ab initio Green-Kubo simulation of heat transport in liquids and glasses

a challenge for theoretical physics, data analysis, and information technology

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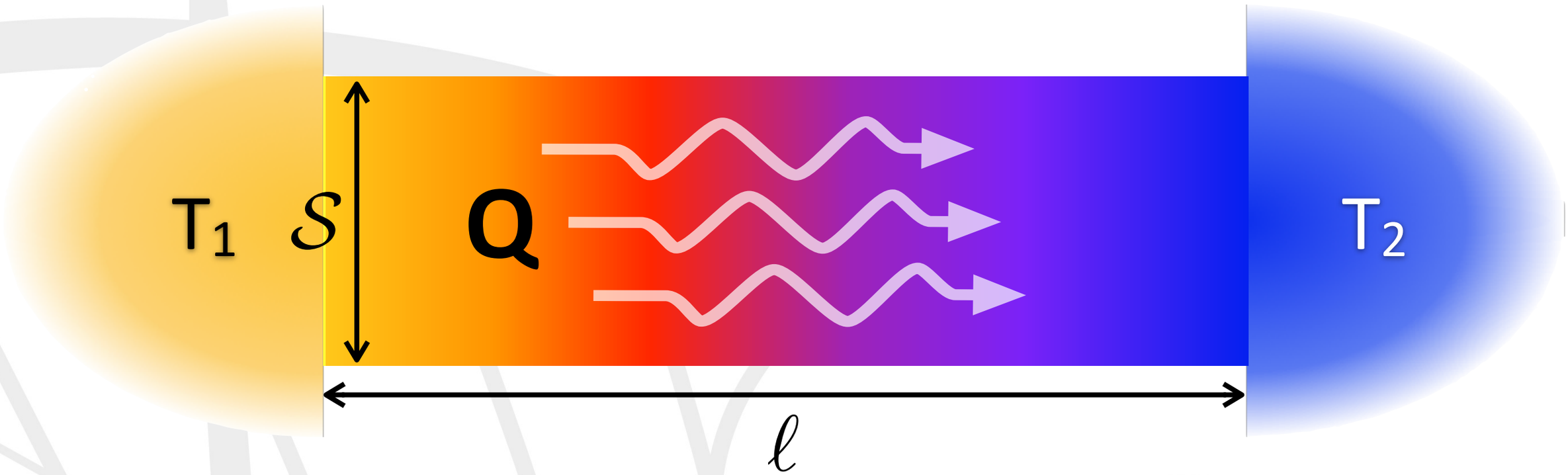
talk given at the MaX Conference on *Materials Design Ecosystem at the Exascale*
the Abdus Salam International Centre for Theoretical Physics, Trieste January 29-31, 2018

what heat transport is all about



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

heat flows from the warm to the cool

as time flows from the past to the future

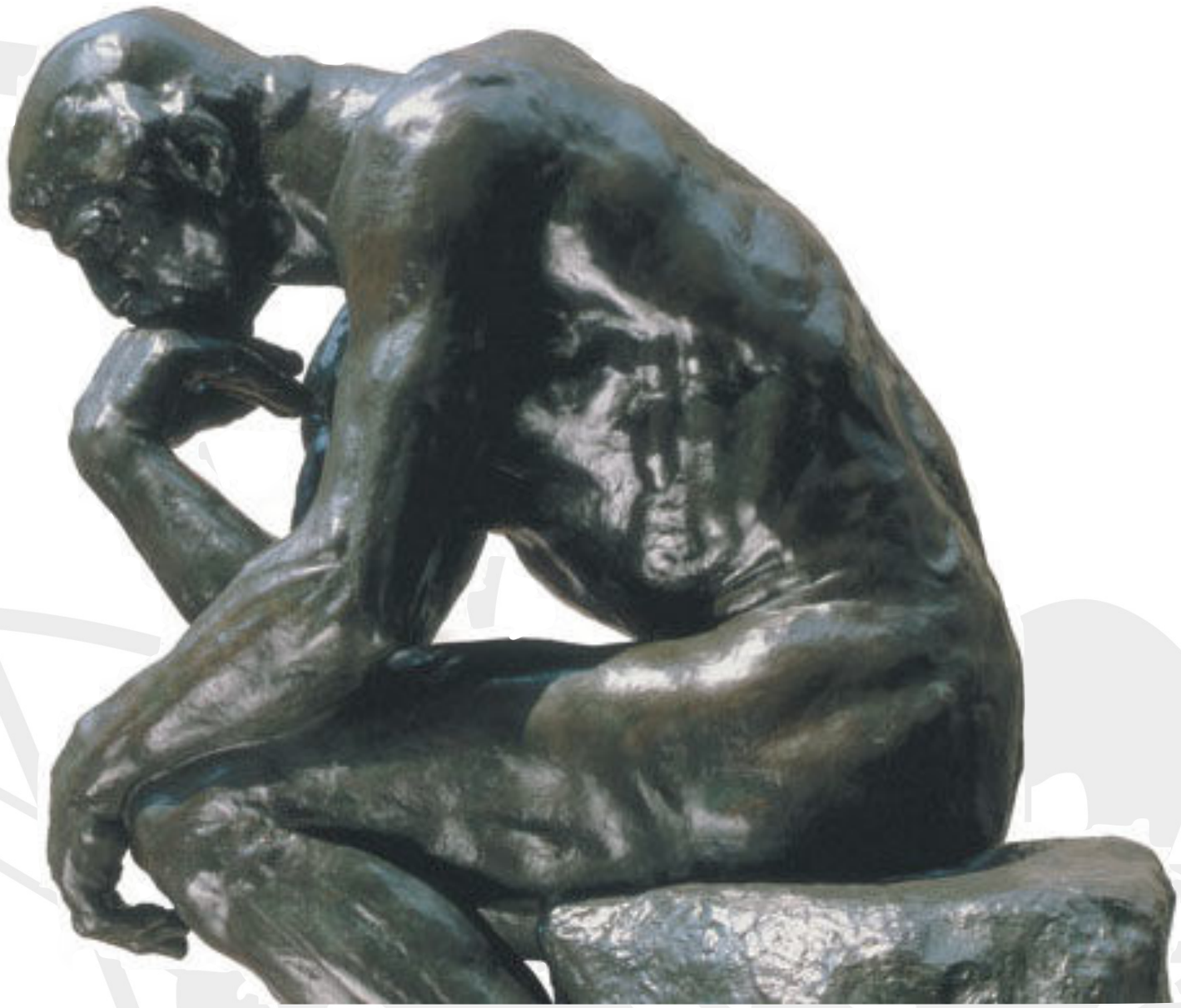
$$\mathbf{j}_Q(\mathbf{r},t) = -\kappa\nabla T(\mathbf{r},t)$$

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

why should we care?

