thermal transport from first principles

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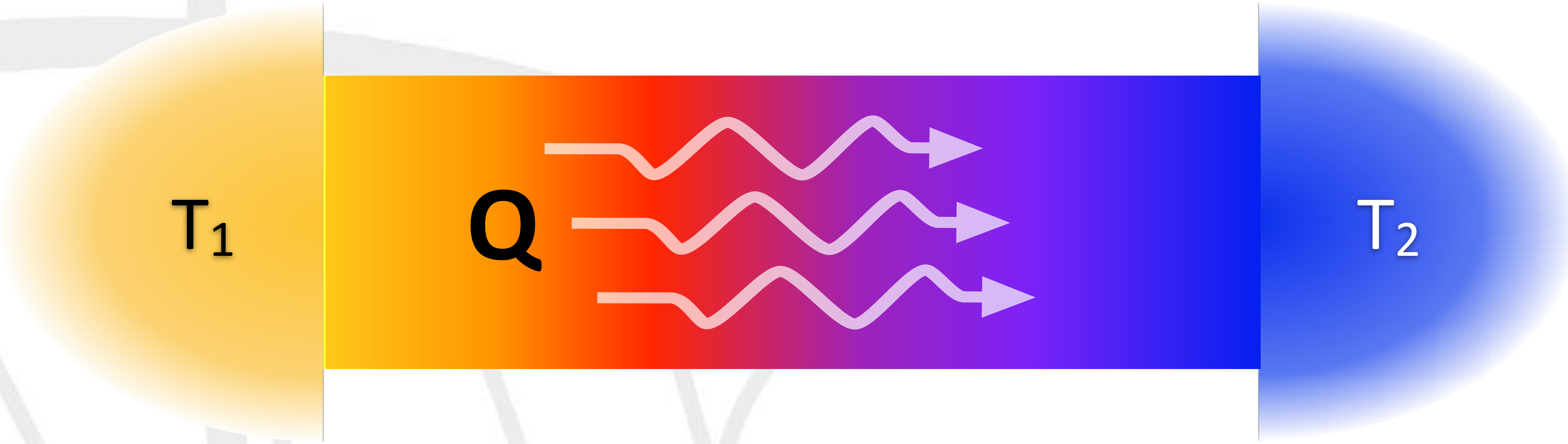
lectures given at the *ICTP Caribbean School on Materials for Clean Energy*, Cartagena de Indias, May 30 — June 5, 2019

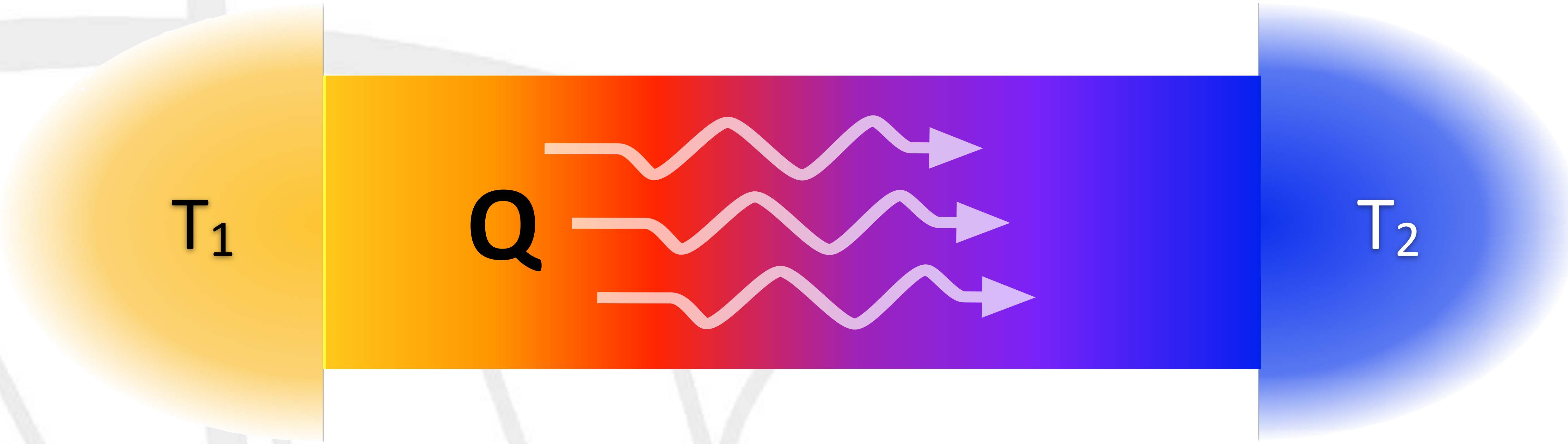
syllabus

- What thermal transport is all about;
- Conserved quantities: continuity and constitutive equations;
- Onsager relations: thermal and electric conductivities, thermoelectric coefficients;
- The Green-Kubo & Einstein-Helfand formulas for transport coefficients;
- The classical energy current;
- Gauge invariance of transport coefficients;
- Density-functional theory of adiabatic heat transport;
- Separating wheat from chaff: the Wiener-Khintchine theorem and cepstral analysis
- Heat conductivity from lattice dynamics: crystals and glasses;
- Lattice dynamics from density-functional perturbation theory (if time allows).

what heat transport is all about

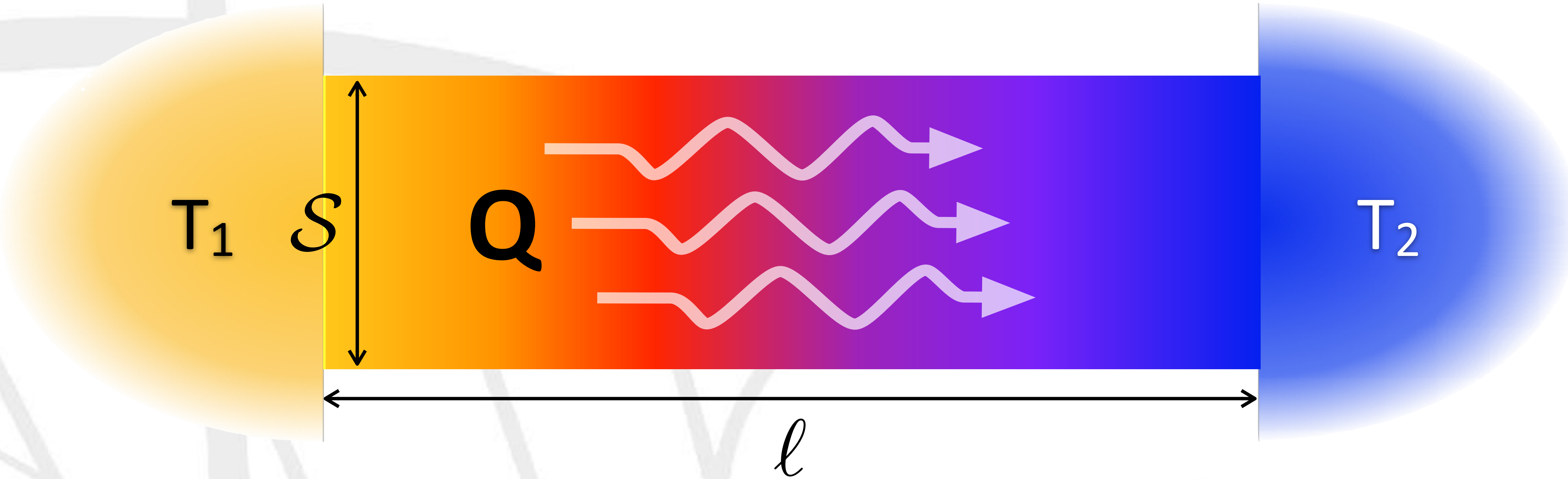


what heat transport is all about



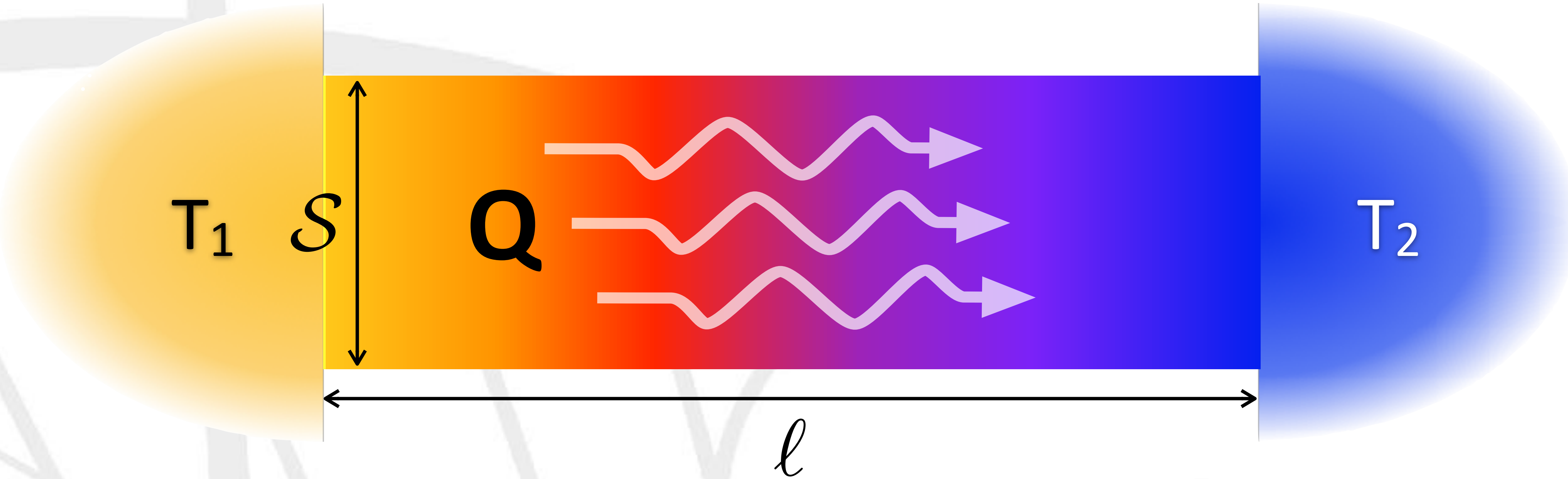
heat flows from the warm to the cool
as time flows from the past to the future

what heat transport is all about



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

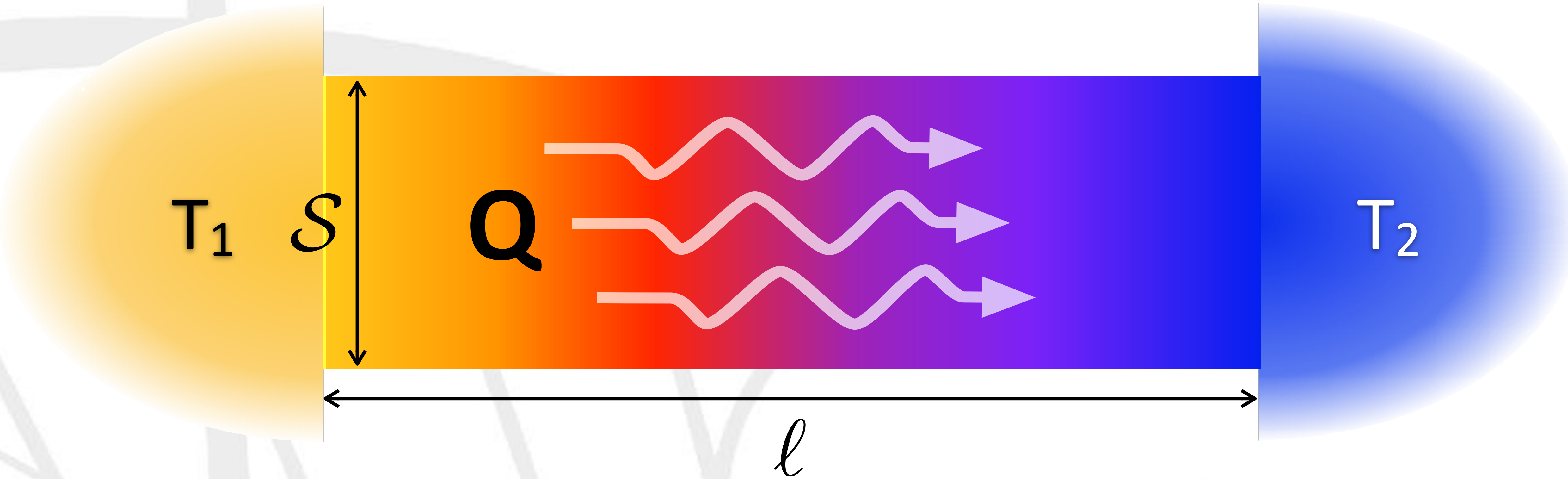
what heat transport is all about



$$\frac{1}{\mathcal{S}}\frac{\mathrm{d}Q}{\mathrm{d}t} = -\kappa\frac{(T_2 - T_1)}{\ell}$$

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

what heat transport is all about



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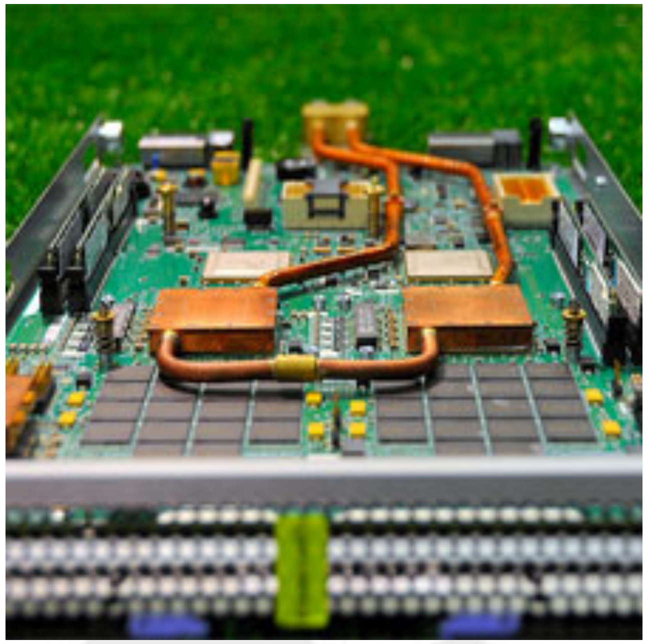
$$\mathbf{j}_Q(\mathbf{r}, t) = -\kappa\nabla T(\mathbf{r}, t)$$

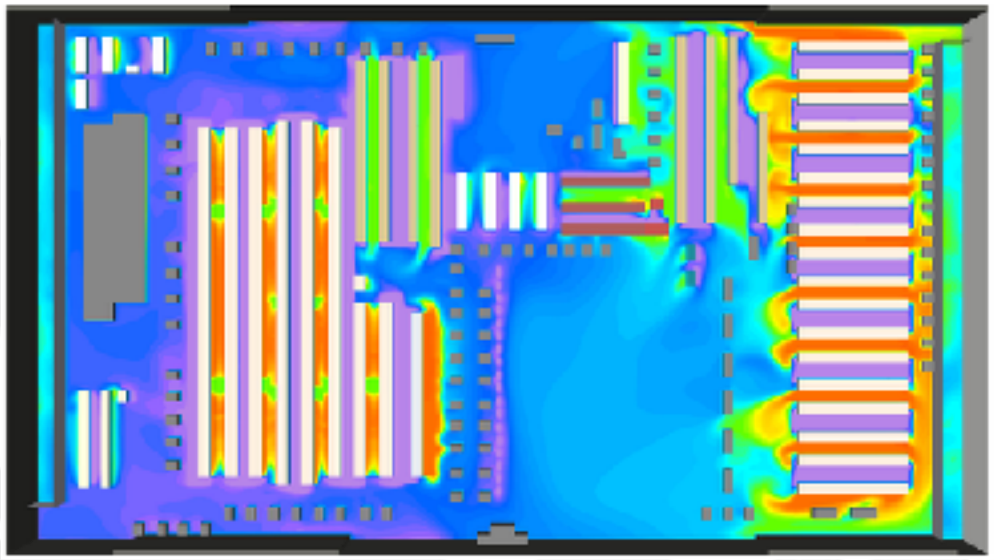
$$\frac{\partial T}{\partial t} = \frac{\kappa}{\rho c_p}\Delta T$$

why should we care?

energy saving

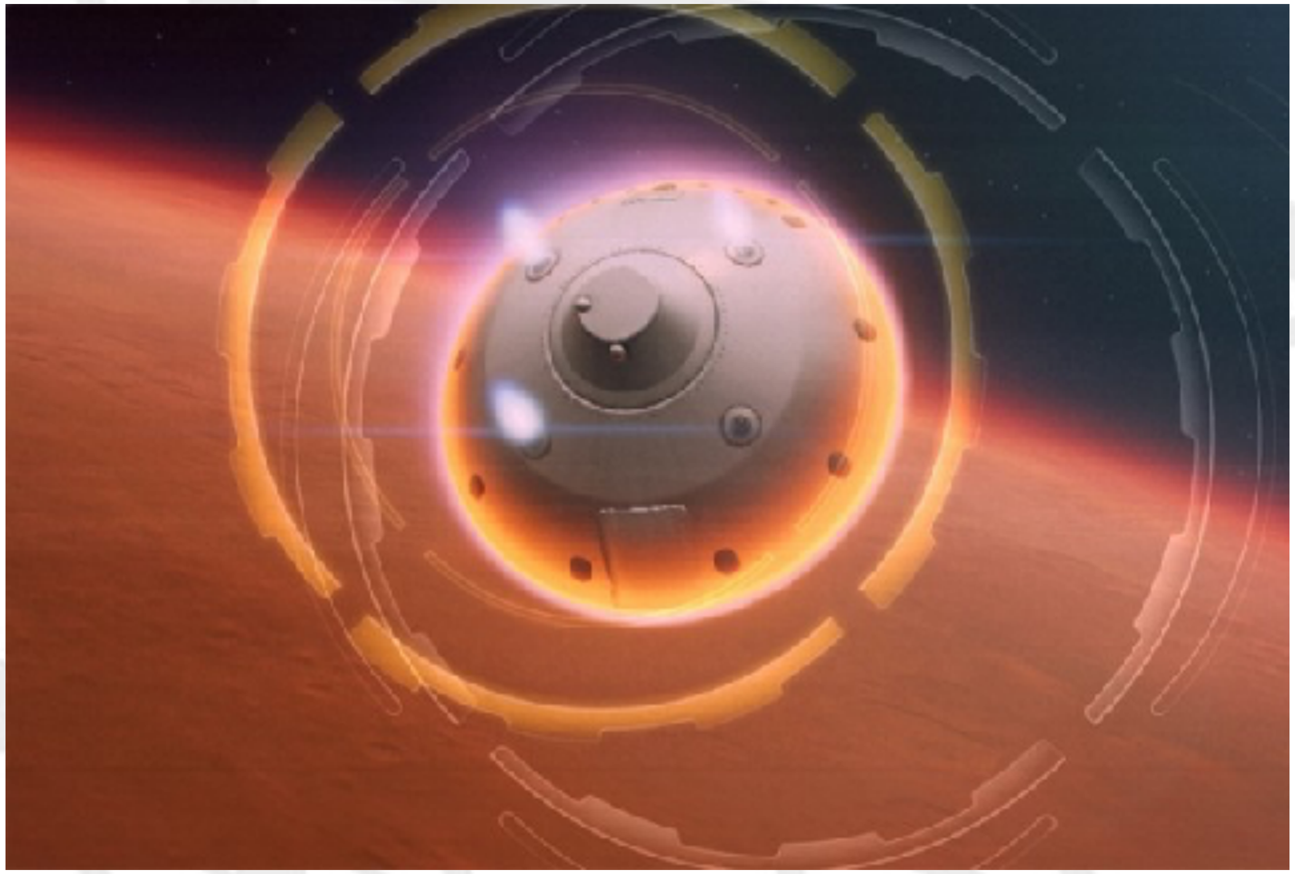
heat dissipation

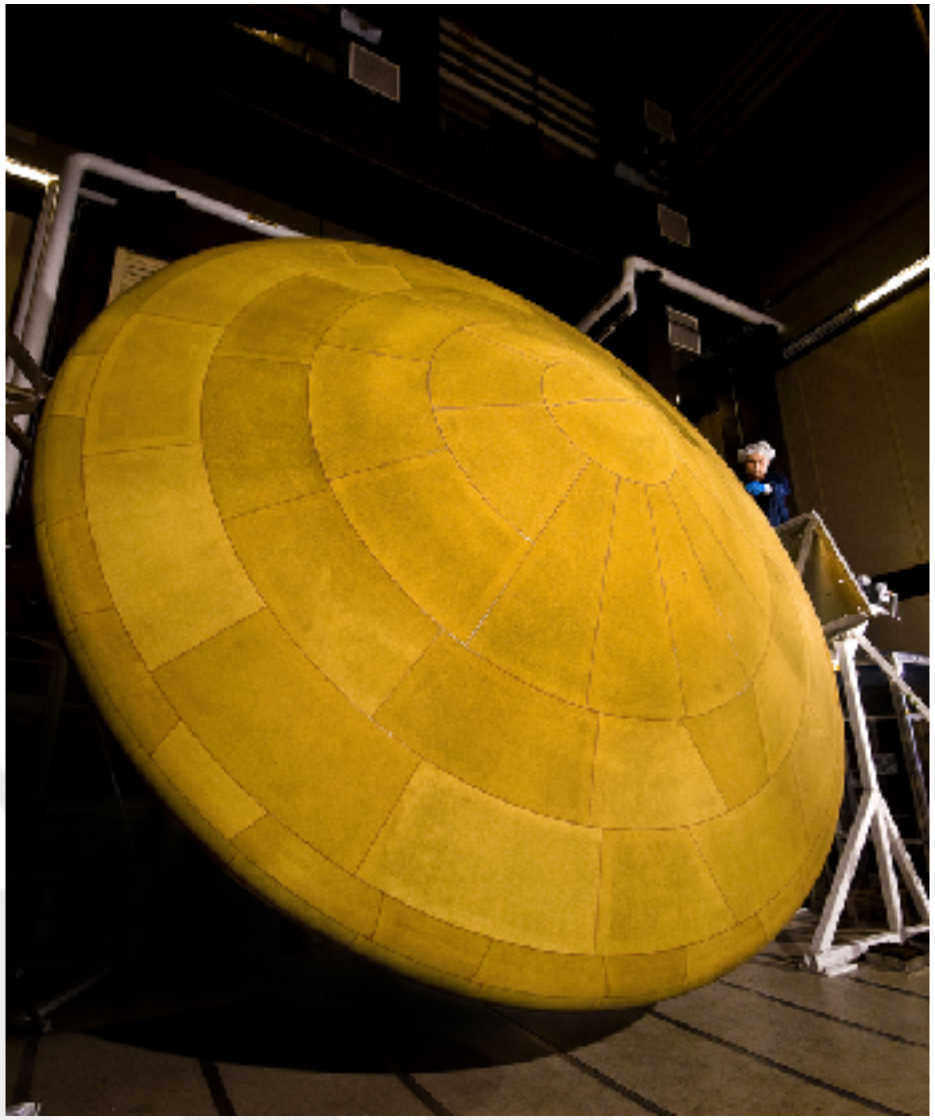




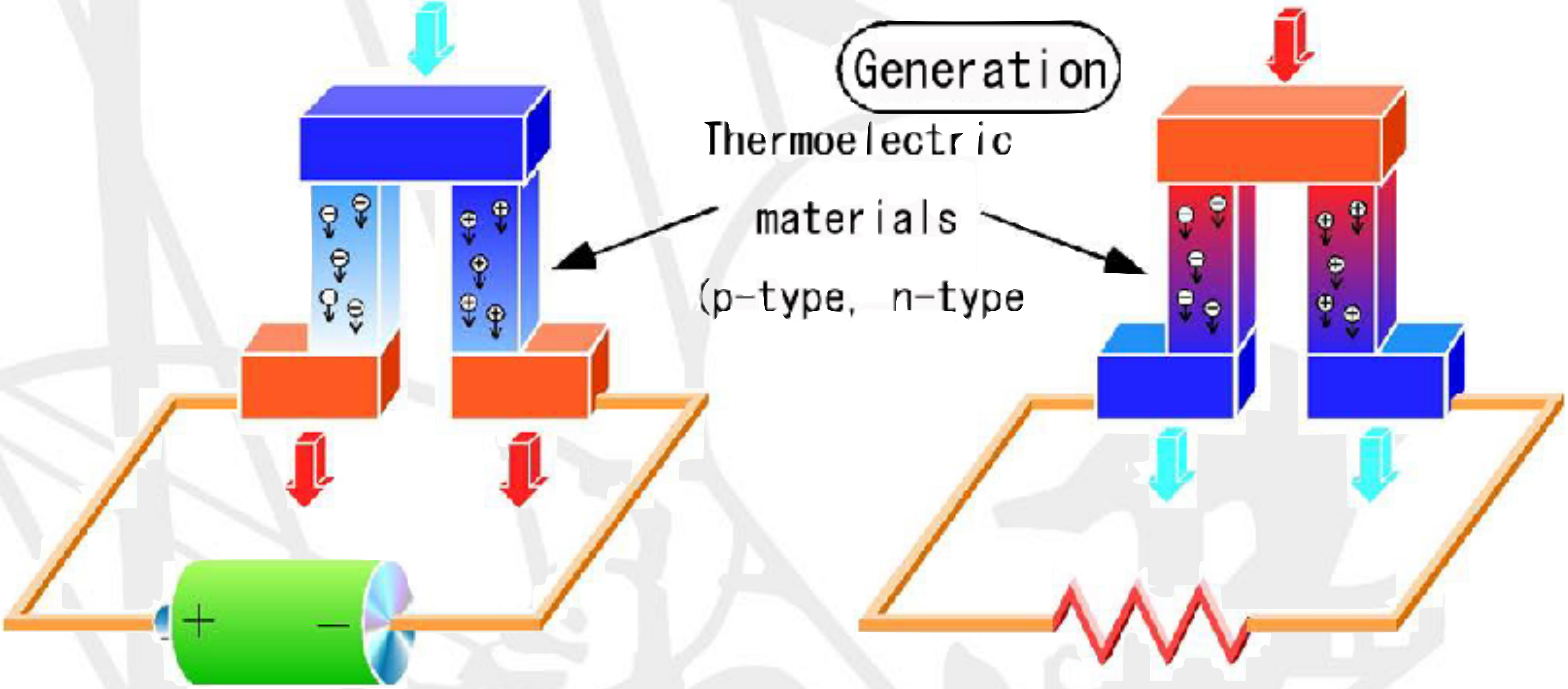
heat shielding

heat shielding

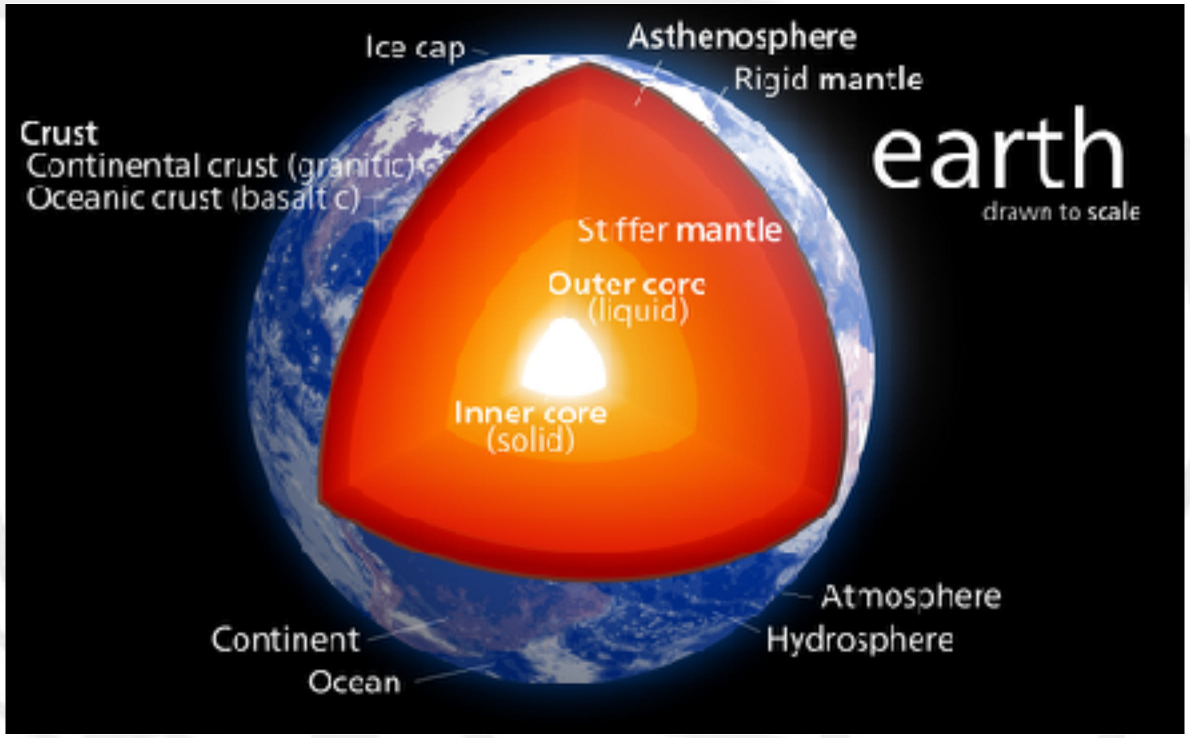


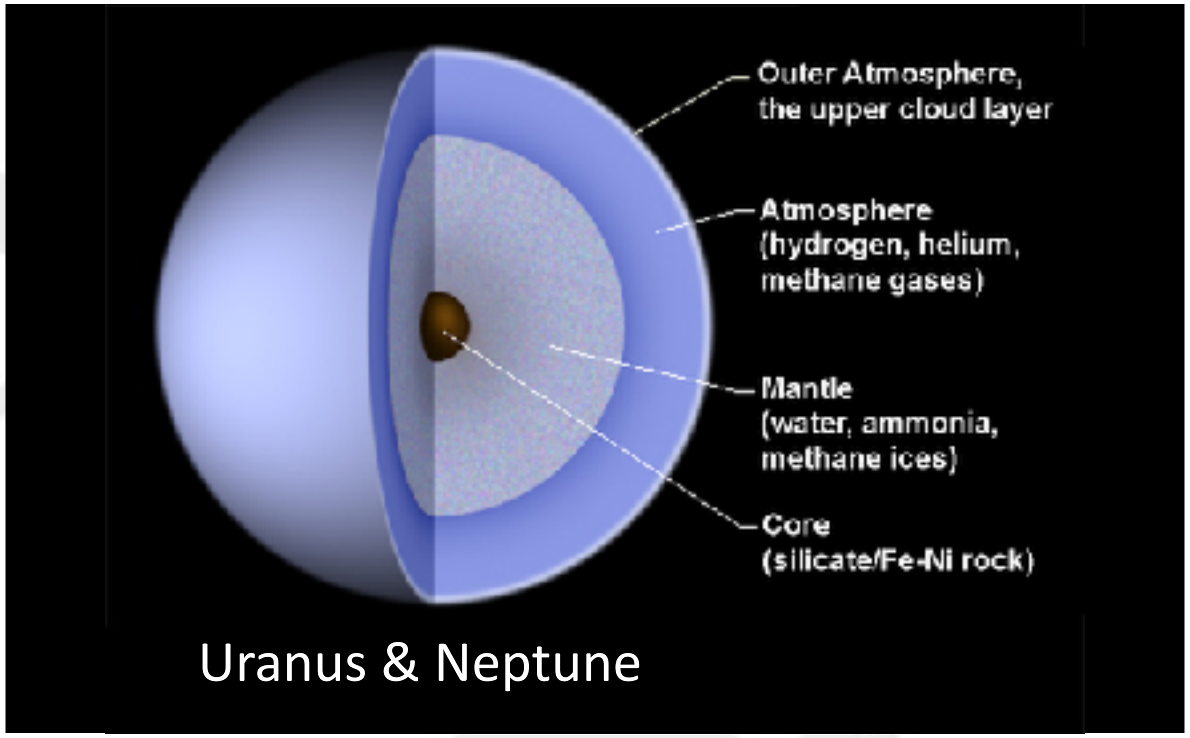


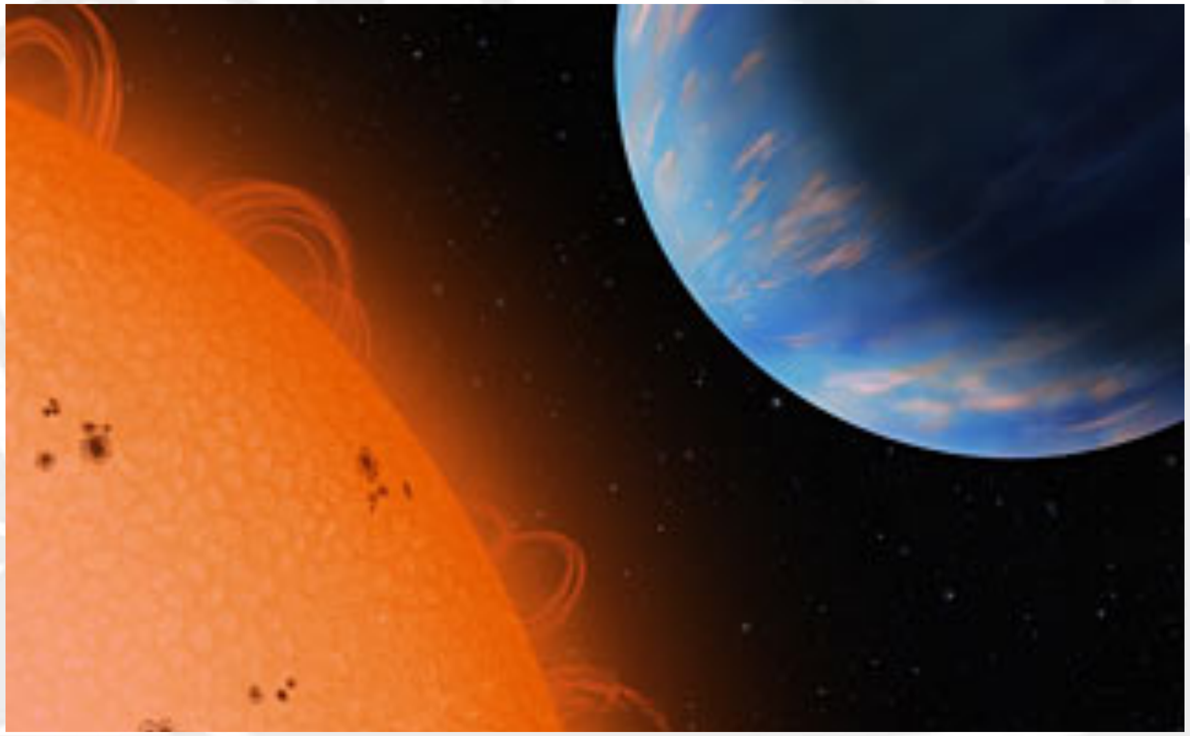
energy conversion

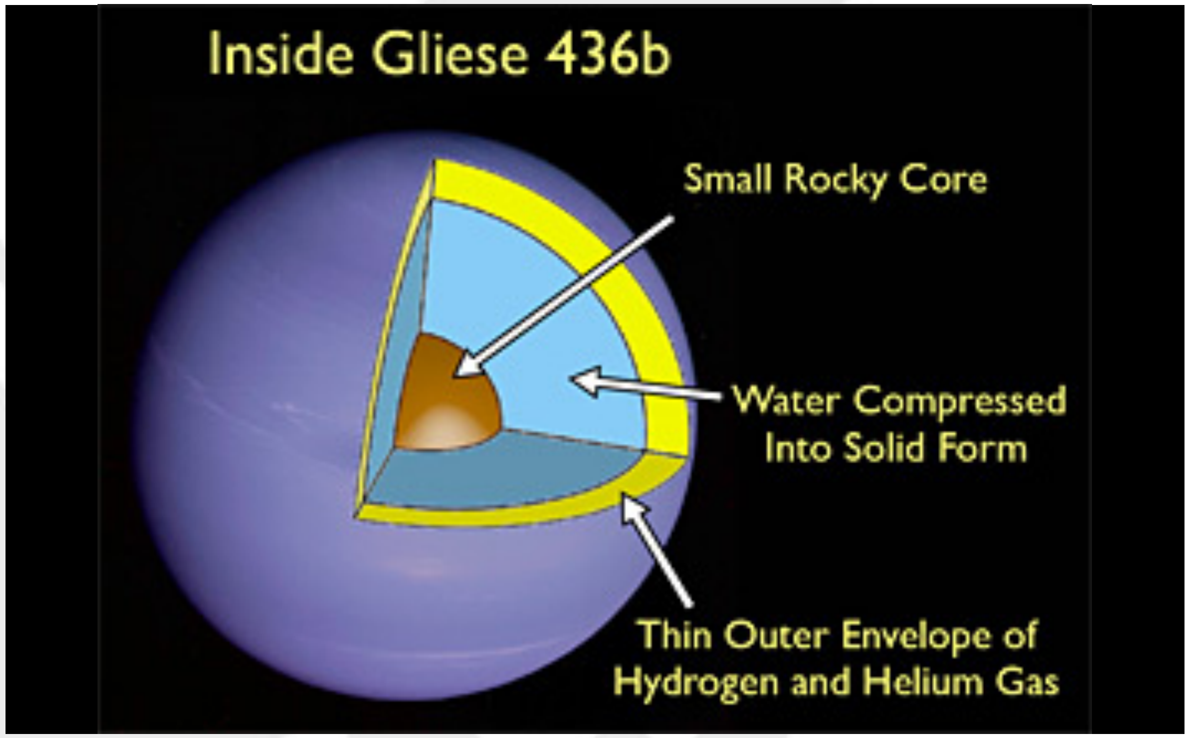


planetary sciences









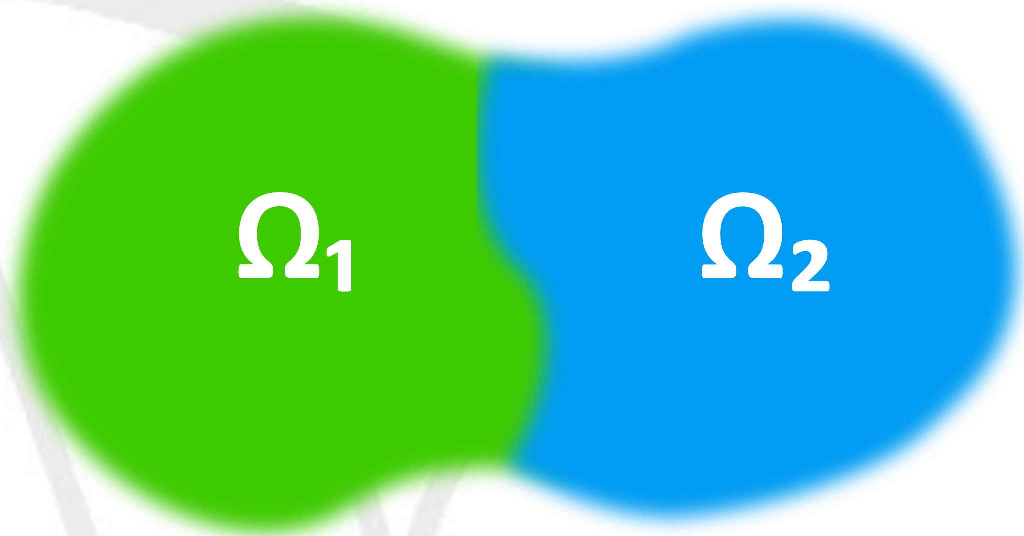
why should we care?

