Car and Parrinello meet Green and Kubo

simulating atomic heat transport from equilibrium ab-initio molecular dynamics

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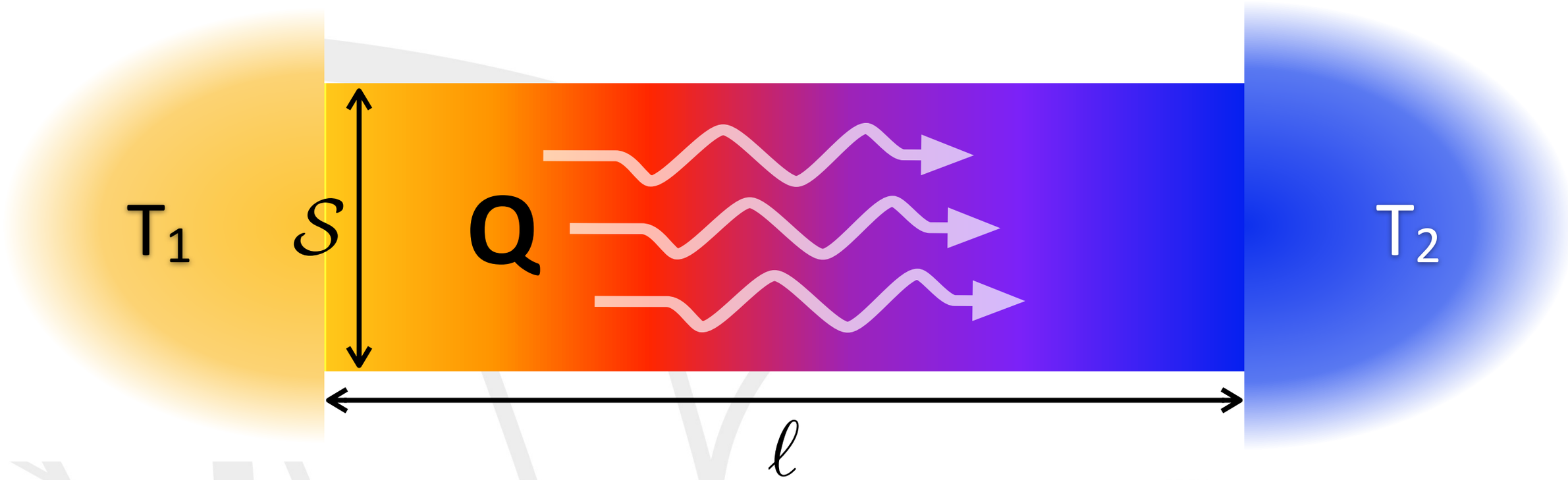
talk given at the Department of Materials, University of Oxford, February 24, 2017

talk given at the Cavendish Laboratory, University of Cambridge, February 23, 2017

talk given at the Department of Earth Sciences, University College London, February 20, 2017

what heat transport is all about



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

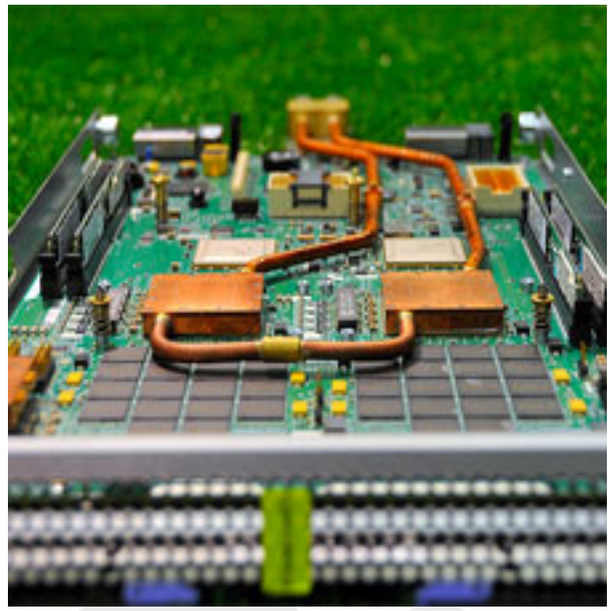
$$\mathbf{J}_Q = -\kappa\nabla T$$

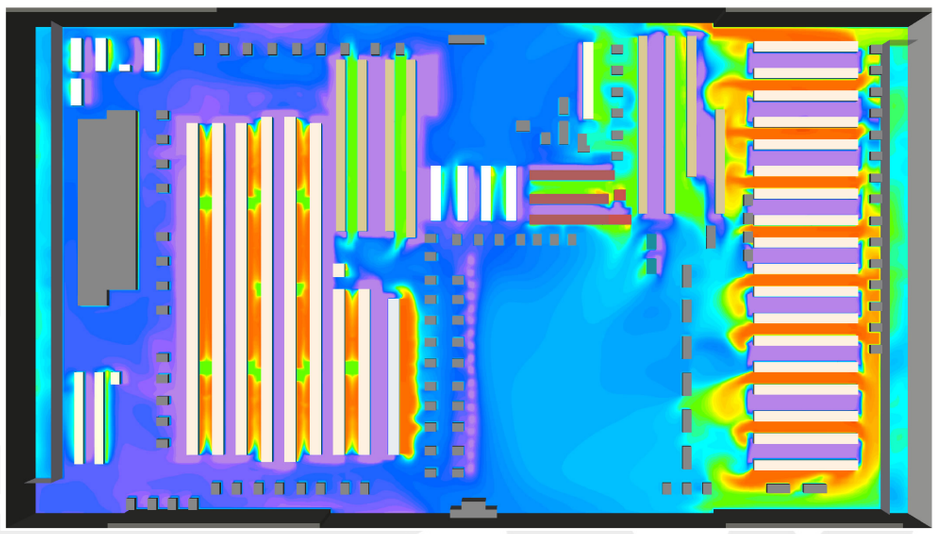
$$\frac{\partial T}{\partial t} = \frac{\kappa}{\rho c_p}\Delta T$$

why should we care?