- 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

Green-Kubo theory

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

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

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

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

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

Green-Kubo theory

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

the classical MD ansatz

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

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

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

hurdles towards an ab initio Green-Kubo theory

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

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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.

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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

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

$$= \text{cnst}$$

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

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

insights from classical mechanics

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

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

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

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

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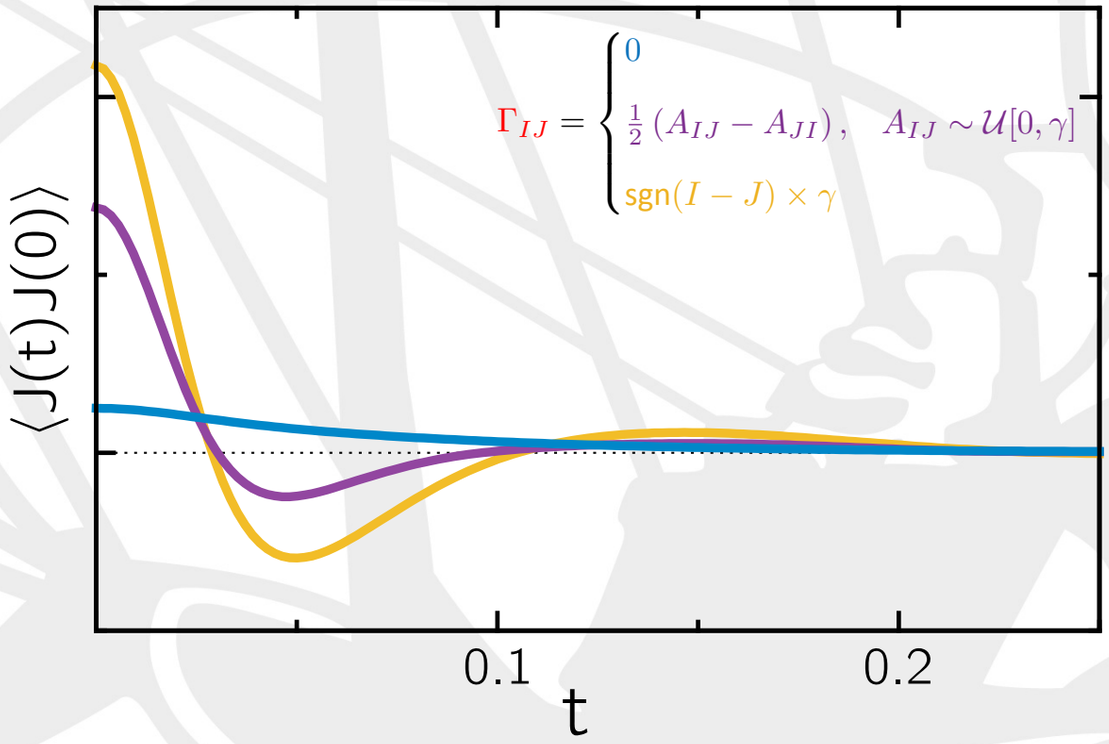
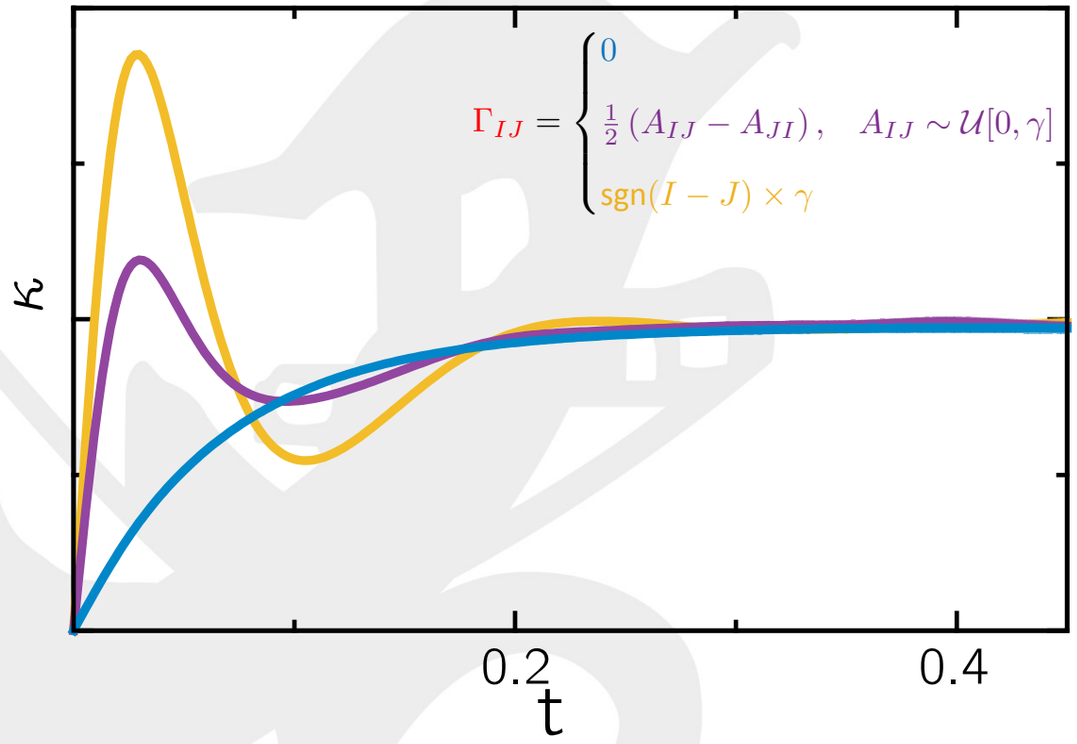




insights from classical mechanics

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

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

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

insights from classical mechanics

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

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

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

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

$$+ \cancel{\langle \mathbf{P}(\infty) \cdot \mathbf{J}(0) \rangle} - \cancel{\langle \mathbf{P}(0) \cdot \mathbf{J}(0) \rangle}$$