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

why should we care?

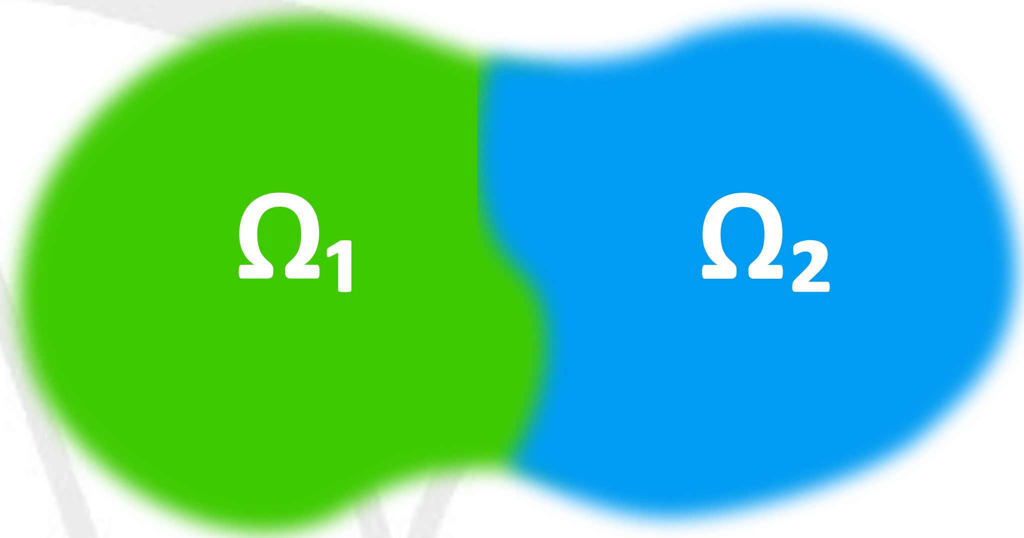
- … because it is important and still poorly understood

extensive properties



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

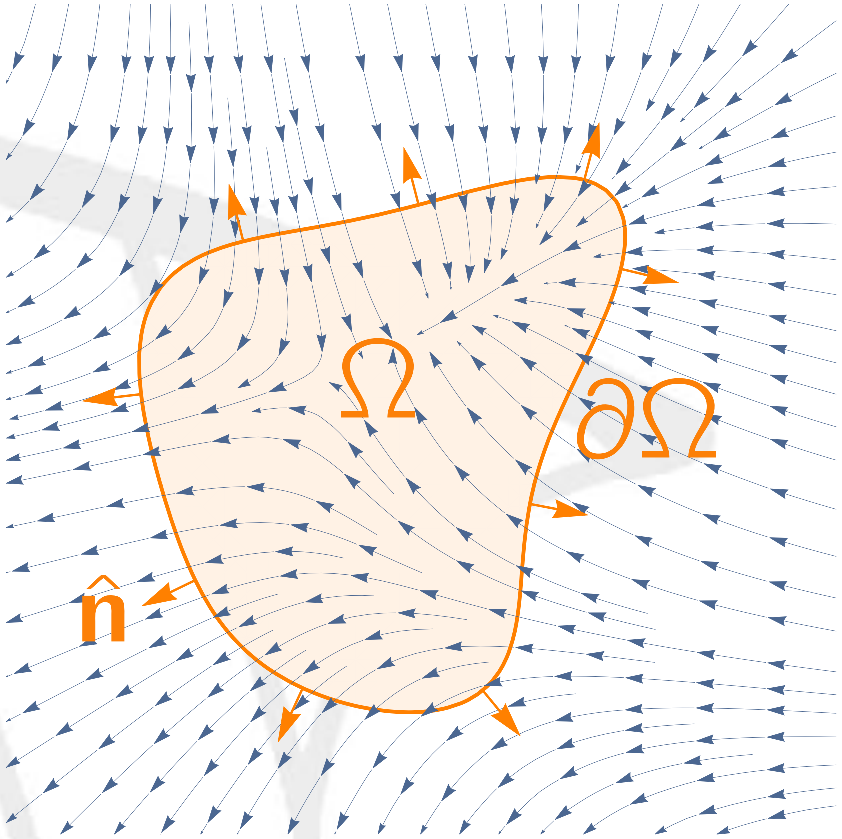
extensive properties



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

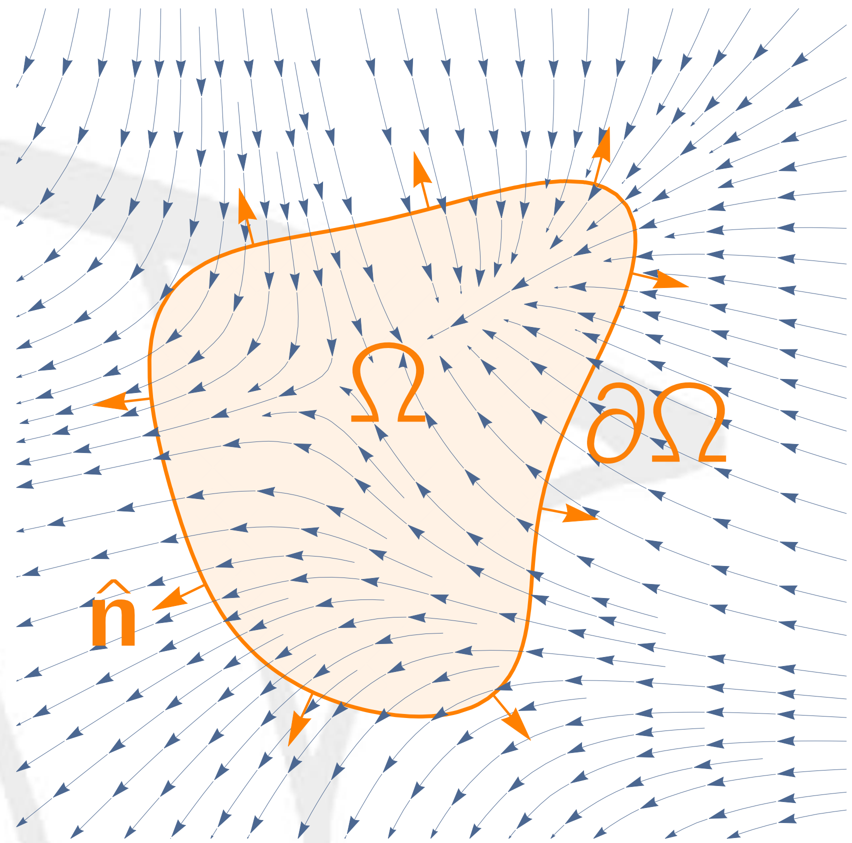
$$E[\Omega] = \int_\Omega \epsilon(\mathbf{r})\, d\mathbf{r}$$

conservation laws



$$\frac{dE(\Omega,t)}{dt} = -\oint_{\partial\Omega} \mathbf{j}(\mathbf{r},t)\cdot\hat{\mathbf{n}}\,dS + \int_{\Omega} \sigma(\mathbf{r},t)\,d\Omega$$

conservation laws



$$\frac{dE(\Omega,t)}{dt} = -\oint_{\partial\Omega} \mathbf{j}(\mathbf{r},t)\cdot\hat{\mathbf{n}}\,dS + \cancel{\int_{\Omega} \sigma(\mathbf{r},t)d\Omega}$$

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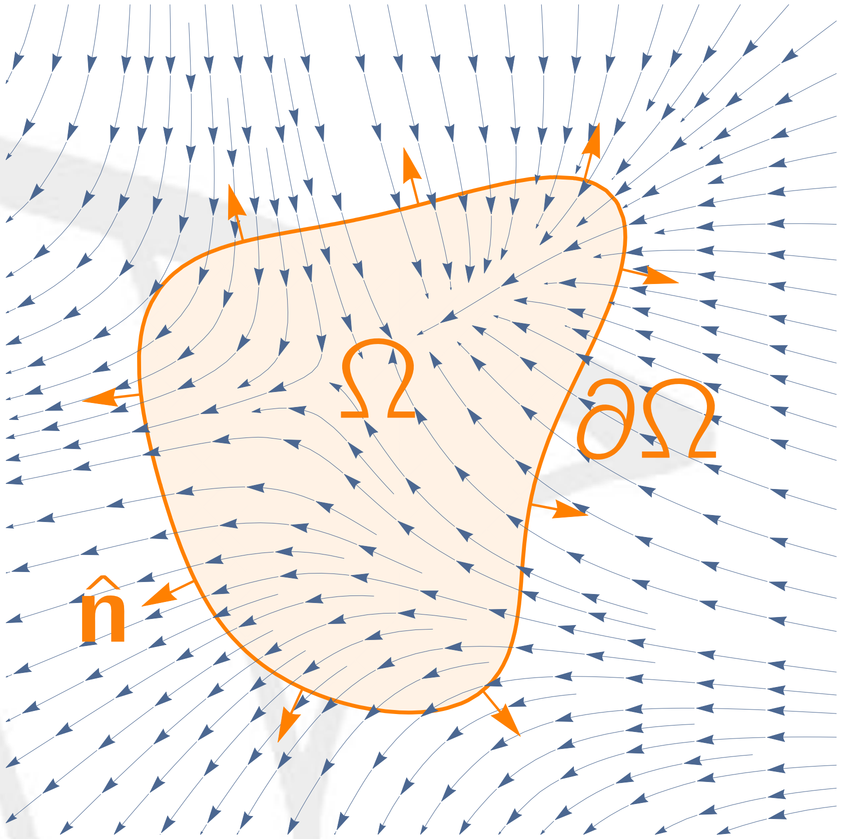

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$$\int_{\Omega} \dot{\epsilon}(\mathbf{r},t)d\Omega = -\int_{\Omega} \nabla\cdot\mathbf{j}(\mathbf{r},t)d\Omega$$

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

continuity equation

adiabatic decoupling of conserved densities

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

$$\dot{\tilde{\epsilon}}(\mathbf{k}, t) = \mathbf{k} \cdot \tilde{\mathbf{j}}(\mathbf{k}, t)$$

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the smaller the wavevector, the slower the dynamics

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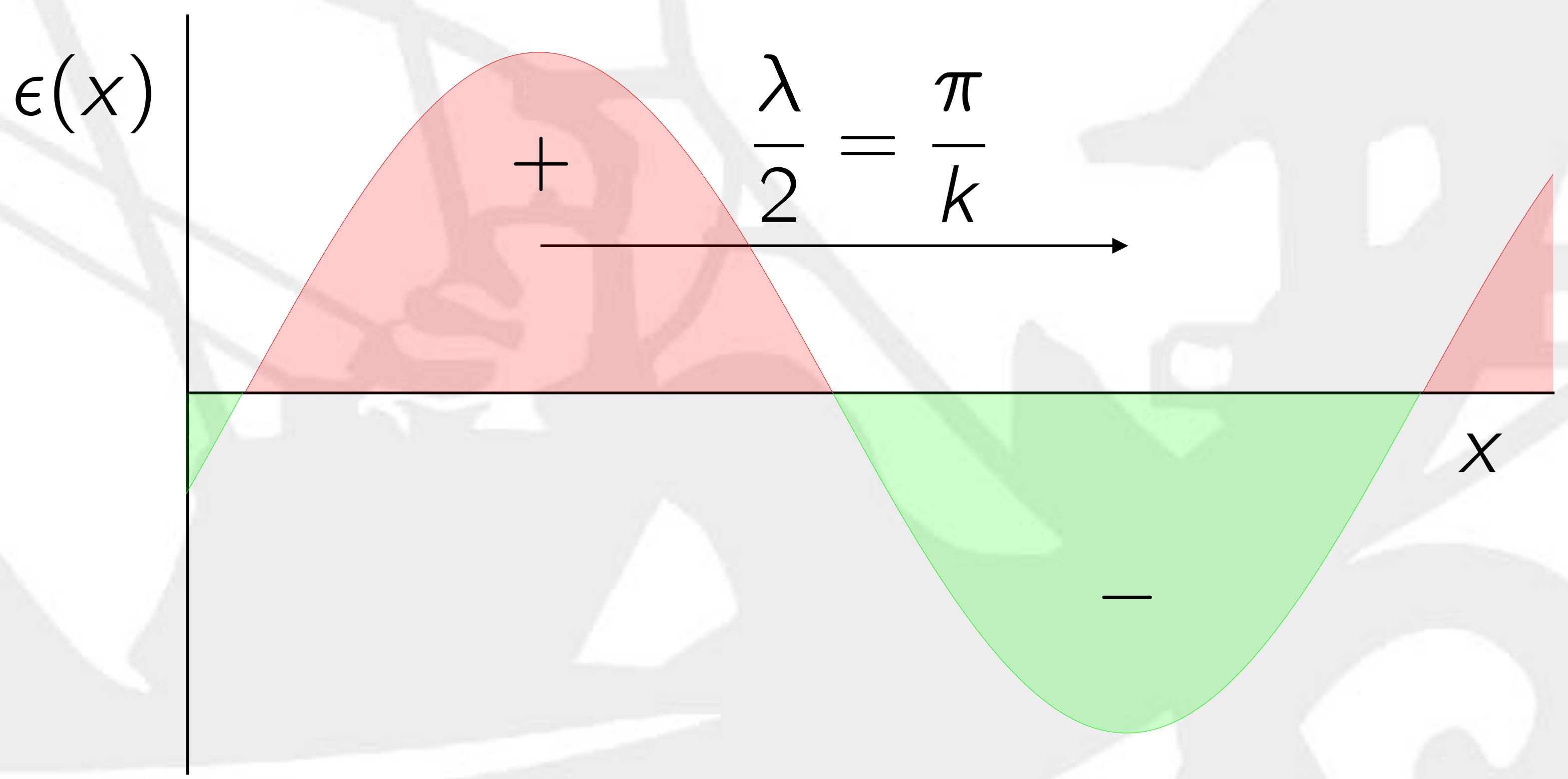

constitutive relations: the heat equation

$$\frac{\partial \epsilon}{\partial t} = -\nabla \cdot \mathbf{j}$$

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$$\alpha = \frac{\kappa}{c_p \rho}$$

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$$\frac{\partial \tilde{T}(\mathbf{k}, t)}{\partial t} = -\alpha k^2 \tilde{T}(\mathbf{k}, t)$$

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$$T(\mathbf{r}, t) = \frac{1}{(4\pi\alpha t)^{\frac{3}{2}}} \int \mathrm{e}^{-\frac{|\mathrm{r}-\mathrm{r}'|^2}{4\alpha t}} T(\mathbf{r}', 0) d\mathbf{r}'$$

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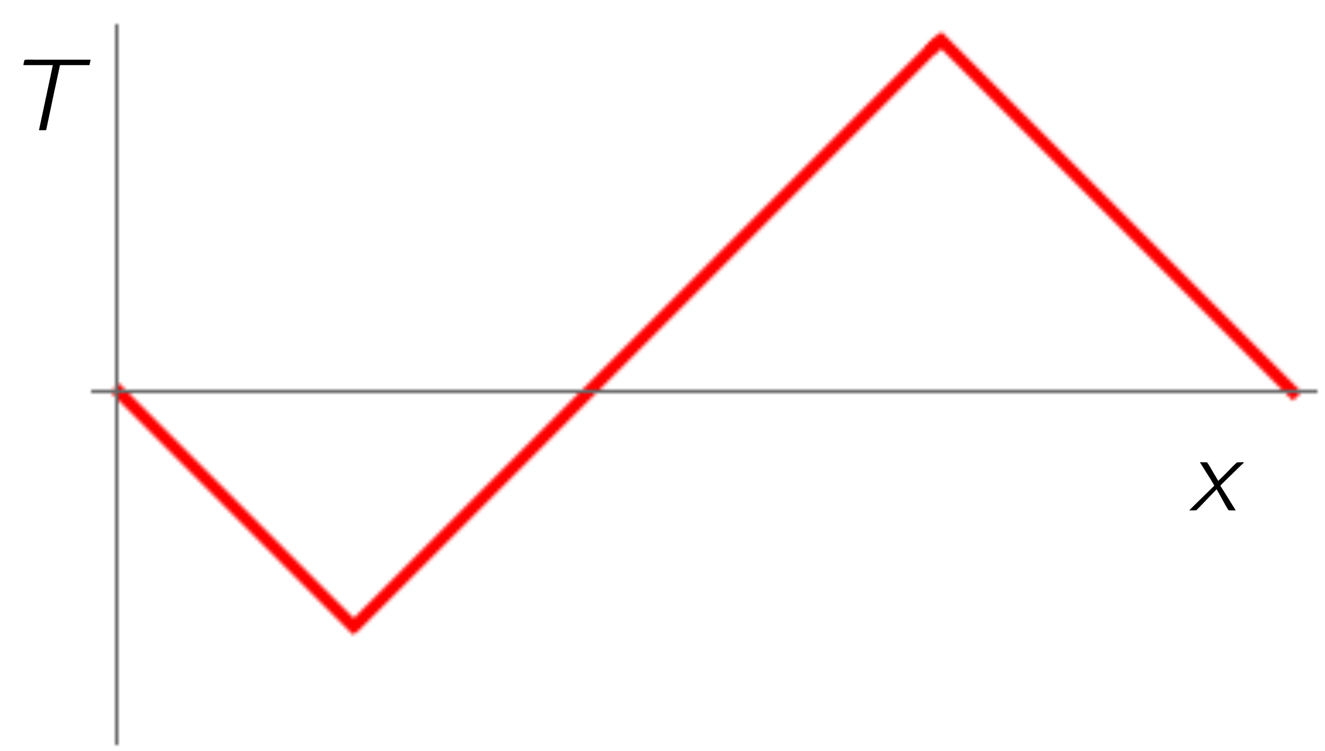

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constitutive relations: Onsager's equations

P conserved quantities: $\big(A_1, A_2, \cdots A_P\big)$

P conserved (current) densities: $\big(a_1(\mathbf{r}), \cdots a_P(\mathbf{r})\big)$, $\big(\mathbf{j}_1(\mathbf{r}), \cdots \mathbf{j}_P(\mathbf{r})\big)$

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$$\frac{\delta}{\delta a_i}\Big(S - \sum_j \lambda_j A_j\Big) = 0$$

$$\frac{\delta S}{\delta a_i} = \alpha_i(\mathbf{r}) = \lambda_i$$

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$$\mathbf{f} = \nabla \alpha$$

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Onsager's linear-response equations

$\Lambda_{ij} = \Lambda_{ji}$

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Onsager's linear-response equations

$$\Lambda_{ij} = \Lambda_{ji}$$

A	$\alpha = \dfrac{\partial S}{\partial A}$
E	$\dfrac{1}{T}$
V	$\dfrac{p}{T}$
N_i	$-\dfrac{\mu_i}{T}$

Green-Kubo linear-response theory

$$\Lambda_{ij} = \frac{\Omega}{k_B} \int_0^\infty \langle J_i(t) J_j(0) \rangle dt$$

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$$J = \frac{1}{\Omega} \int_{\Omega} j(\mathbf{r}) d\mathbf{r}$$

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$$\begin{aligned} J(t) &= J(\Gamma_t) \\ &= J(t, \Gamma_0) \end{aligned}$$

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$$\begin{aligned} \langle J(t) J(0) \rangle &= \int J(t, \Gamma_0) J(0, \Gamma_0) P^\circ(\Gamma_0) d\Gamma_0 \\ &\approx \frac{1}{T-t} \int_0^{T-t} J(t+\tau, \Gamma_0) J(\tau, \Gamma_0) d\tau \end{aligned}$$

Einstein-Helfand relations

Einstein (1905)

$$\left\langle |x(t) - x(0)|^2 \right\rangle = \left\langle \left| \int_0^t v(t')dt' \right|^2 \right\rangle$$

$$\approx 2Dt$$

$$D = \int_0^\infty \langle v(t)v(0) \rangle dt$$

Einstein-Helfand relations

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Helfand (1960)

$$\left\langle \left| \int_0^t J(t')dt' \right|^2 \right\rangle \approx 2\Lambda t$$

$$\Lambda = \int_0^\infty \langle J(t)J(0) \rangle dt$$

the classical energy current

$$\mathbf{J} = \frac{1}{\Omega}\int_{\Omega} \mathbf{j}(\mathbf{r})\,d\mathbf{r}$$

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the classical energy current

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$$\nabla\cdot\mathbf{j}(\mathbf{r}) = -\dot{\epsilon}(\mathbf{r})$$

$$\int_\Omega \mathbf{r}\big(\nabla\cdot\mathbf{j}(\mathbf{r})\big)d\mathbf{r} = -\int_\Omega \mathbf{r}\dot{\epsilon}(\mathbf{r})d\mathbf{r}$$

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$$\int_\Omega \mathbf{j}(\mathbf{r})d\mathbf{r} = \int_\Omega \mathbf{r}\dot{\epsilon}(\mathbf{r})d\mathbf{r} + \text{surface terms}$$

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

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

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$$\mathbf{J} = \sum_I \big(\dot{\mathbf{R}}_I e_I + \mathbf{R}_I \dot{e}_I\big)$$

the classical energy current

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

hurdles 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*
Department of Geological Sciences, University of Michigan, Ann Arbor, Michigan, 48109-1005, USA

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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.

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

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

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

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

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

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

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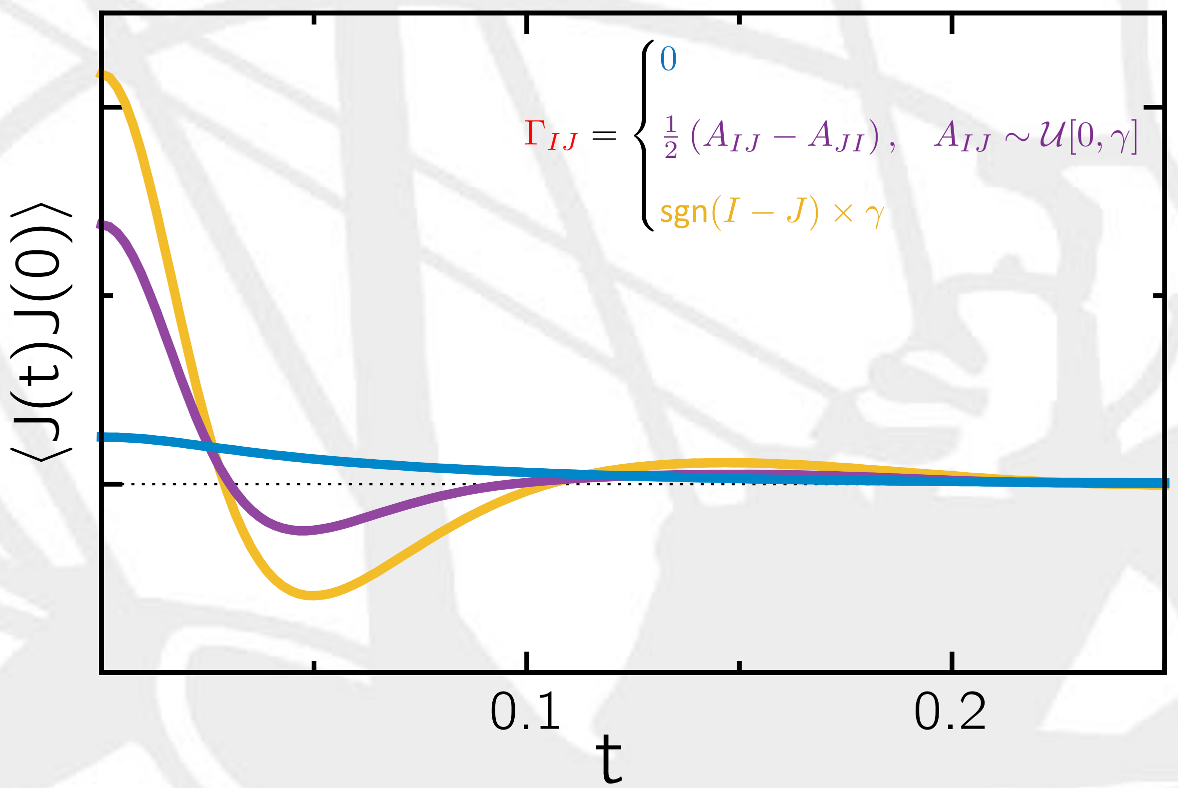
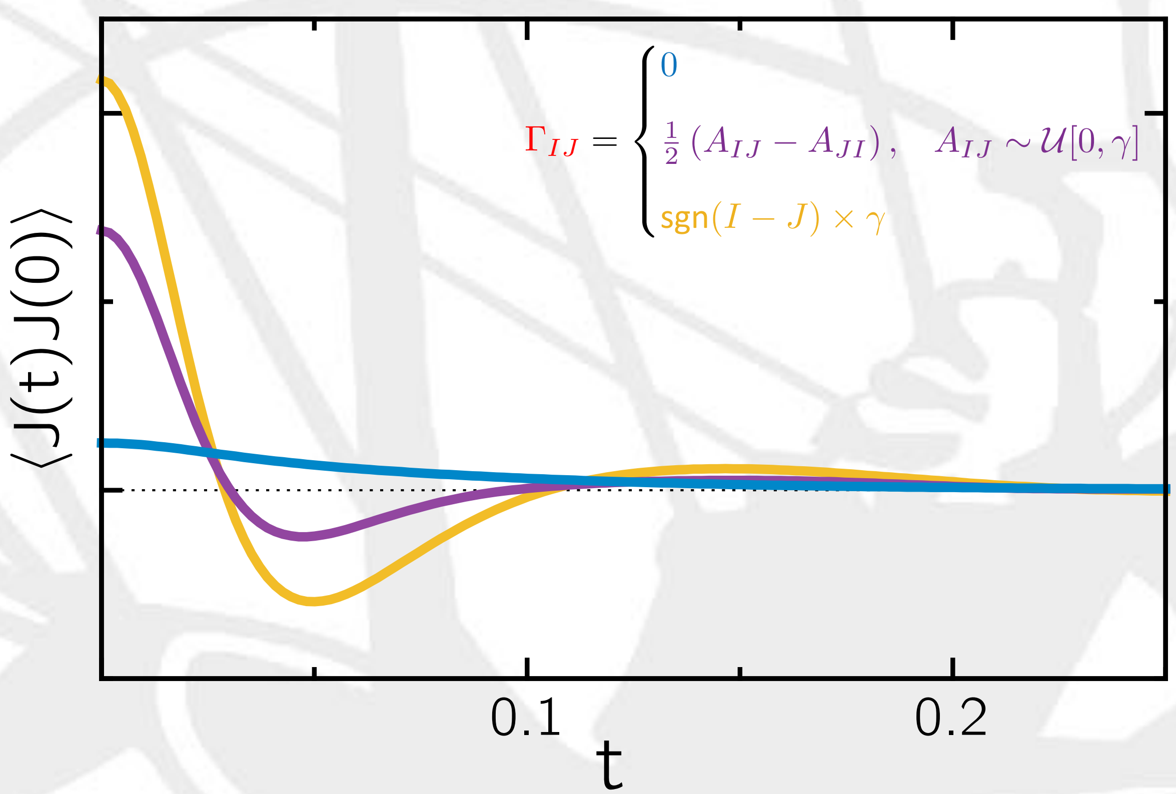
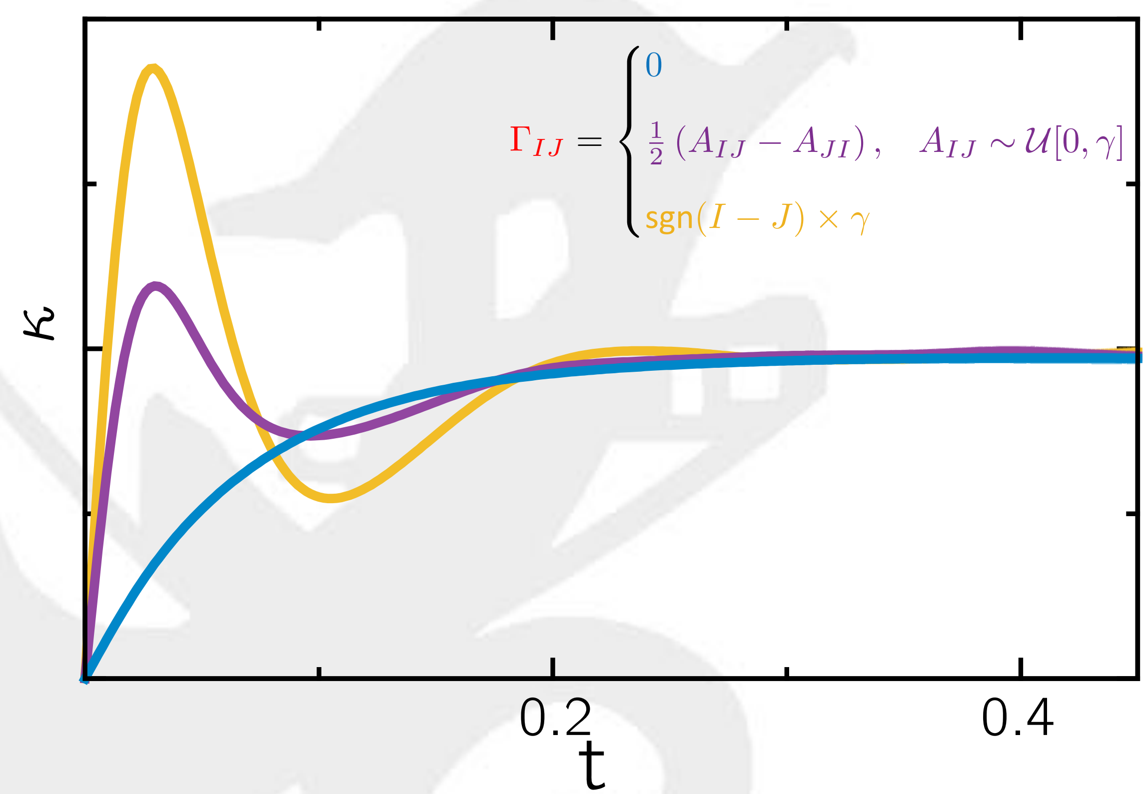


insights from classical mechanics

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





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

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

insights from classical mechanics

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insights from classical mechanics

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$$\mathrm{var}\left[\mathbf{D}'(t)\right] = \mathrm{var}\left[\mathbf{D}(t)\right] + \mathrm{var}\left[\Delta\mathbf{P}(t)\right] + 2\mathrm{cov}\left[\mathbf{D}(t)\cdot\Delta\mathbf{P}(t)\right]$$

insights from classical mechanics

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

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

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$$\mathrm{var}\left[\mathbf{D}'(t)\right] = \underbrace{\mathrm{var}\left[\mathbf{D}(t)\right]}_{\mathcal{O}(t)} + \underbrace{\cancel{\mathrm{var}\left[\Delta\mathbf{P}(t)\right]} + \cancel{2\mathrm{cov}\left[\mathbf{D}(t)\cdot\Delta\mathbf{P}(t)\right]}}_{\mathcal{O}(1)}$$

insights from classical mechanics

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

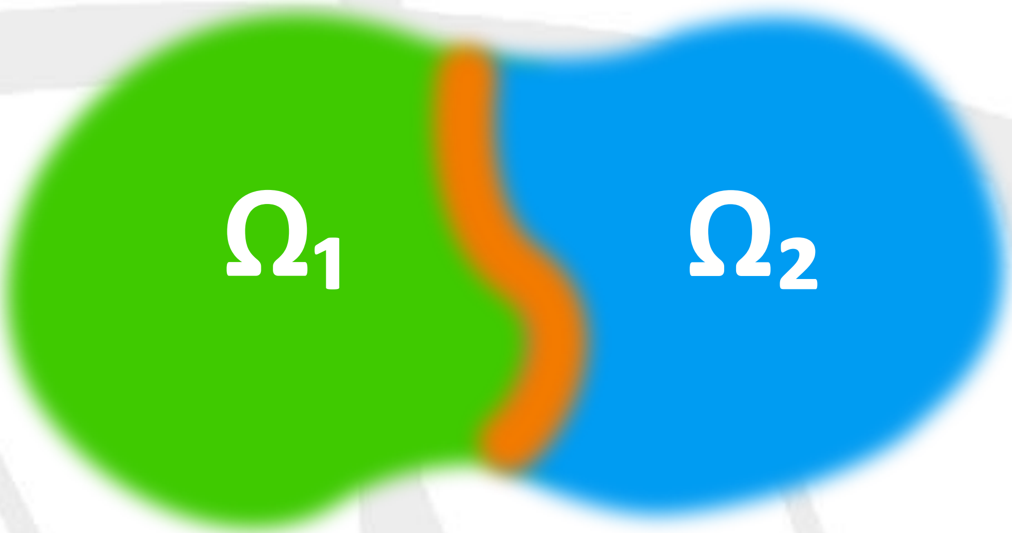
$$\kappa \sim \frac{1}{2t}\mathrm{var}\left[\mathbf{D}(t)\right] \qquad \mathbf{D}(t) = \int_0^t \mathbf{J}(t')dt'$$

