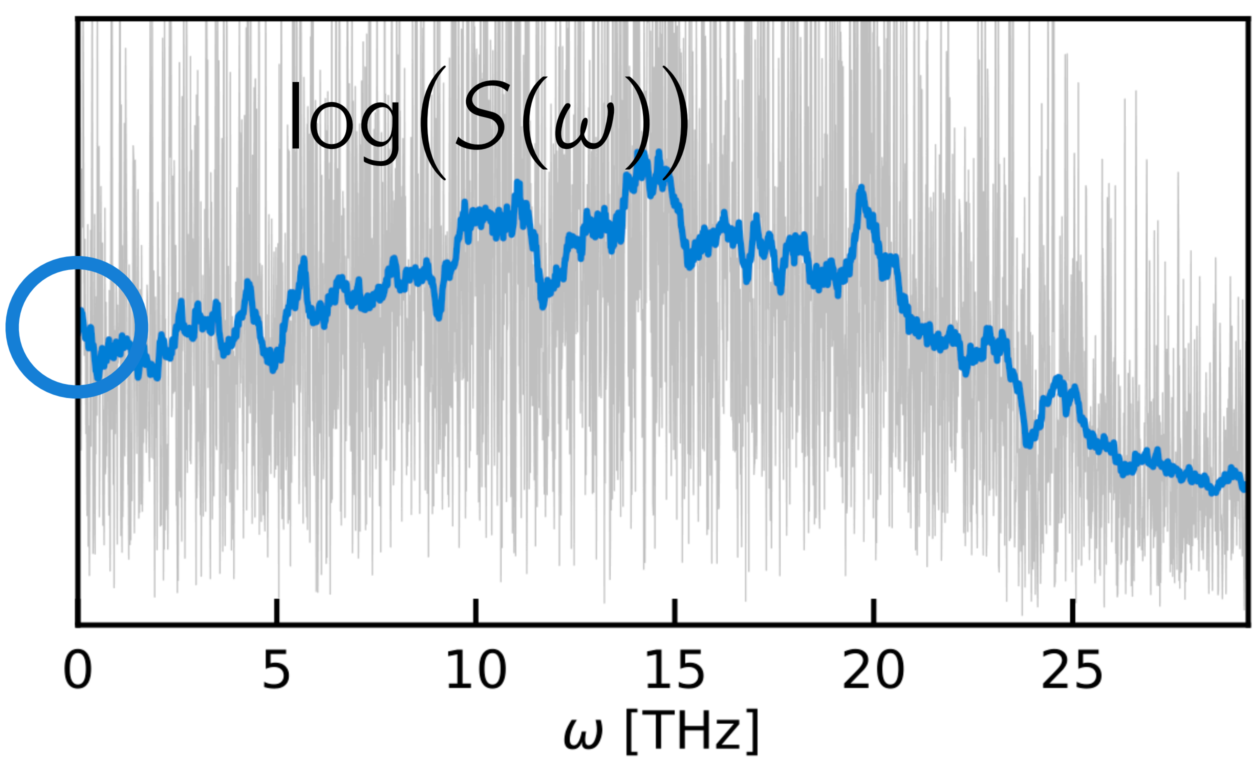


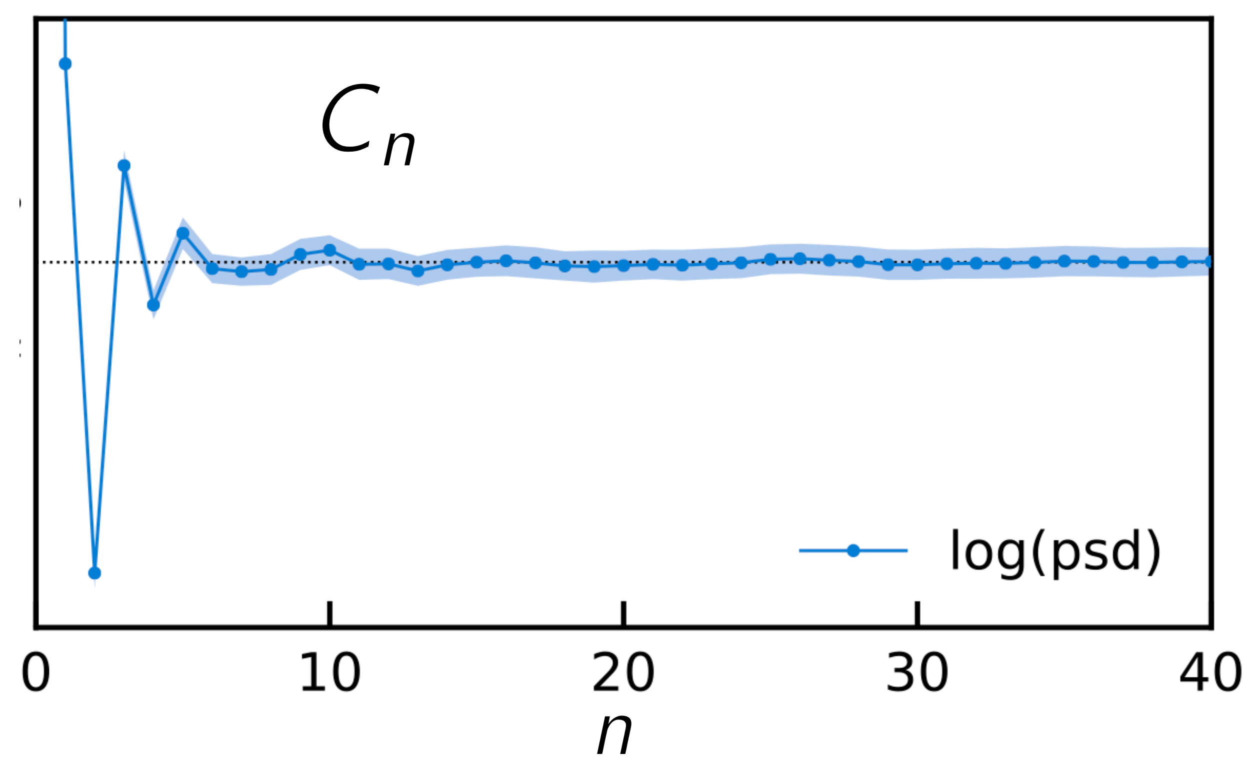


separating wheat from chaff

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

$$\frac{1}{N}\sum_{k=0}^{N-1}\log\left(\hat{S}(k)\right)e^{-i\frac{2\pi kn}{N}} = C_n + \text{white noise}$$