$$+ \cancel{\langle \mathbf{P}(0) \cdot \mathbf{J}(0) \rangle} - \cancel{\langle \mathbf{P}(-\infty) \cdot \mathbf{J}(0) \rangle}$$

$$+ \cancel{\langle \mathbf{P}(\infty) \cdot \dot{\mathbf{P}}(0) \rangle} - \cancel{\langle \mathbf{P}(0) \cdot \dot{\mathbf{P}}(0) \rangle}$$

insights from classical mechanics

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

$$\kappa' = \kappa$$

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

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

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

the DFT energy density

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

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

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

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

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

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

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

the DFT energy current

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

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

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

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

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

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

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

the DFT energy current

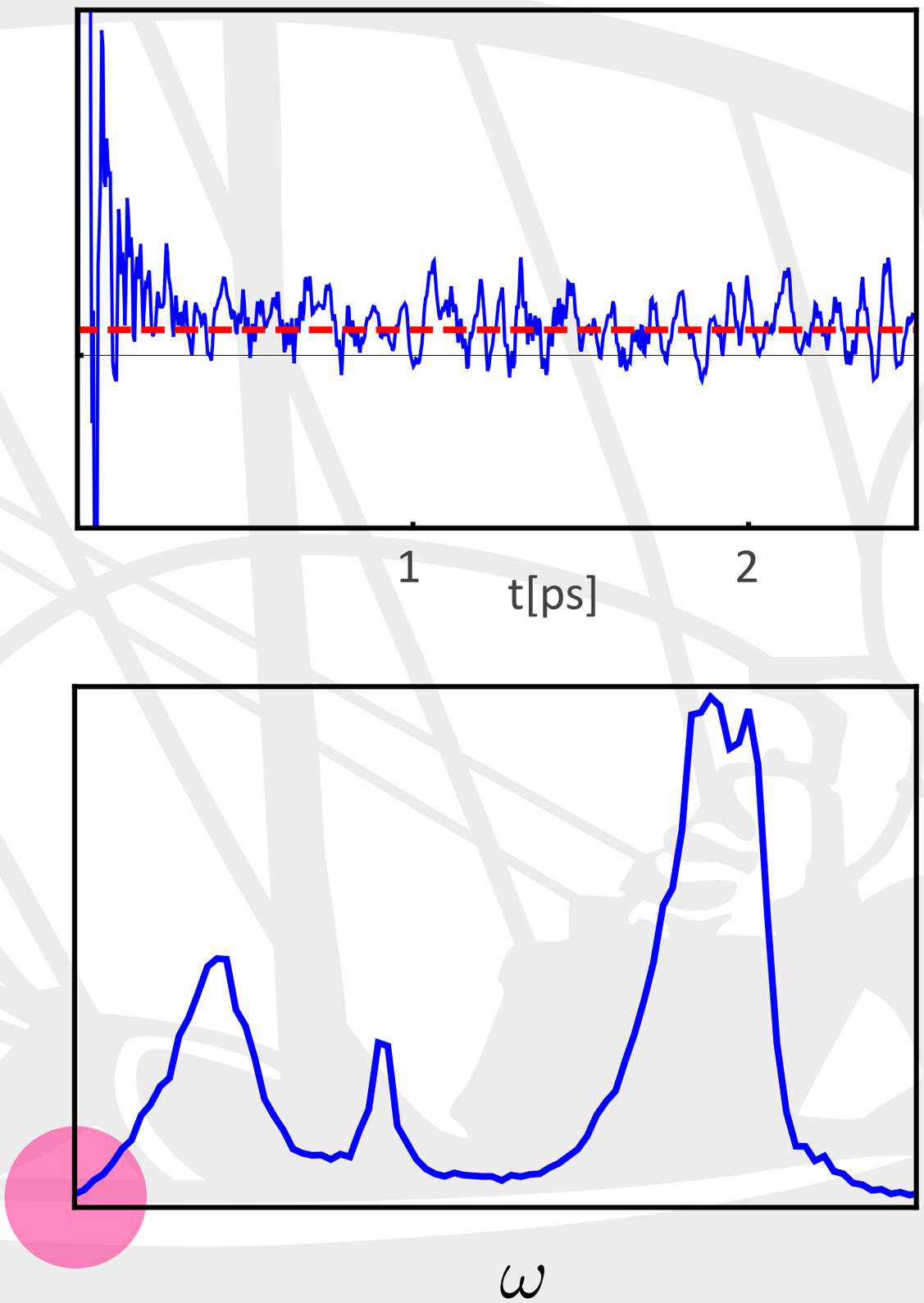
$$\mathbf{J}_{DFT} = \int \mathbf{r}\dot{e}_{DFT}(\mathbf{r},t)d\mathbf{r}$$

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

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

- $|\dot{\varphi}_v\rangle$ 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