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

$$\kappa' = \kappa$$

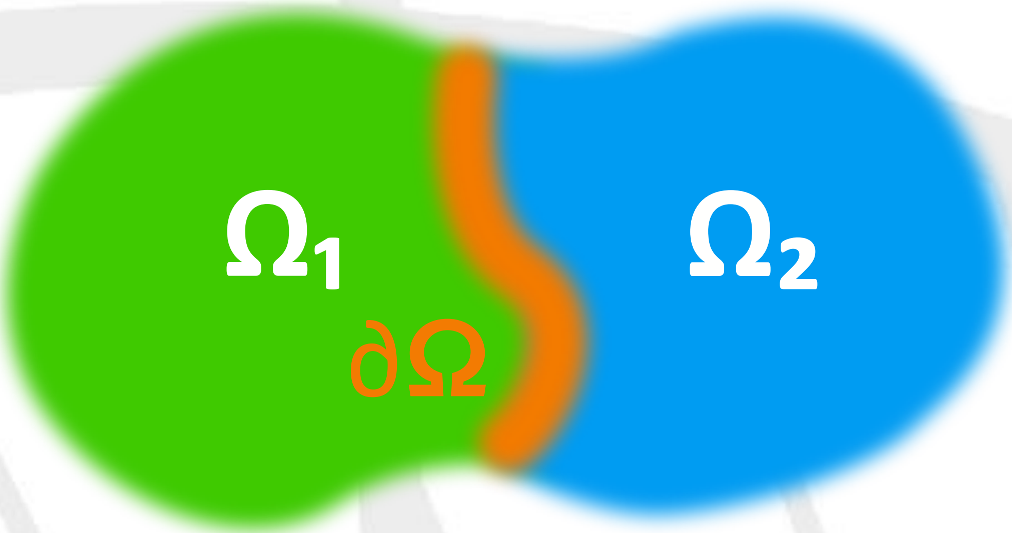
$$\mathrm{var}\left[\mathbf{D}'(t)\right] = \mathrm{var}\left[\mathbf{D}(t)\right] + \cancel{\mathrm{var}\left[\Delta\mathbf{P}(t)\right]} + \cancel{2\mathrm{cov}\left[\mathbf{D}\cdot\Delta\mathbf{P}(t)\right]}$$

gauge invariance



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

gauge invariance



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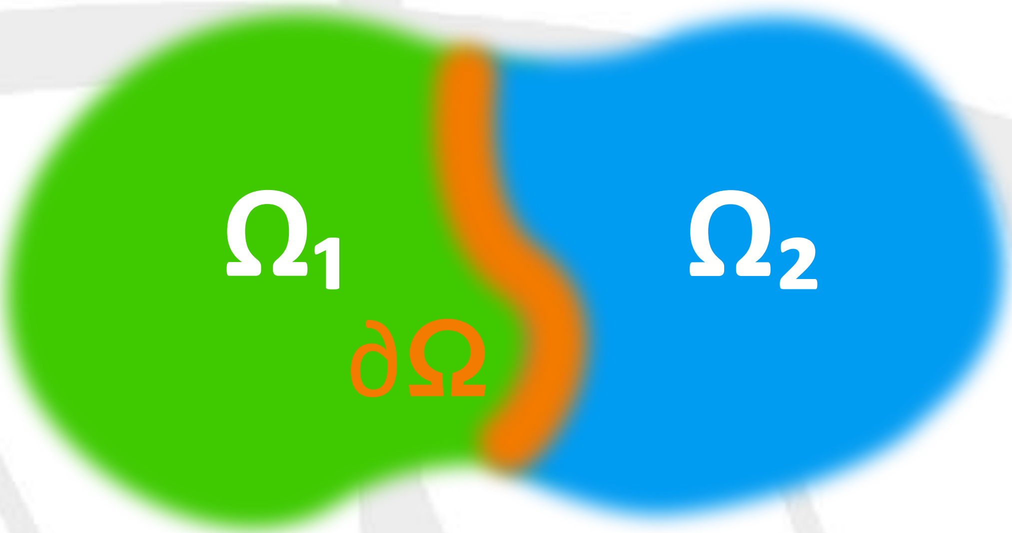
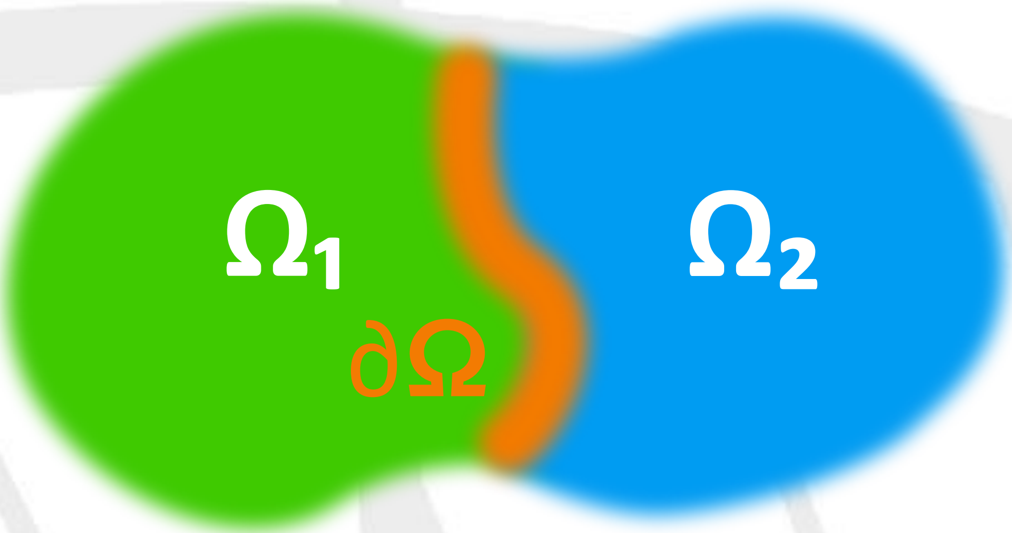


$$\mathsf{E}[\Omega_1 \cup \Omega_2] = \mathsf{E}[\Omega_1] + \mathsf{E}[\Omega_2] + \mathsf{W}[\partial\Omega]$$
$$\stackrel{?}{=} \mathcal{E}[\Omega_1] + \mathcal{E}[\Omega_2]$$
$$\mathcal{E}[\Omega] = \int_\Omega e(\mathbf{r})d\mathbf{r}$$

gauge invariance



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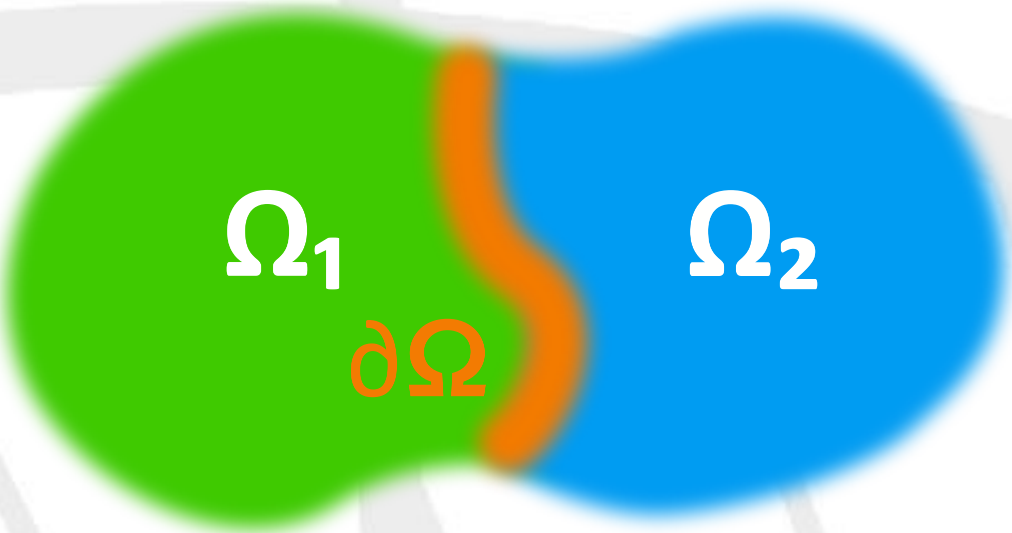
gauge invariance



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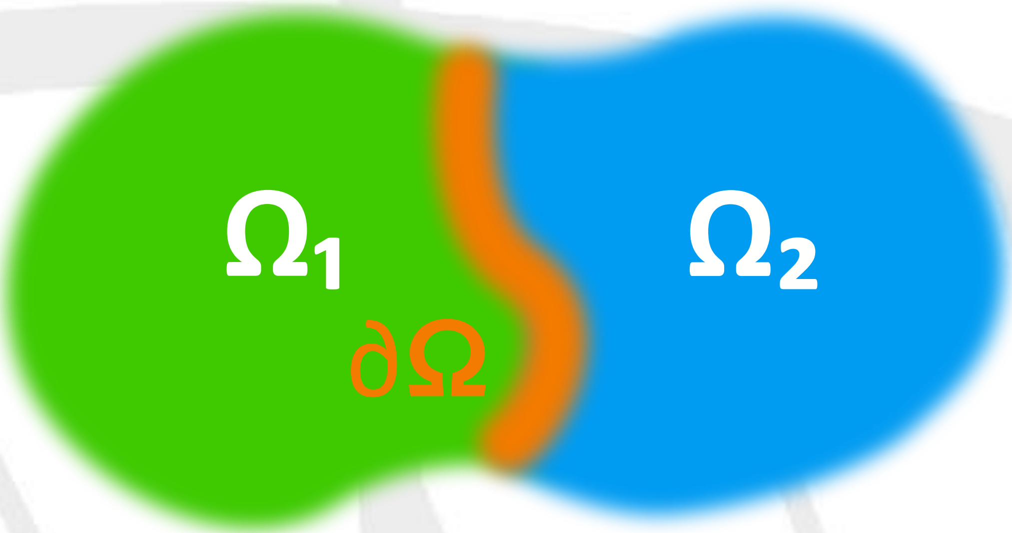
$$e'(\mathbf{r}) = e(\mathbf{r}) - \nabla \cdot \mathbf{p}(\mathbf{r})$$

gauge invariance



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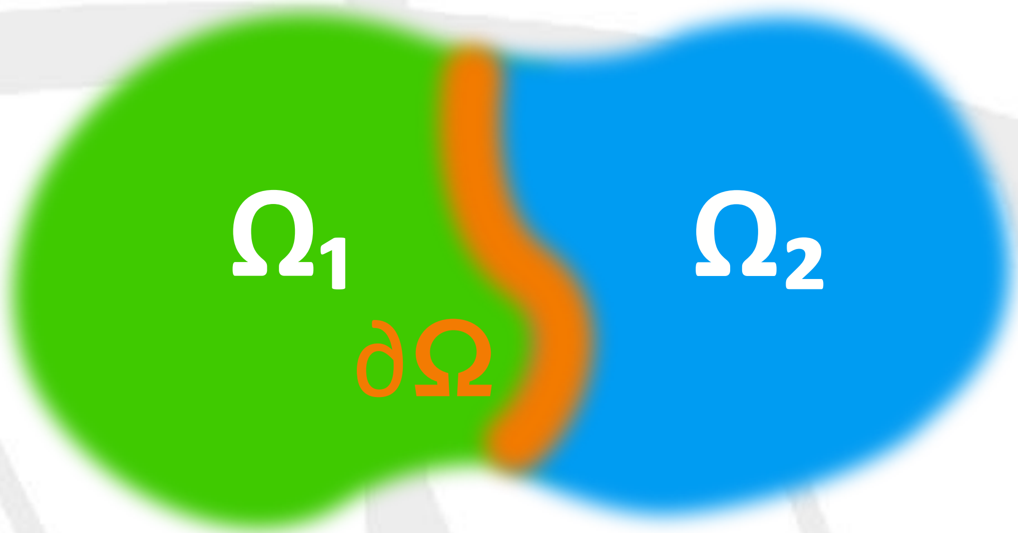
$$e'(\mathbf{r}) = e(\mathbf{r}) - \nabla \cdot \mathbf{p}(\mathbf{r})$$

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

gauge invariance



$$
\begin{aligned}
\mathsf{E}[\Omega_1 \cup \Omega_2] &= \mathsf{E}[\Omega_1] + \mathsf{E}[\Omega_2] + \mathsf{W}[\partial\Omega] \\
&\stackrel{?}{=} \mathcal{E}[\Omega_1] + \mathcal{E}[\Omega_2]
\end{aligned}
$$

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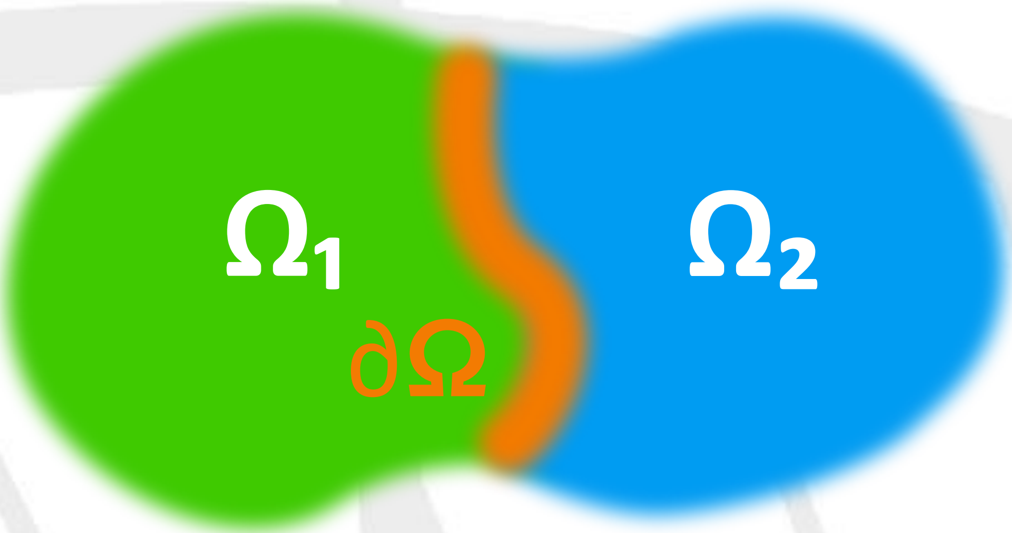
gauge invariance



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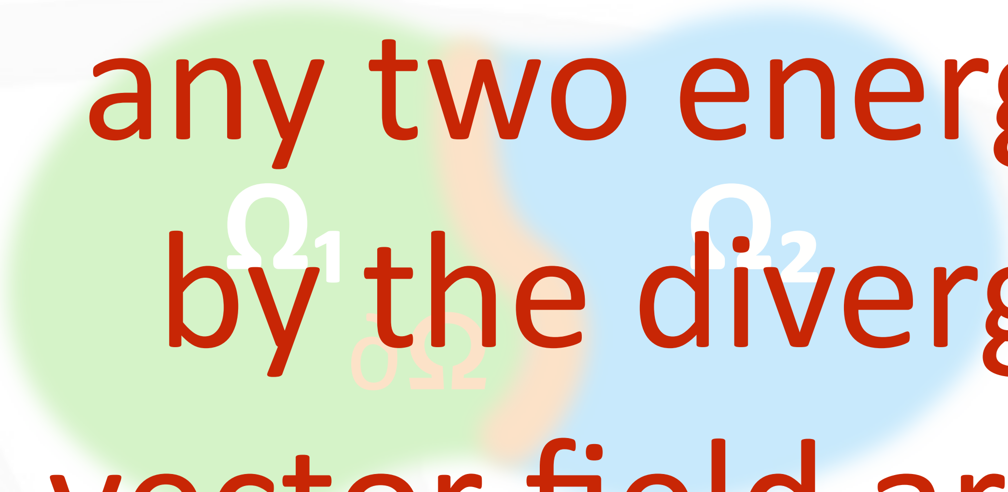
$$\boxed{\mathbf{J}'(t) = \mathbf{J}(t) + \dot{\mathbf{P}}(t)}$$

gauge invariance

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



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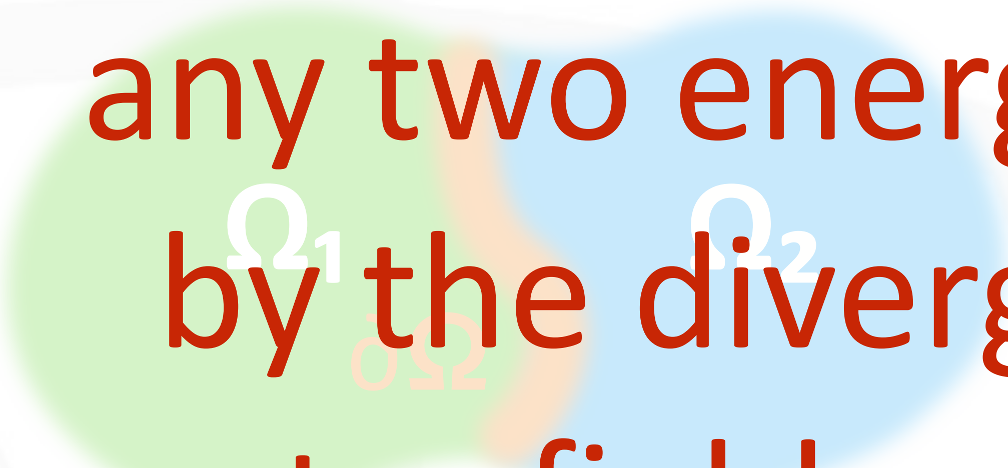
$$\boxed{\mathbf{J}'(t) = \mathbf{J}(t) + \dot{\mathbf{P}}(t)}$$

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



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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

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

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

the DFT energy density

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

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

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

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

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

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

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

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

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

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

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

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

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

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

the DFT energy current

$$\mathbf{J}_{DFT} = \int \mathbf{r}\dot{e}_{DFT}(\mathbf{r},t)d\mathbf{r}$$
$$= \mathbf{J}_{KS} + \mathbf{J}_H + \mathbf{J}_0' + \mathbf{J}_0 + \mathbf{J}_{XC}$$

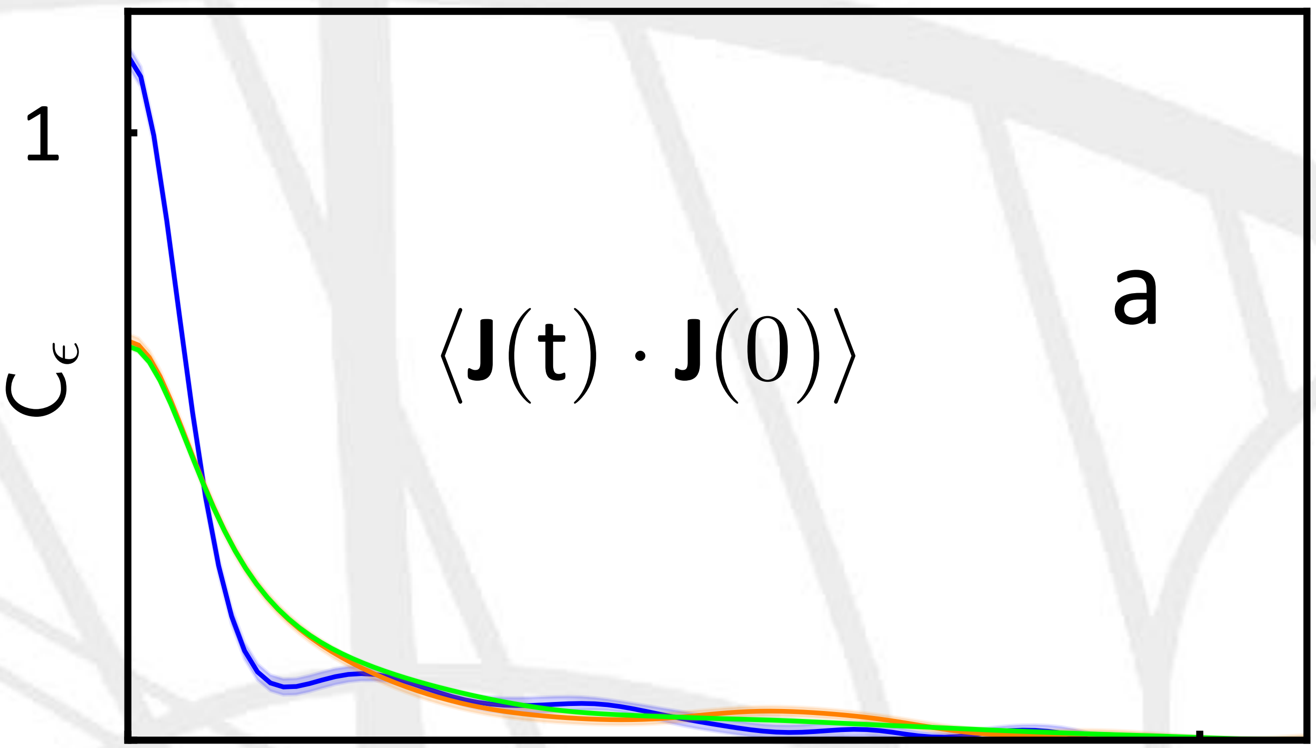
$$\mathbf{J}_{KS} = \sum_v \left(\langle \varphi_v | \mathbf{r} \hat{H}_{KS} | \dot{\varphi}_v \rangle + \varepsilon_v \langle \dot{\varphi}_v | \mathbf{r} | \varphi_v \rangle \right)$$

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

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

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

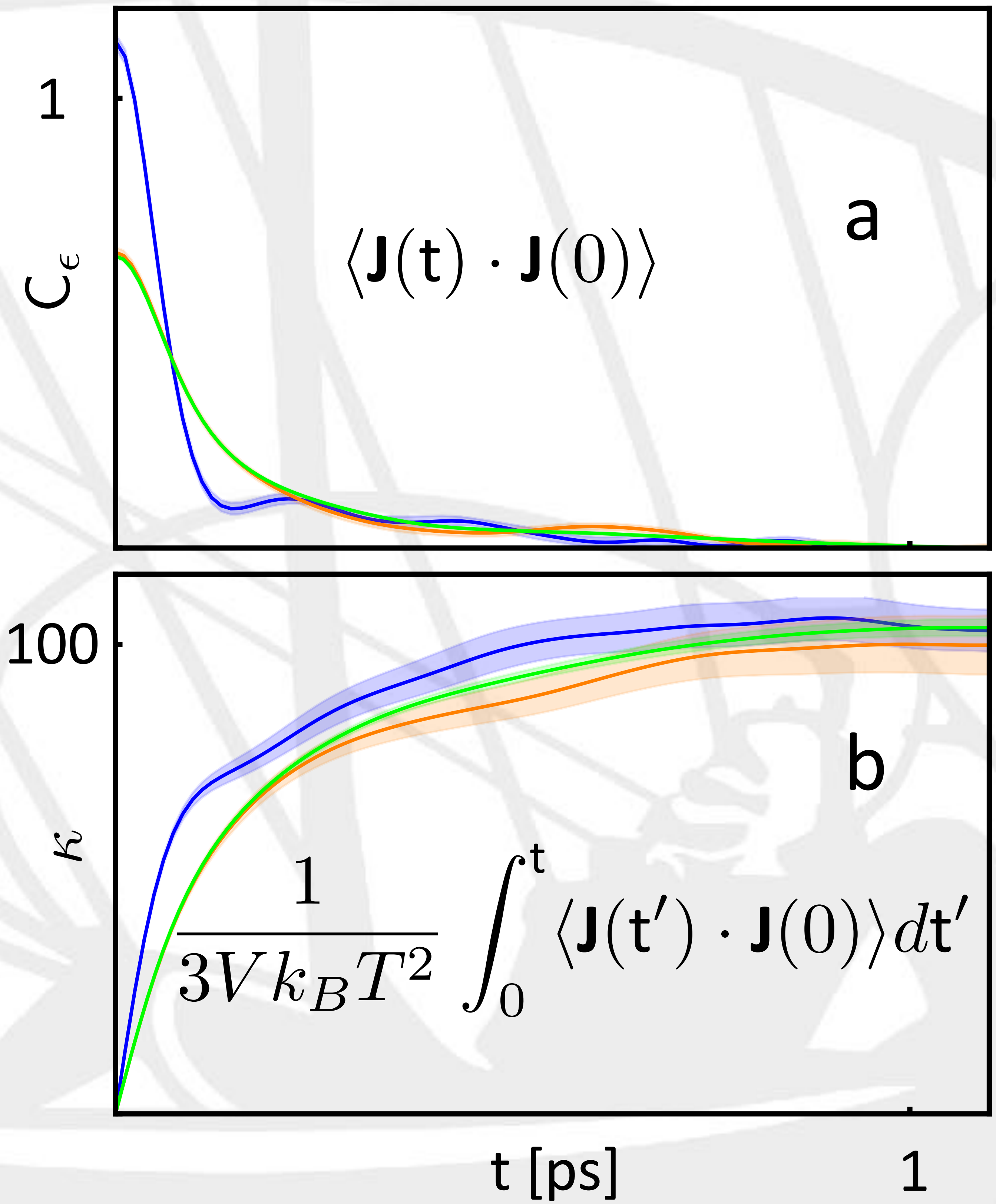
a benchmark



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



108 “LDA Ar” atoms
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100 ps CP trajectory
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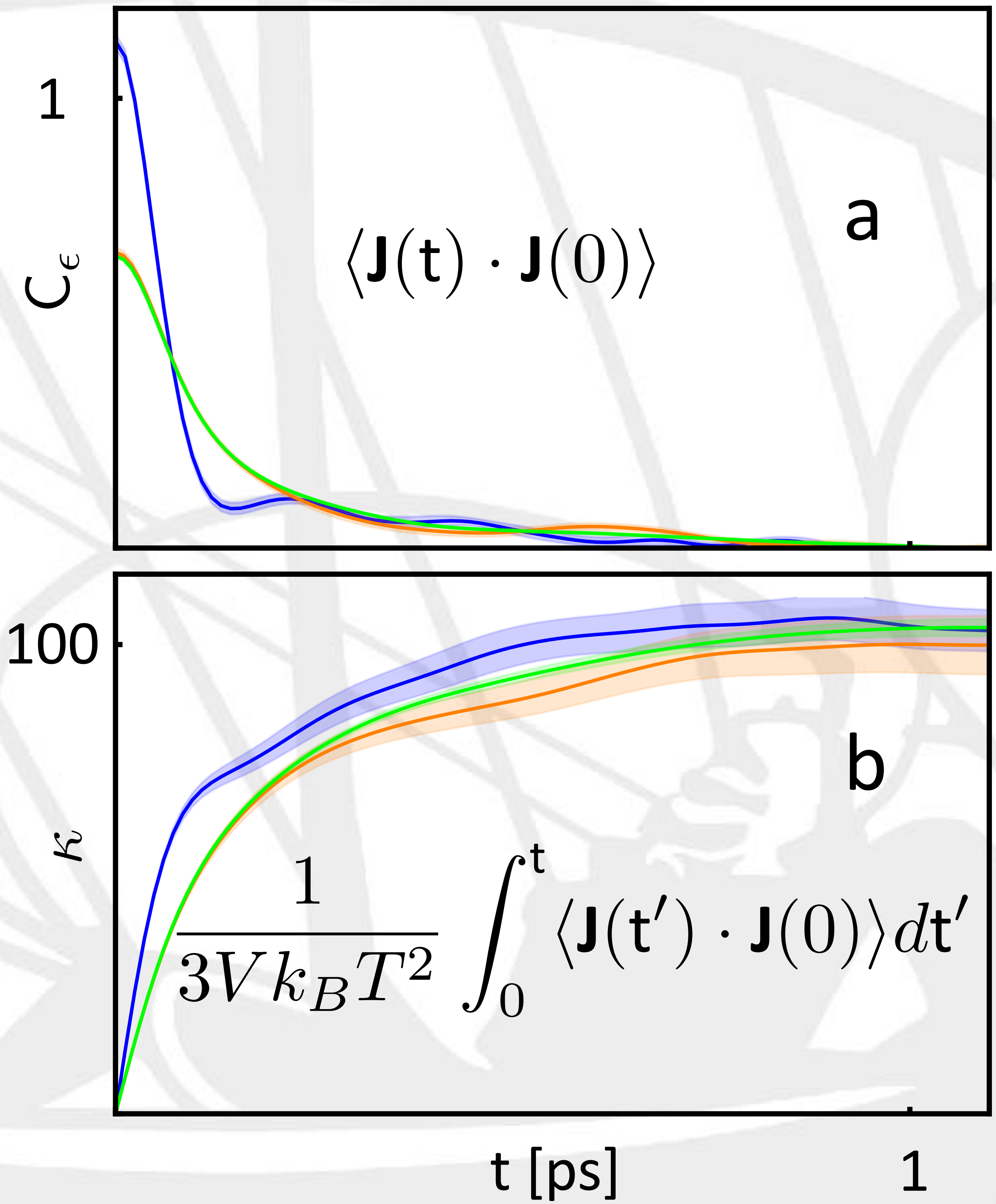
a benchmark

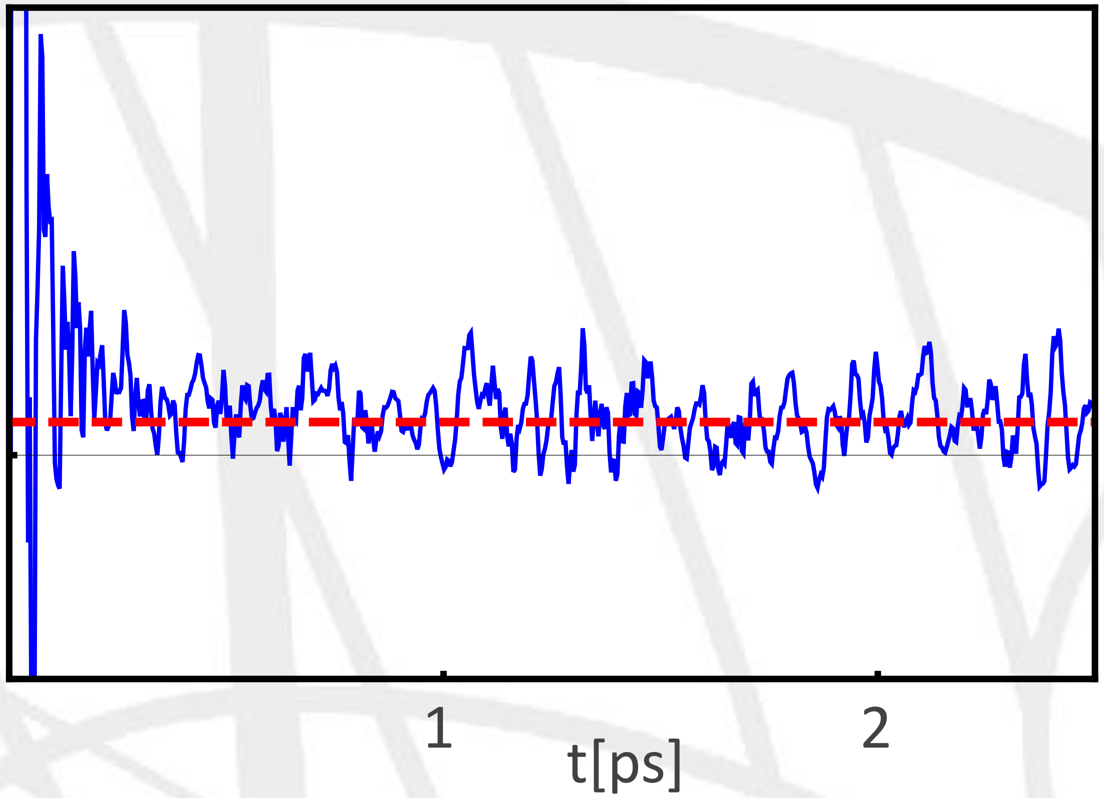


108 "LDA Ar" atoms
@bp density, T= 250 K

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

same behavior at T=400 K

liquid (heavy) water

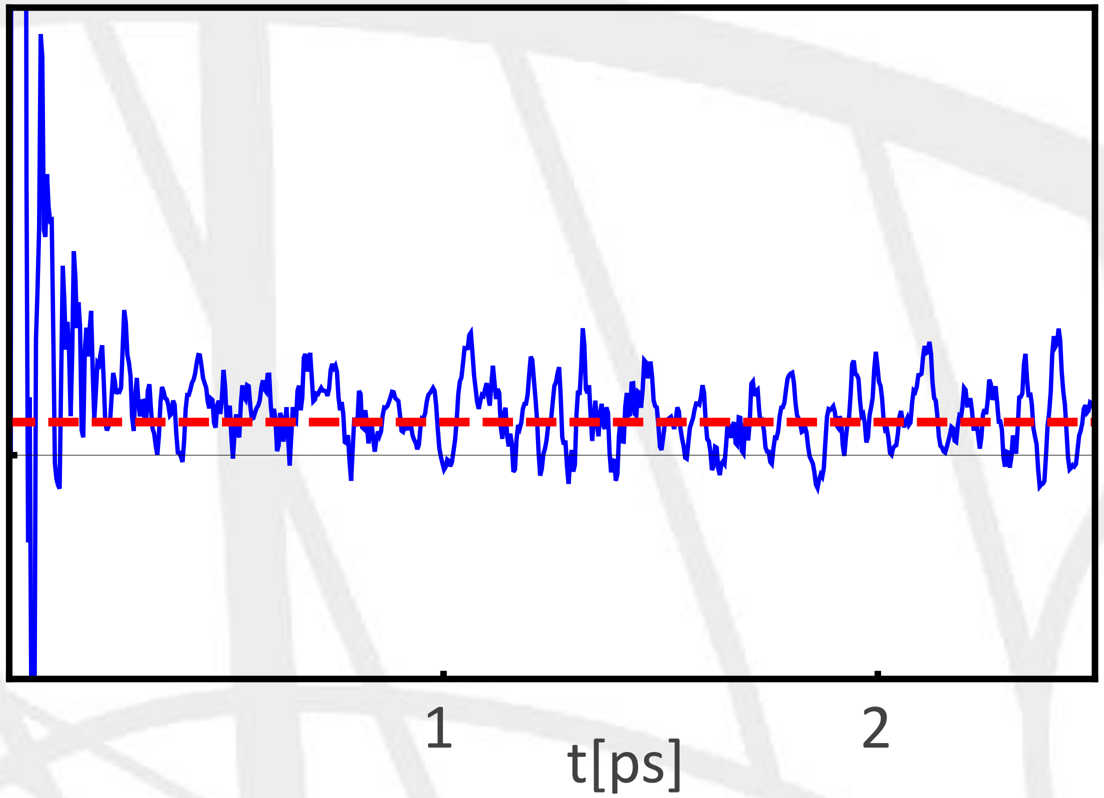


64 molecules, T=385 K
expt density @ac

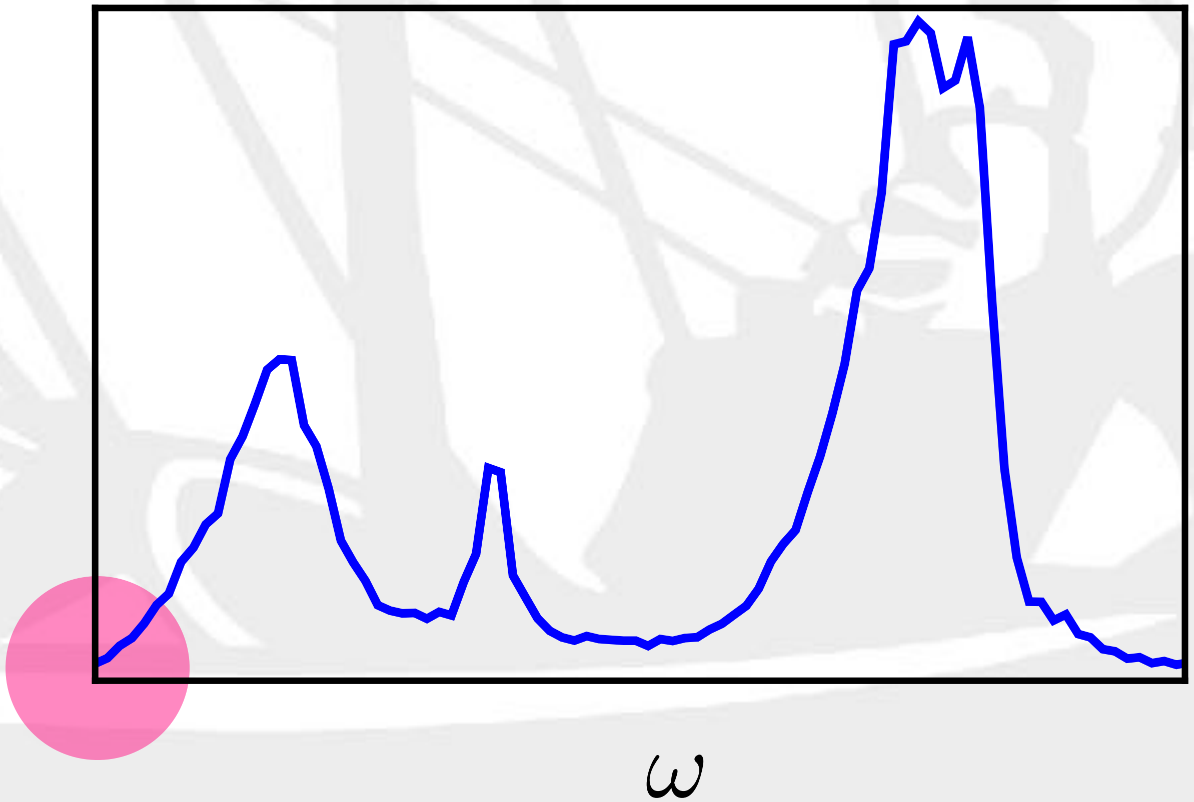
$$\frac{1}{3Vk_BT^2}\int_0^{\mathsf{t}}\langle \mathbf{J}(\mathsf{t}')\cdot\mathbf{J}(0)\rangle d\mathsf{t}'$$

liquid (heavy) water

64 molecules, T=385 K
expt density @ac

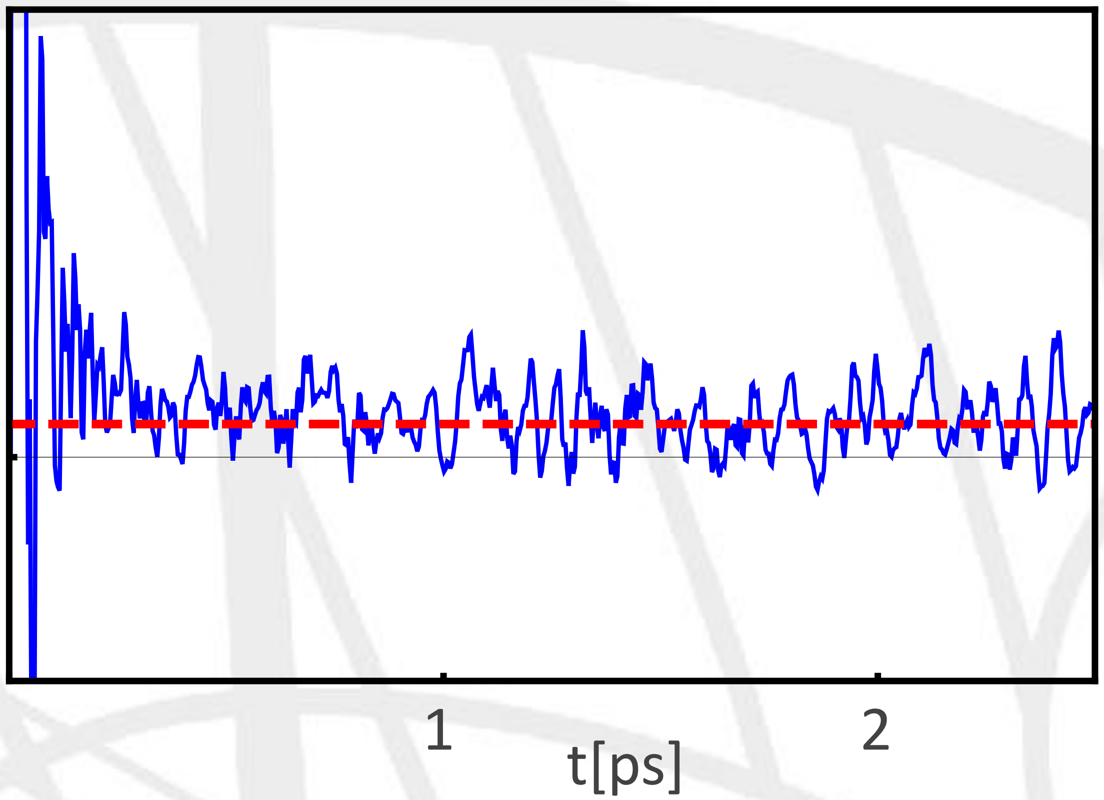


$$\frac{1}{3Vk_BT^2}\int_0^{\mathrm{t}}\langle \mathbf{J}(\mathrm{t}')\cdot\mathbf{J}(0)\rangle d\mathrm{t}'$$