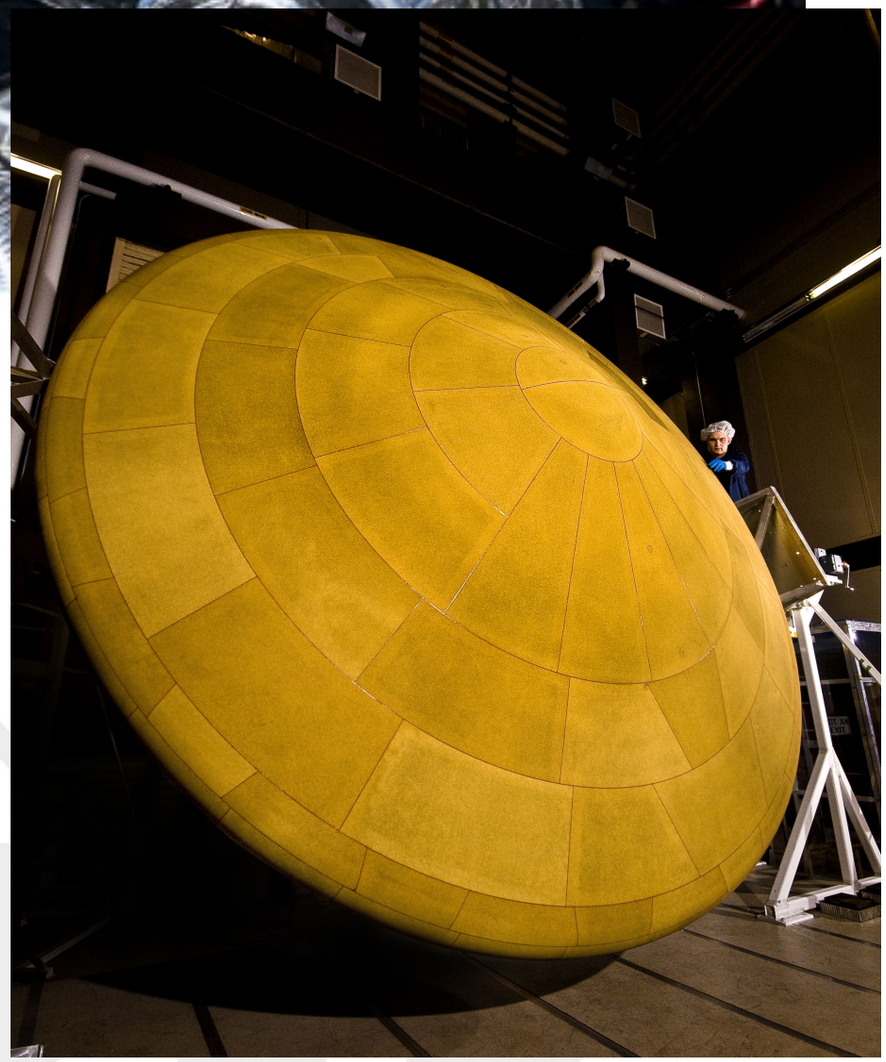
energy saving

heat dissipation

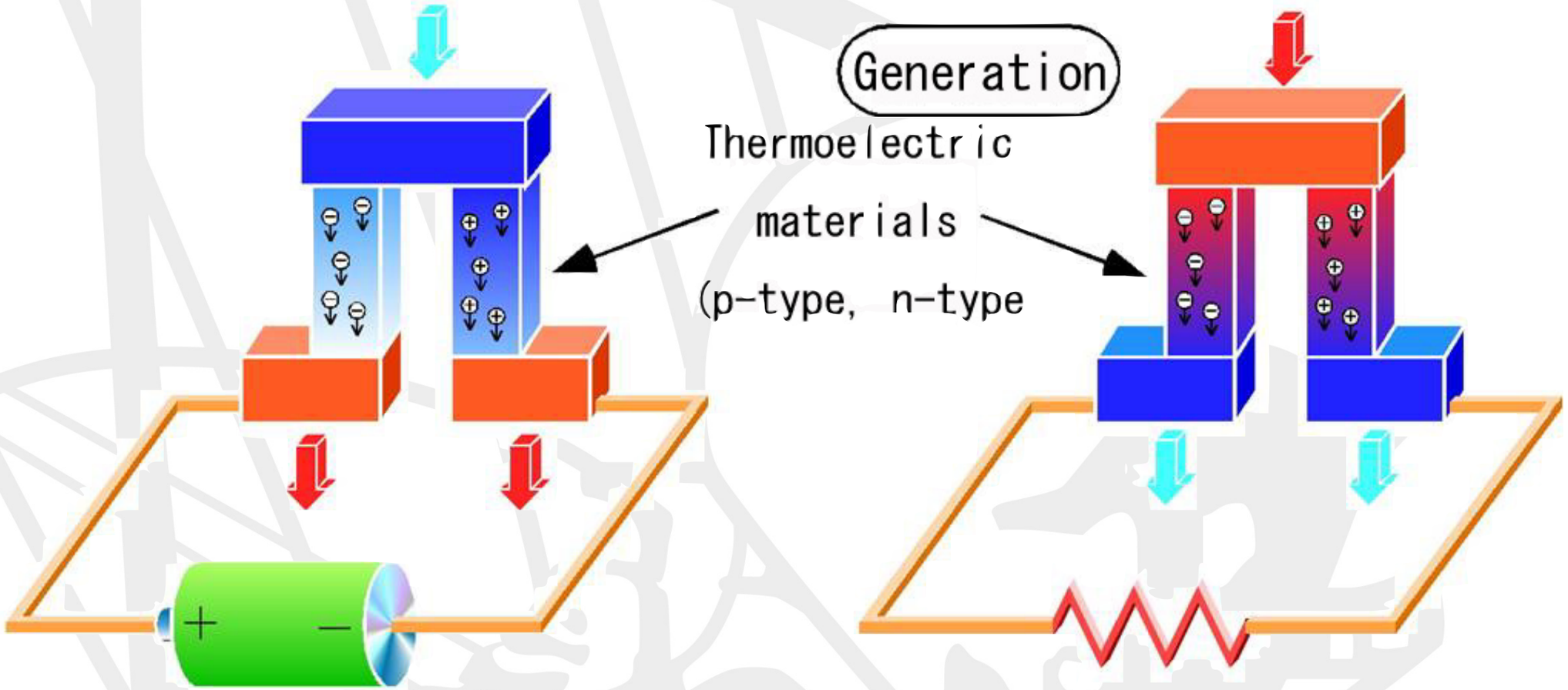




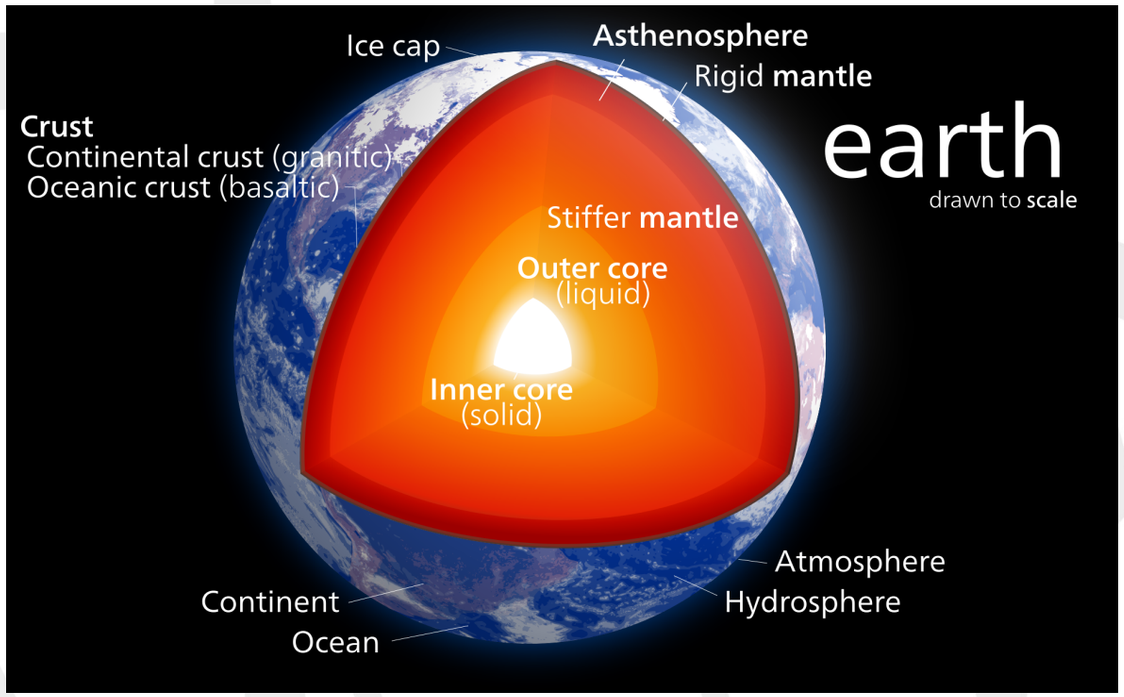
heat shielding

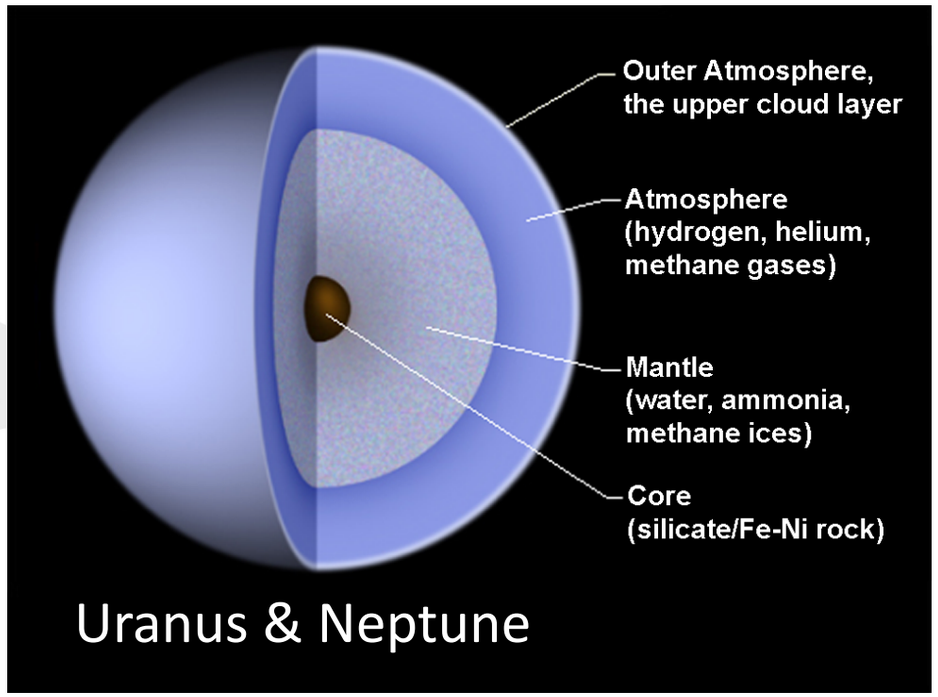


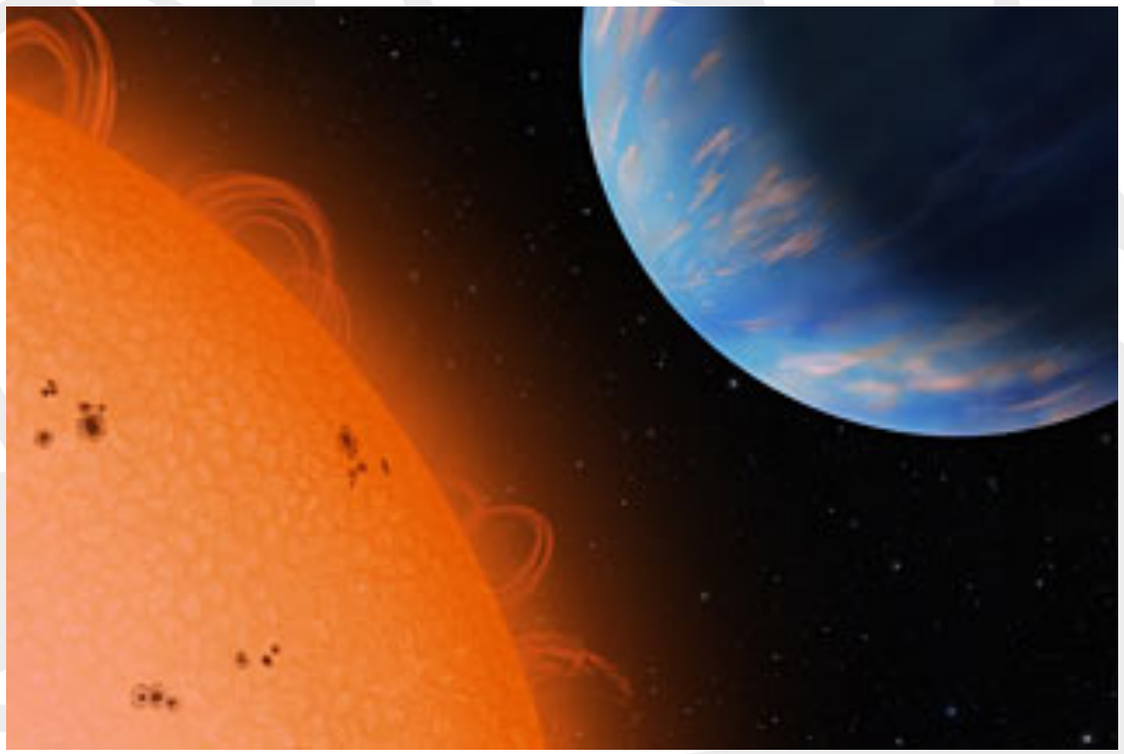
energy conversion

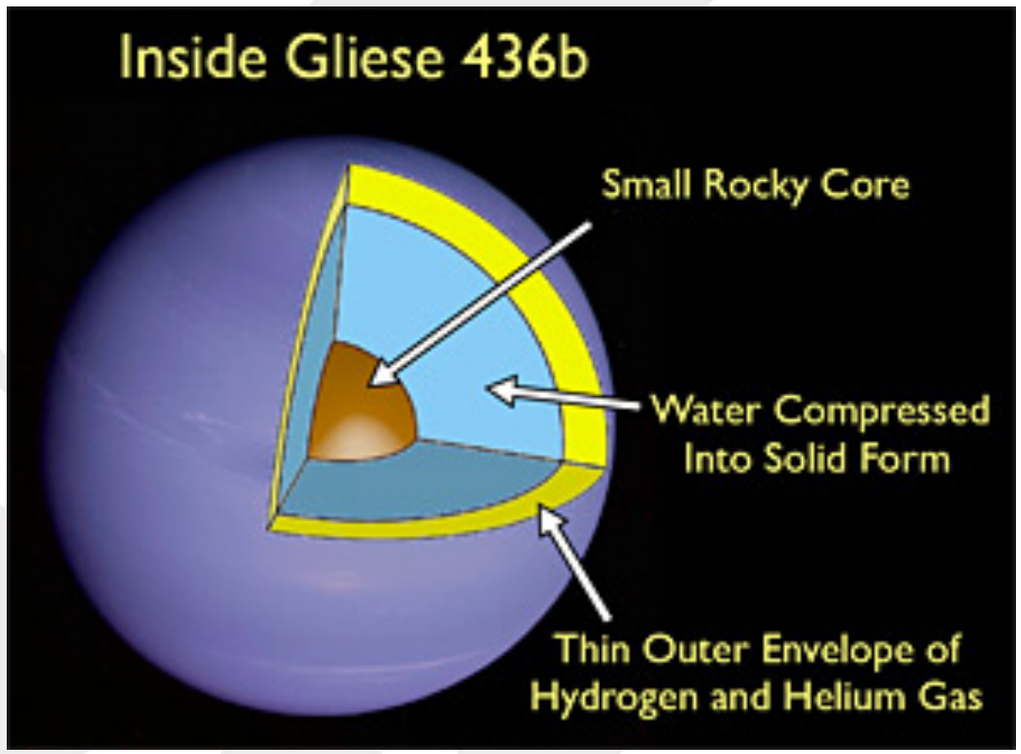


planetary sciences









why heat transport

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

hydrodynamic fluctuations

Extensive, conserved, quantities are characterised by two properties:

$$A[\Omega_1 \cup \Omega_2] = A[\Omega_1] + A[\Omega_2] \Rightarrow A[\Omega] = \int_\Omega a(\mathbf{r}) d\mathbf{r}$$