liquid (heavy) water

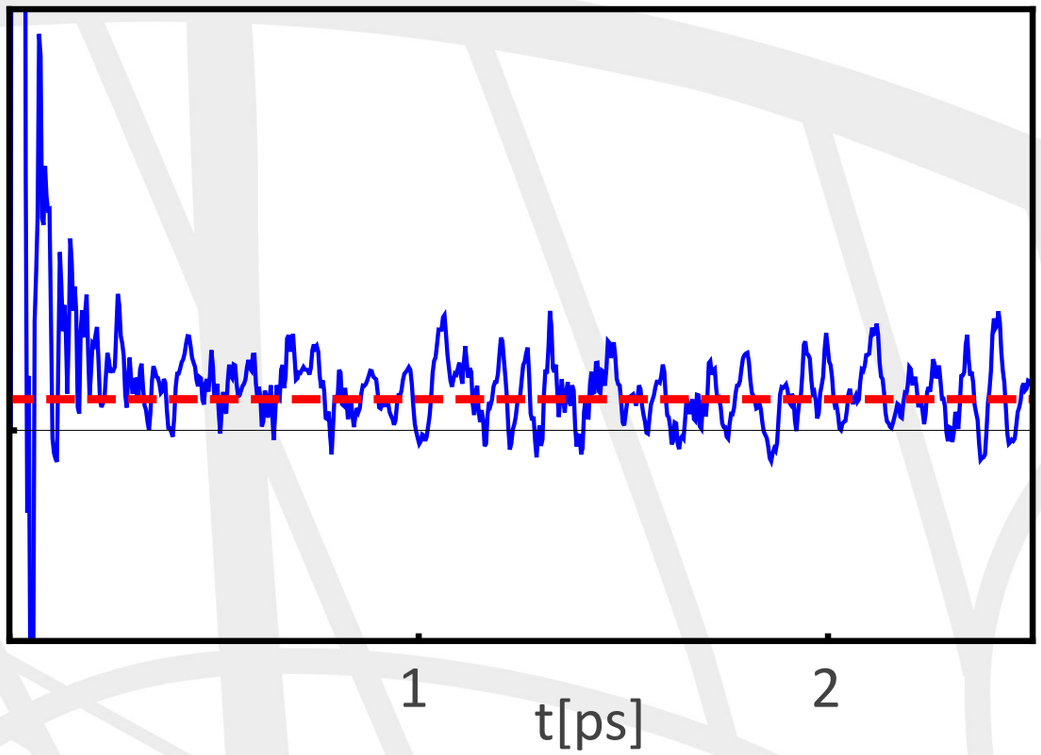


64 molecules, T=385 K
expt density @ac

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

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

liquid (heavy) water



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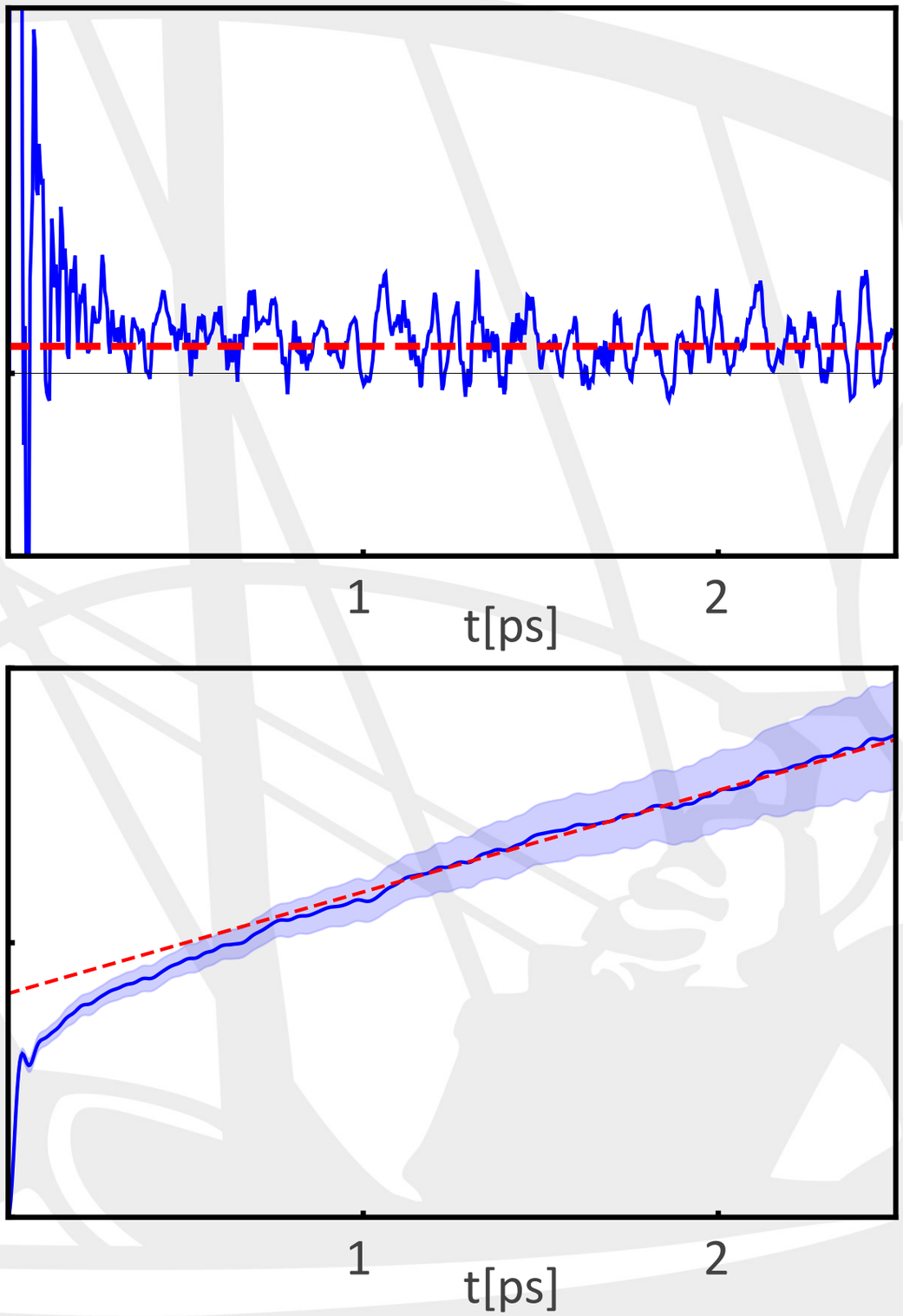
$$\frac{1}{3Vk_BT^2}\int_0^{\mathrm{t}}\langle \mathbf{J}(\mathrm{t}')\cdot\mathbf{J}(0)\rangle d\mathrm{t}'$$

Einstein's relation

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

liquid (heavy) water



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

$\kappa_{\mathrm{DFT}} = 0.74 \pm 0.12$ 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

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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

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

$$\kappa \propto S(\omega = 0) \qquad S(\omega) = \int_{-\infty}^{\infty} C(t)\mathrm{e}^{-i\omega t}dt$$