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

liquid (heavy) water



64 molecules, T=385 K
expt density @ac

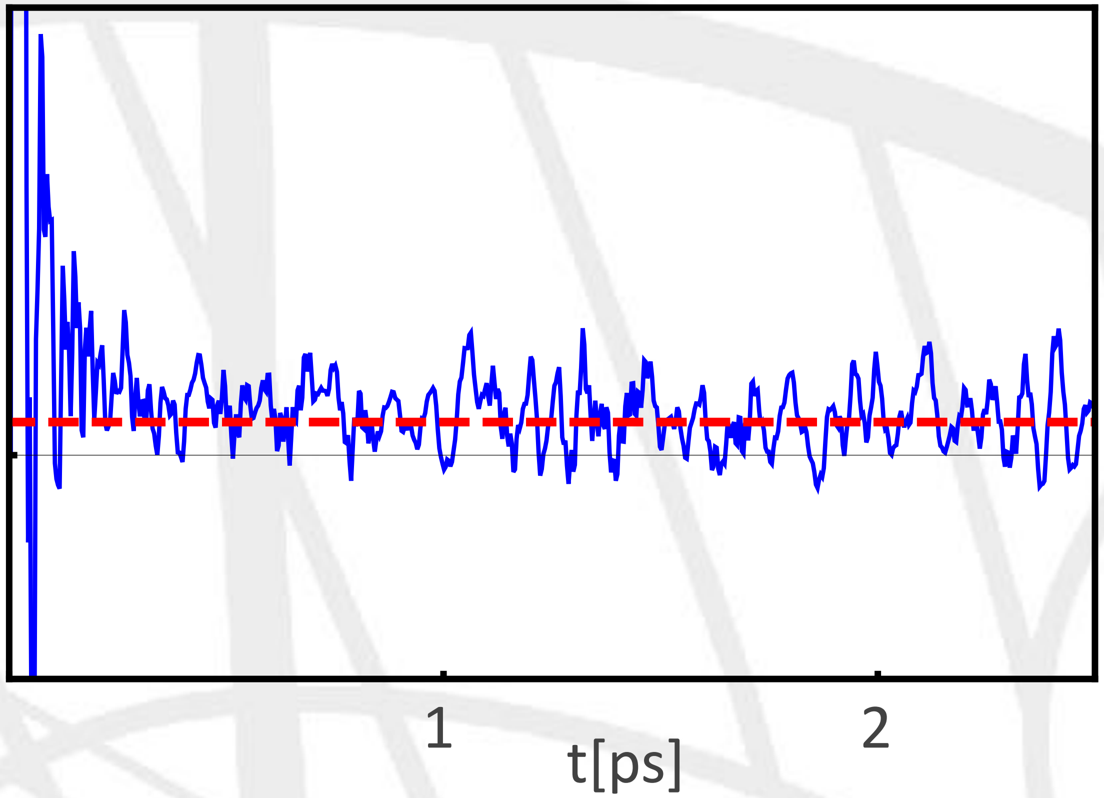
$$\frac{1}{3Vk_BT^2}\int_0^{\mathsf{t}}\langle \mathbf{J}(\mathsf{t}')\cdot\mathbf{J}(0)\rangle d\mathsf{t}'$$

Einstein's relation

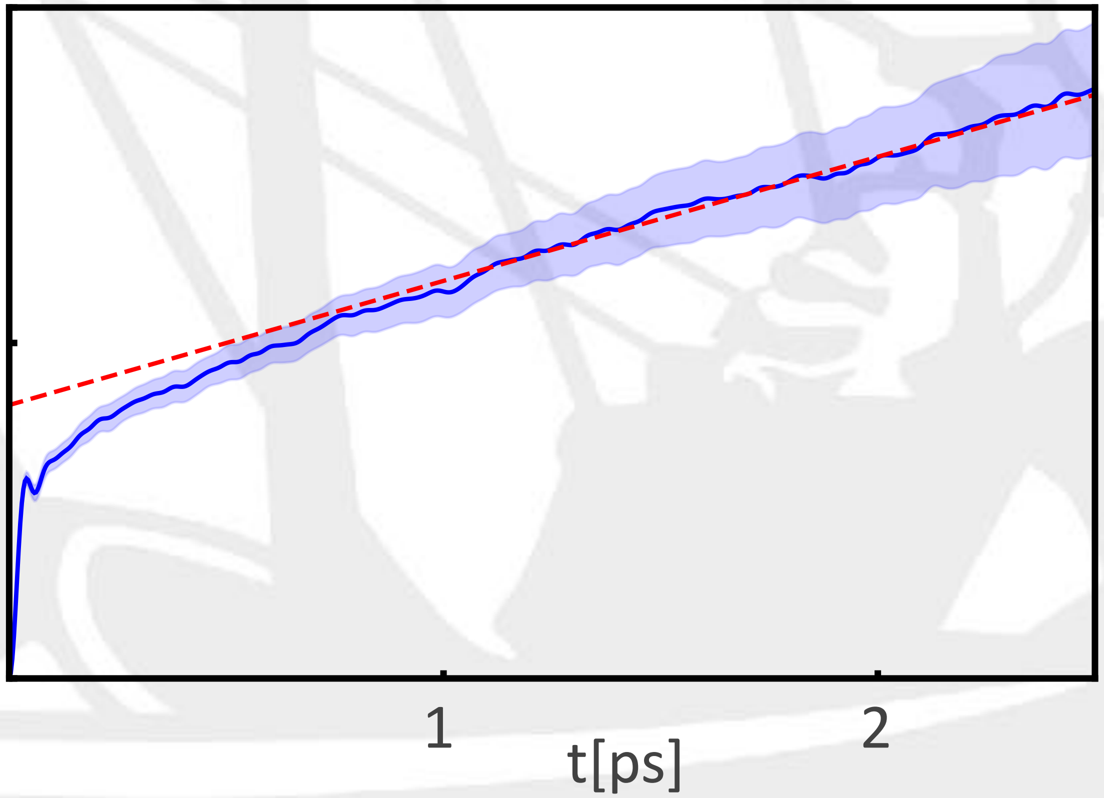
$$\frac{\mathsf{t}}{3Vk_BT^2}\int_0^{\mathsf{t}}\langle \mathbf{J}(\mathsf{t}')\cdot\mathbf{J}(0)\rangle d\mathsf{t}' \approx \frac{1}{6Vk_BT^2}\left\langle\left|\int_0^{\mathsf{t}}\mathbf{J}(\mathsf{t}')d\mathsf{t}'\right|^2\right\rangle$$

liquid (heavy) water

64 molecules, T=385 K
expt density @ac

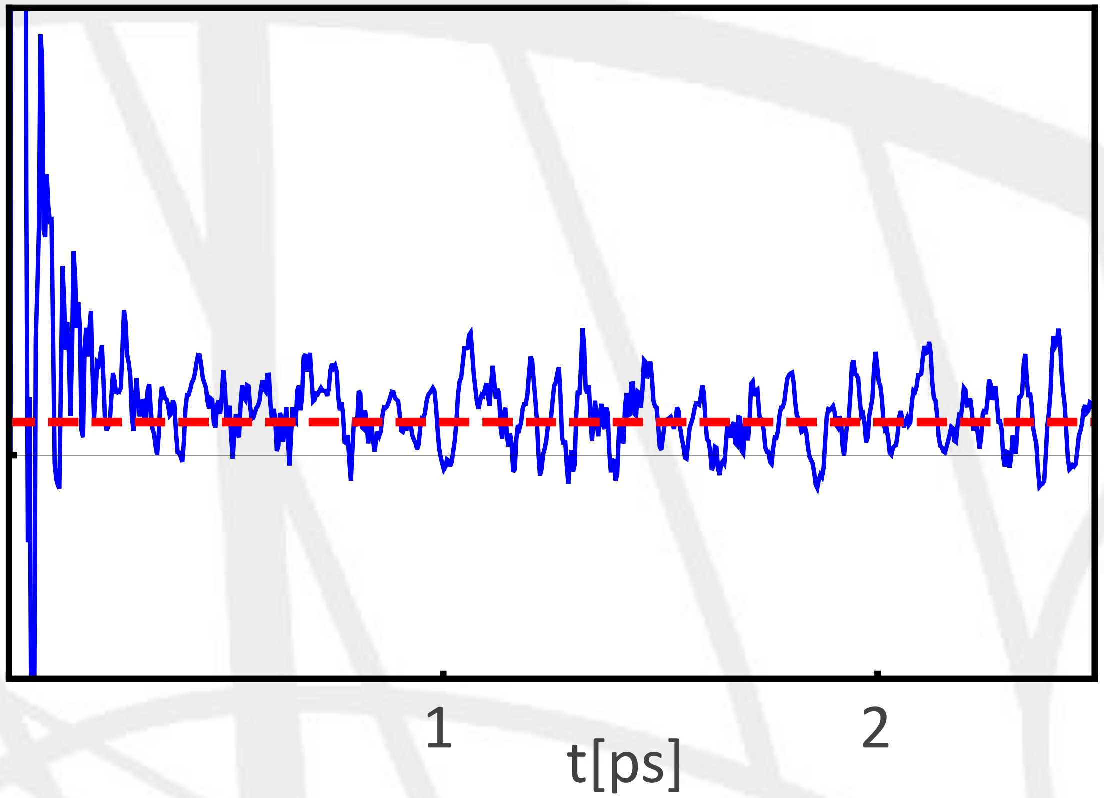


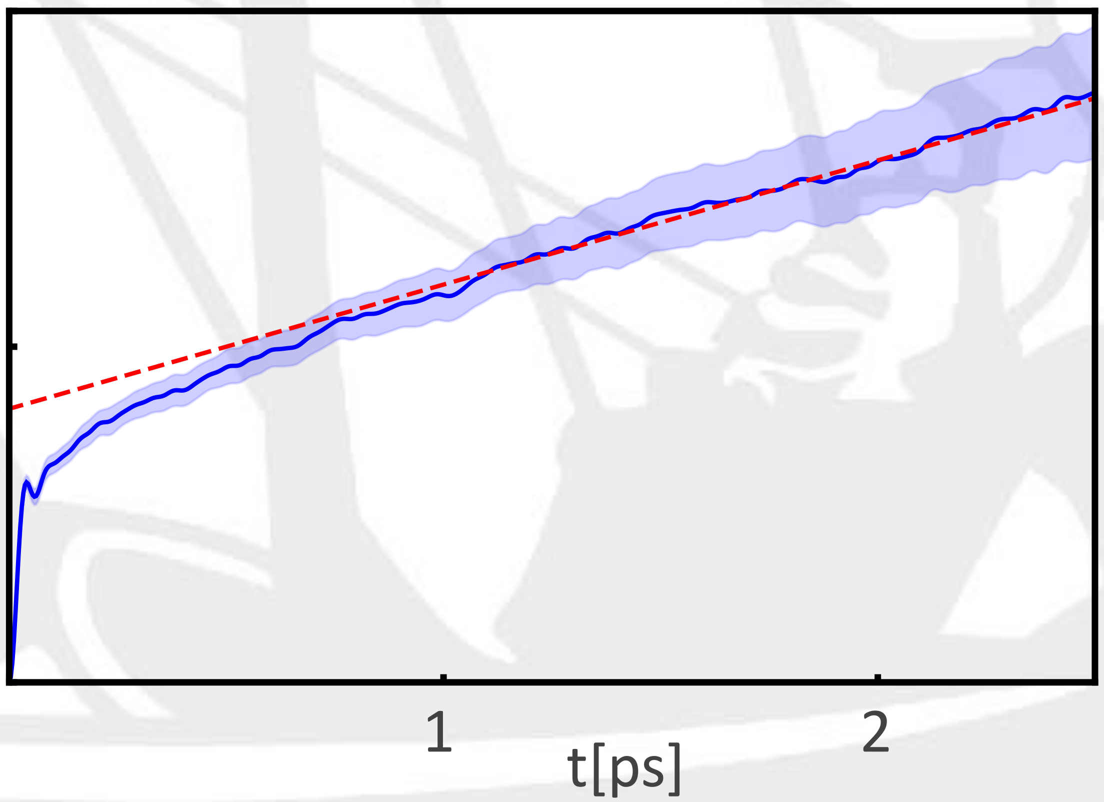
$$\frac{1}{3Vk_BT^2}\int_0^{\mathrm{t}}\langle \mathbf{J}(\mathrm{t}')\cdot\mathbf{J}(0)\rangle d\mathrm{t}'$$



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

liquid (heavy) water





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

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

$$\kappa_{\mathrm{expt}} = 0.61 \quad (\mathrm{light@AC})$$

$$\kappa_{\mathrm{DFT}} = 0.60 \quad (\mathrm{heavy@AC})$$

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

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.

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

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Christian Carbogno, Rampi Ramprasad, and Matthias Scheffler

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Green-Kubo *vs.* Einstein-Helfand

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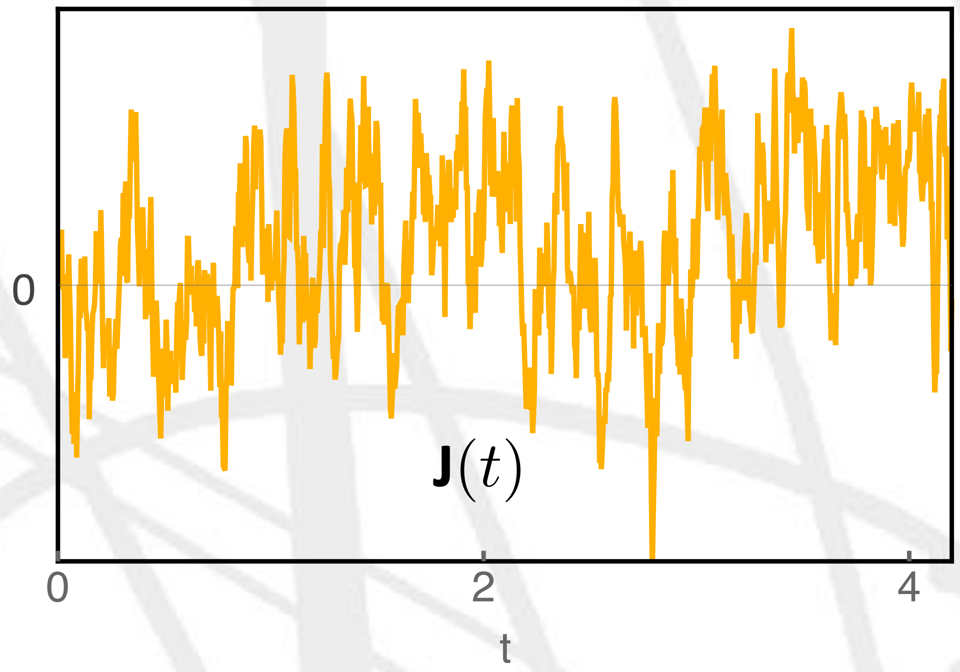

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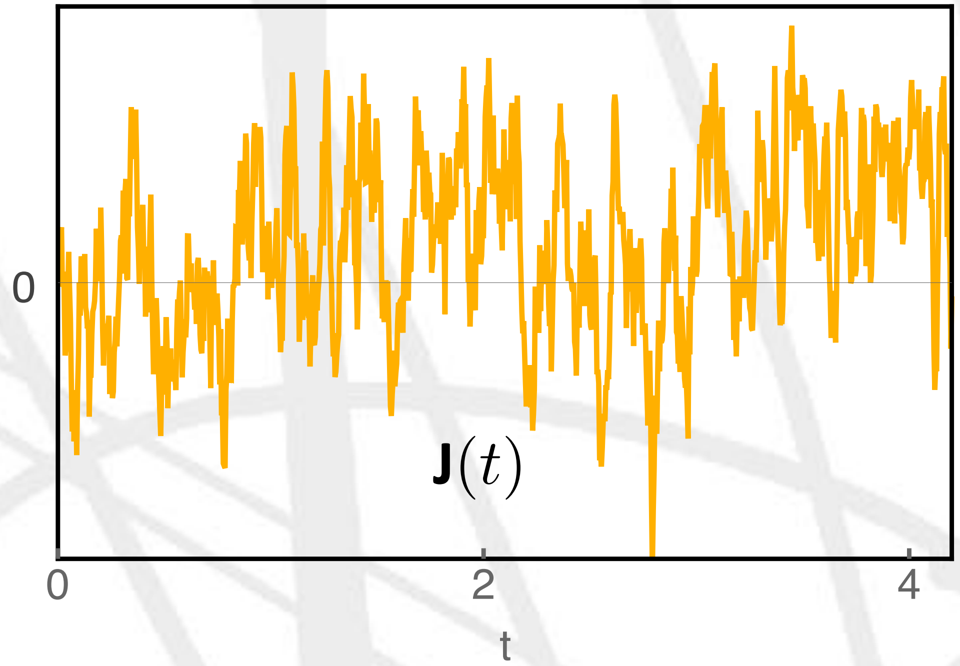

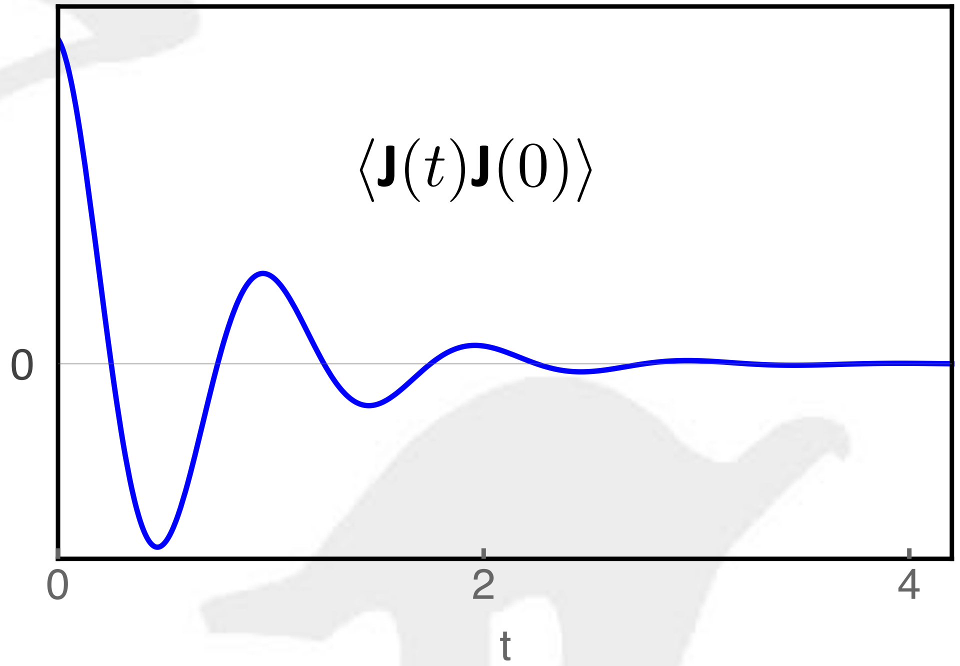

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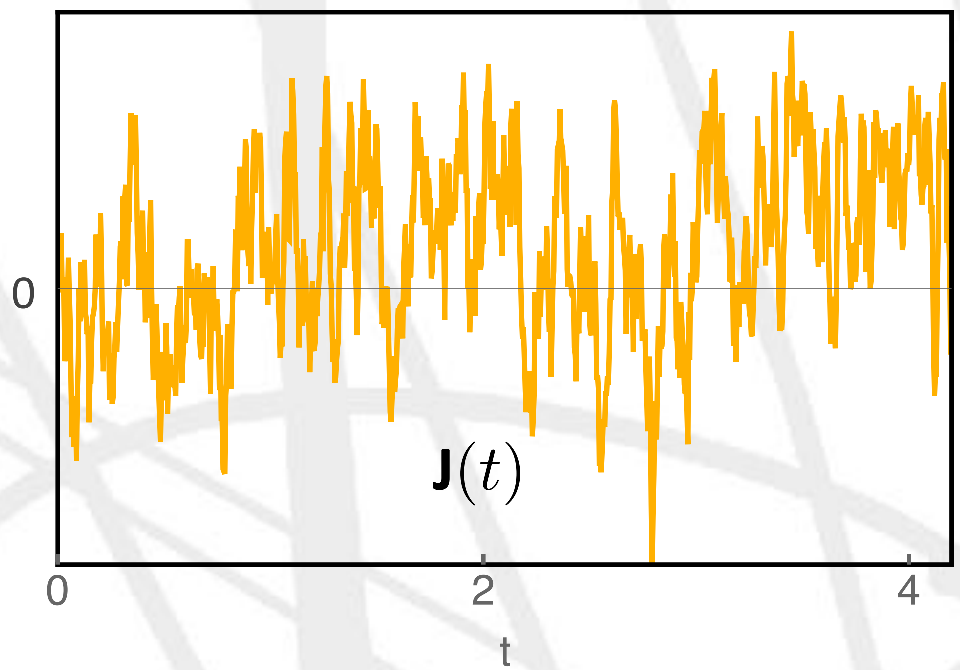

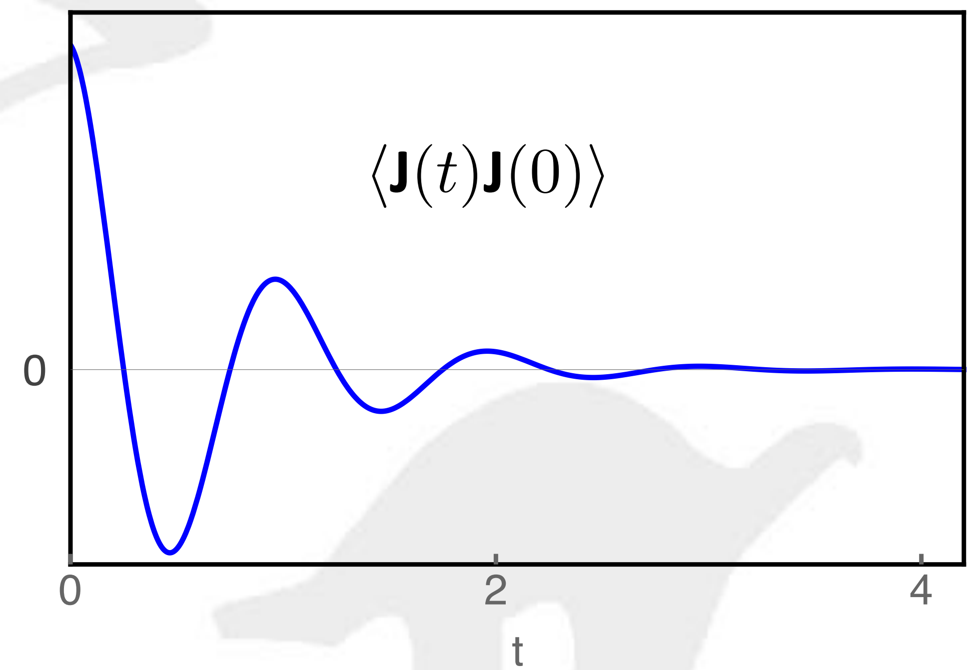

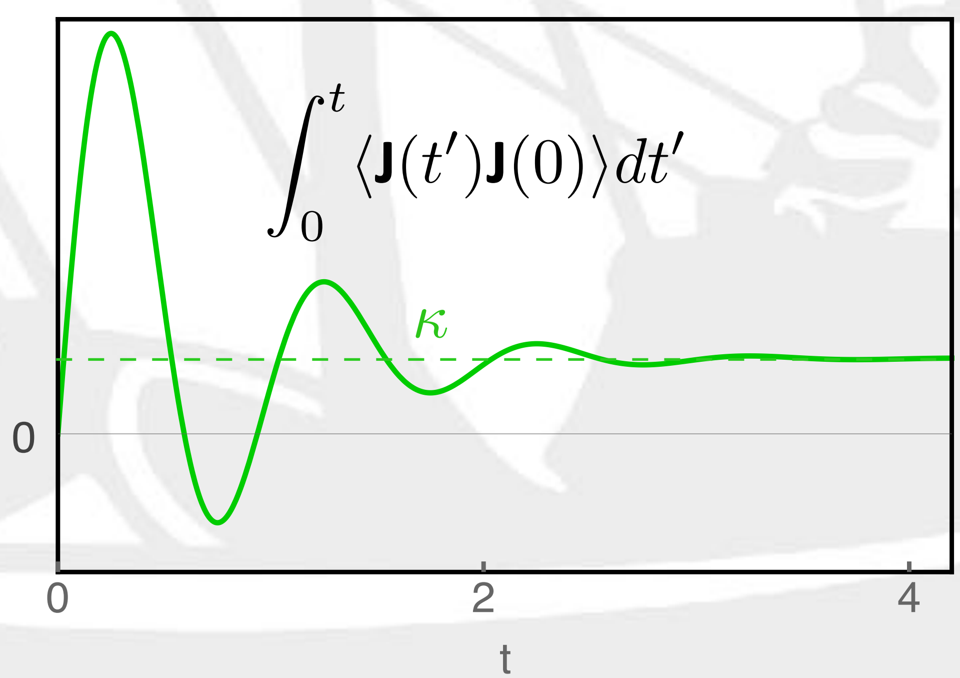

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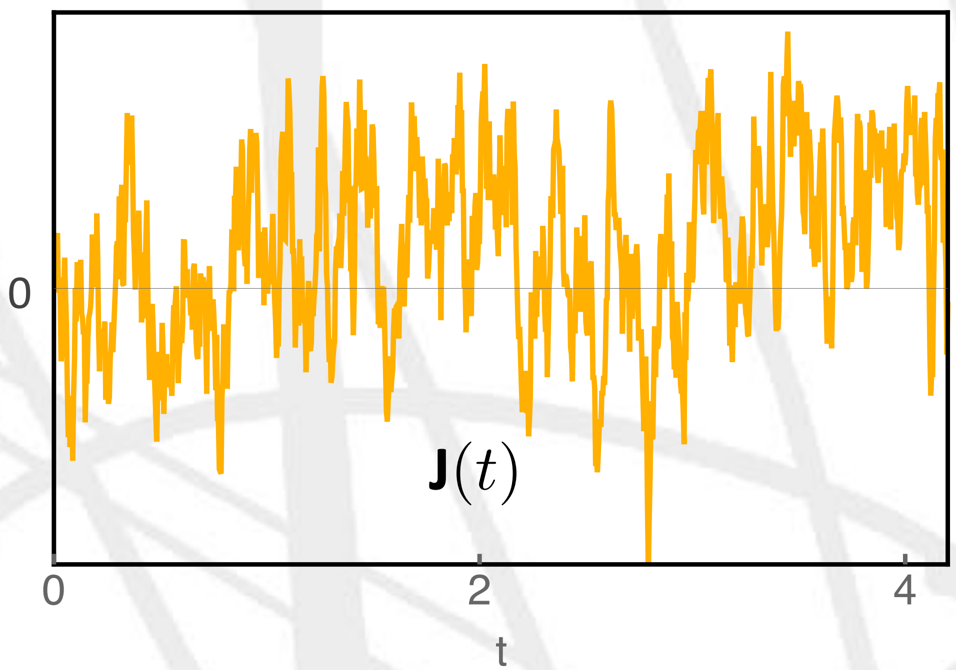

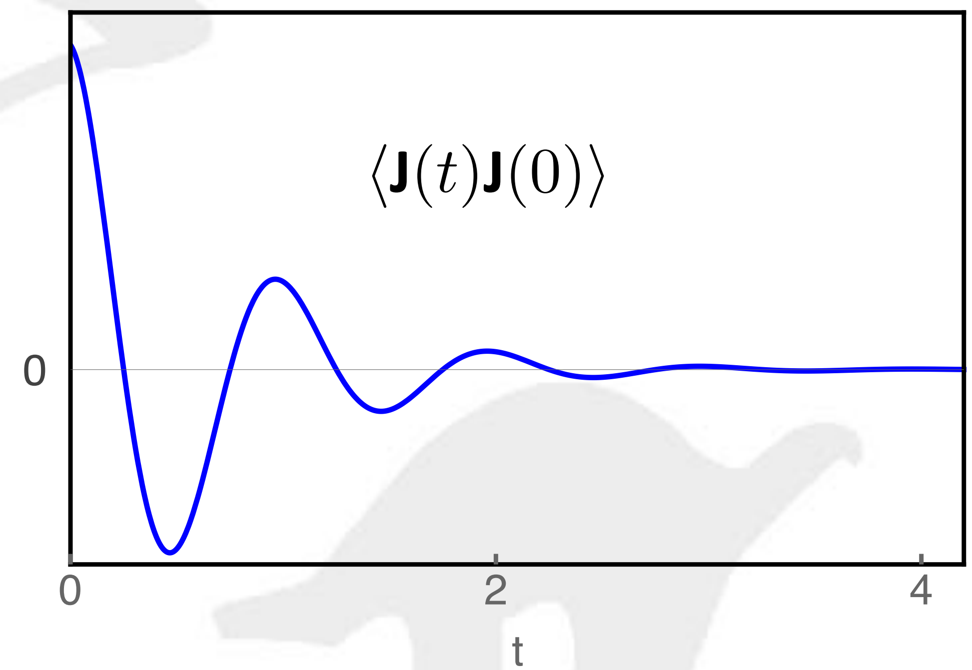

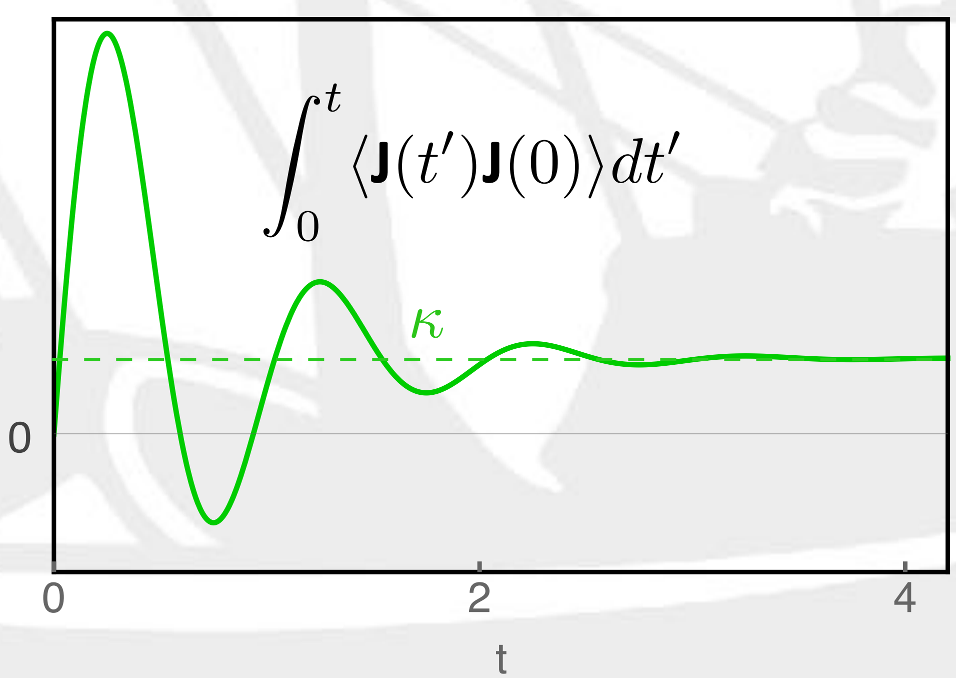

$$\left\langle \left| \int_0^t \mathbf{J}(t')dt' \right|^2 \right\rangle \approx 2t \int_0^\infty \langle \mathbf{J}(t')\mathbf{J}(0)\rangle dt'$$