$$\frac{dA}{dt} = 0 \quad \Rightarrow \quad \frac{\partial a(\mathbf{r},t)}{\partial t} = -\nabla \cdot \mathbf{j}_a(\mathbf{r},t)$$

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

the longer the wavelength, the slower the mode

Green-Kubo theory

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

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

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

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

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

the classical MD ansatz

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

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

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

ab initio simulations

Thermal Conductivity of Periclase (MgO) from First Principles

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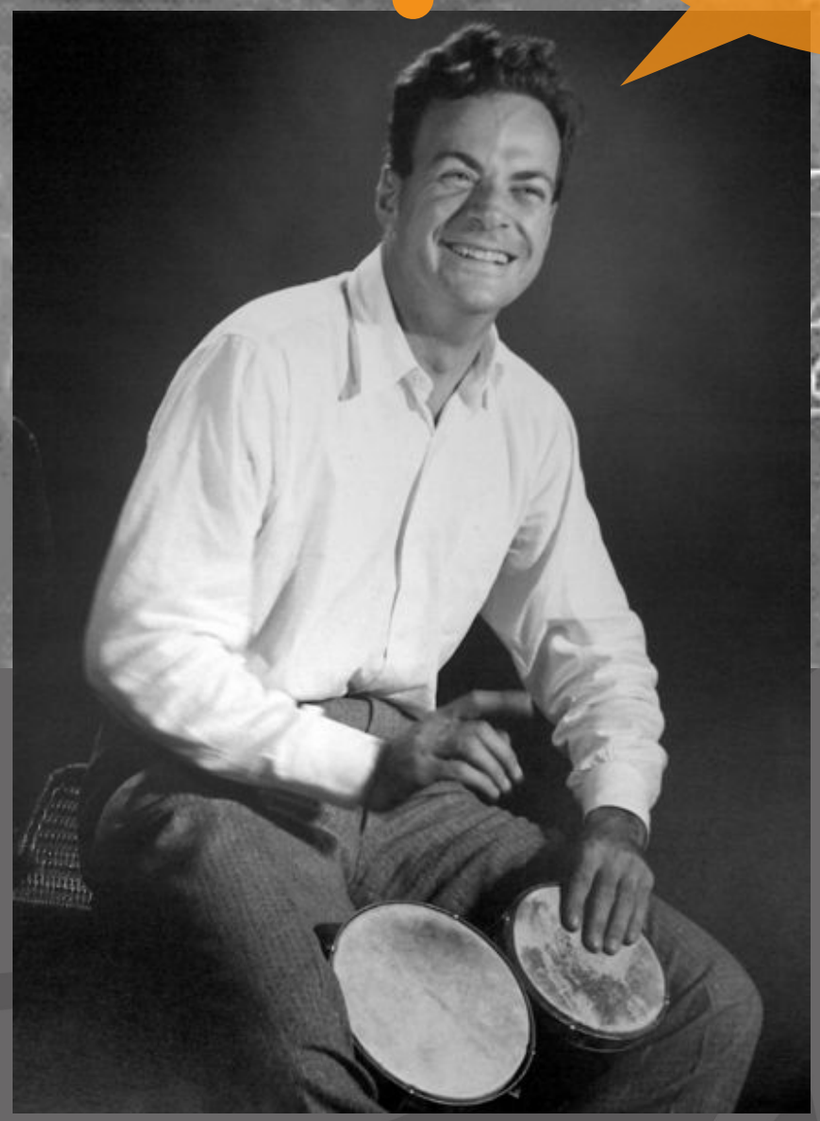
sensitive to the form of the potential. The widely used Green-Kubo relation [14] does not serve our purposes, because in first-principles calculations it is impossible to uniquely decompose the total energy into individual contributions from each atom.