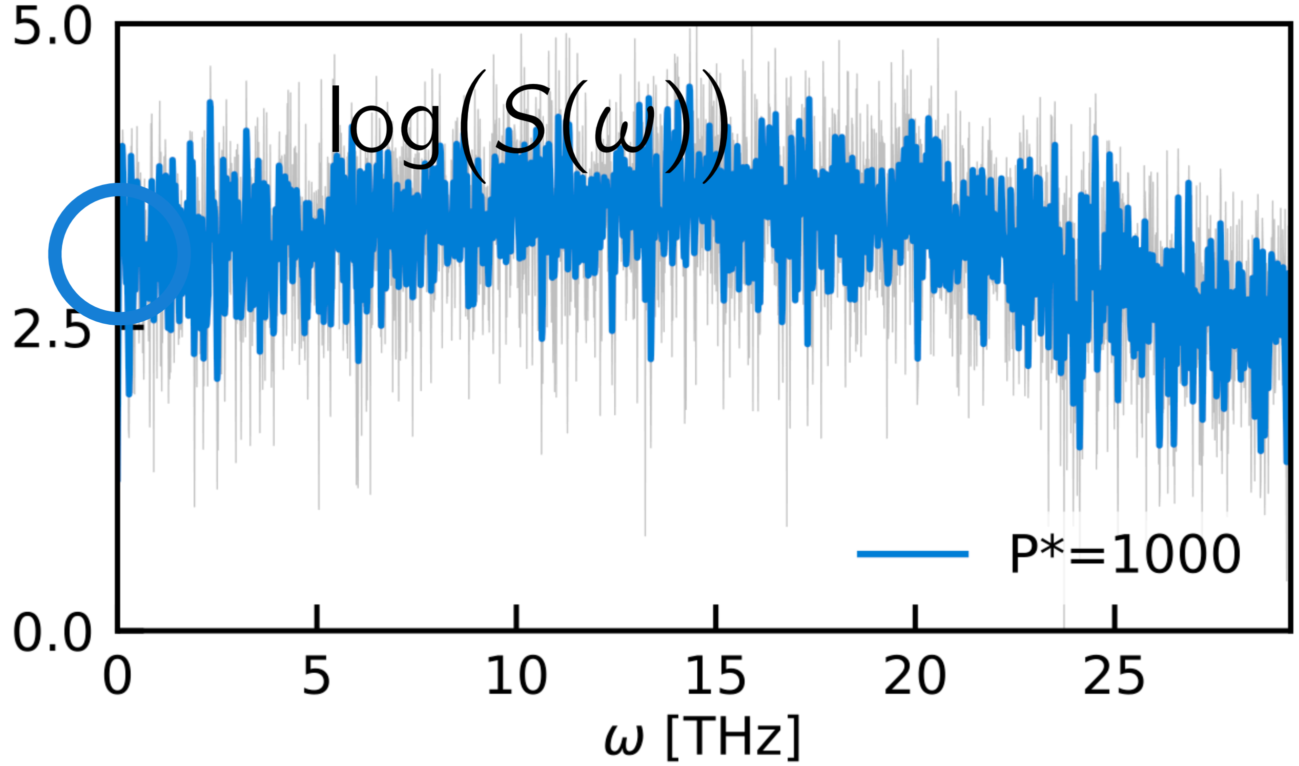


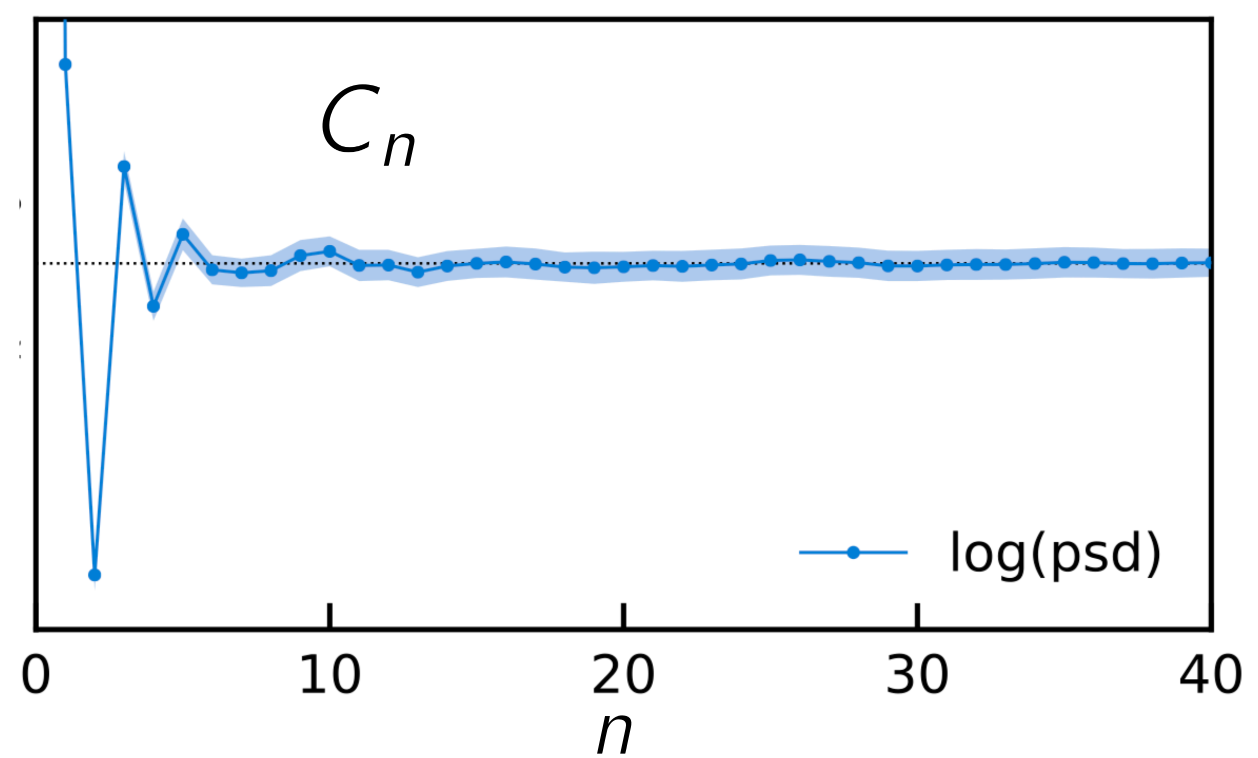
separating wheat from chaff

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

$$\frac{1}{N}\sum_{k=0}^{N-1} \log\left(\hat{S}(k)\right) e^{-i\frac{2\pi k n}{N}} = C_n + \text{white noise}$$

$$\log\left(S(\omega_k)\right) = \sum_{n=0}^{P^*-1} C_n e^{i\frac{2\pi k n}{N}} + \text{less noise}$$