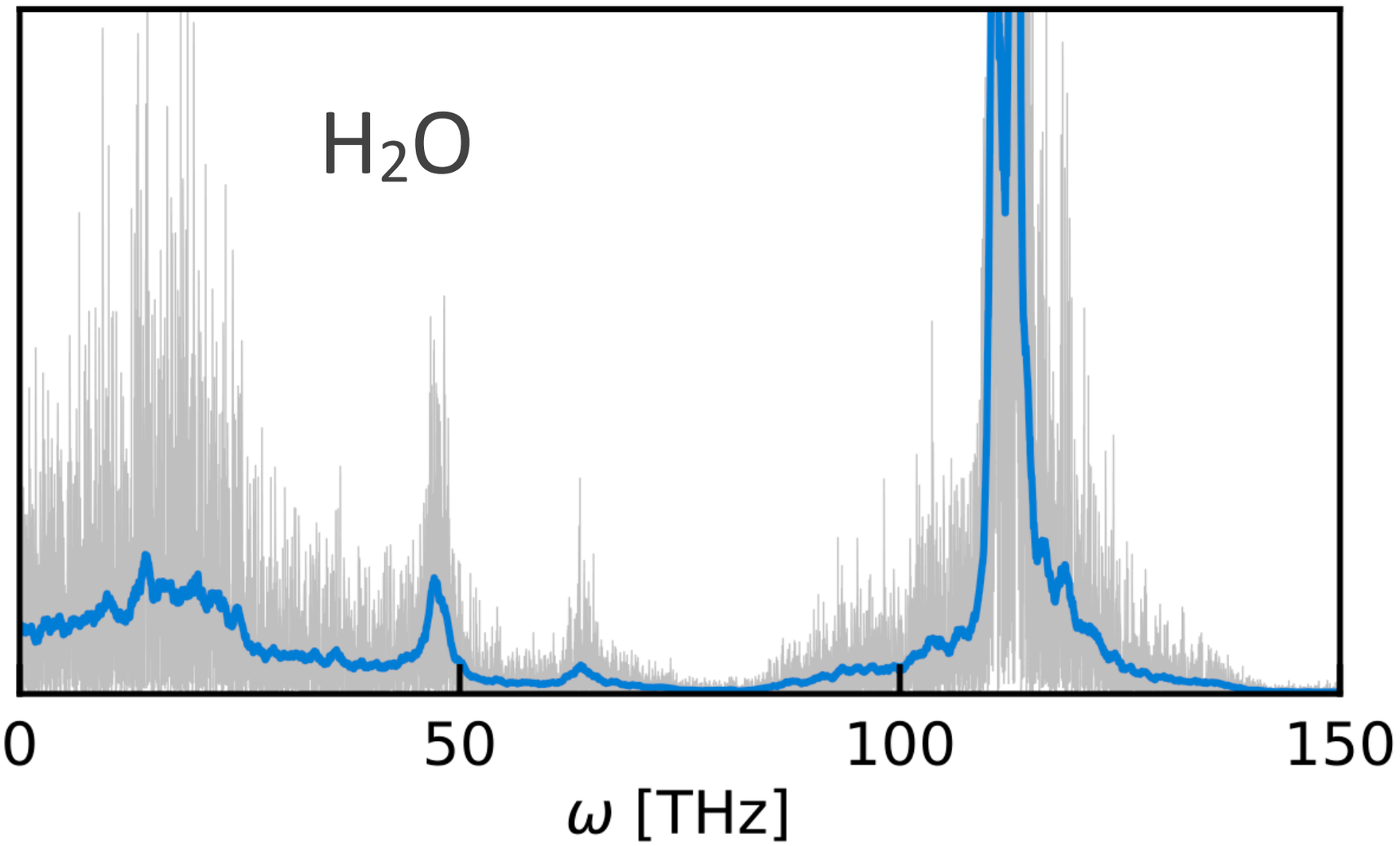
the Wiener-Kintchine theorem

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

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

separating wheat from chaff

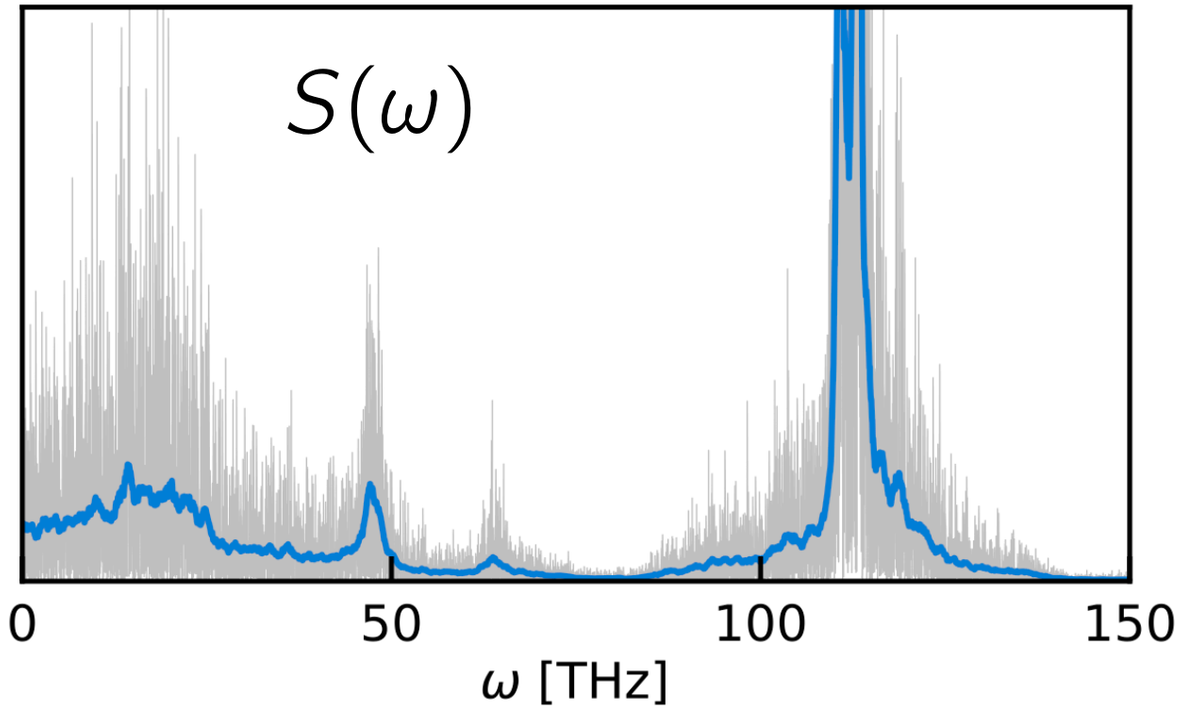
$$\hat{S}(k) = \frac{\epsilon}{N} \left| \tilde{J}(k) \right|^2$$
$$= \frac{1}{2} S(\omega_k) \times \chi_2^2$$