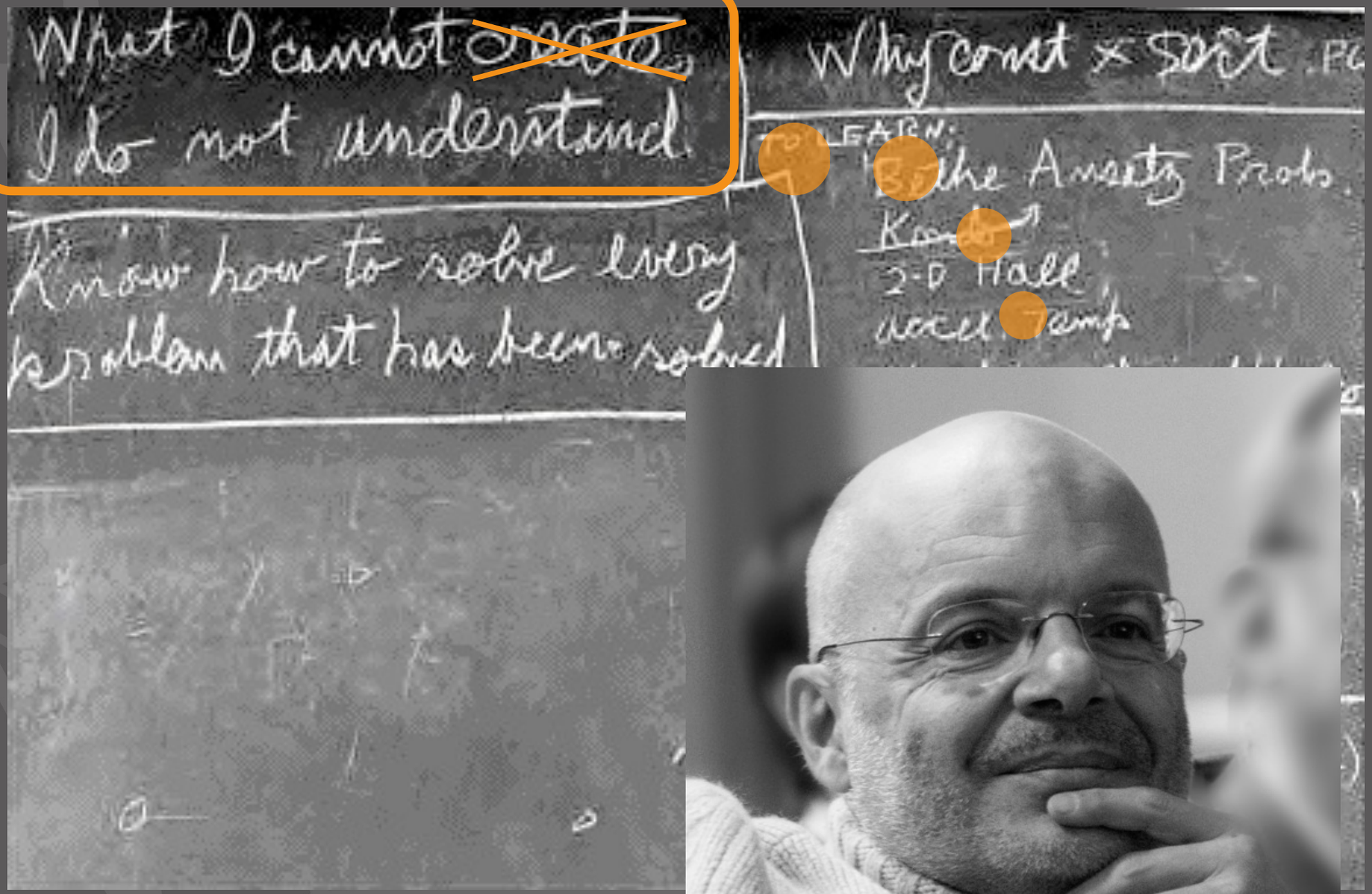
What I cannot create,
I do not understand.

$$A \sim \int \mathrm{e}^{-\frac{i}{\hbar}\mathcal{S}[x(\cdot)]}\mathcal{D}[x(\cdot)]$$



I can safely say
that nobody
understands quantum
mechanics

compute


What I cannot create,
I do not understand.
Know how to solve every
problem that has been solved
Why const × sort
LEARN:
2-D Hall

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

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

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

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

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

insights from classical mechanics

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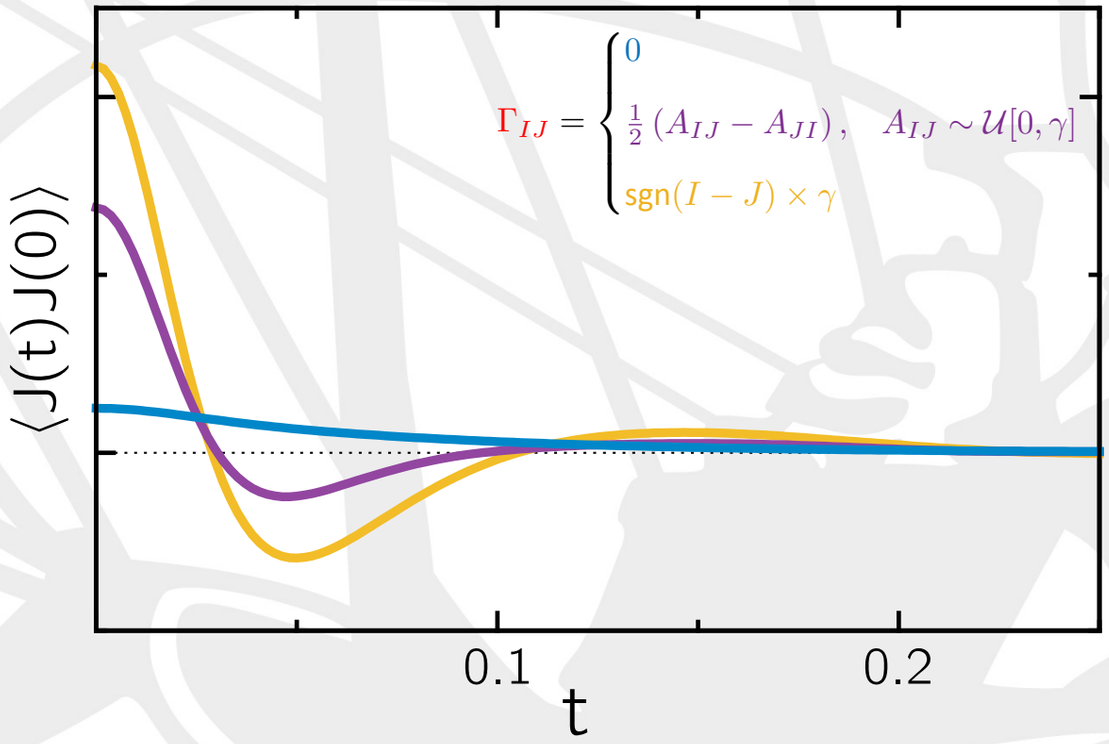