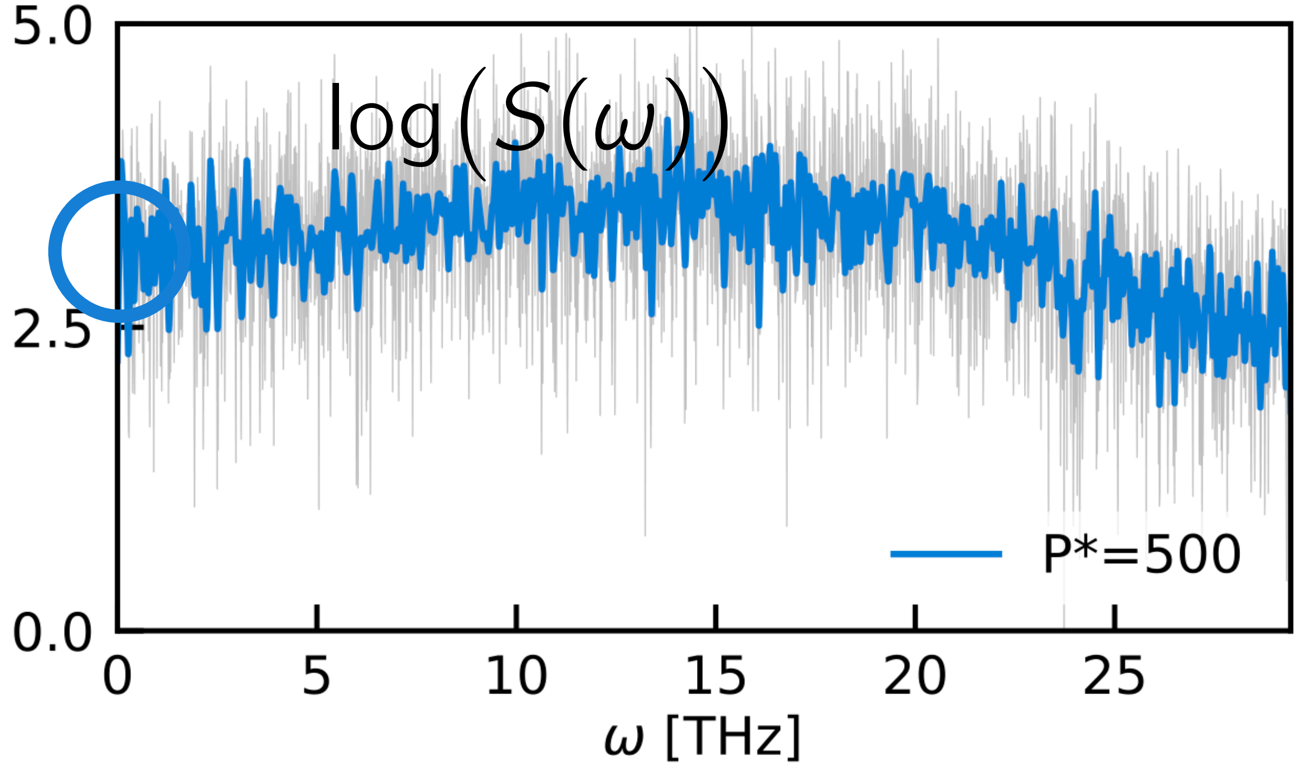


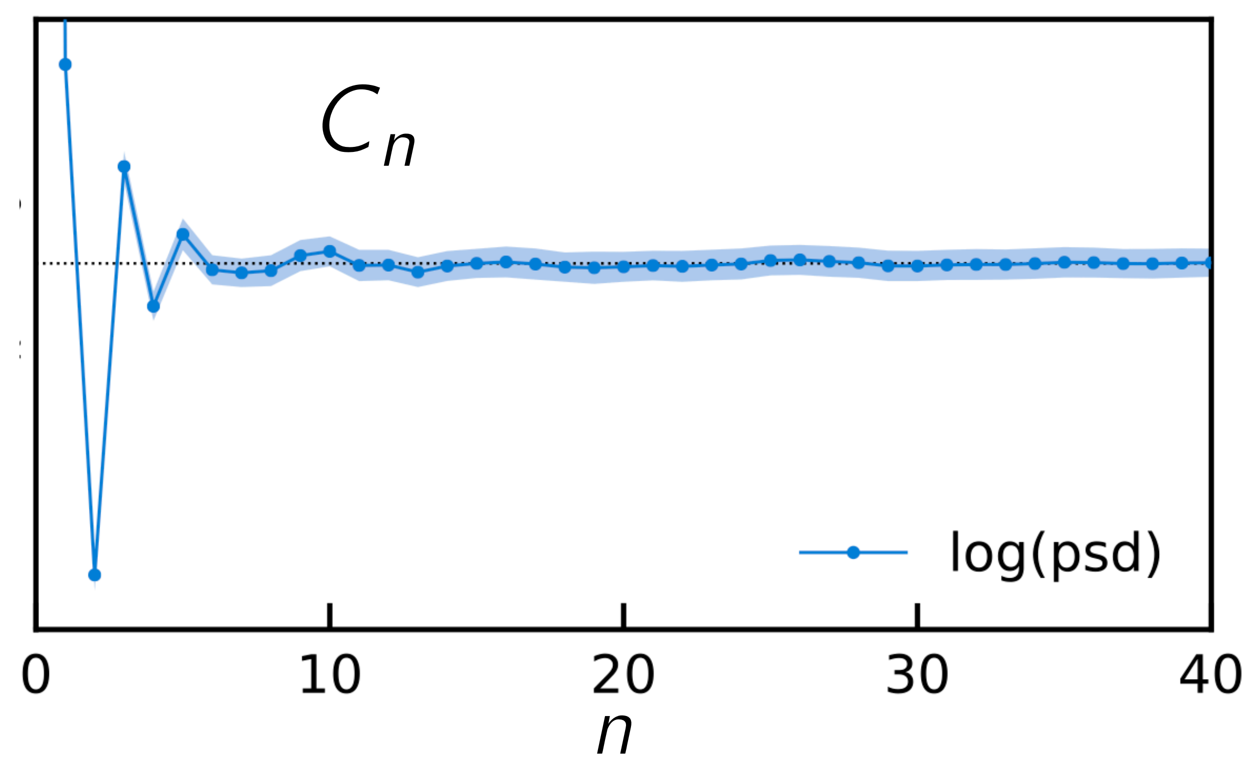
separating wheat from chaff

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

$$\frac{1}{N}\sum_{k=0}^{N-1} \log\left(\hat{S}(k)\right) e^{-i\frac{2\pi k n}{N}} = C_n + \text{white noise}$$

$$\log\left(S(\omega_k)\right) = \sum_{n=0}^{P^*-1} C_n e^{i\frac{2\pi k n}{N}} + \text{less noise}$$