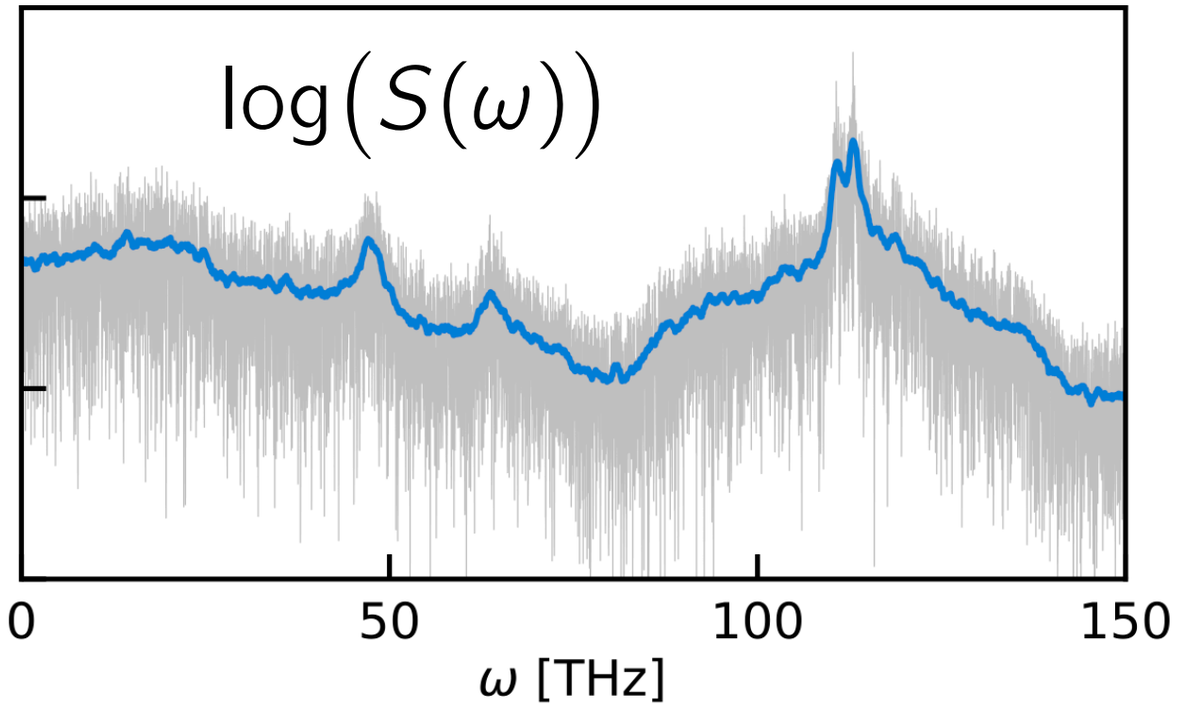


separating wheat from chaff

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

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





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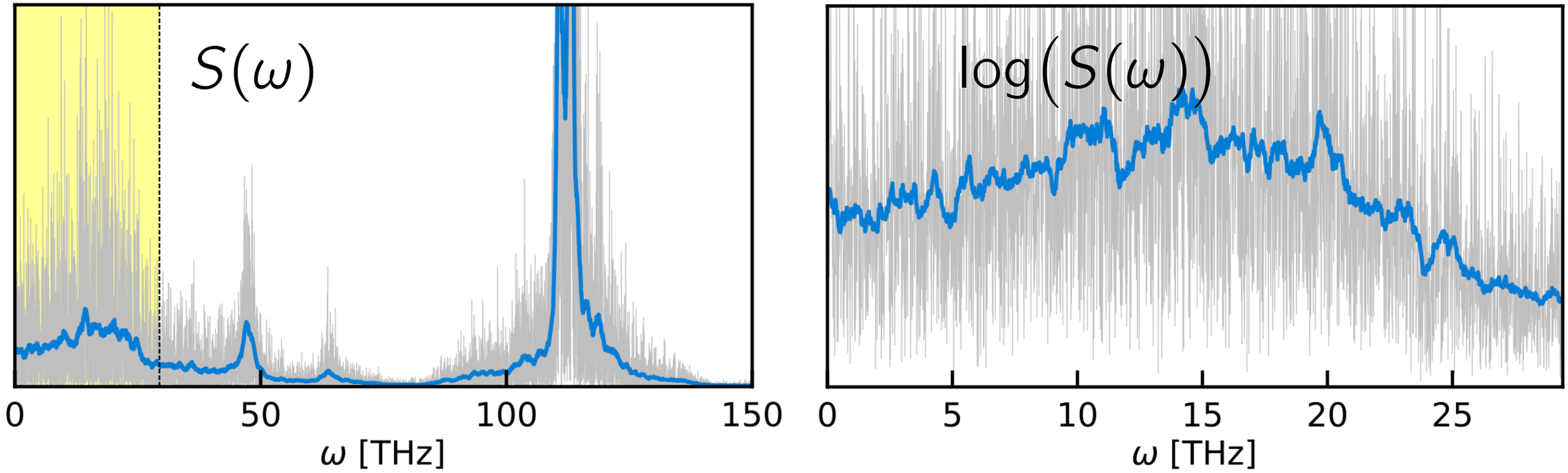