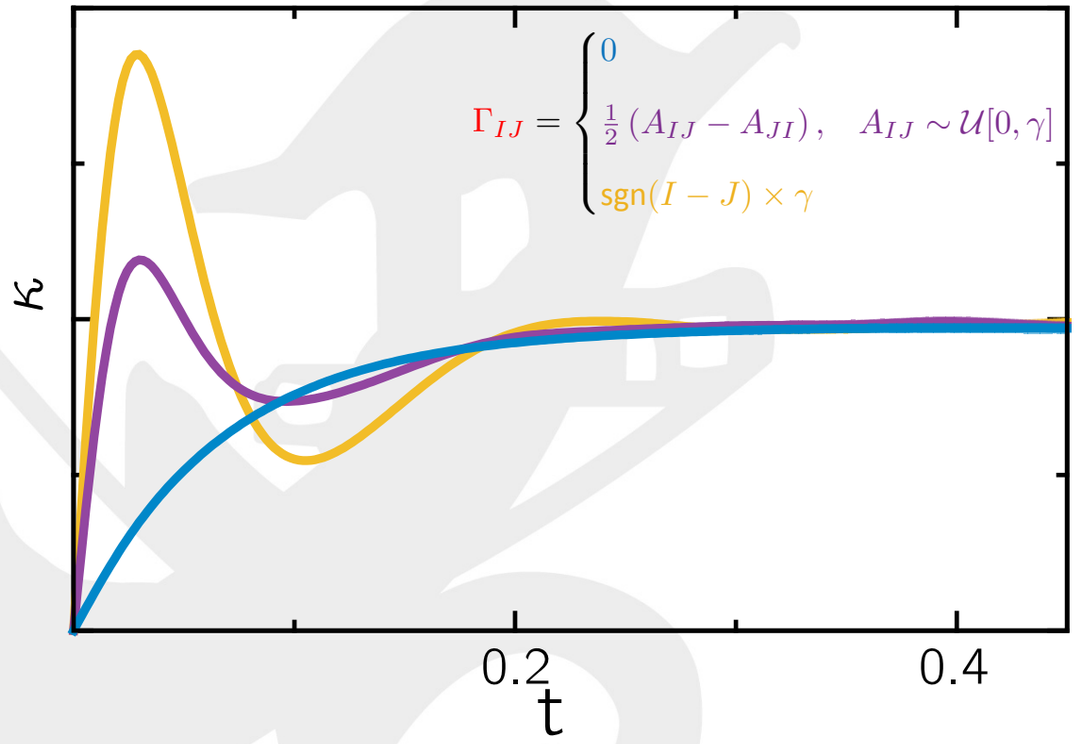

insights from classical mechanics

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

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

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

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

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

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

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

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

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

$$\kappa' = \kappa$$

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

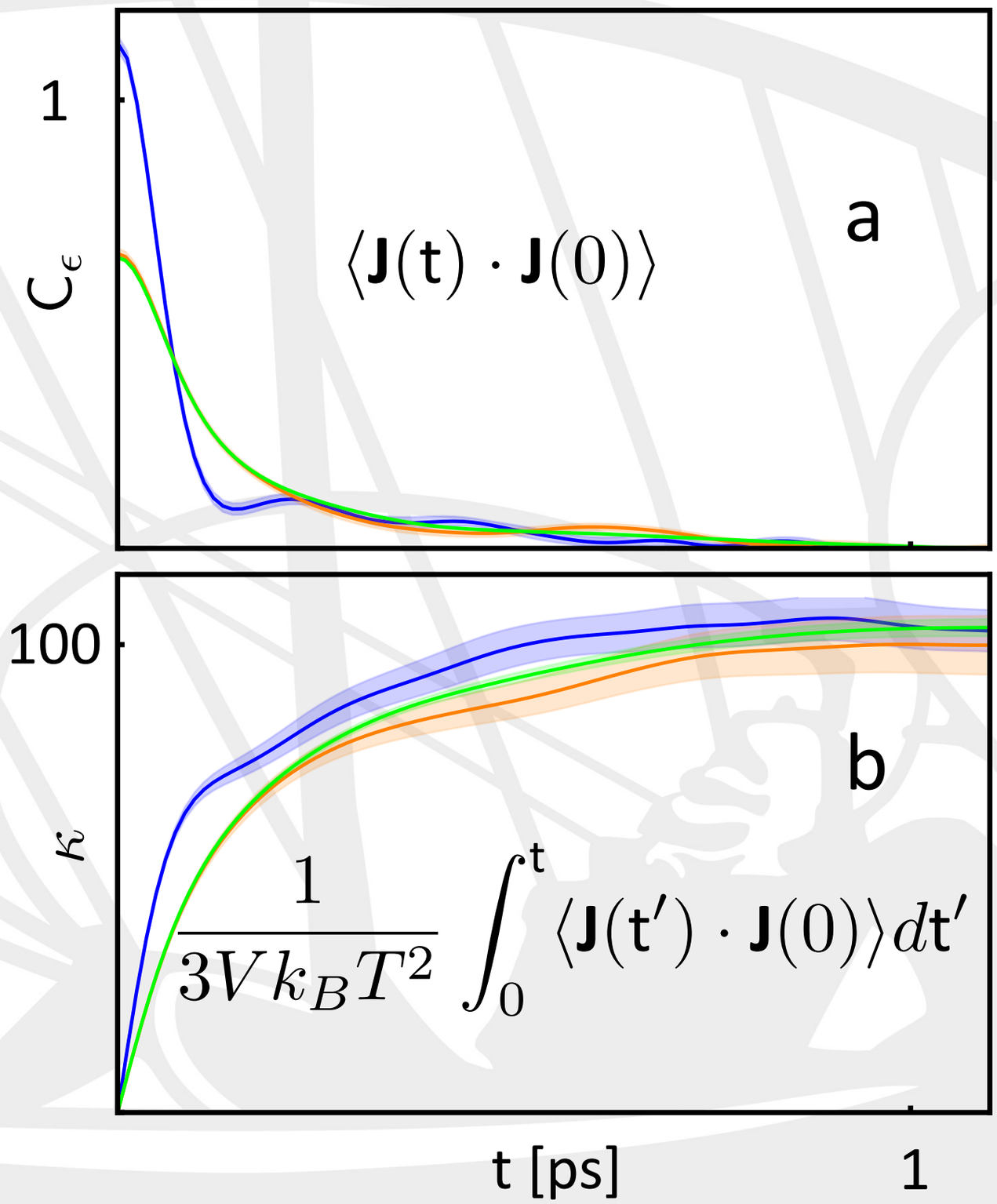
$$\mathbf{J}_{DFT} = \int \mathbf{r}\dot{e}_{DFT}(\mathbf{r},t)d\mathbf{r}$$