Green-Kubo *vs.* Einstein-Helfand

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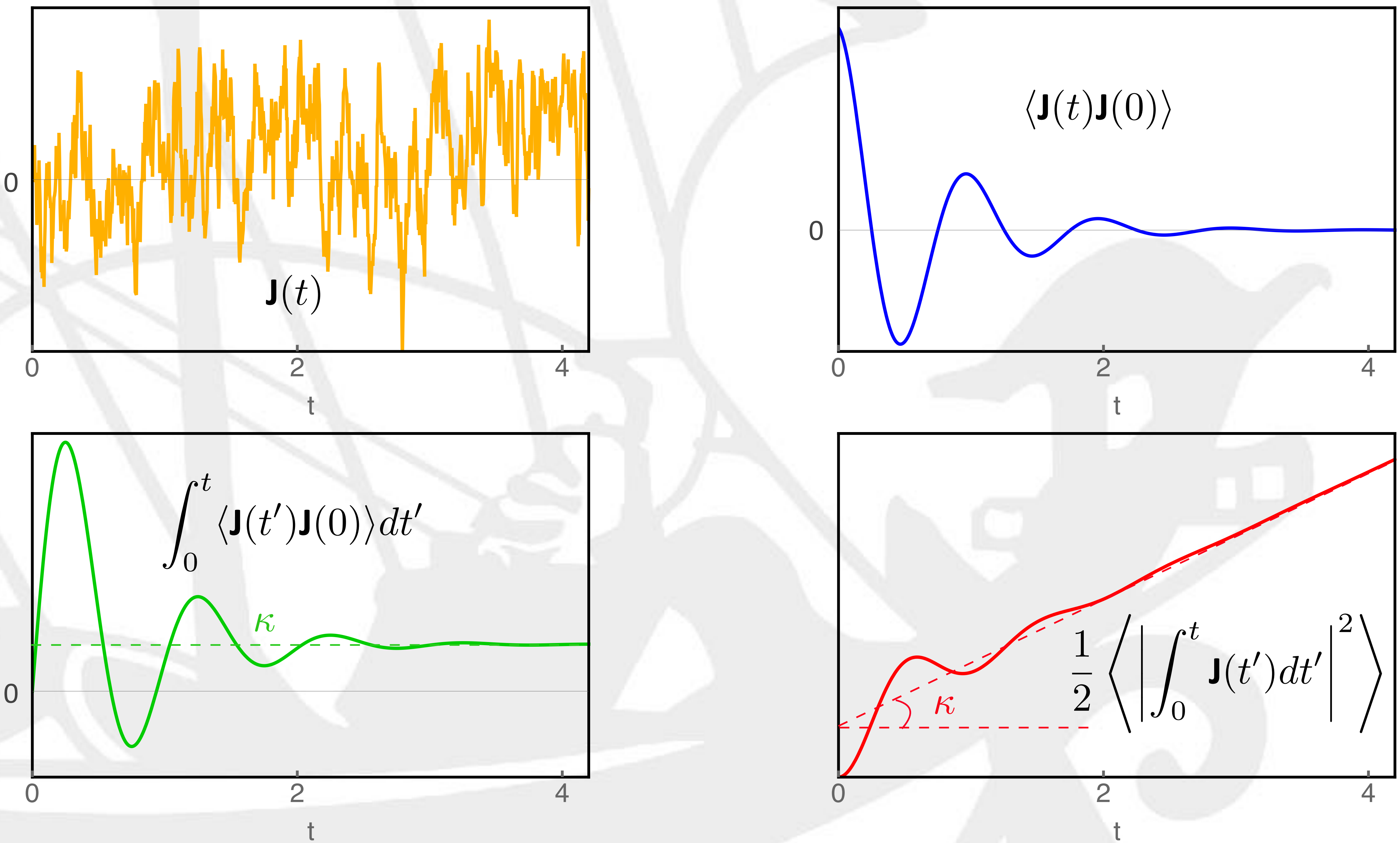
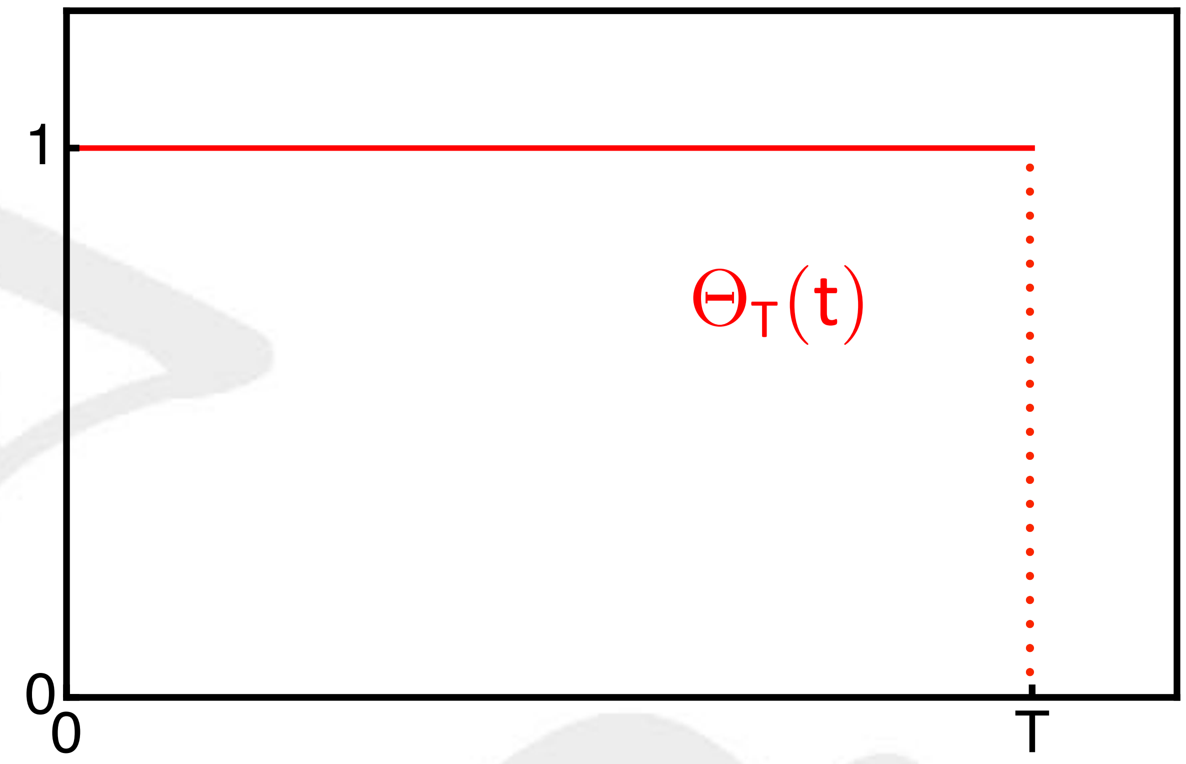


Einstein *vs.* Green-Kubo

$$\kappa_{\mathsf{GK}}(\mathsf{T}) = \int_0^{\mathsf{T}} \langle \mathsf{v}(\mathsf{t})\mathsf{v}(0)\rangle \mathsf{dt}$$

Einstein *vs.* Green-Kubo

$$\kappa_{GK}(T) = \int_0^T \langle v(t)v(0)\rangle dt$$
$$= \int_0^\infty \langle v(t)v(0)\rangle \Theta_T(t) dt$$



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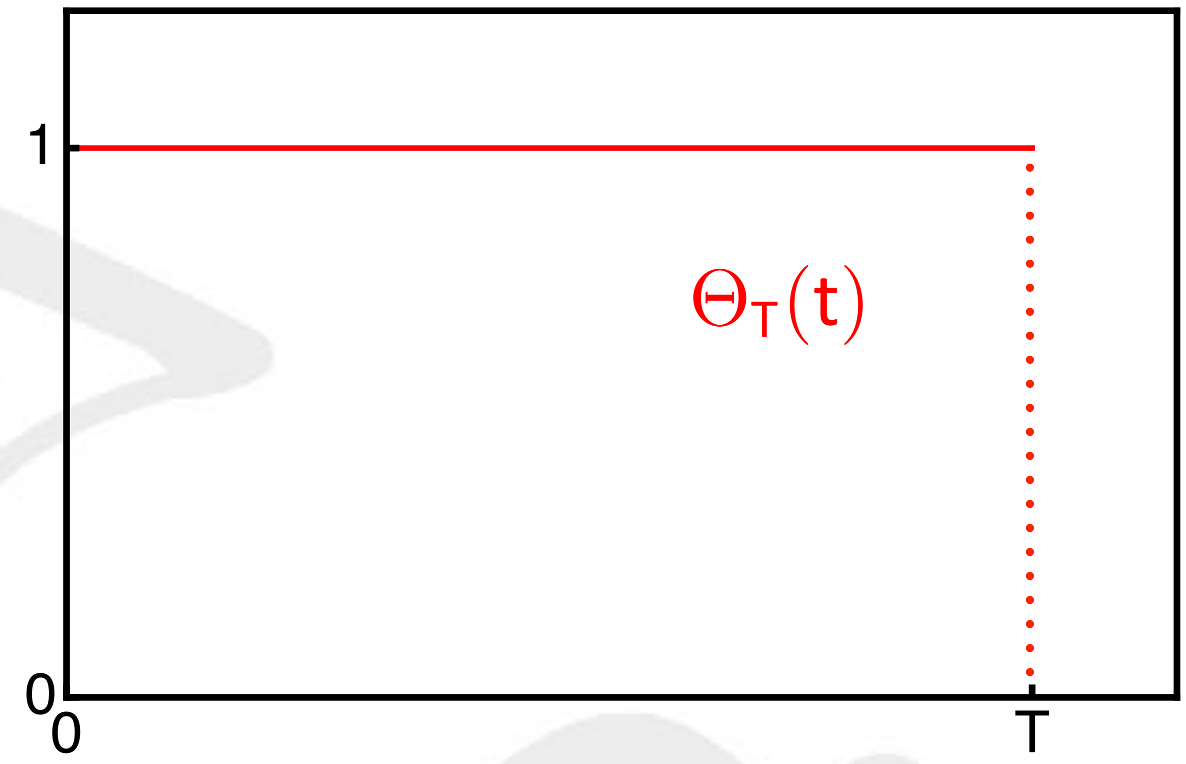

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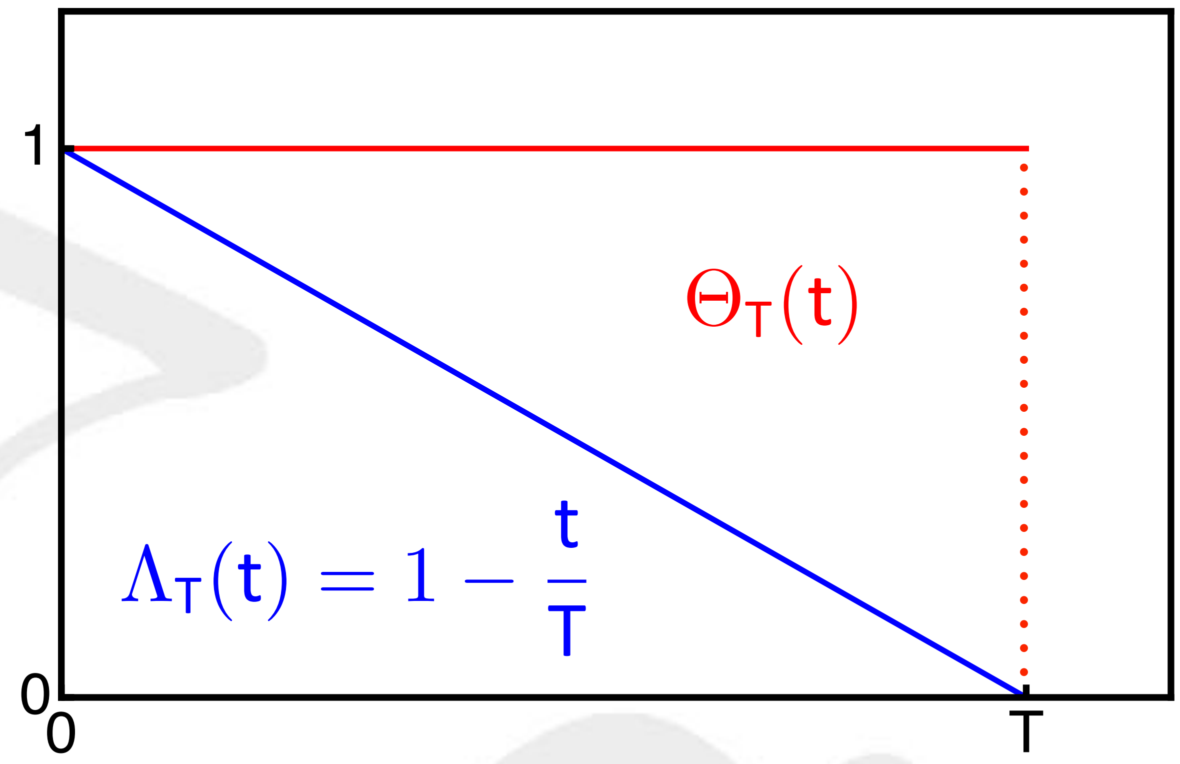

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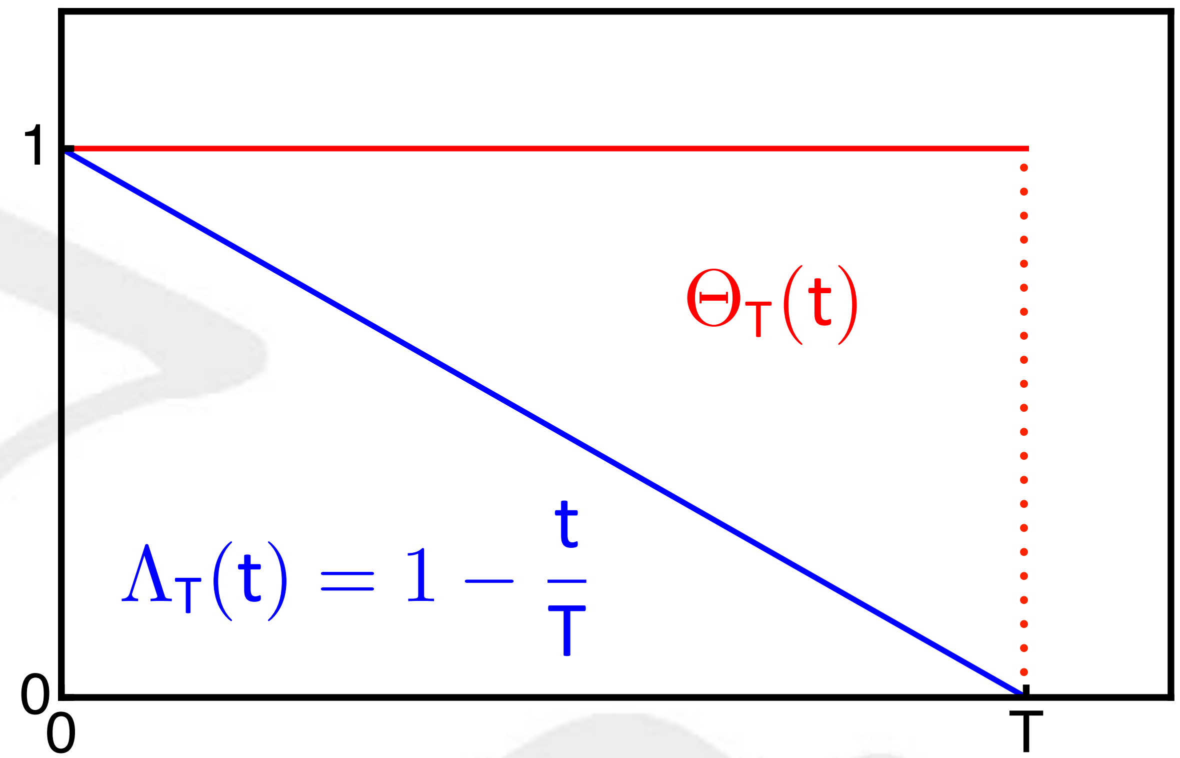

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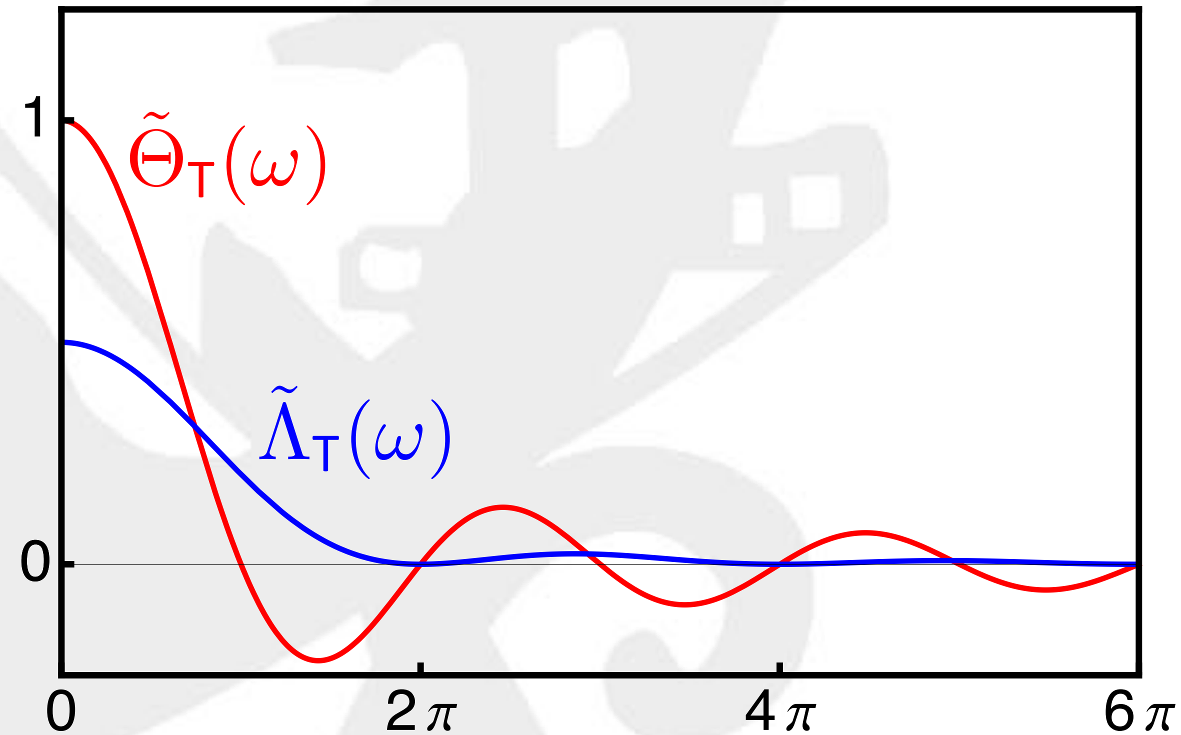

separating wheat from chaff

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

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

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

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

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the Wiener-Khintchine theorem

$$S(\omega) = \lim_{T\to\infty} \left\langle \left| \frac{1}{T} \int_{-\frac{T}{2}}^{\frac{T}{2}} J(t)\mathrm{e}^{i\omega t} \right|^2 \right\rangle$$

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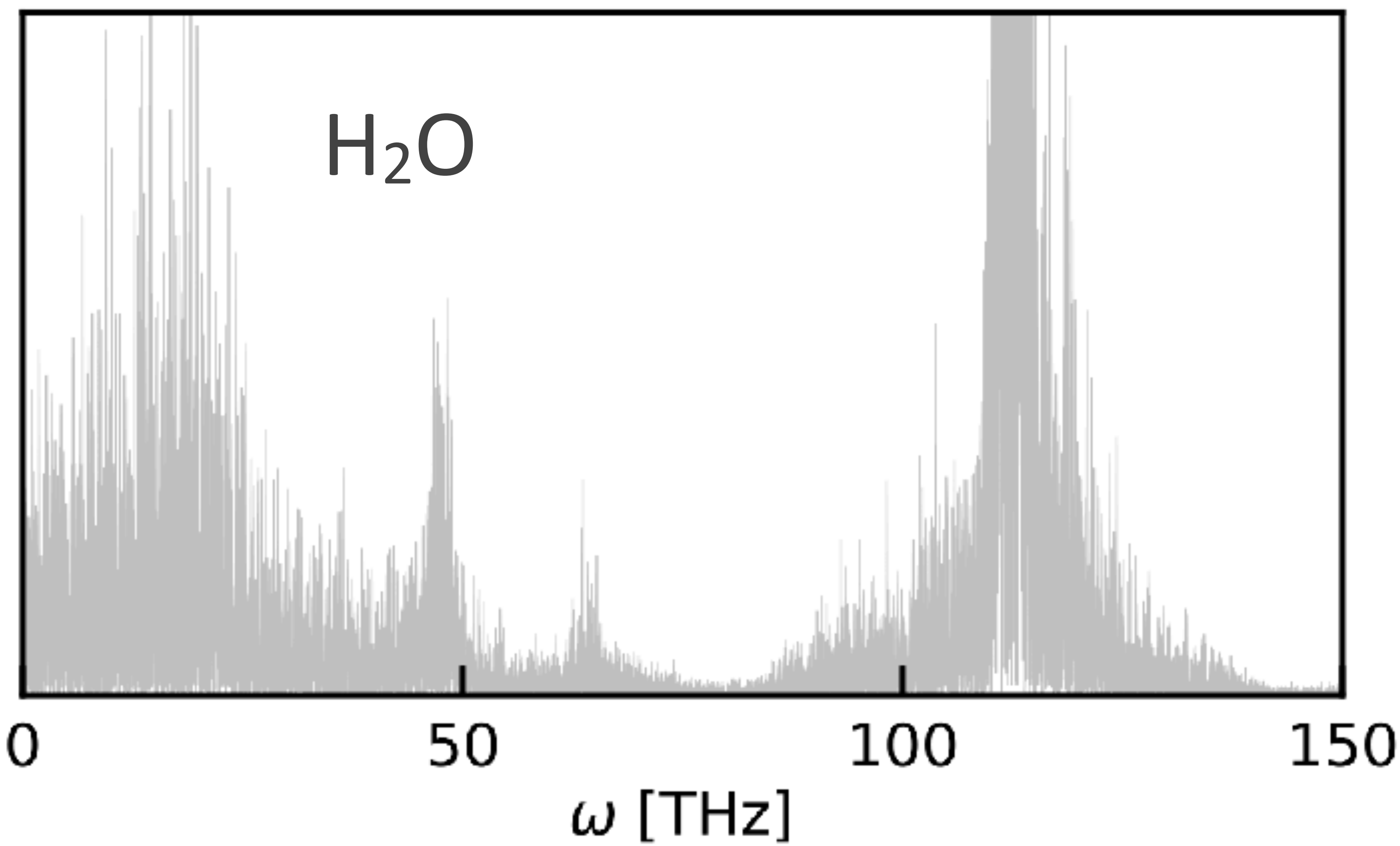
in practice:

$$S\left(\omega_k\right) = \frac{\epsilon}{N} \left\langle \left| \sum_{n=0}^{N-1} J_n \mathrm{e}^{-i\frac{2\pi nk}{N}} \right|^2 \right\rangle$$

separating wheat from chaff

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



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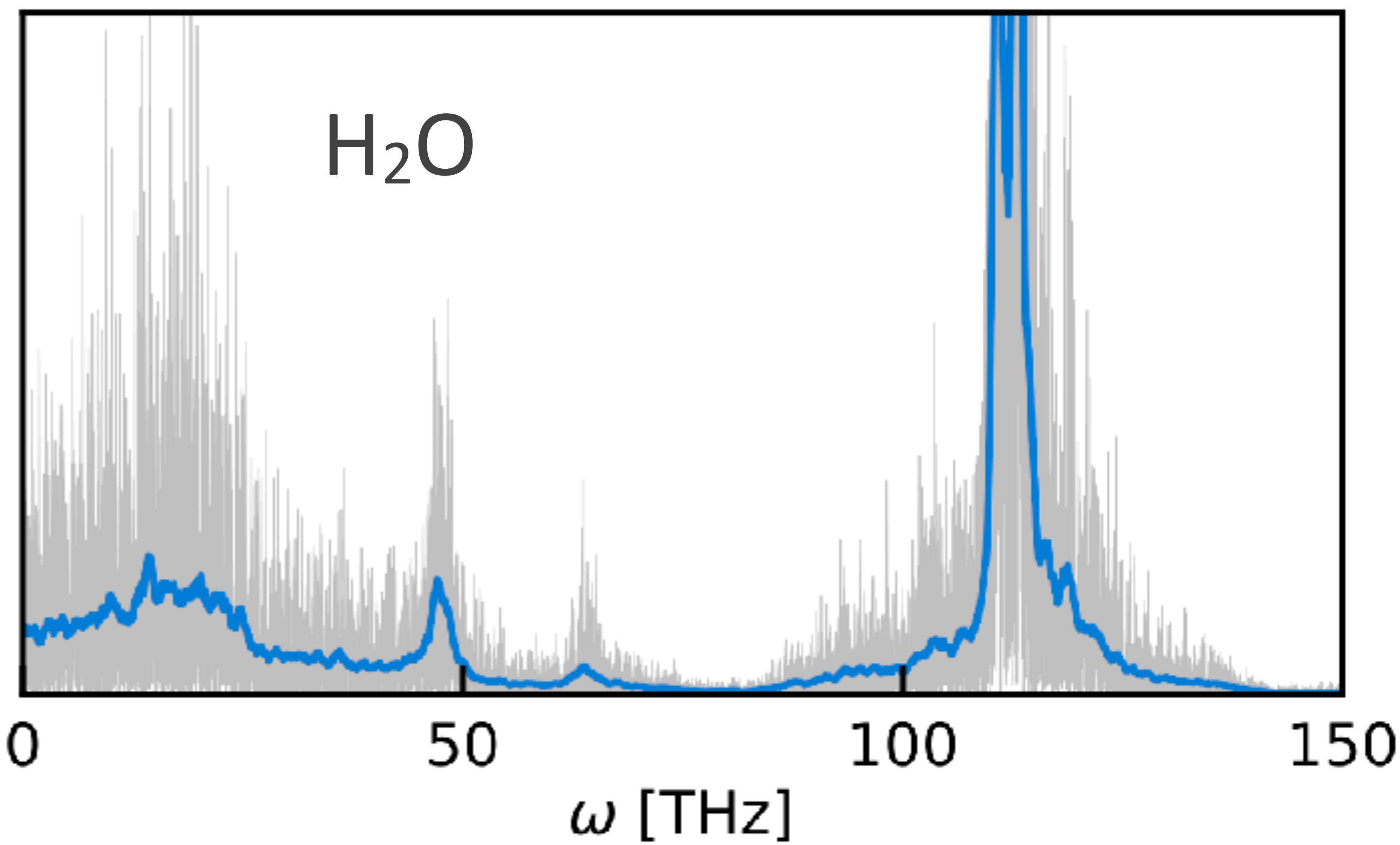

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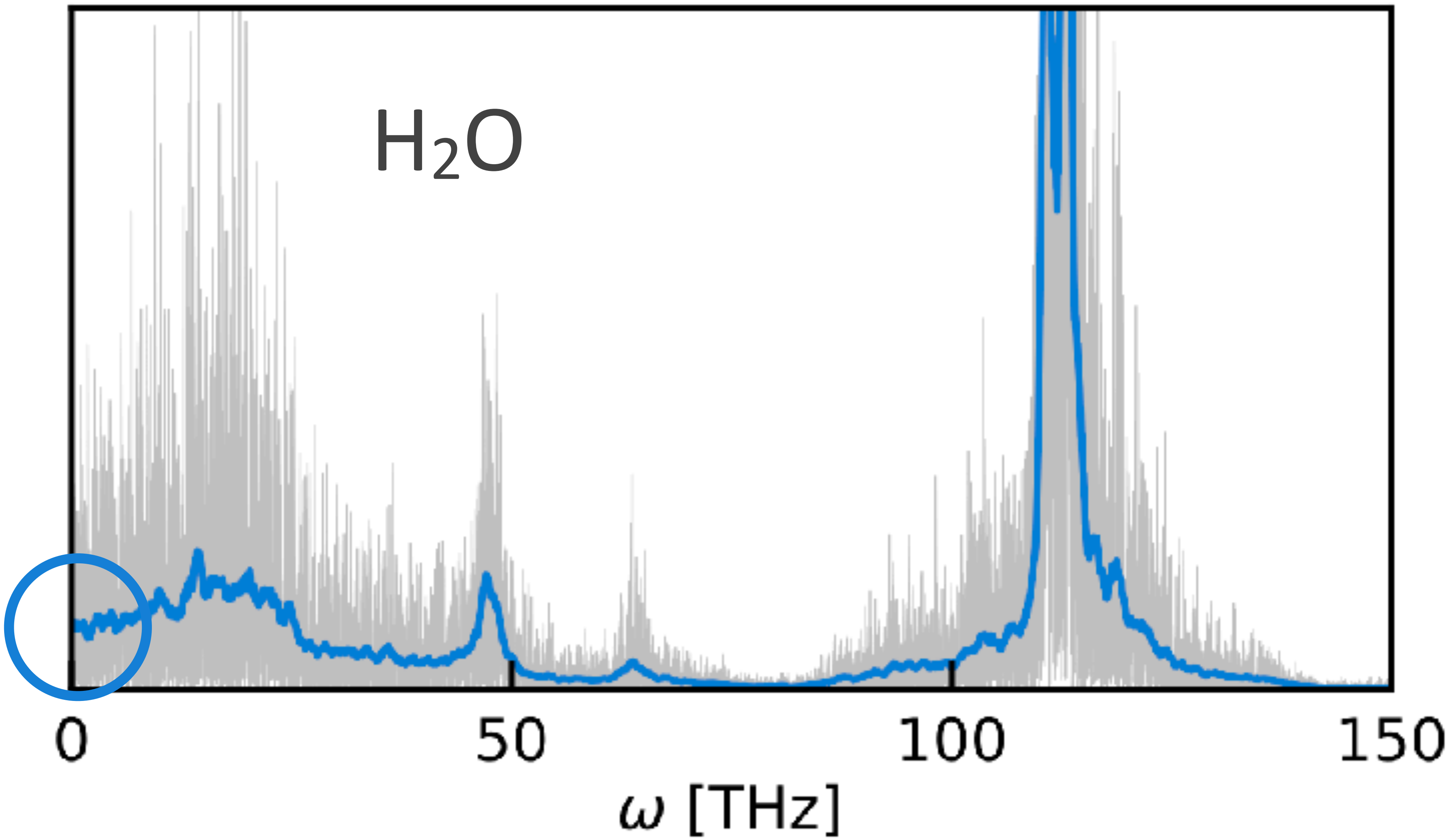

separating wheat from chaff

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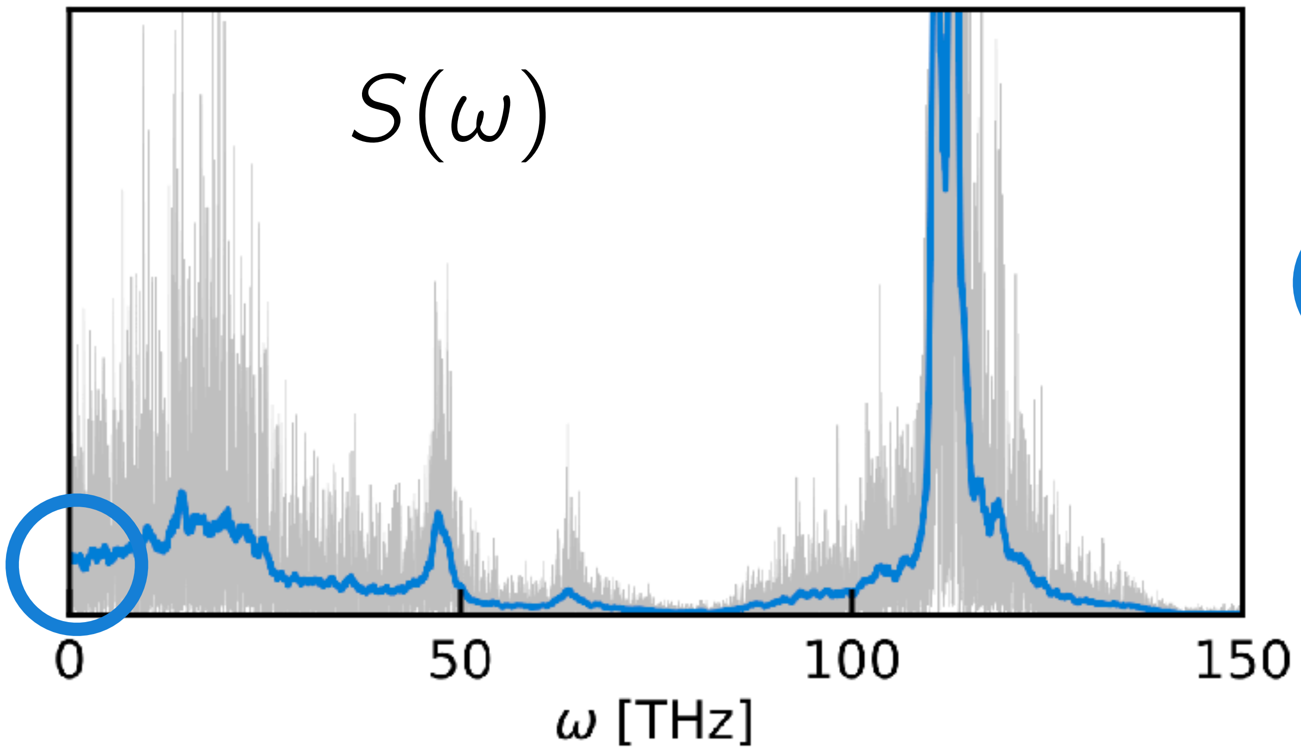