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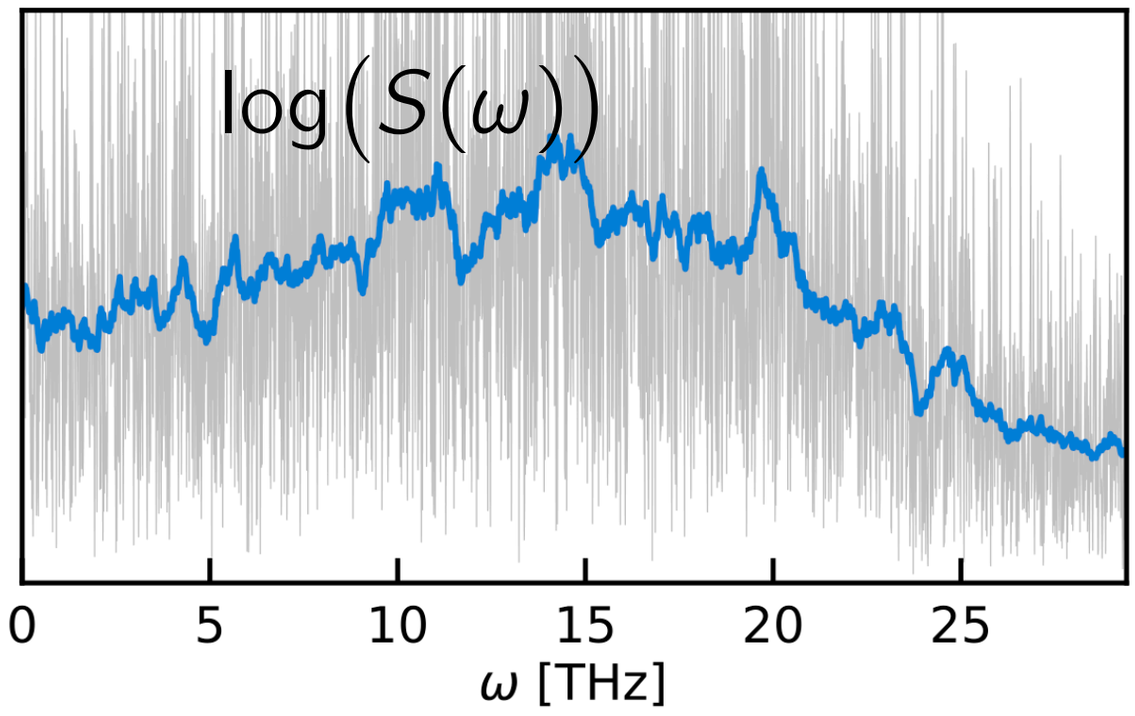
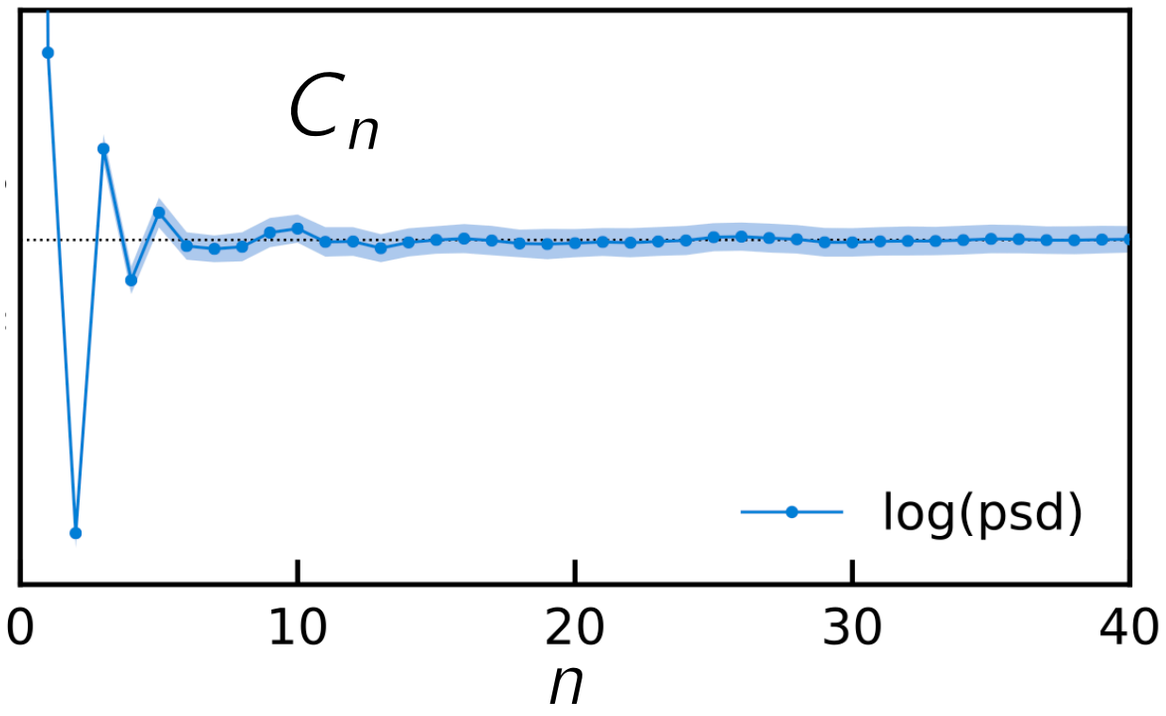
$$\log\big(\hat{S}(k)\big) = \log\big(S(\omega_k)\big) + \log\big(\hat{\xi}_k\big)$$

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





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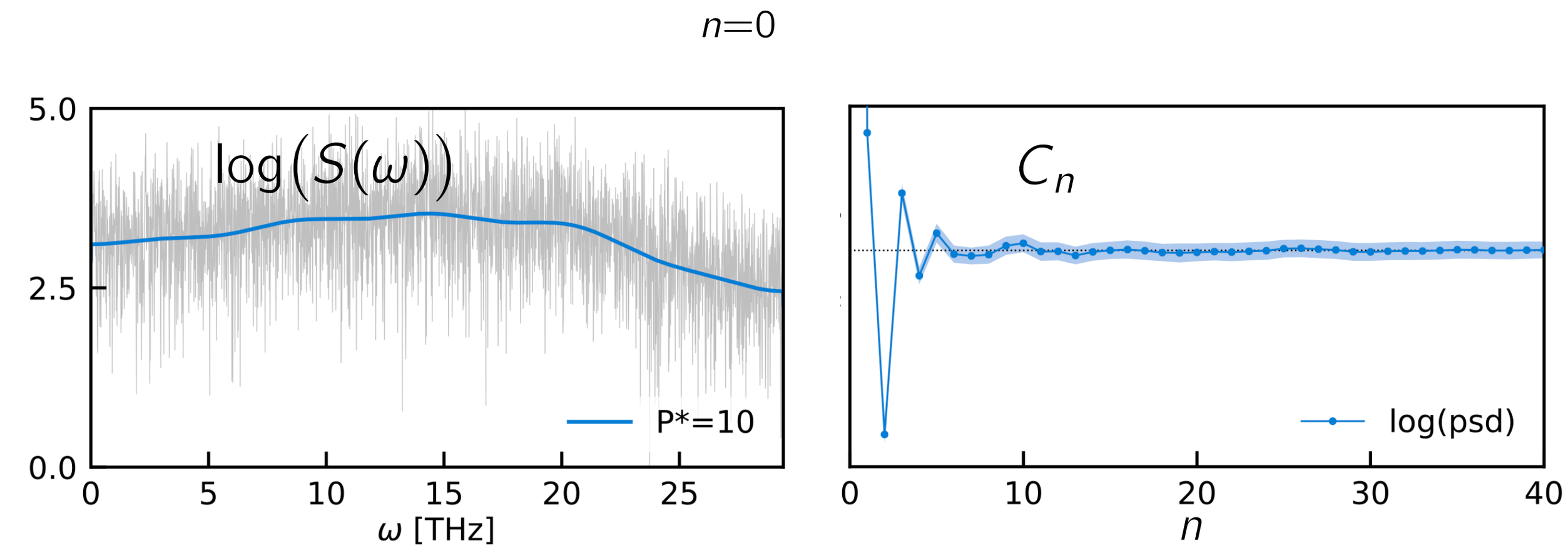
$$\log\big(S(\omega_k)\big) = \sum^{P^*-1} C_n \mathrm{e}^{i\frac{2\pi kn}{N}} + \text{less noise}$$