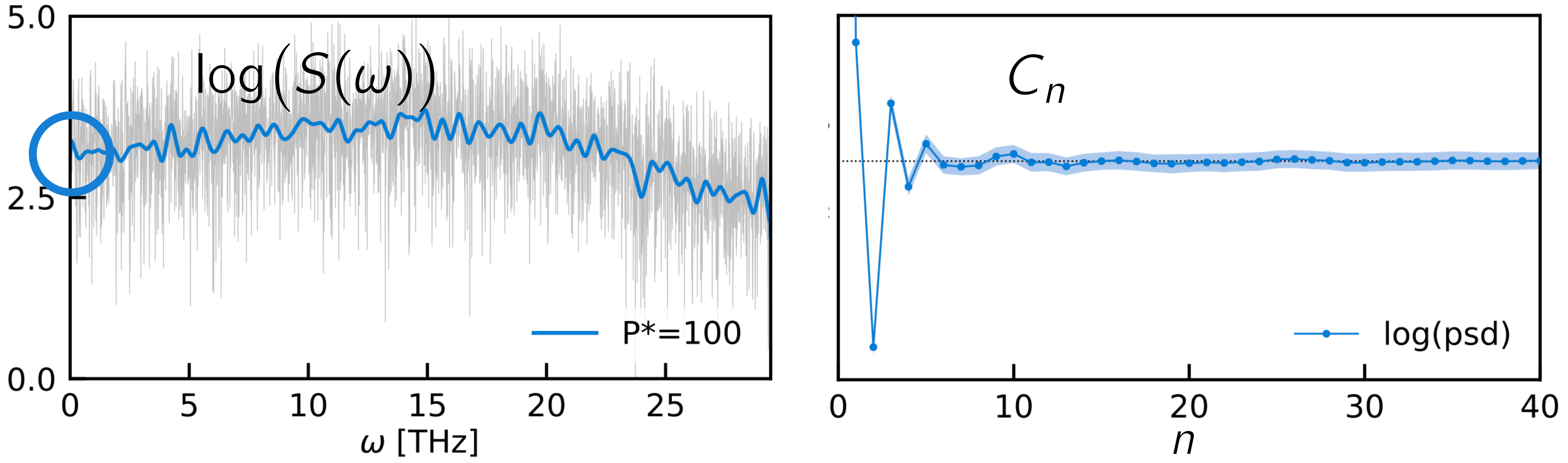


separating wheat from chaff

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

$$\frac{1}{N}\sum_{k=0}^{N-1}\log\left(\hat{S}(k)\right)e^{-i\frac{2\pi kn}{N}} = C_n + \text{white noise}$$

$$\log\left(S(\omega_k)\right) = \sum_{n=0}^{P^*-1} C_n e^{i\frac{2\pi kn}{N}} + \text{less noise}$$