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

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

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

a benchmark

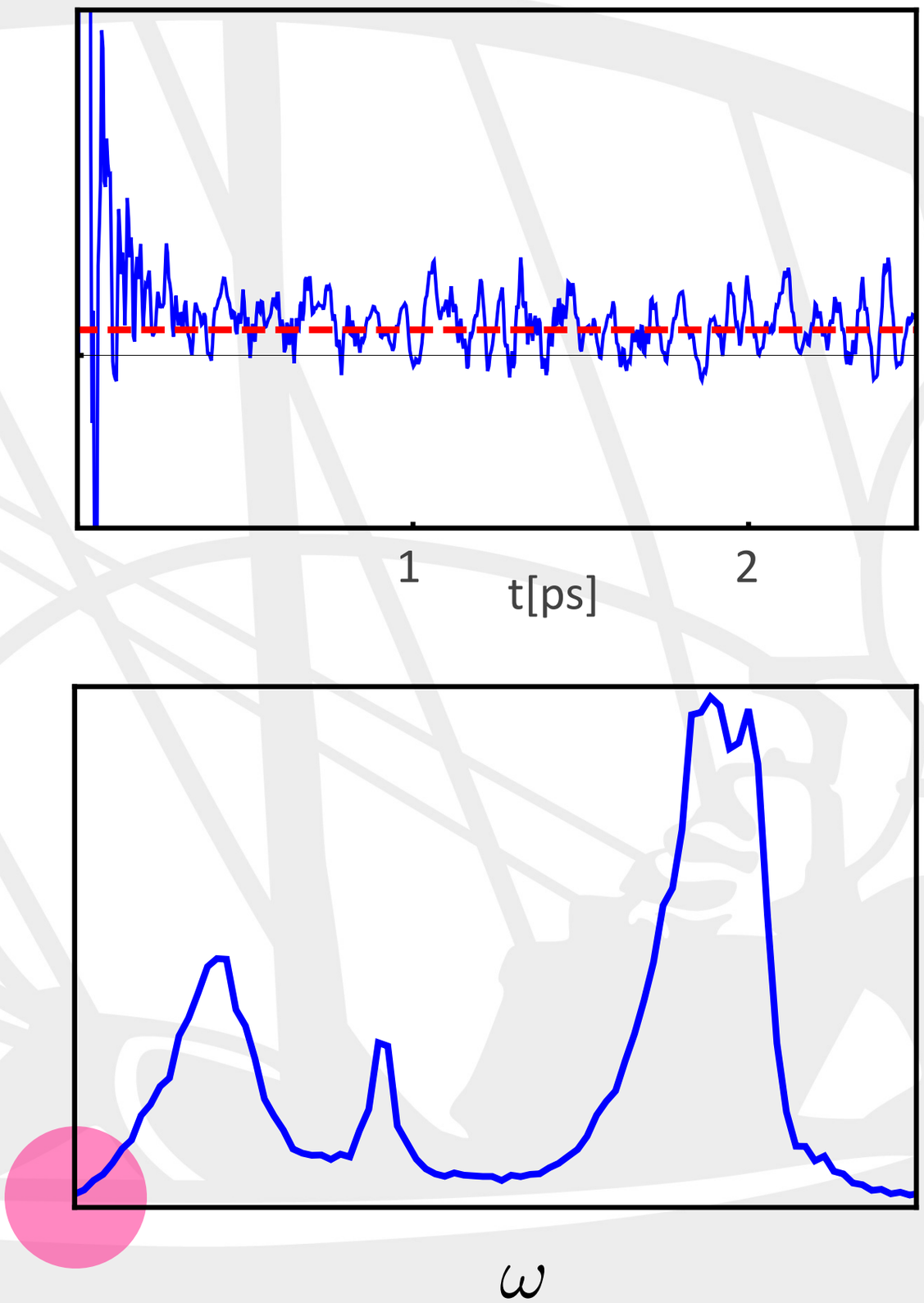


108 “LDA Ar” atoms
@bp density, T= 250 K

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

same behavior at T=400 K

liquid (heavy) water

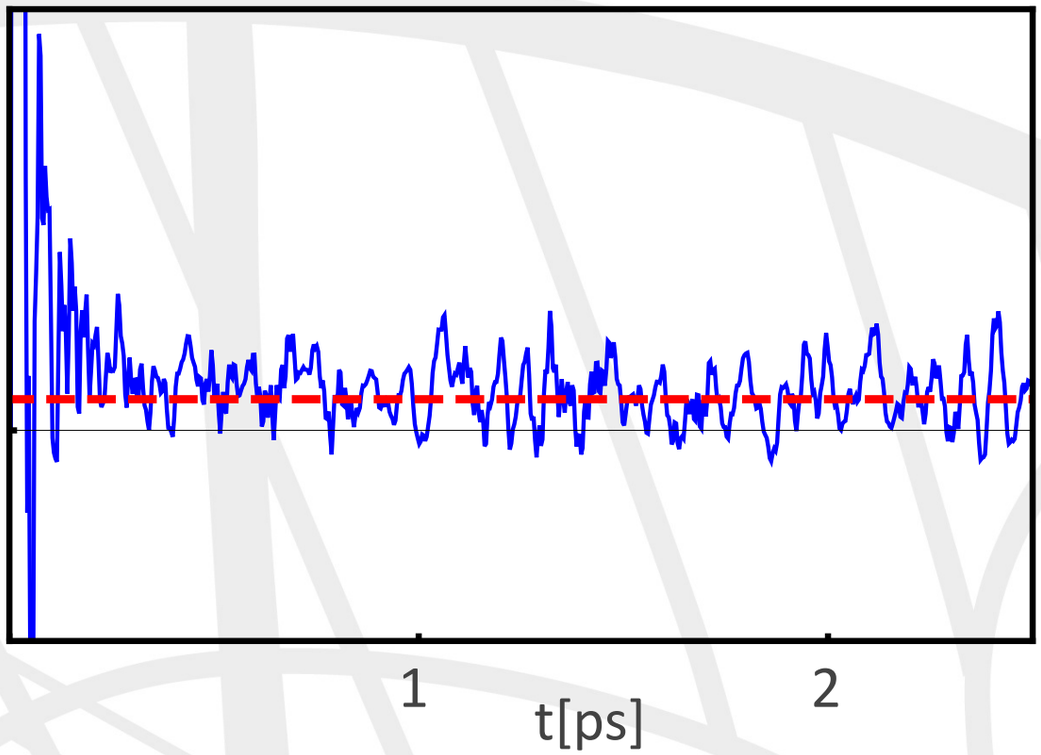


64 molecules, T=385 K
expt density @ac

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

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

liquid (heavy) water



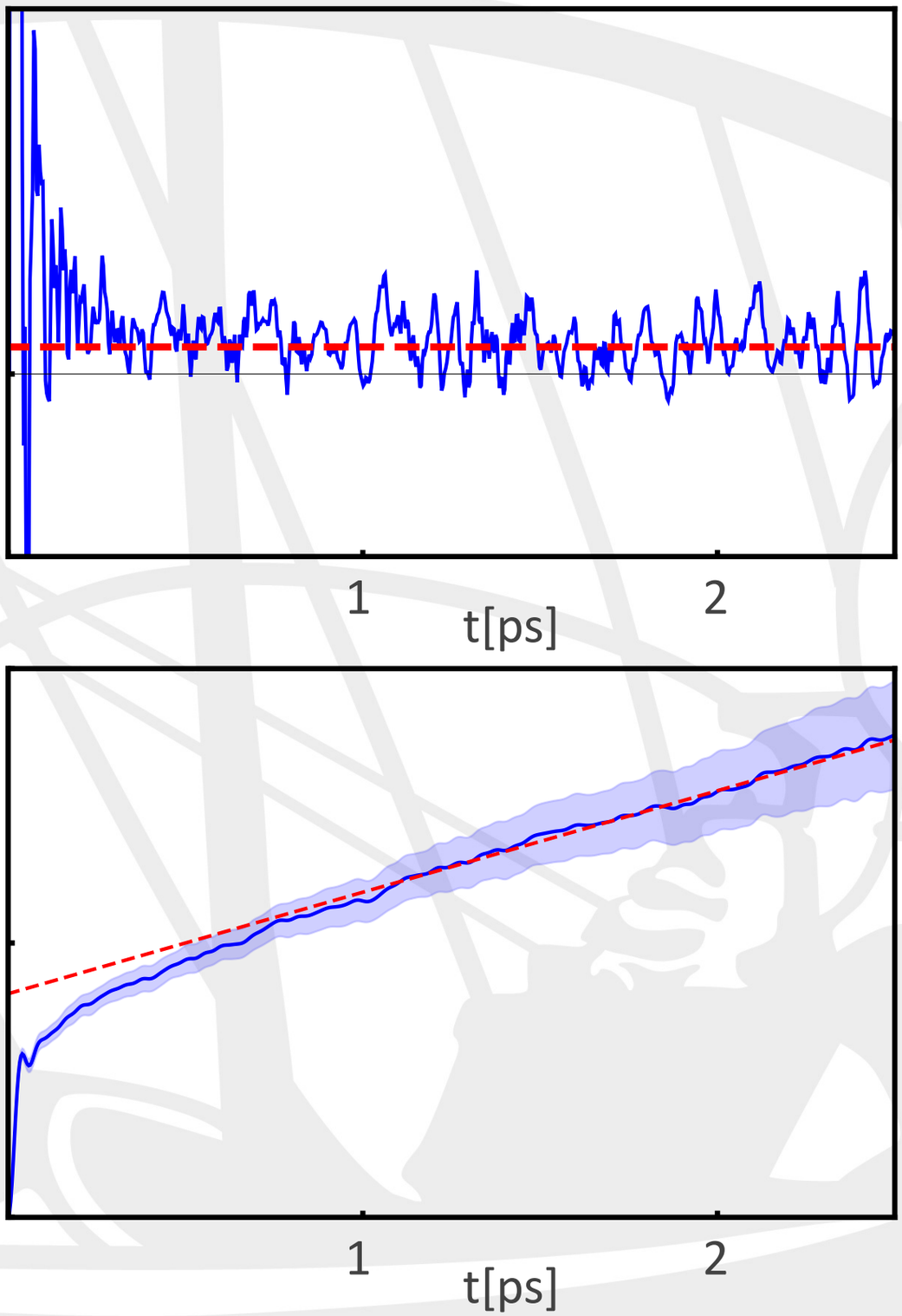
64 molecules, T=385 K
expt density @ac