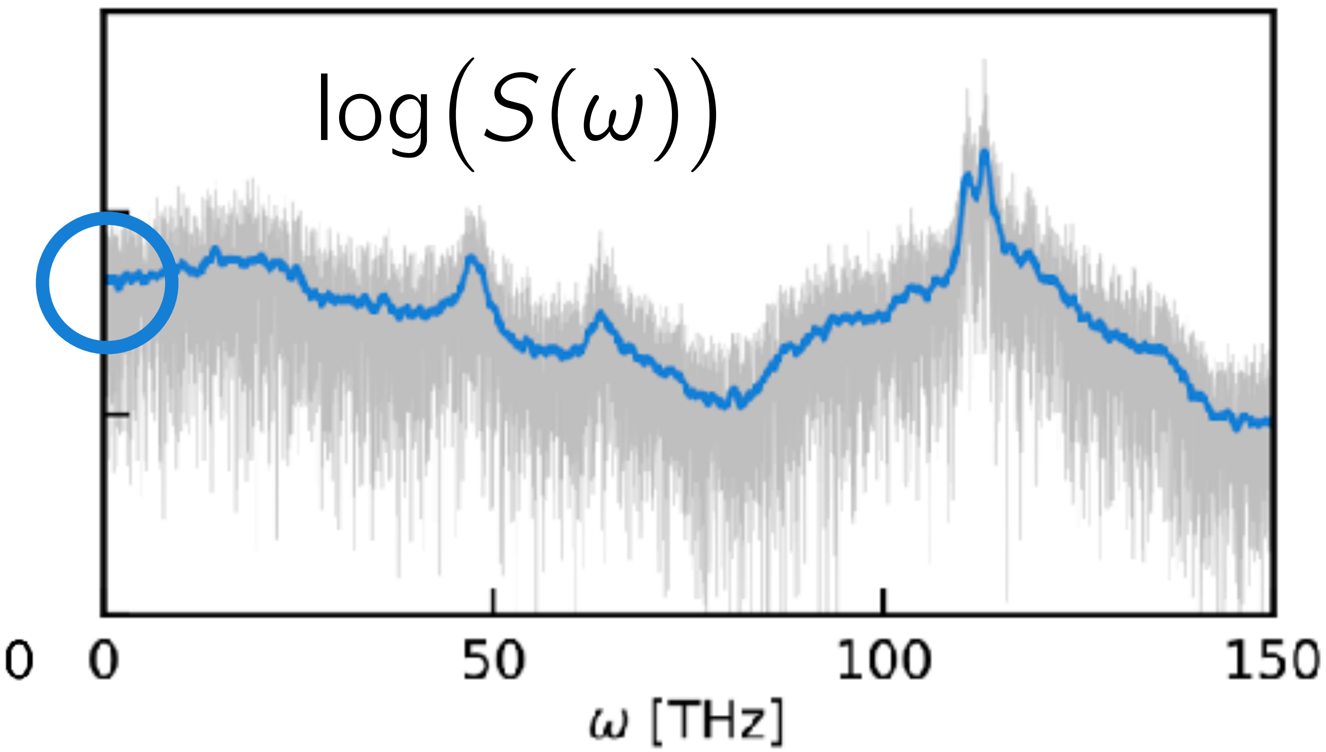

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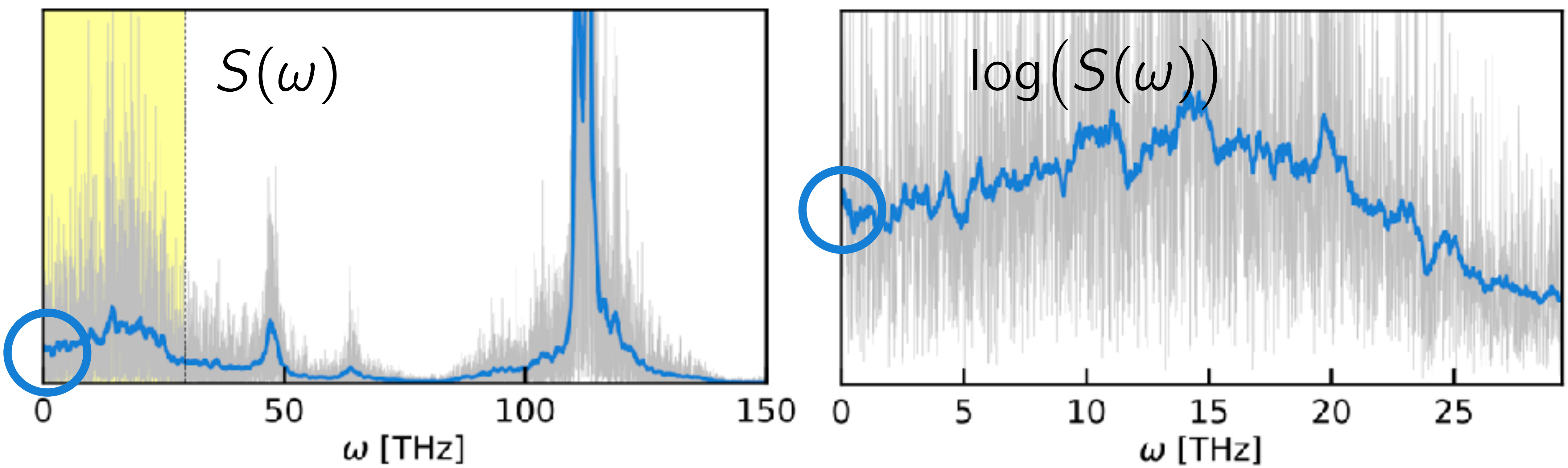

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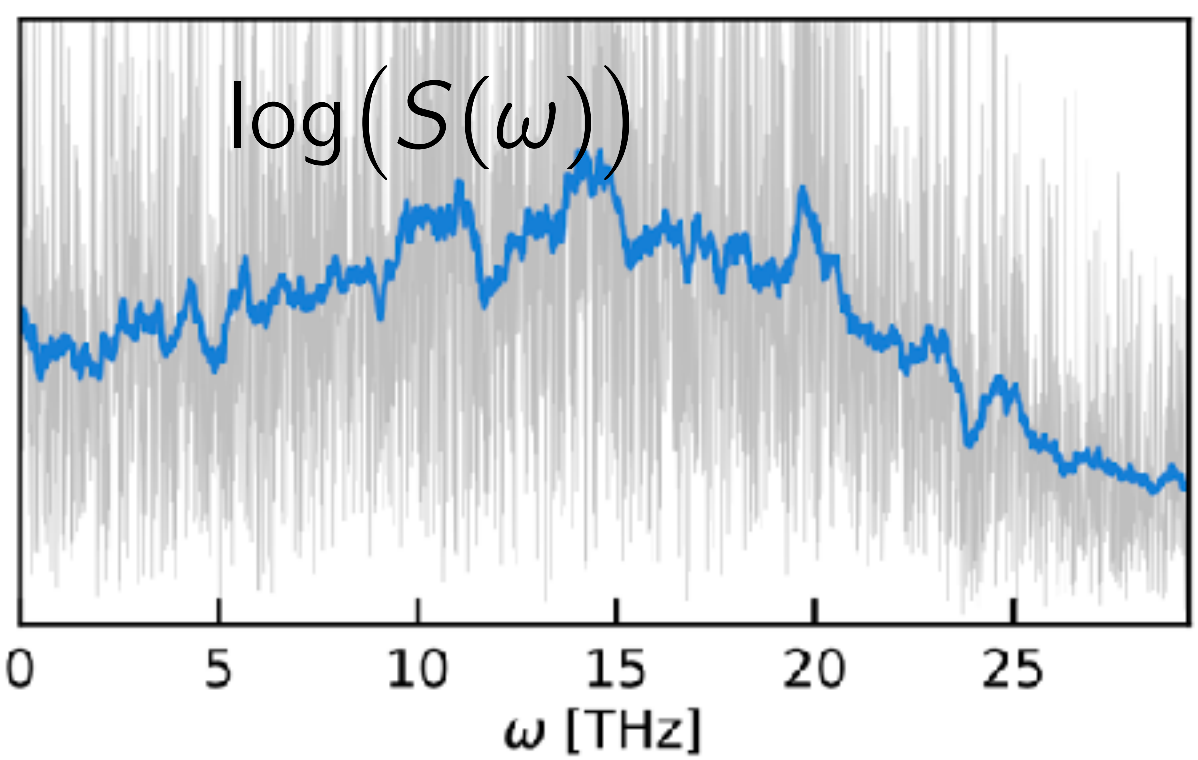

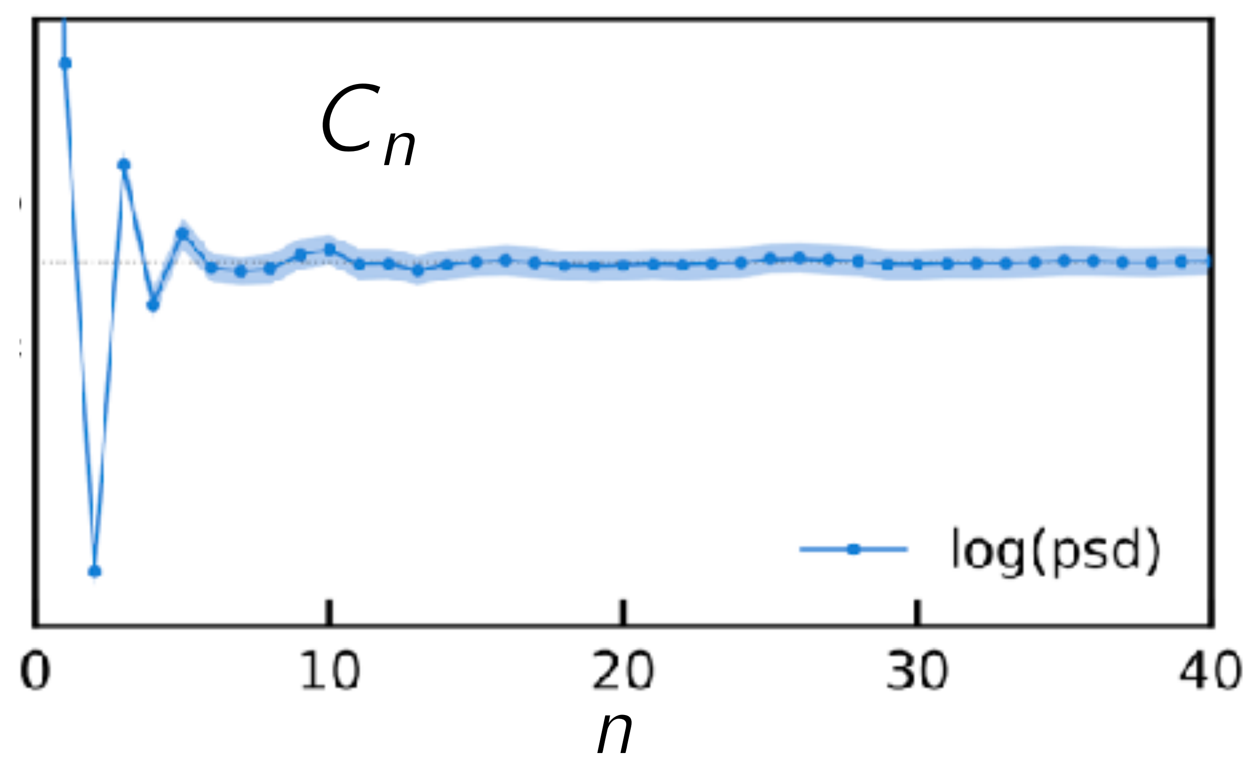

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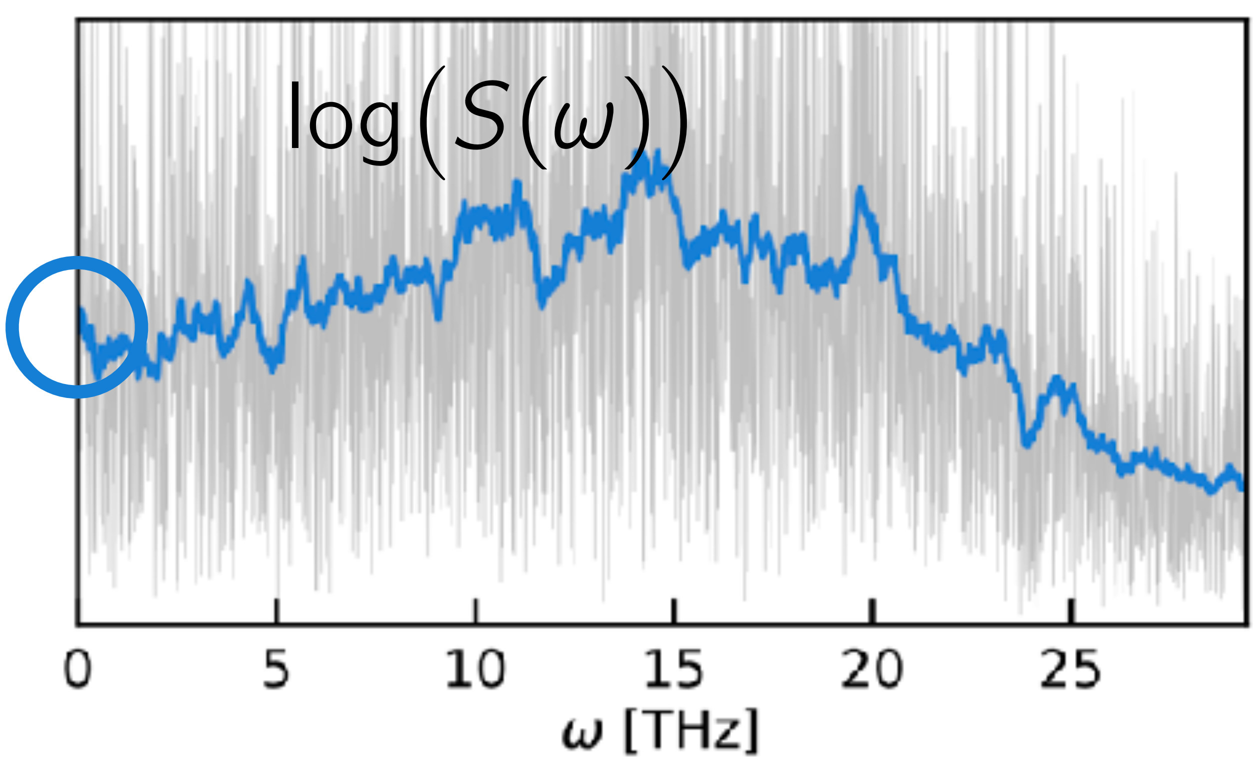

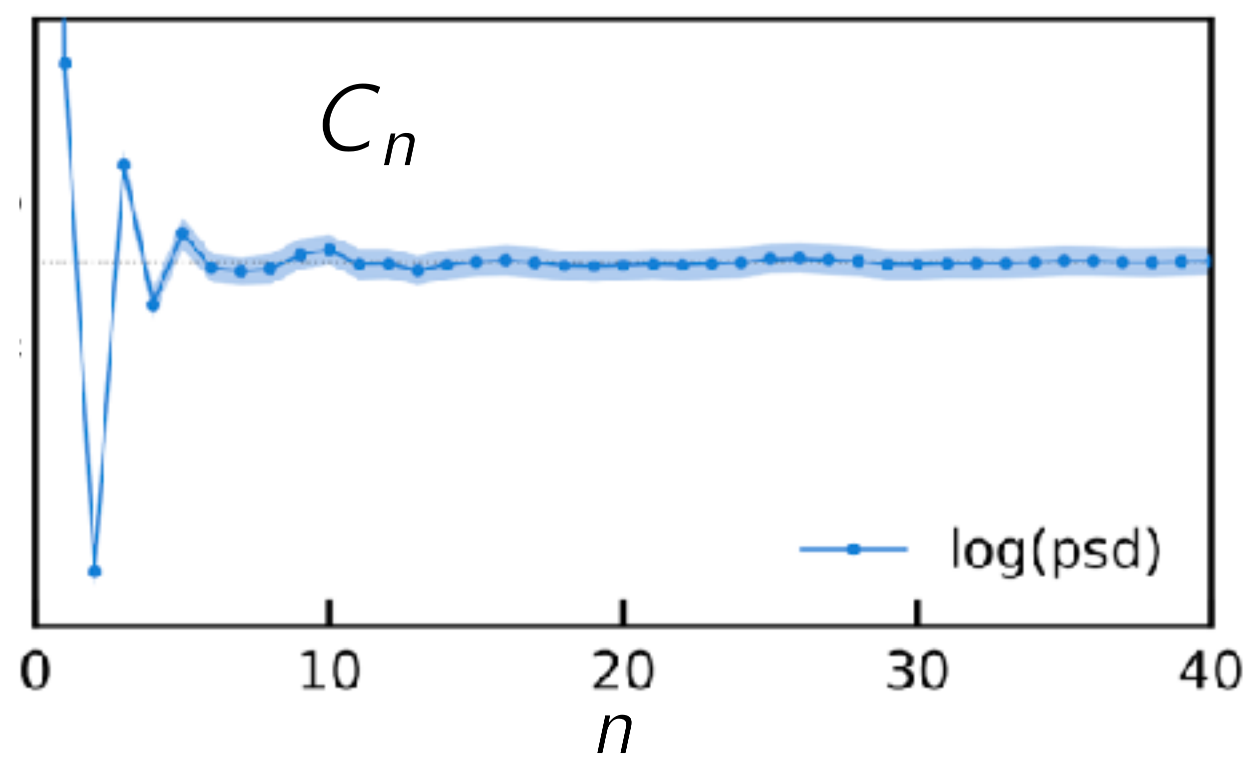

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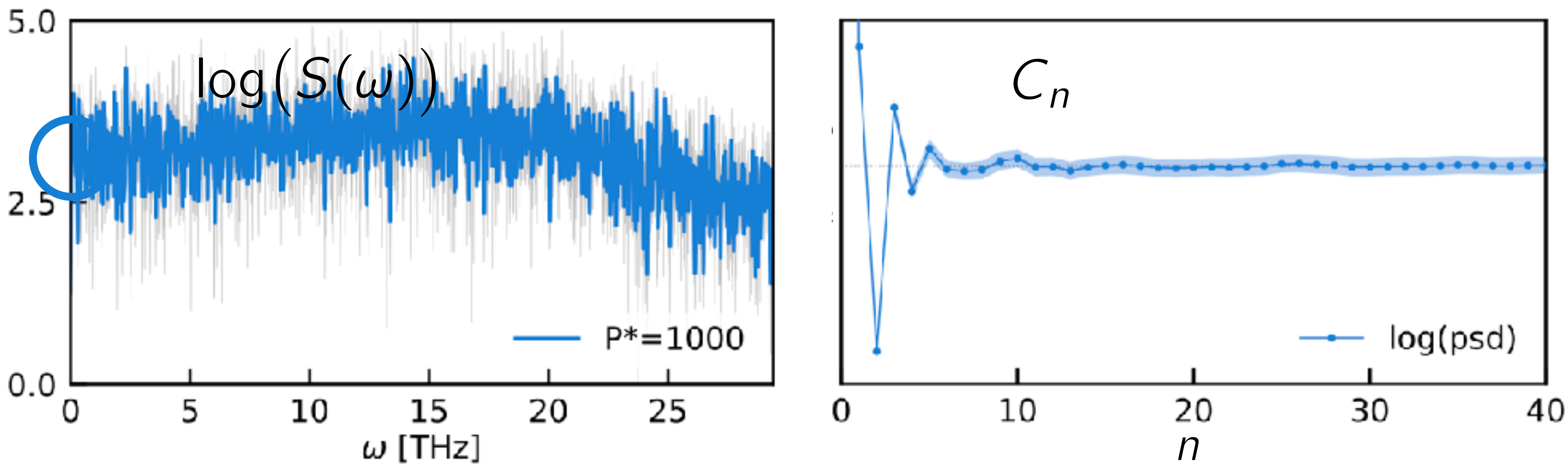

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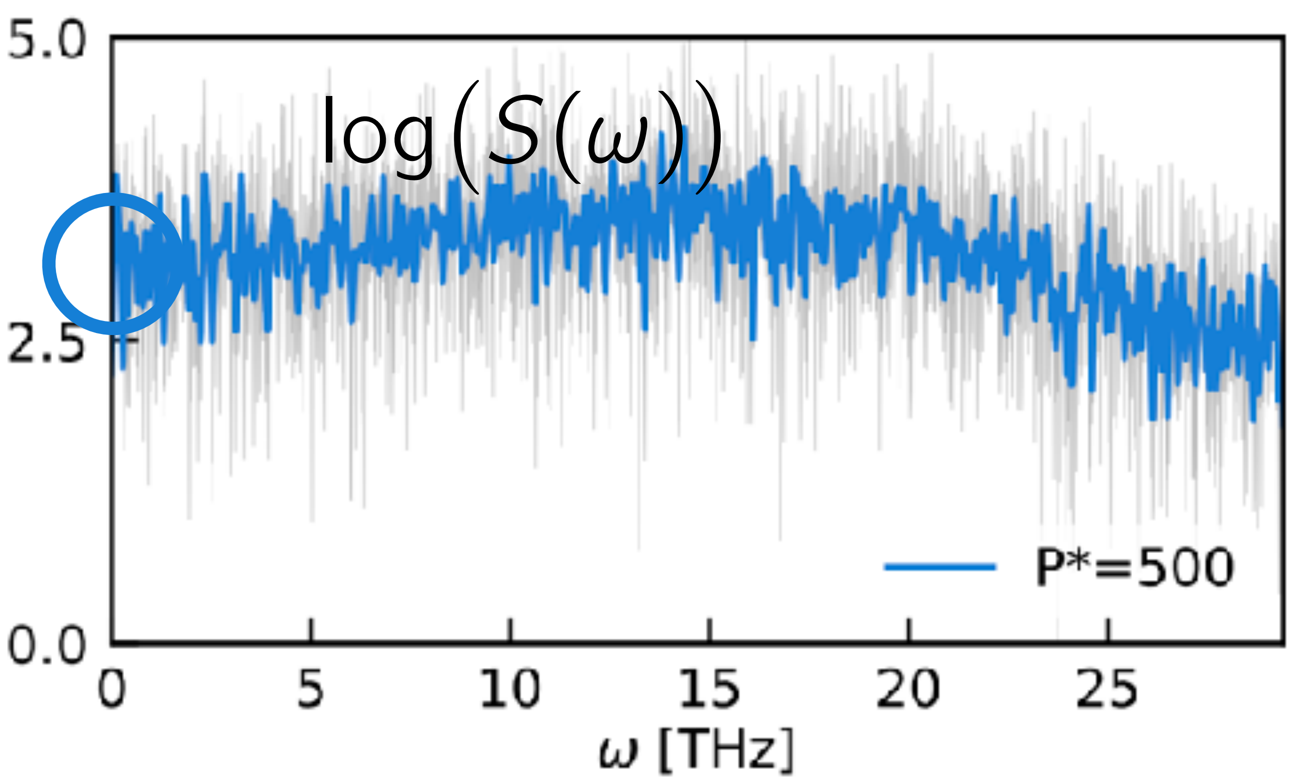

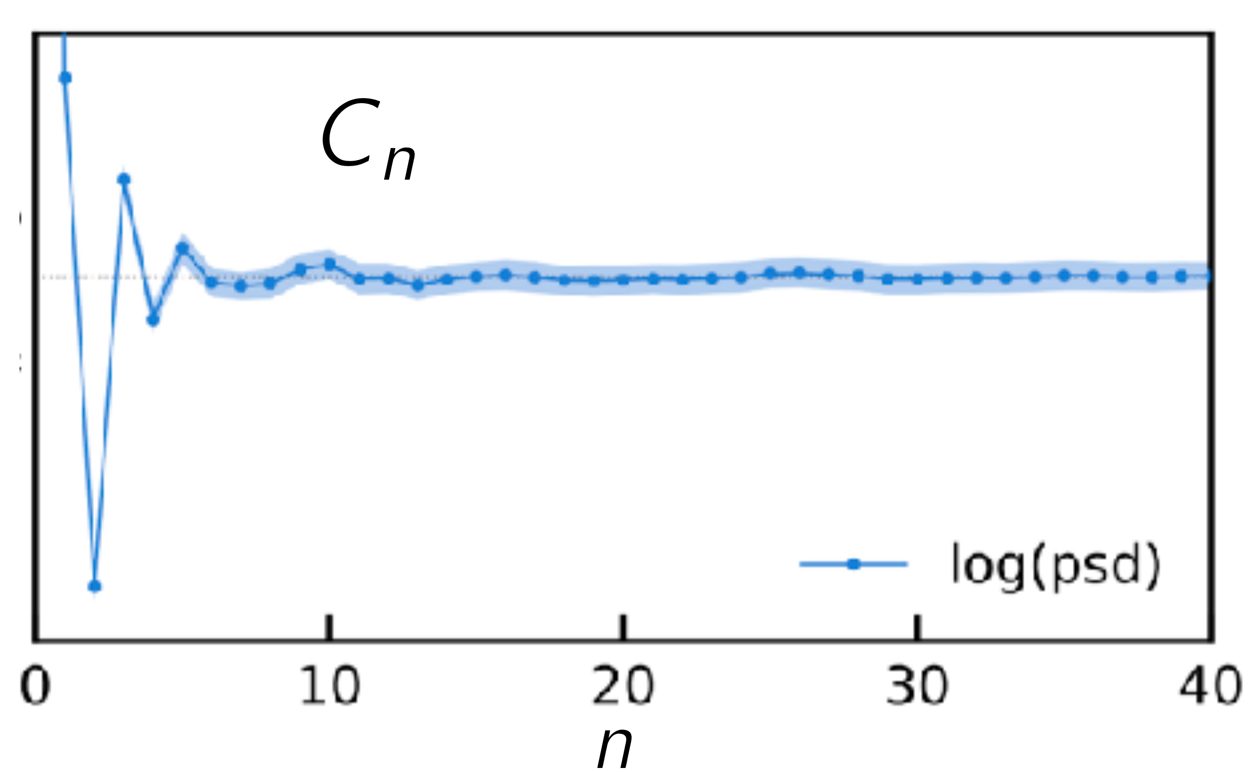

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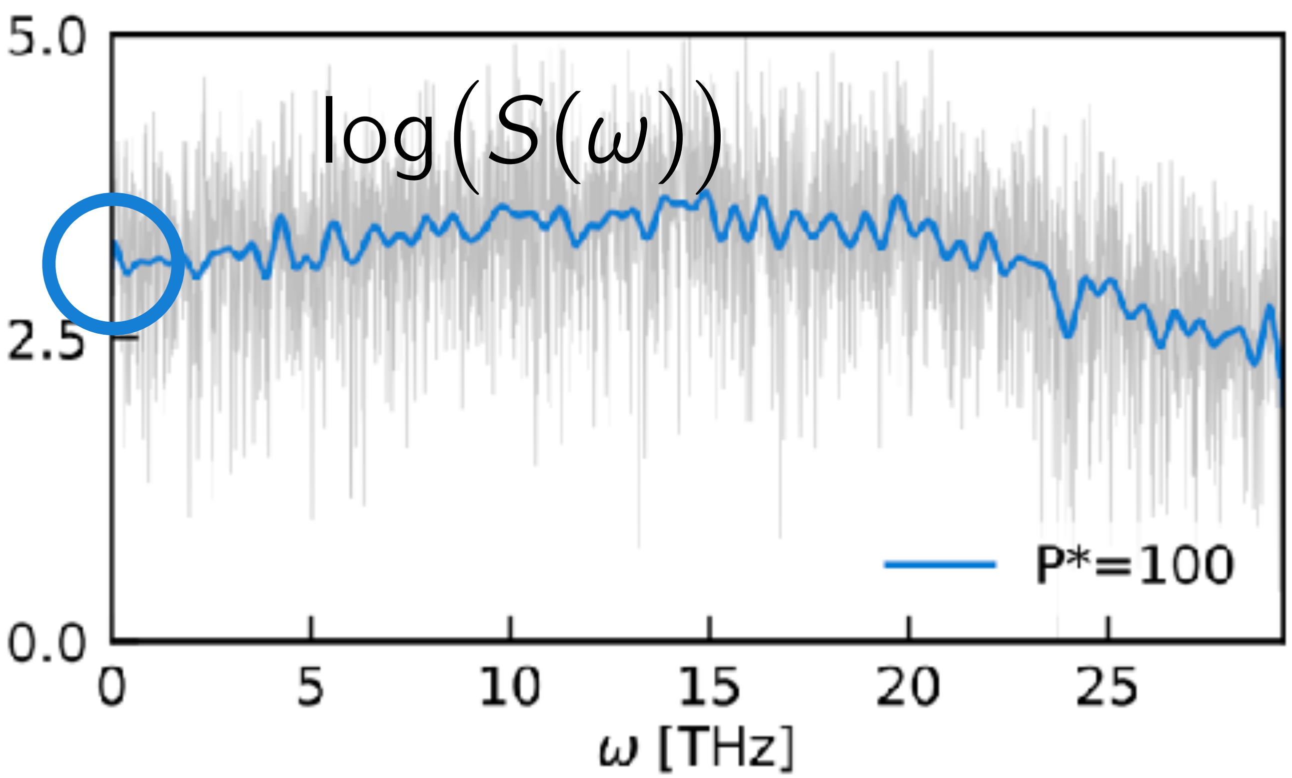

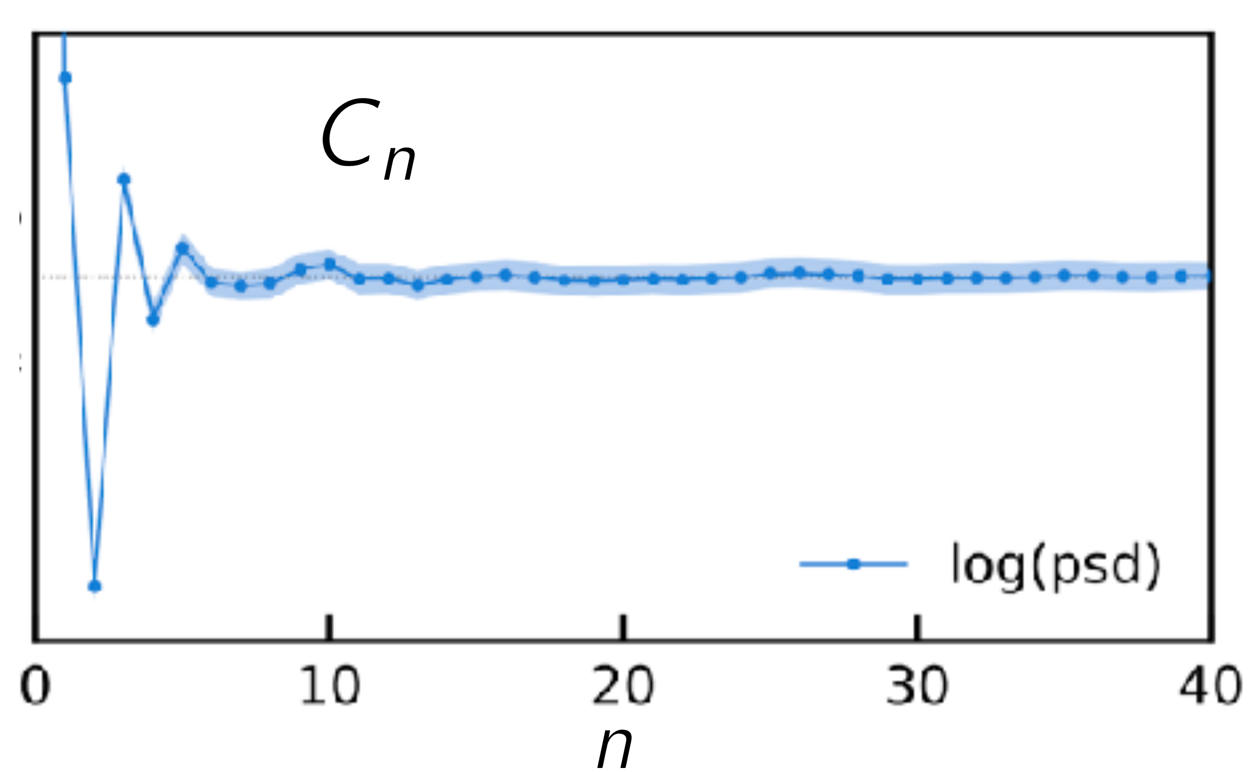

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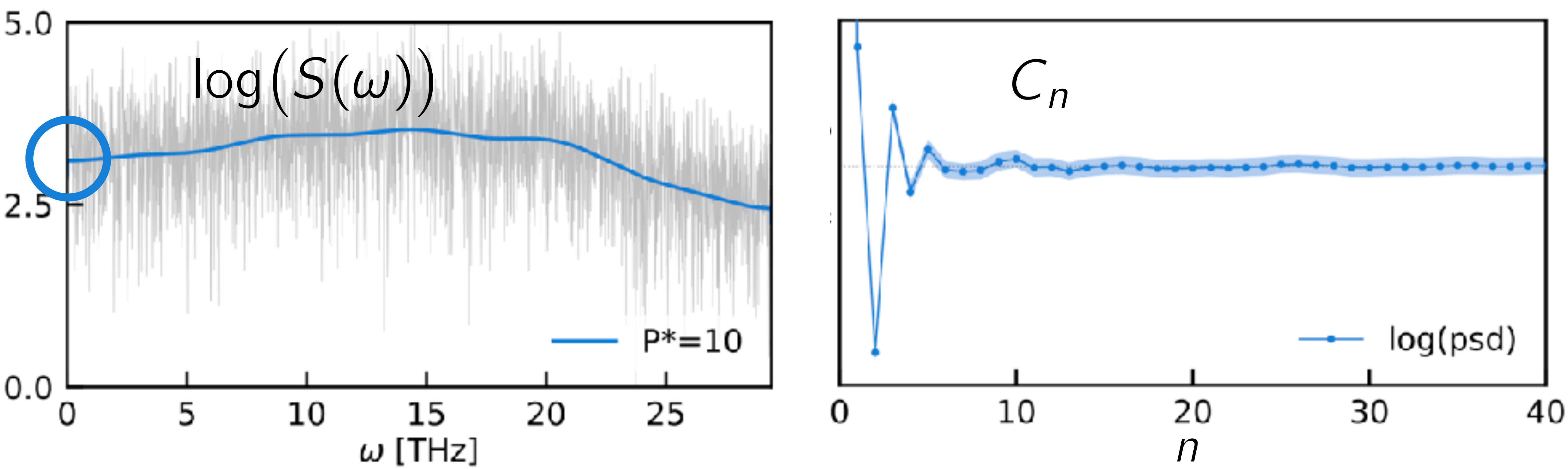

separating wheat from chaff

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constants independent of the time series being sampled

separating wheat from chaff

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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

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Stephen Stackhouse, Lars Stixrude, and Bijaya B. Karki

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

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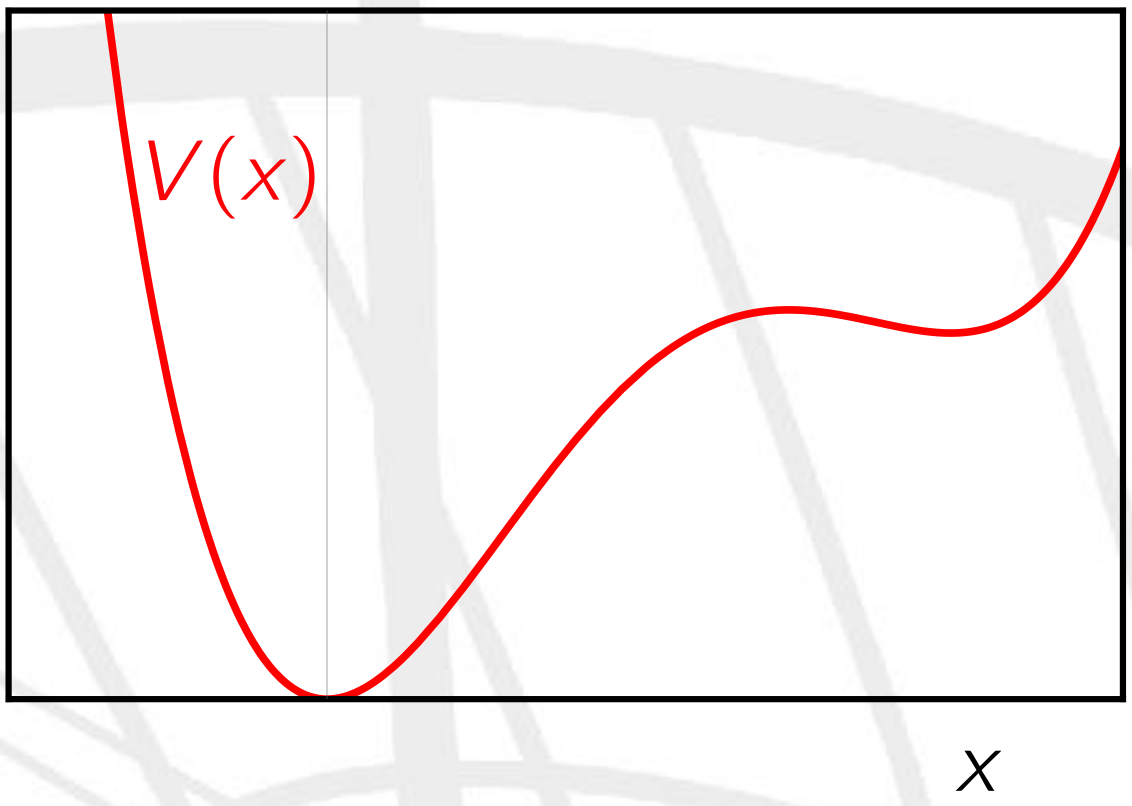
do BTE!

what about glasses and alloys?