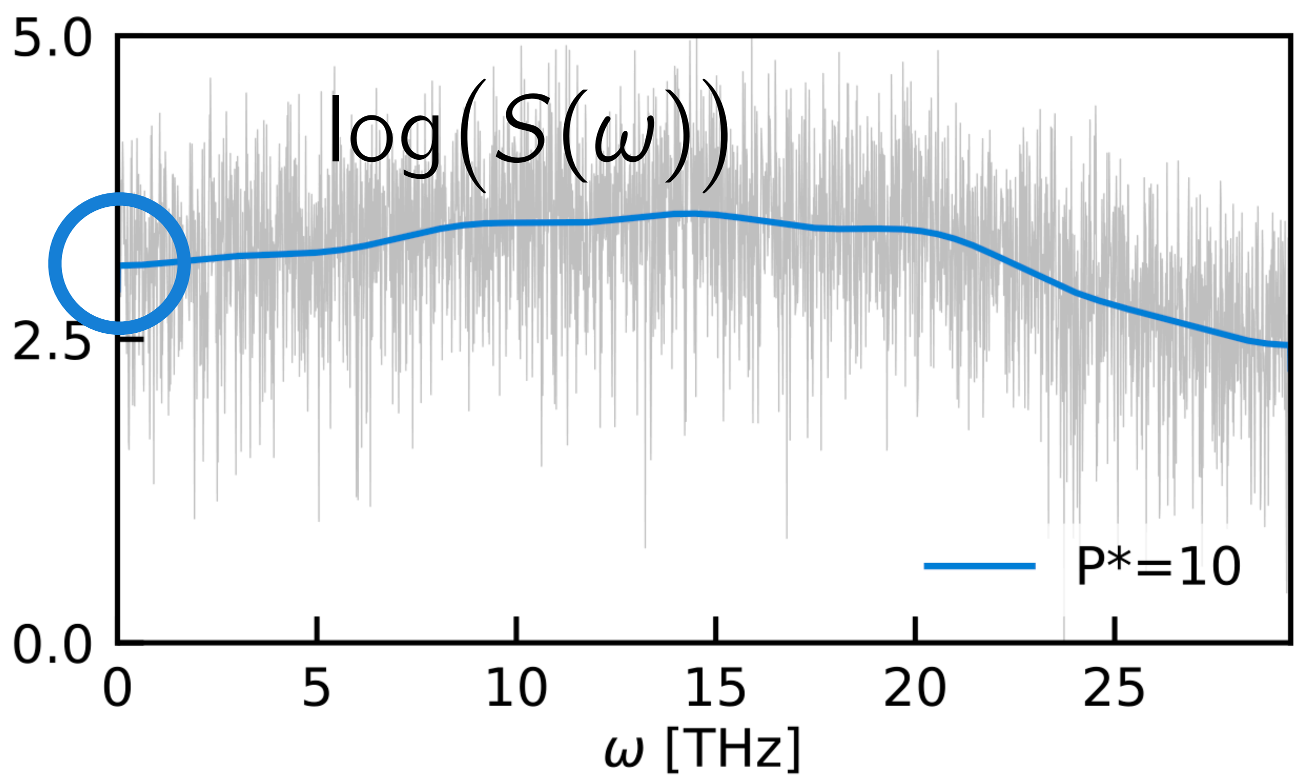


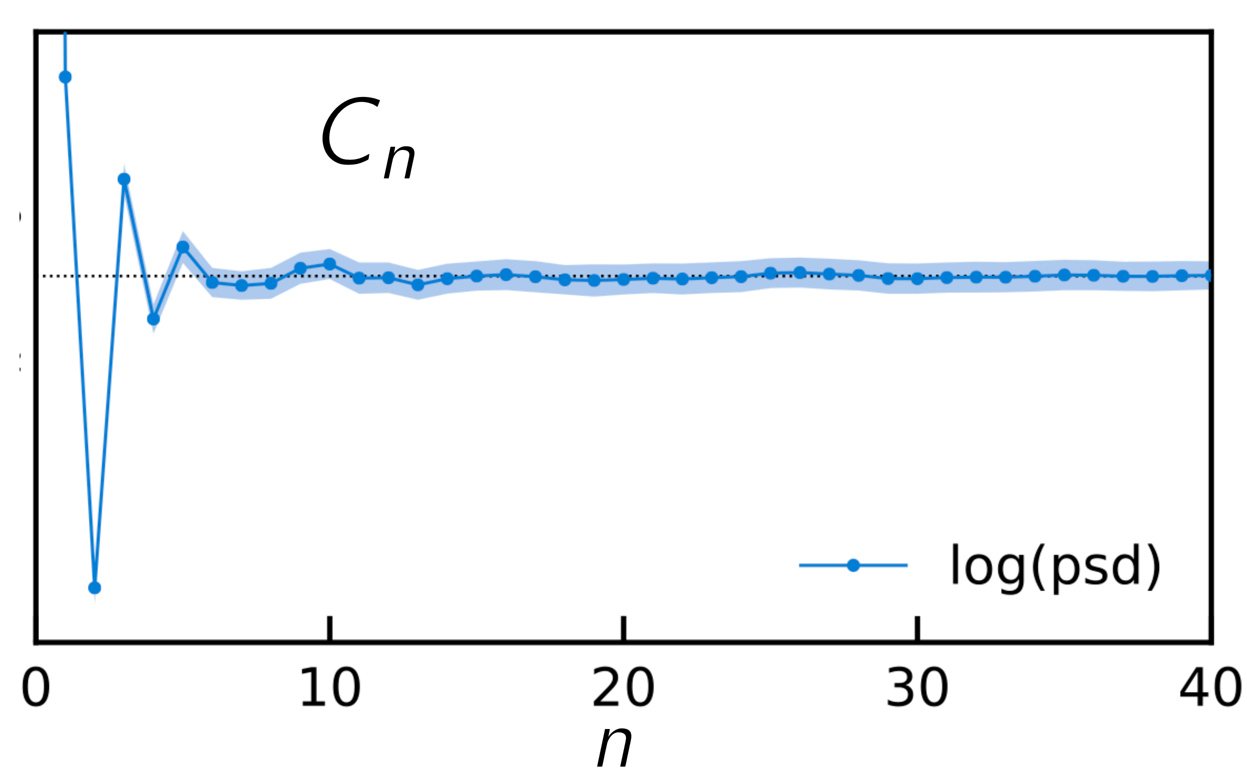
separating wheat from chaff

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

$$\frac{1}{N}\sum_{k=0}^{N-1}\log\left(\hat{S}(k)\right)e^{-i\frac{2\pi kn}{N}} = C_n + \text{white noise}$$

$$\log\left(S(\omega_k)\right) = \sum_{n=0}^{P^*-1} C_n e^{i\frac{2\pi kn}{N}} + \text{less noise}$$





separating wheat from chaff

$$\log\big(S(\omega_k)\big) = \sum_{n=0}^{P^*-1} C_n e^{i\frac{2\pi k n}{N}} + \text{less noise}$$

optimal number of coefficients, to be determined

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

constants independent of the time series being sampled

separating wheat from chaff

$$\log\left(S(\omega_k)\right) = \sum_{n=0}^{P^*-1} C_n e^{i\frac{2\pi k n}{N}} + \text{less noise}$$

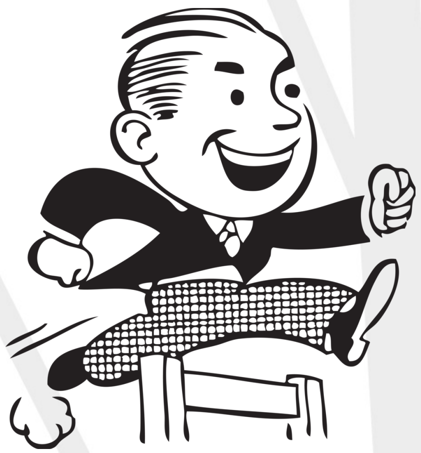
optimal number of coefficients, to be determined

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

constants independent of the time series being sampled

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

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).

thanks to:

Loris Ercole, SISSA

Aris Marcolongo, SISSA
now @EPFL

Federico Grasselli, SISSA

Riccardo Bertossa, SISSA

thanks to:

QUANTUMESPRESSO

QUANTUM ESPRESSO
FOUNDATION

MAX

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]*

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

CrossMark

Gauge Invariance of Thermal Transport Coefficients

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

SCIENTIFIC REPORTS

OPEN

Received: 14 August 2017
Accepted: 2 November 2017
Published online: 20 November 2017

Accurate thermal conductivities from optimally short molecular dynamics simulations

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

SCIENTIFIC REPORTS | 7: 15835 | DOI:10.1038/s41598-017-15843-2 1

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