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

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

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a heavy workflow

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

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

$$= \sum_v \langle \bar{\varphi}_v | (\hat{H}_{KS} + \varepsilon_v) | \dot{\varphi}_v \rangle$$

$$(\hat{H}_{KS} - \varepsilon_v) \bar{\varphi}_v = \hat{P}_c [\hat{H}_{KS}, \mathbf{r}] \varphi_v$$

density-functional perturbation theory

a heavy workflow

density-functional perturbation theory

$$(\hat{H}_{KS} - \varepsilon_v)\bar{\varphi}_v = \hat{P}_c[\hat{H}_{KS}, \mathbf{r}]\varphi_v$$

estimator evaluation (almost) as heavy as configuration sampling

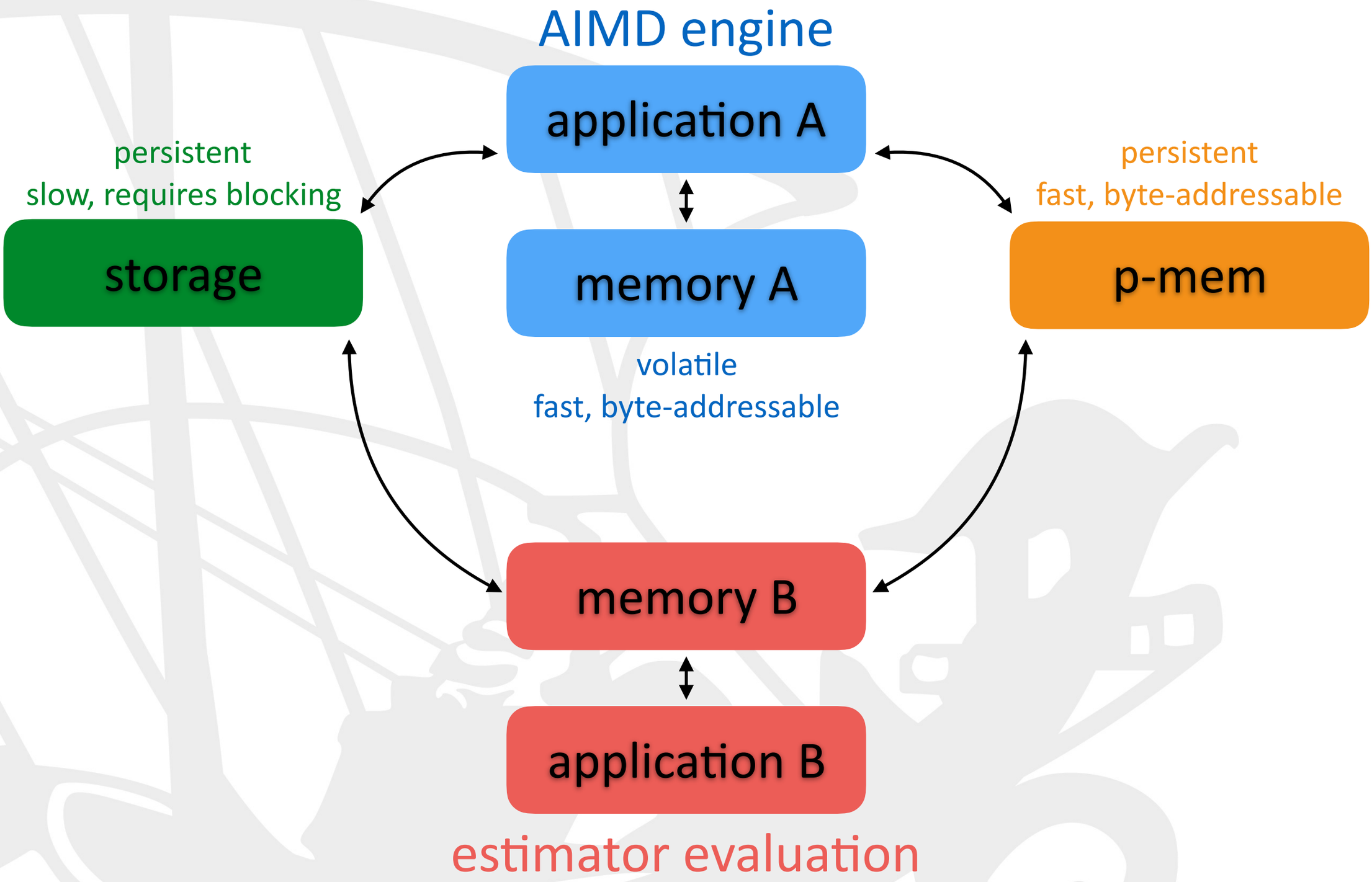
two approaches:

- evaluate estimators in post-processing mode **expensive**
- integrate estimator evaluation in ab initio MD codes **unwieldy**

third way:

- share big data amongst executable through *persistent memory*

persistent memory



summary

- heat currents are intrinsically ill-defined at the atomic scale;
- a *gauge invariance* principle exists, making heat transport coefficients independent of such and indeterminacy and computable within Green-Kubo AIMD;
- the statistical theory of time series can be leveraged to estimate and significantly improve the accuracy of the transport coefficients computed from MD;
- when stretched to extreme-scale simulations, the resulting computational workflow sets considerable challenges to IT; persistent memory may be an asset to win the challenge.

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ARTICLES

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Microscopic theory and quantum simulation of atomic heat transport

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

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DOI 10.1007/s10909-016-1617-6

Gauge Invariance of Thermal Transport Coefficients

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

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Accurate thermal conductivities from optimally short molecular dynamics simulations

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

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