Lattice dynamics in the harmonic approximation



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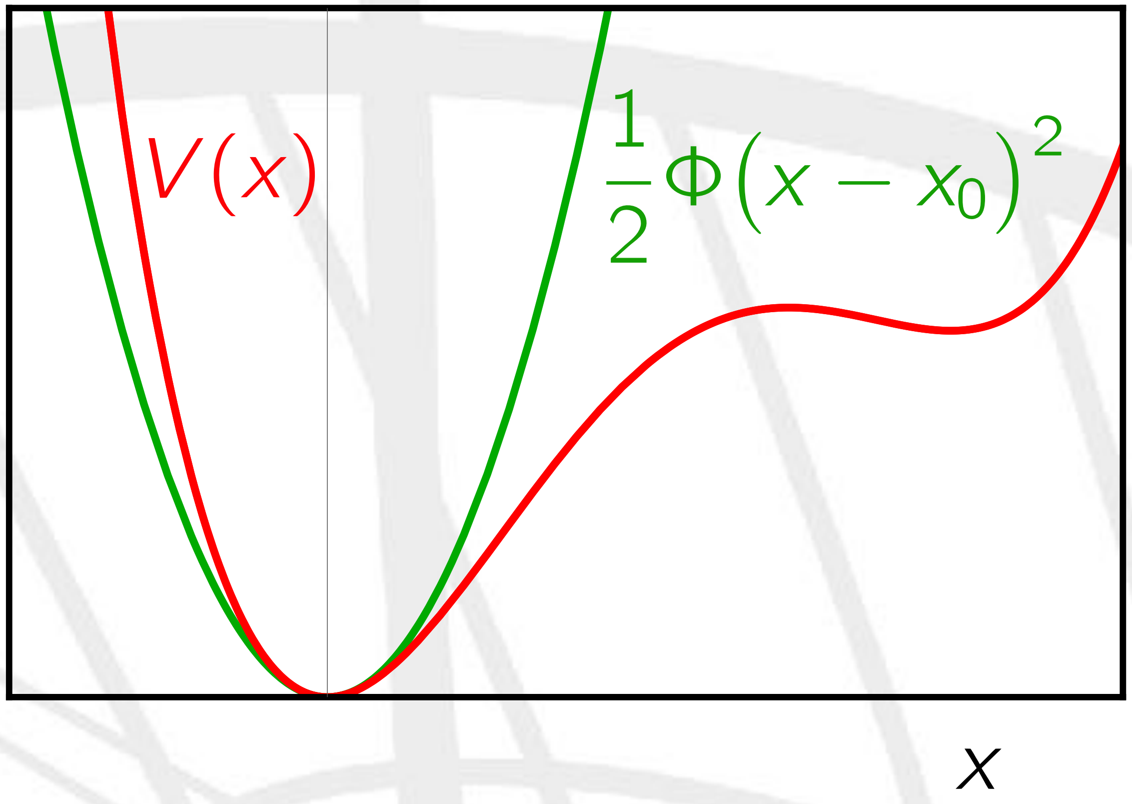
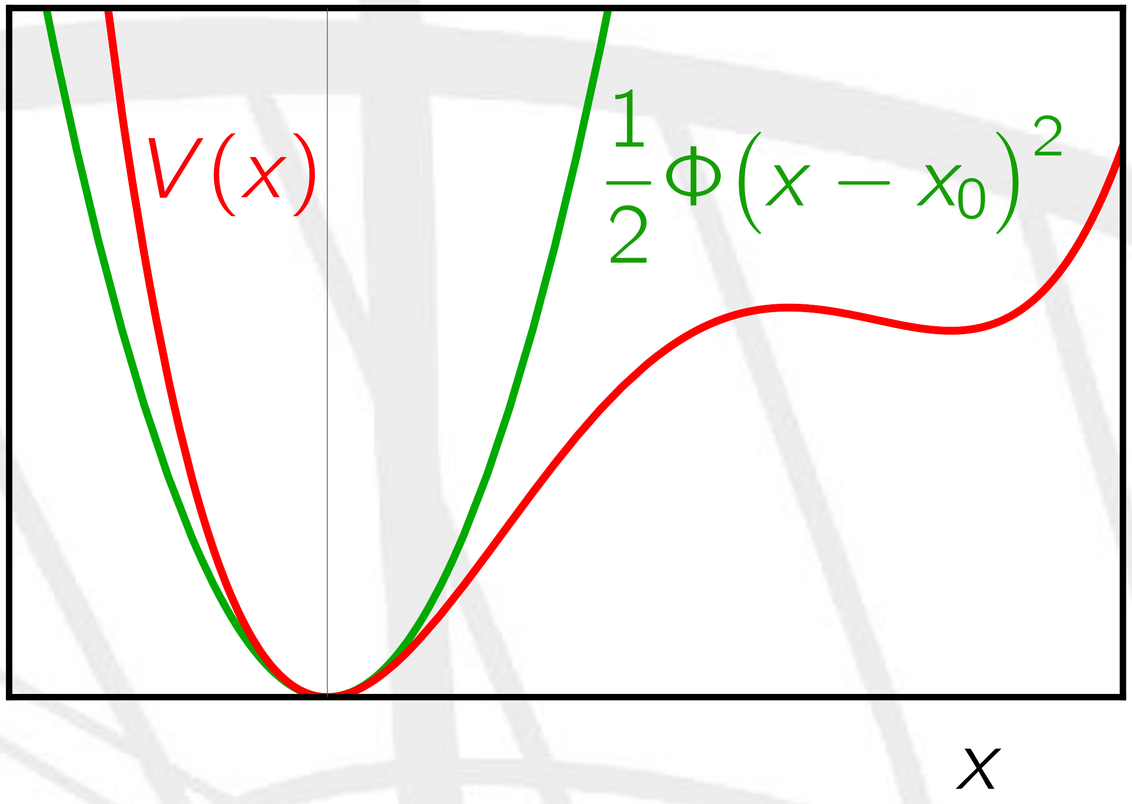
Lattice dynamics in the harmonic approximation



$$M\ddot{x} = -\frac{\partial V}{\partial x}$$

$$V(x_0+u) \approx V(x_0) + \frac{1}{2}\Phi u^2 + \mathcal{O}(u^3)$$

Lattice dynamics in the harmonic approximation



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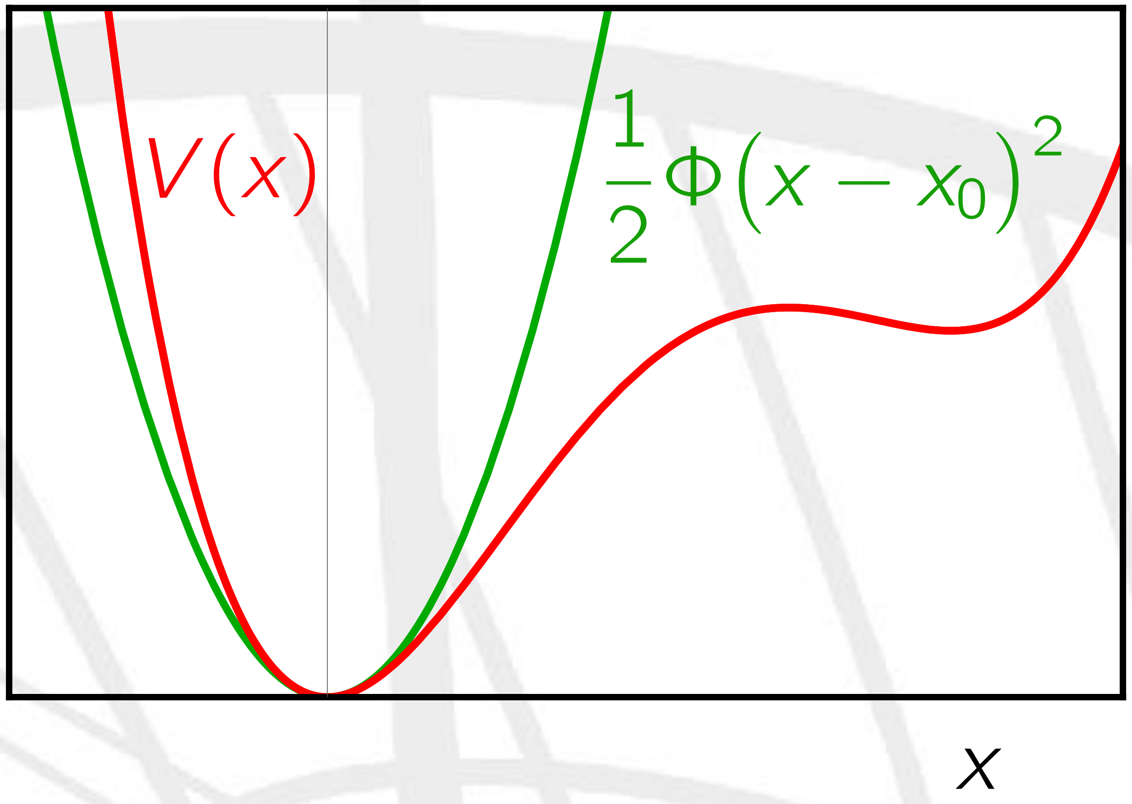

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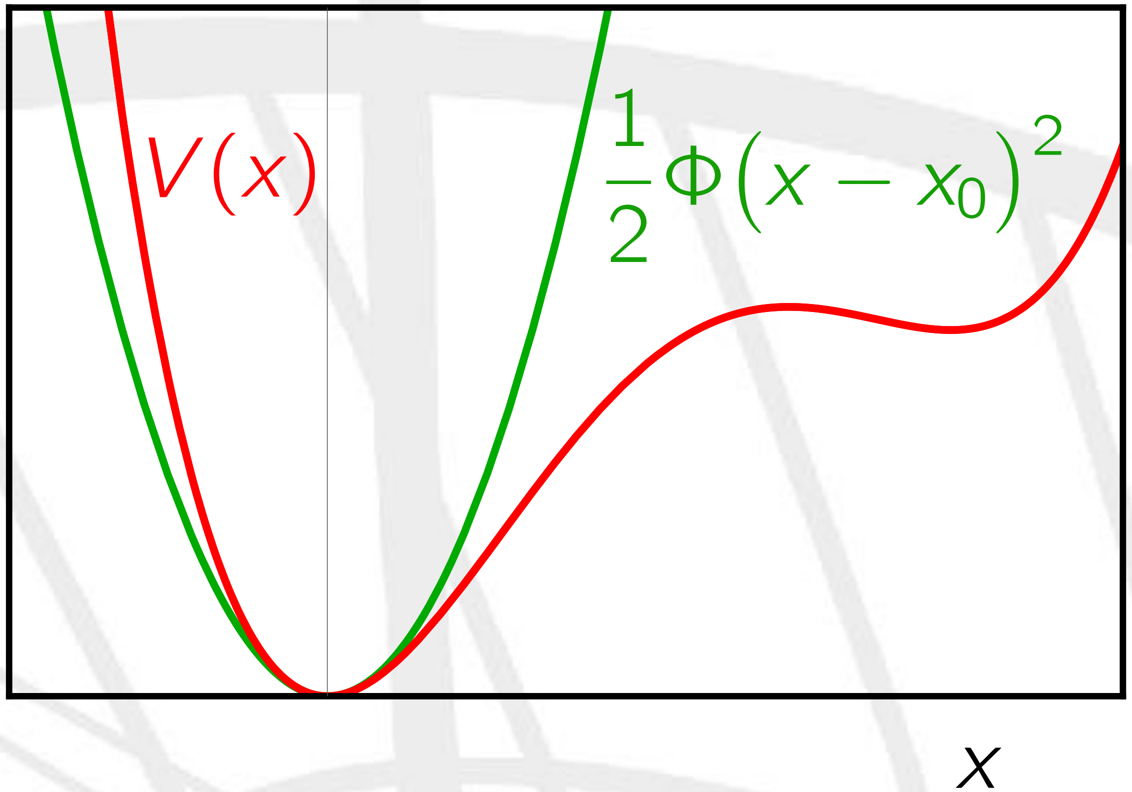

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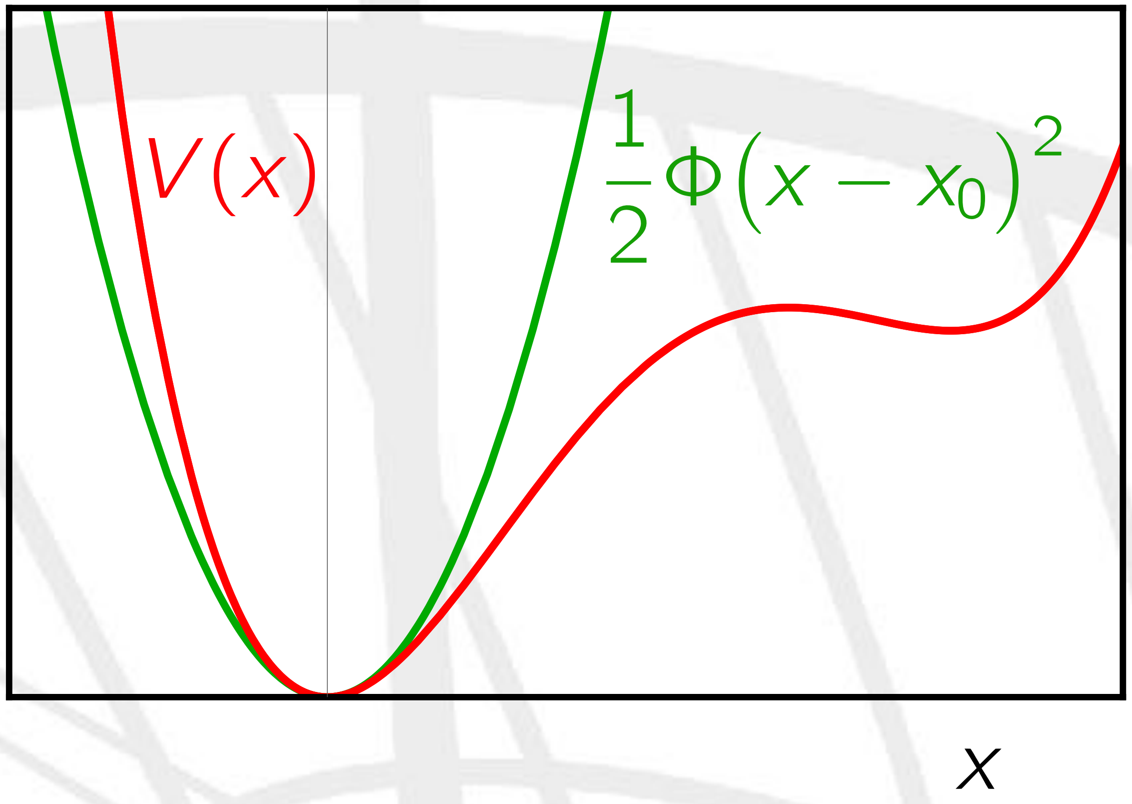

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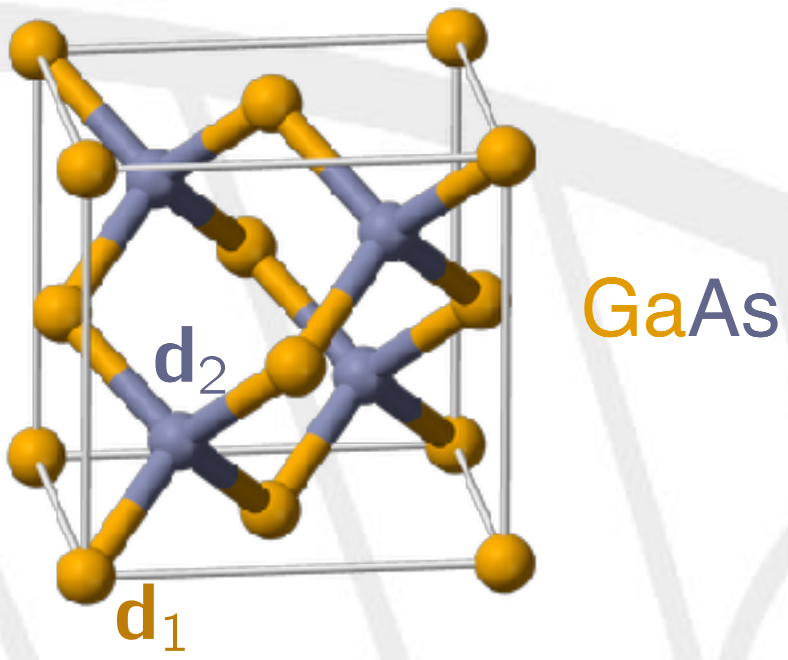
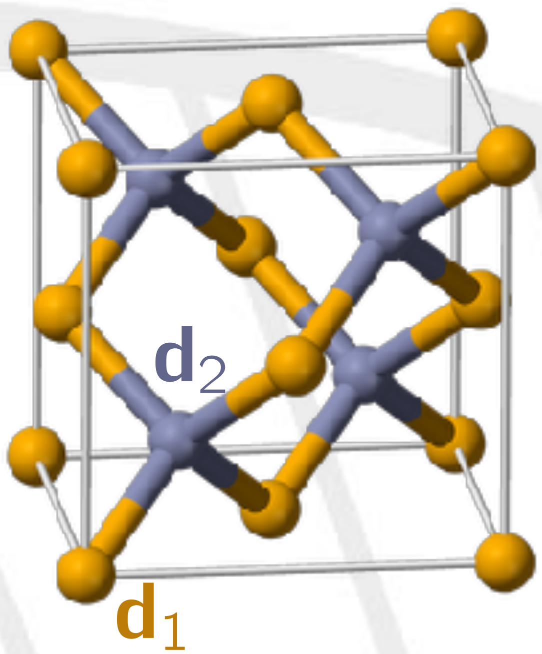
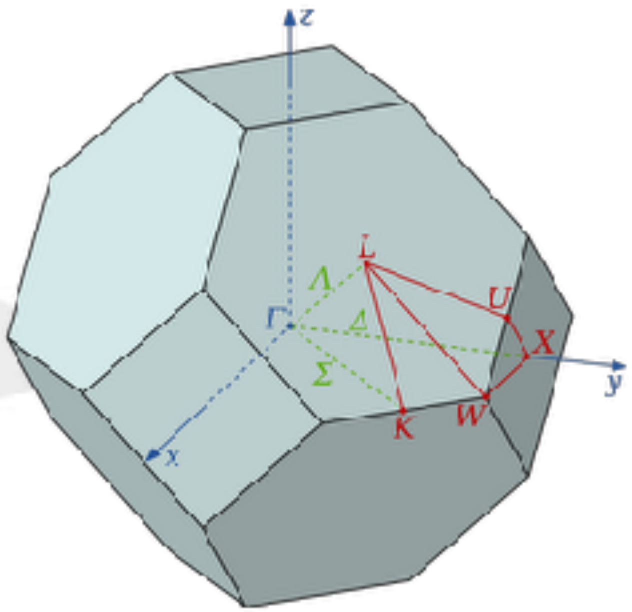
Periodic systems



$$\mathbf{R}_i^\circ = \boldsymbol{\tau}_i + \mathbf{d}_i$$

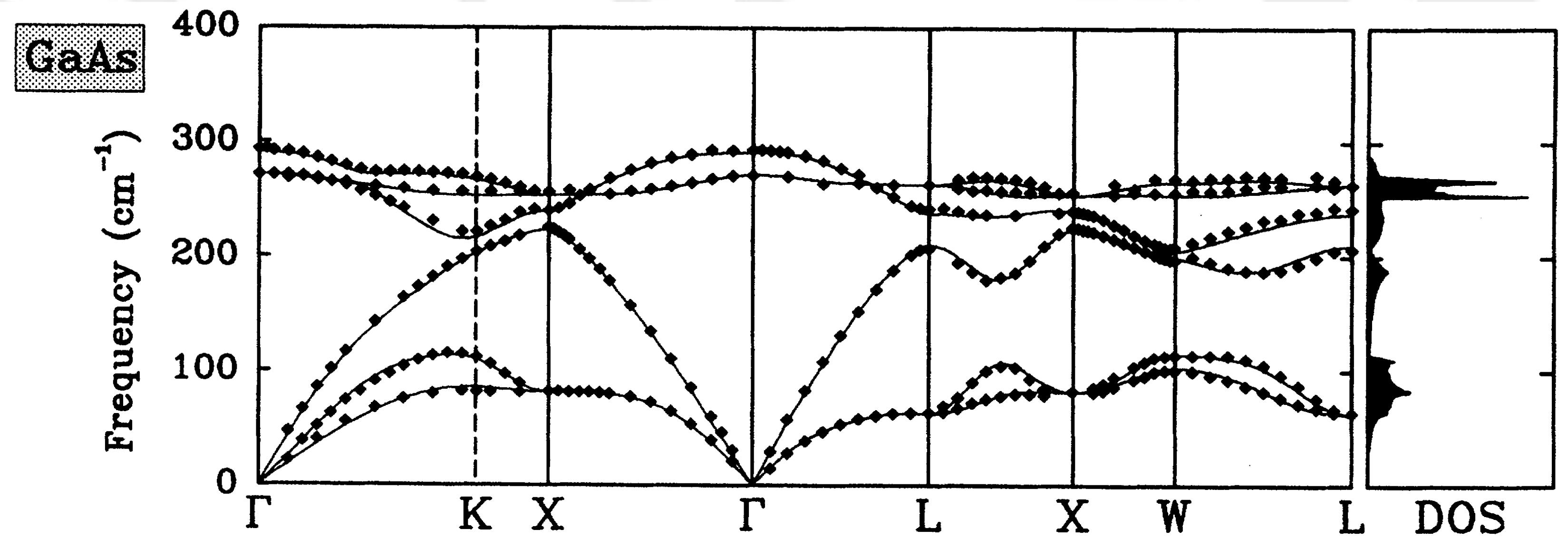
Periodic systems





$$\mathbf{R}_i^\circ = \boldsymbol{\tau}_i + \mathbf{d}_i$$

$$\omega_n = \omega_\nu(\mathbf{q})$$



P. Giannozzi, S. de Gironcoli, P. Pavone, and S. Baroni, Phys. Rev. B **43**, 7231 (1991)

Anharmonic lifetimes

$$u_\nu u_{\nu'} u_{\nu''} \sim \left(\hat{a}_\nu + \hat{a}^\dagger_\nu\right)\left(\hat{a}_{\nu'} + \hat{a}^\dagger_{\nu'}\right)\left(\hat{a}_{\nu''} + \hat{a}^\dagger_{\nu''}\right)$$

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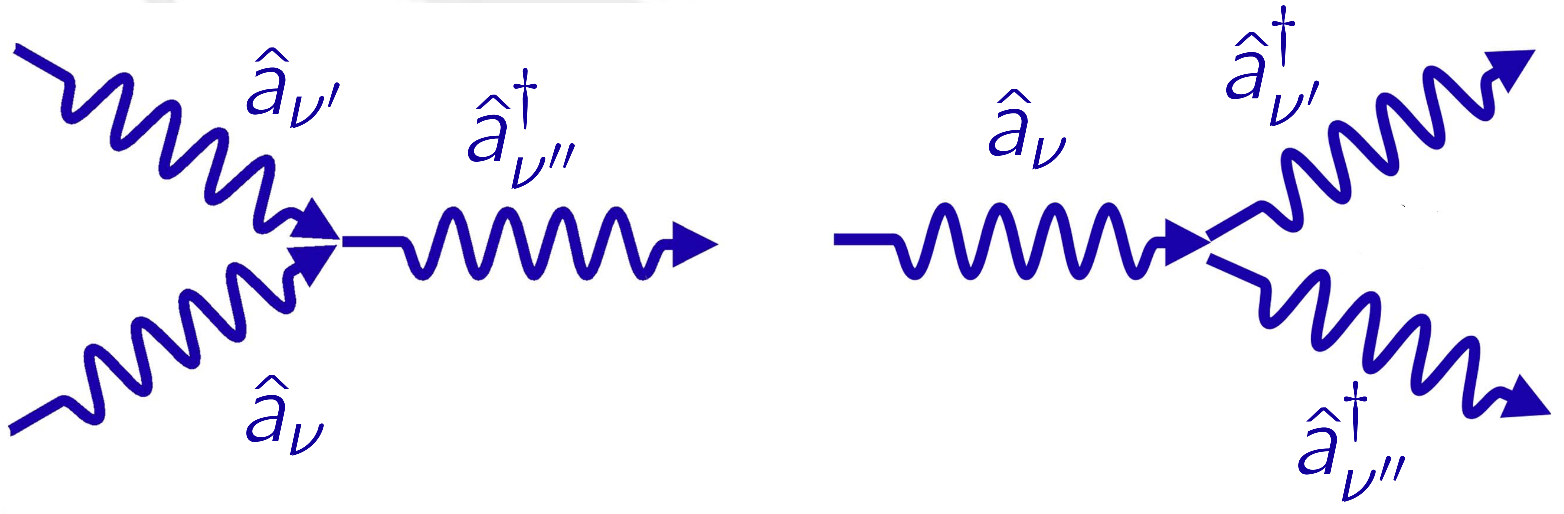

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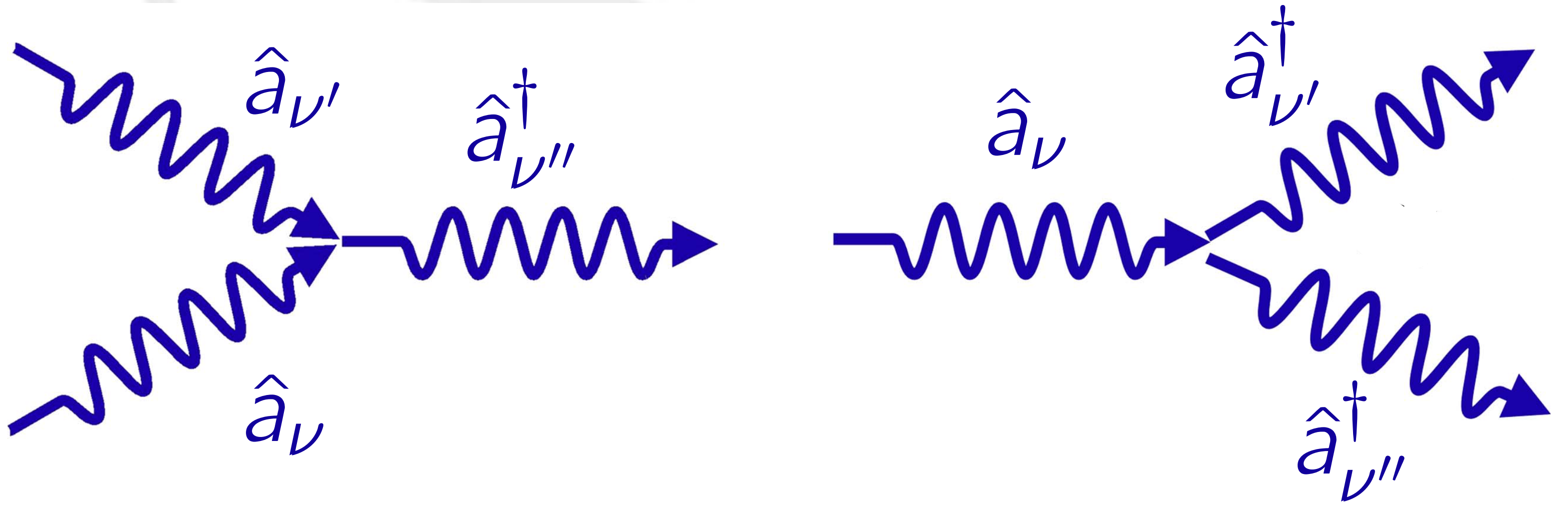

$$\tau_i^{-1} = \frac{2\pi}{\hbar}\sum_f \delta(E_i - E_f)\left|V_{if}\right|^2$$

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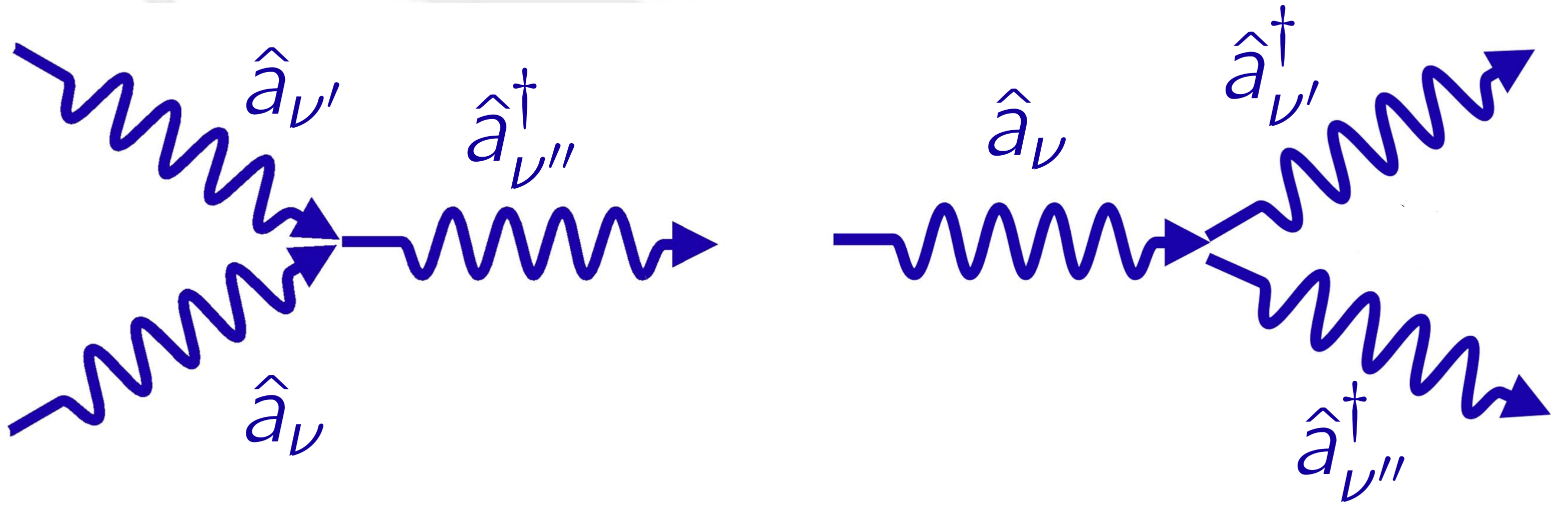

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Anharmonic lifetimes

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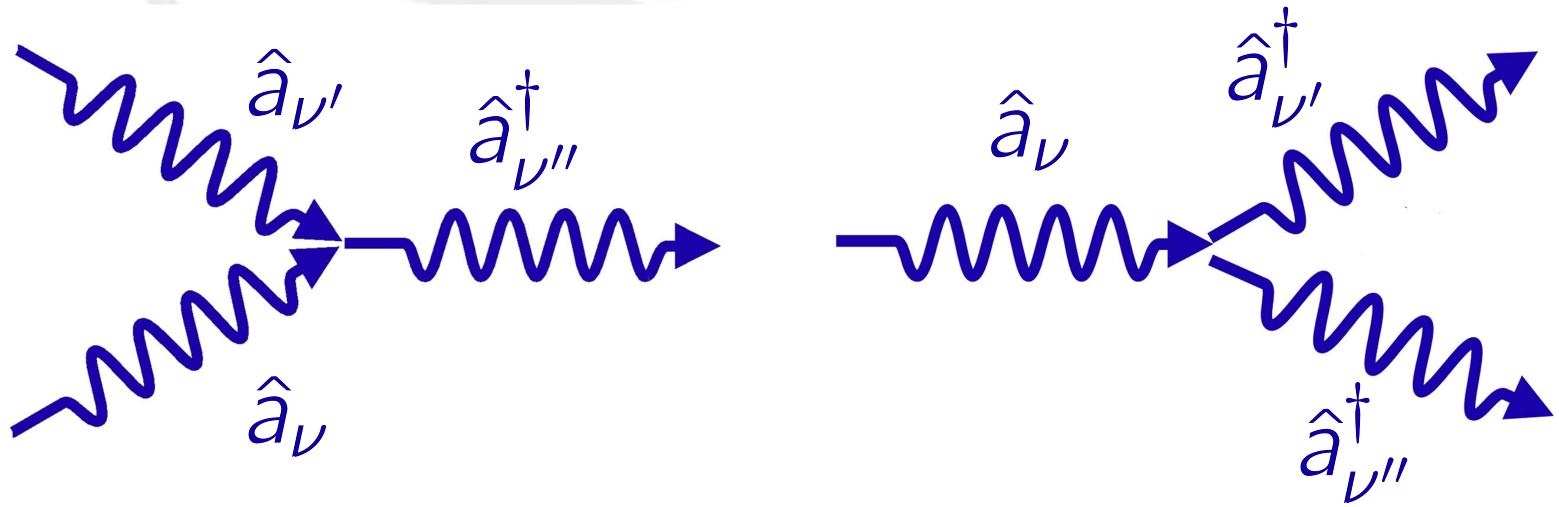

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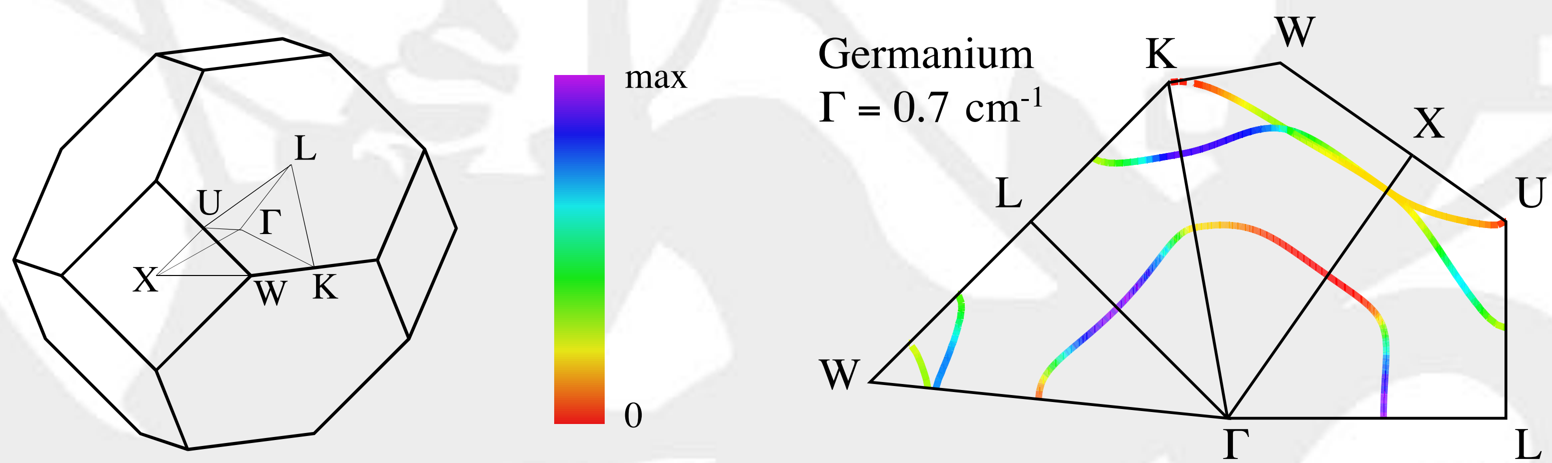

Alberto Debernardi, Stefano Baroni, and Elisa Molinari, Phys. Rev. Lett. **75**, 1819 (1995)

Heat transport from lattice dynamics

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

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

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

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

$$c_{nm} = \frac{\hbar\omega_n\omega_m}{T}\,\frac{n(\omega_m) - n(\omega_n)}{\omega_m - \omega_n}$$

$$n(\omega) = \frac{1}{e^{\frac{\hbar\omega}{k_B T}} - 1}$$

$$c_{nn} = k_B\left(\frac{\hbar\omega_n}{k_B T}\right)^2 \frac{e^{\hbar\omega_n/k_B T}}{(e^{\hbar\omega_n/k_B T} - 1)^2}$$

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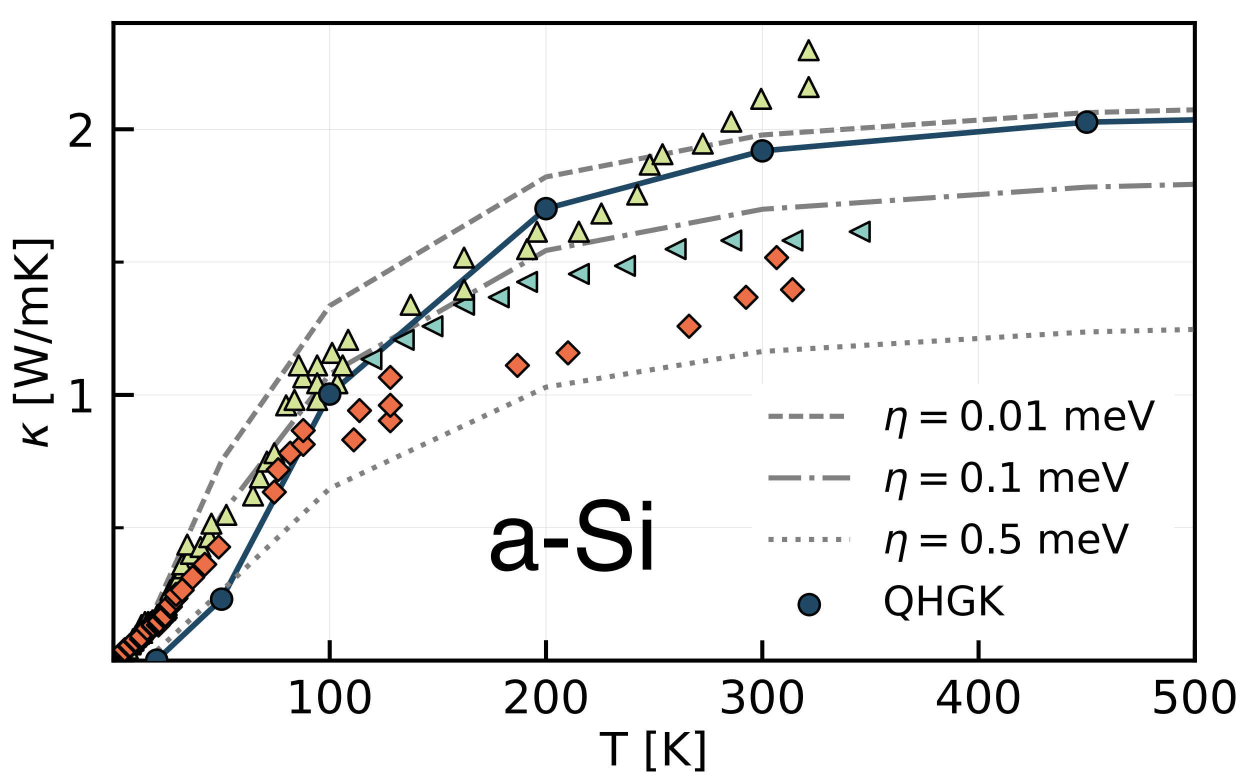

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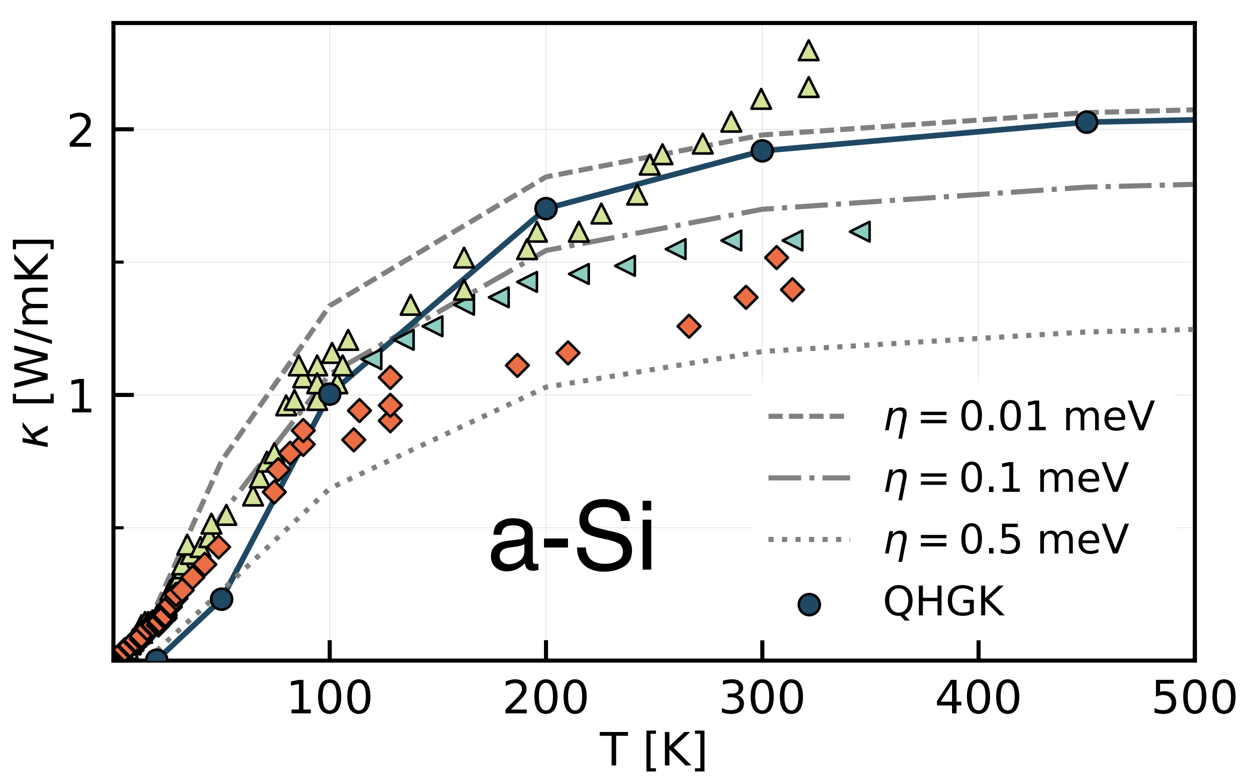

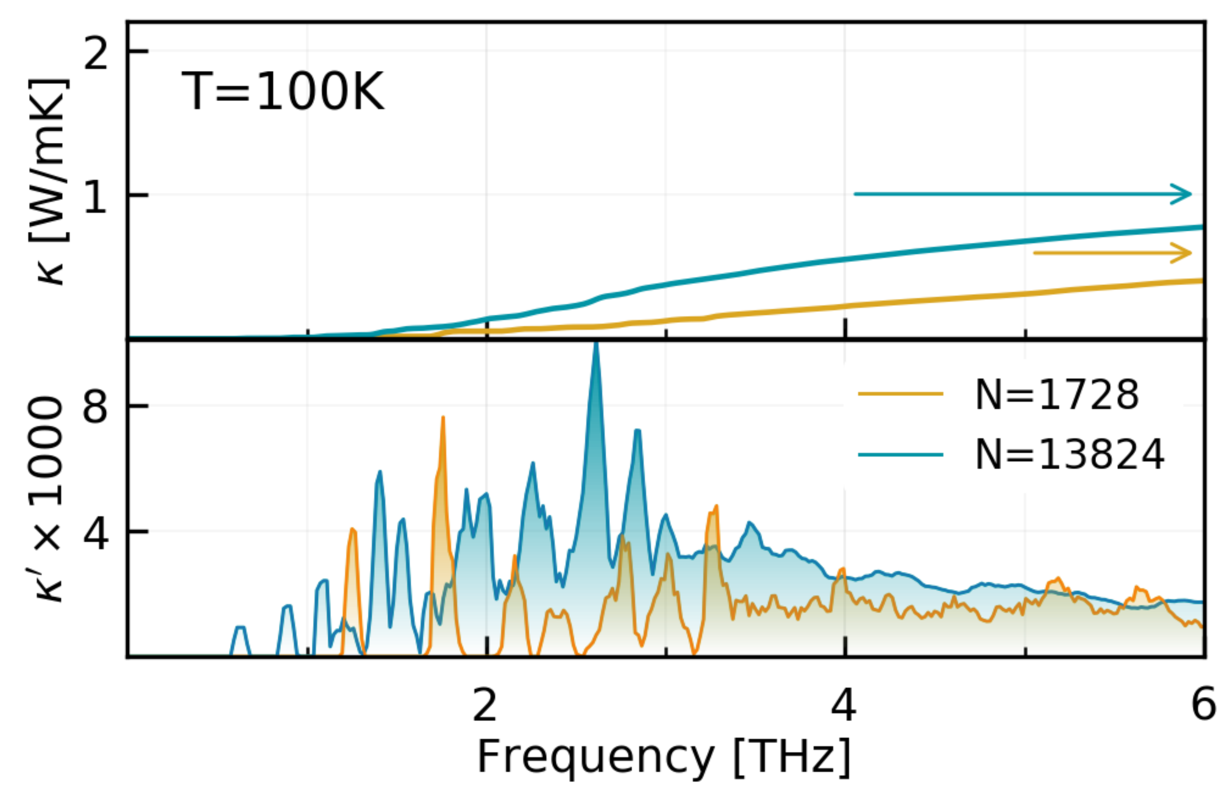

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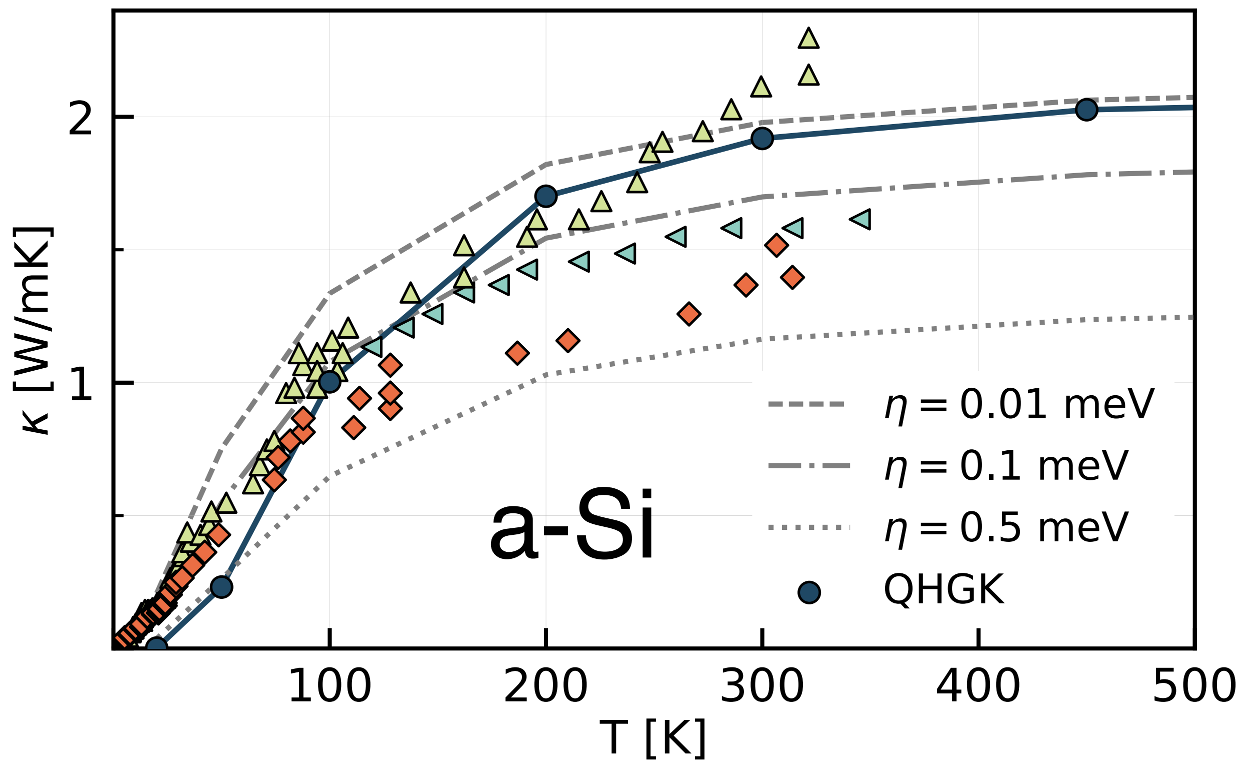

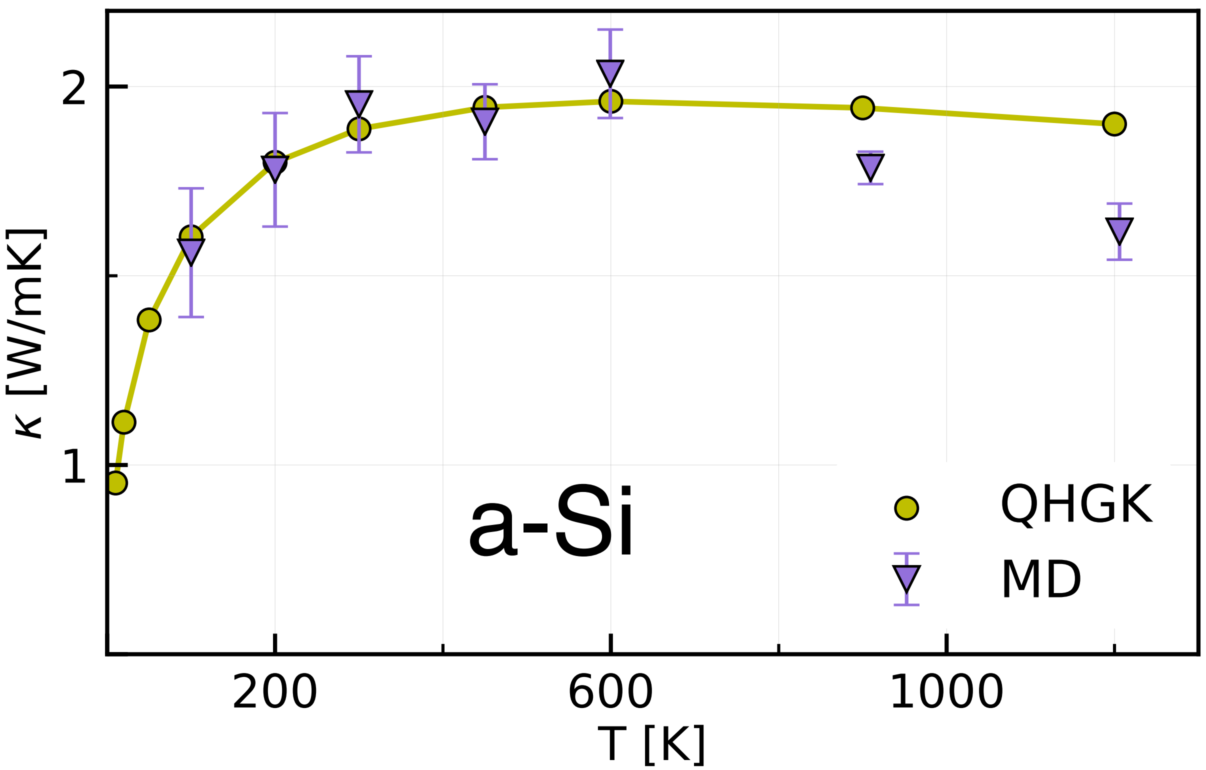

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BTE

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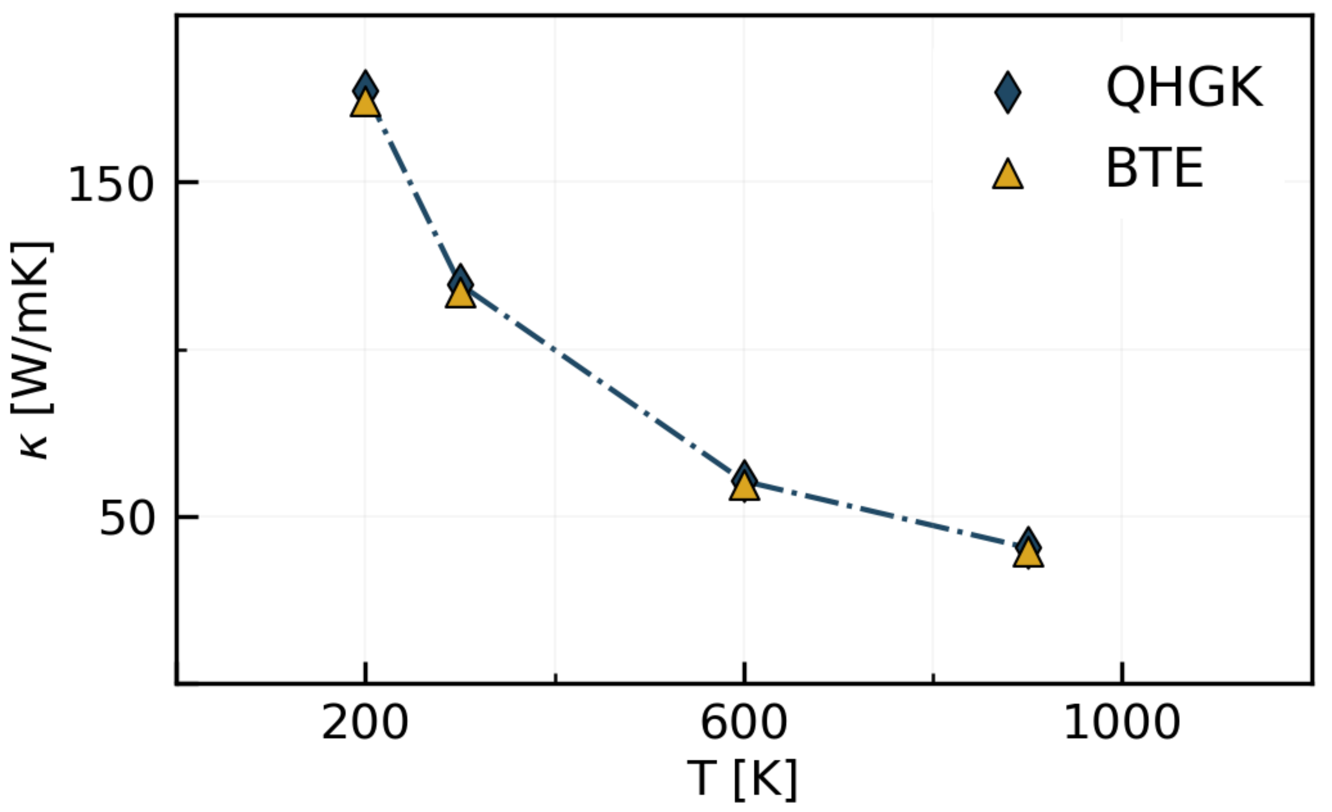

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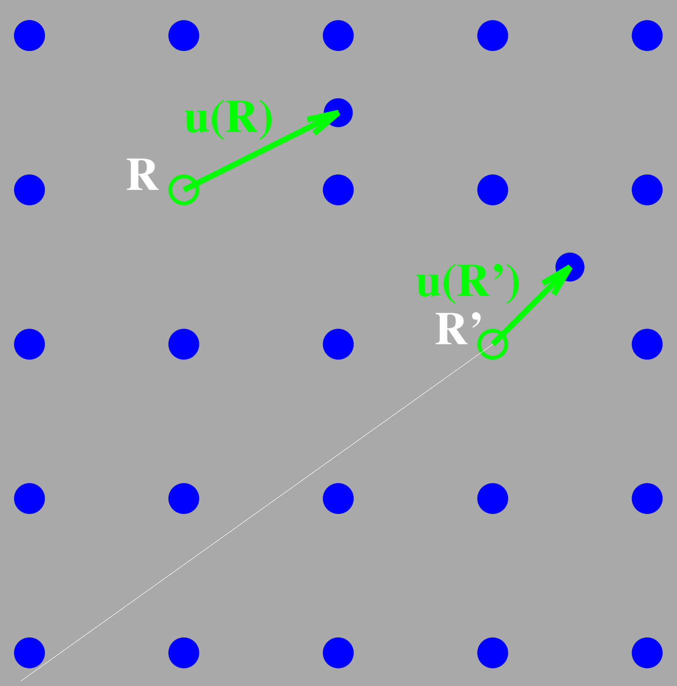
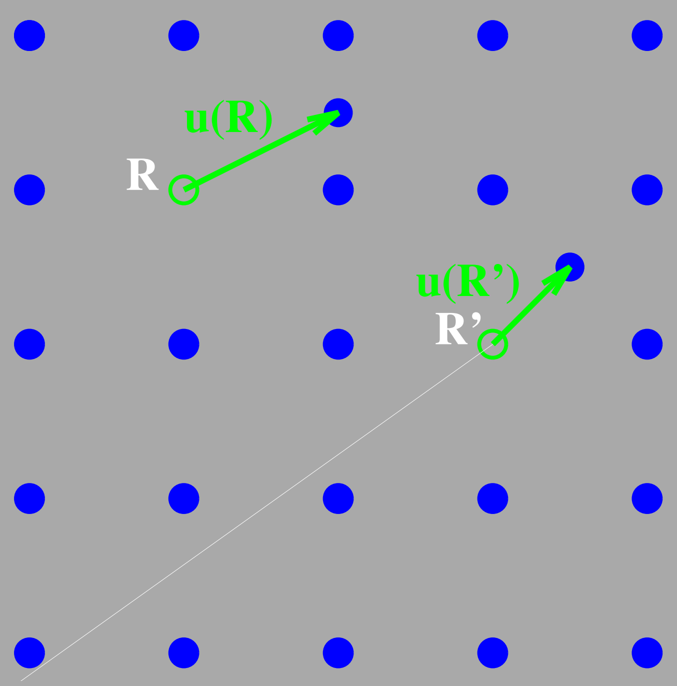
lattice dynamics
from density-functional perturbation theory

lattice dynamics



$$V(\mathbf{r}) = V_0(\mathbf{r}) + \sum_{\mathbf{R}} \mathbf{u}(\mathbf{R}) \cdot \frac{\partial v(\mathbf{r}-\mathbf{R})}{\partial \mathbf{R}} + \cdots$$

lattice dynamics



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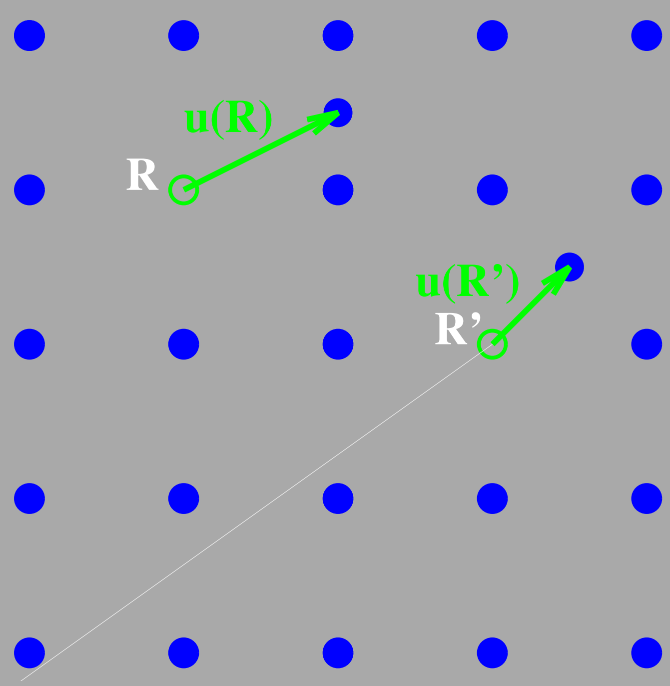
lattice dynamics



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DFT

DPFT

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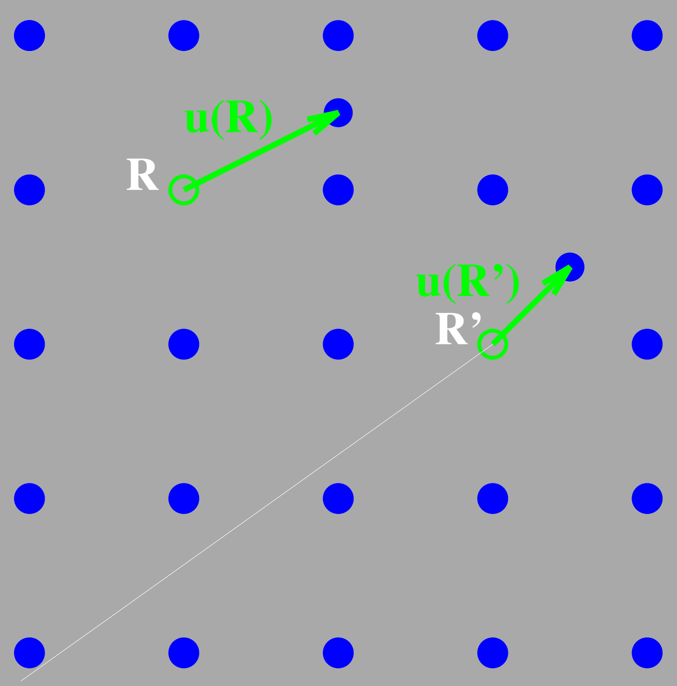

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$$\det\left[\frac{\partial^2 E}{\partial \mathbf{u}(\mathbf{R})\partial \mathbf{u}(\mathbf{R}')} - \omega^2 M(\mathbf{R})\delta_{\mathbf{R},\mathbf{R}'}\right] = 0$$

density-functional perturbation theory

$$V_\lambda(\mathbf{r}) = V_0(\mathbf{r}) + \sum_i \lambda_i v_i(\mathbf{r})$$

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$$\boxed{\frac{\partial^2 E(\lambda)}{\partial \lambda_i \partial \lambda_j} = \int \frac{\partial n_\lambda(\mathbf{r})}{\partial \lambda_j} v_i(\mathbf{r}) d\mathbf{r}}$$ DFPT

calculating the response

$$n(\mathbf{r}) = \sum_v |\phi_v(\mathbf{r})|^2$$

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$$\phi_v' = \sum_c \phi_c^{\circ} \frac{\langle \phi_c^{\circ} | V' | \phi_v^{\circ} \rangle}{\epsilon_v^{\circ} - \epsilon_c^{\circ}}$$

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$$= 2\mathrm{Re}\sum_{cv} \rho_{vc}'\phi_v^{\circ *}(\mathbf{r})\phi_c^{\circ}(\mathbf{r})$$

$$\phi_v' = \sum_c \phi_c^\circ \frac{\langle\phi_c^\circ|V'|\phi_v^\circ\rangle}{\epsilon_v^\circ - \epsilon_c^\circ}$$

$$\boxed{(H^\circ - \epsilon_v^\circ)\phi_v' = -P_c V'\phi_v^\circ}$$

calculating the response

$$n'(\mathbf{r}) = 2\mathrm{Re}\sum_v \phi_v^{\circ *}(\mathbf{r})\phi_v'(\mathbf{r})$$

$$(H^\circ - \epsilon_v^\circ)\phi_v' = -P_c V' \phi_v^\circ$$

DFPT: the equations

DFT

$$V_0(\mathbf{r}) \leftrightarrows n(\mathbf{r})$$

$$V_{SCF}(\mathbf{r}) = V_0(\mathbf{r}) + \int \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' + \mu_{xc}(\mathbf{r})$$

$$n(\mathbf{r}) = \sum_{\epsilon_v < E_F} |\phi_v(\mathbf{r})|^2$$

$$\boxed{\big(-\Delta + V_{SCF}(\mathbf{r})\big)\phi_v(\mathbf{r}) = \epsilon_v \phi_v(\mathbf{r})}$$

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DFPT

$$V'(\mathbf{r}) \leftrightarrows n'(\mathbf{r})$$

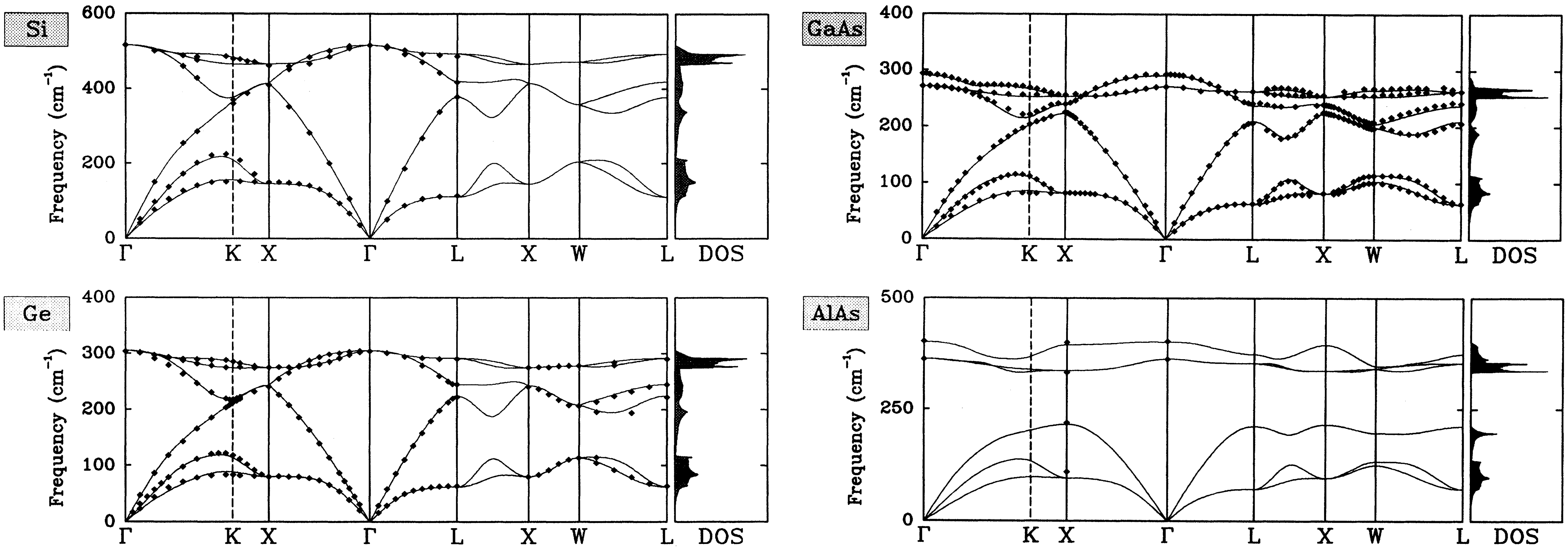
$$V'_{SCF}(\mathbf{r}) = V'(\mathbf{r}) + \int \frac{n'(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' + \mu'_{xc}(\mathbf{r})$$

$$n'(\mathbf{r}) = 2\ \mathrm{Re} \sum_{\epsilon_v < E_F} \phi_v^*(\mathbf{r})\phi'_v(\mathbf{r})$$

$$\boxed{(-\Delta + V_{SCF}(\mathbf{r}) - \epsilon_v)\phi'_v(\mathbf{r}) = P_c V'_{SCF}(\mathbf{r})\phi_v(\mathbf{r})}$$

SB, P. Giannozzi, and A. Testa, Phys. Rev. Lett. **58**, 1861 (1987)

phonons from DFPT



P. Giannozzi, S. de Gironcoli, P. Pavone, and SB, Phys. Rev. B **43**, 7231 (1991)

the “2n+1” theorem

$$\Phi = \Phi_0 + \mathcal{O}(\epsilon) \Rightarrow E = E_0 + \mathcal{O}(\epsilon^2)$$

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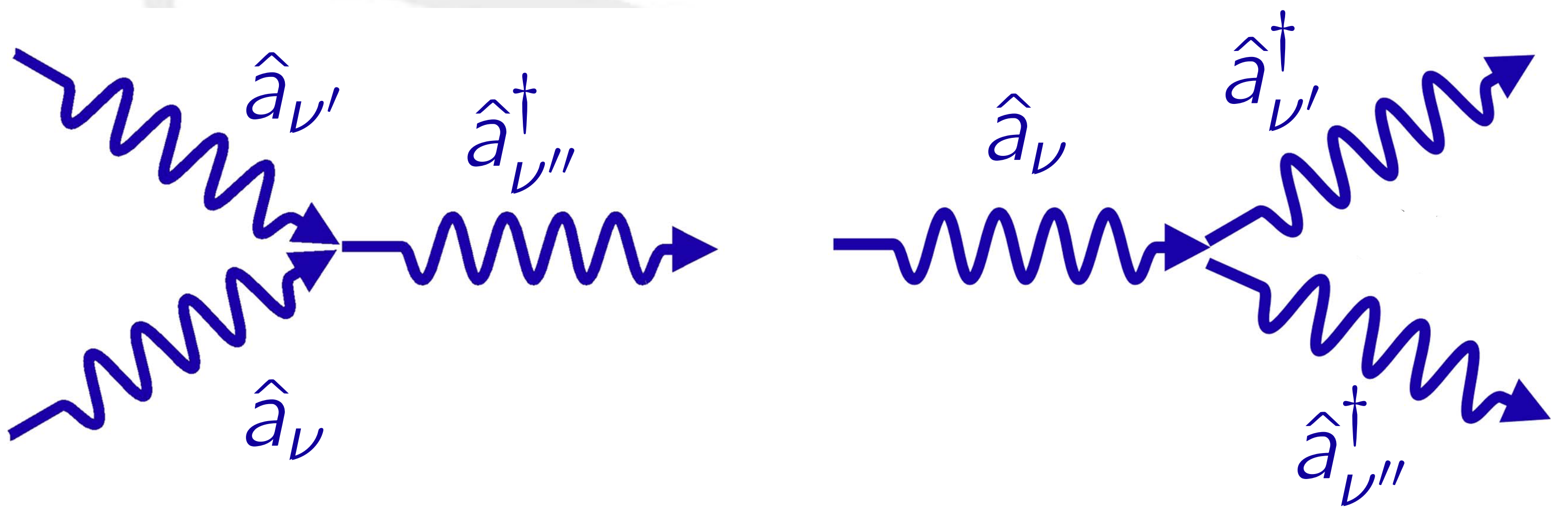
$$E^{(3)} = \langle \Phi' | V' | \Phi' \rangle - \langle \Phi' | \Phi' \rangle \langle \Phi_0 | V' | \Phi_0 \rangle$$

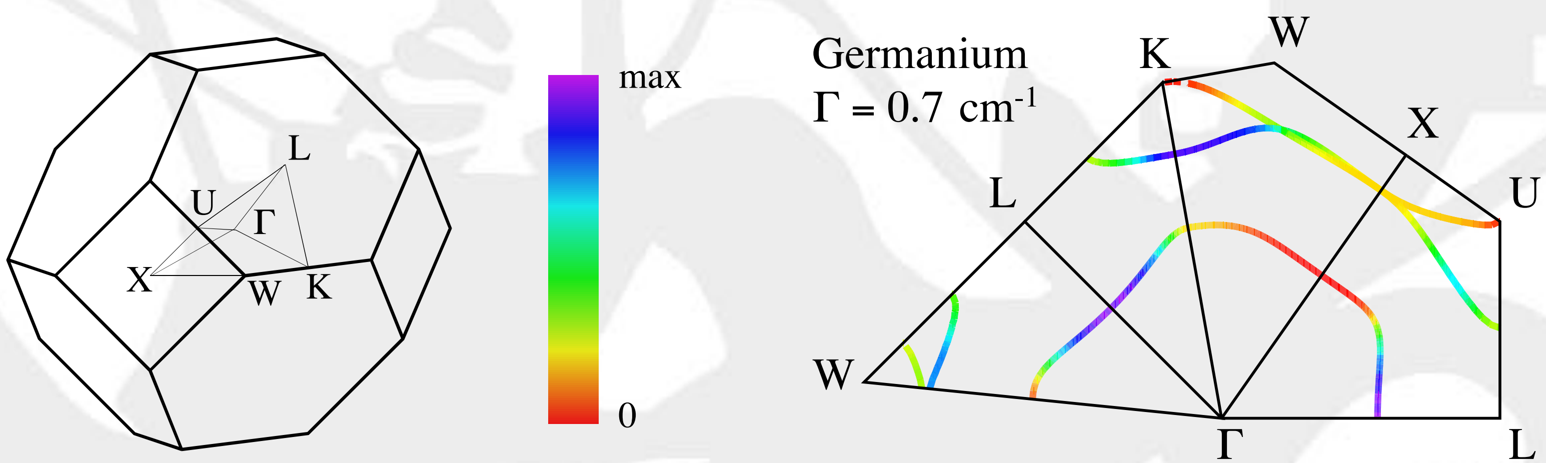
Anharmonic lifetimes

$$u_\nu u_{\nu'} u_{\nu''} \sim \left(\hat{a}_\nu + \hat{a}_\nu^\dagger\right)\left(\hat{a}_{\nu'} + \hat{a}_{\nu'}^\dagger\right)\left(\hat{a}_{\nu''} + \hat{a}_{\nu''}^\dagger\right)$$



$$\tau_\nu^{-1} = \frac{2\pi}{\hbar} \sum_{\nu'\nu''} \left(V_{\nu\nu'\nu''}\right)^2 \times \Big(\delta(\epsilon_\nu - \epsilon_{\nu'} - \epsilon_{\nu''}) n_\nu (n_{\nu'} + 1)(n_{\nu''} + 1) +$$

$$\delta(\epsilon_\nu + \epsilon_{\nu'} - \epsilon_{\nu''}) n_\nu n_{\nu'} (n_{\nu''} + 1)\Big)$$



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Riccardo Bertossa, SISSA

Leyla Isaeva, SISSA


That's all Folks!
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