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

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



64 molecules, T=385 K
expt density @ac

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

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

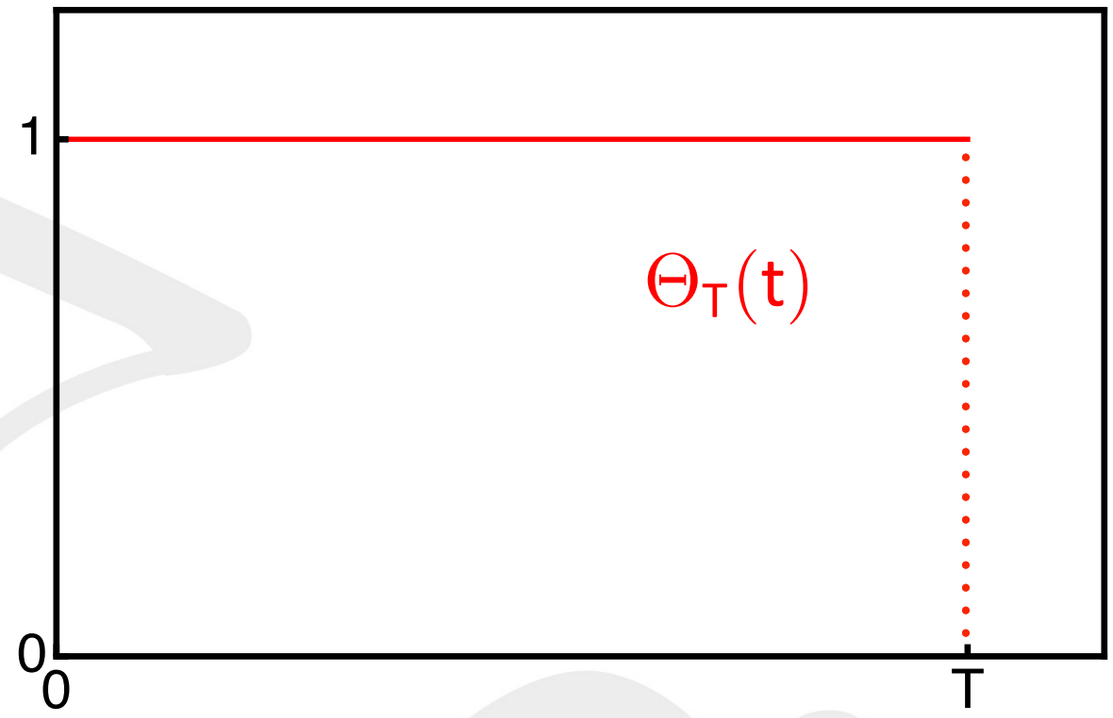
$\kappa_{\mathrm{expt}} = 0.61$ (light@AC)

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

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

Einstein *vs.* Green-Kubo

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



Einstein *vs.* Green-Kubo

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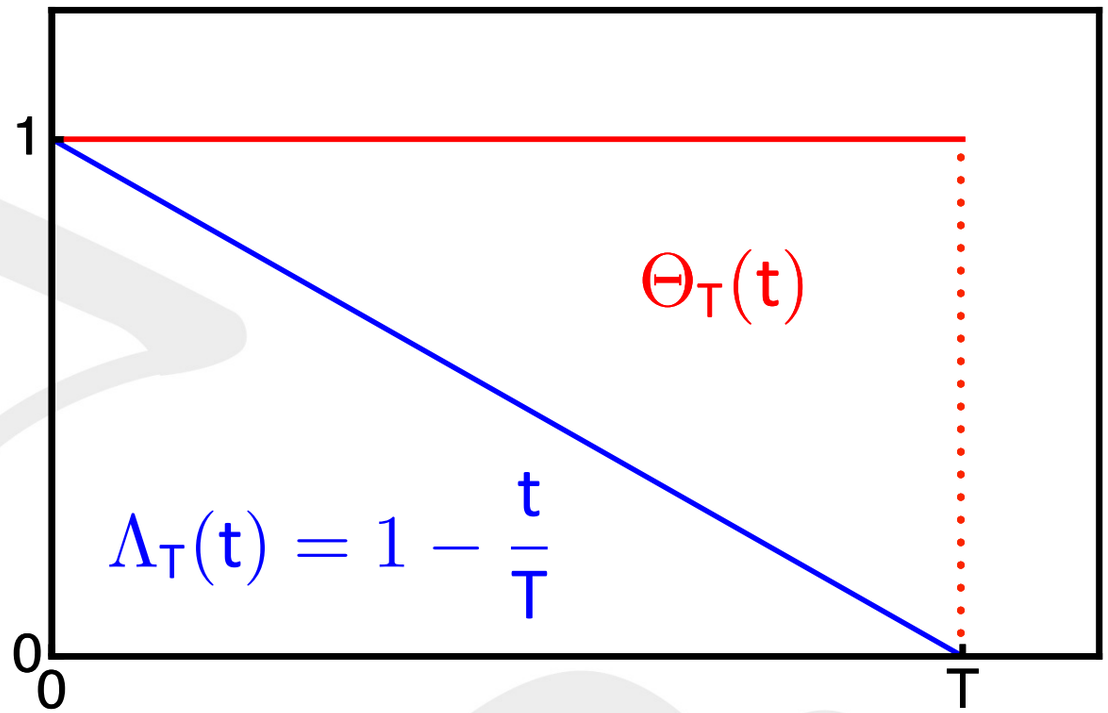
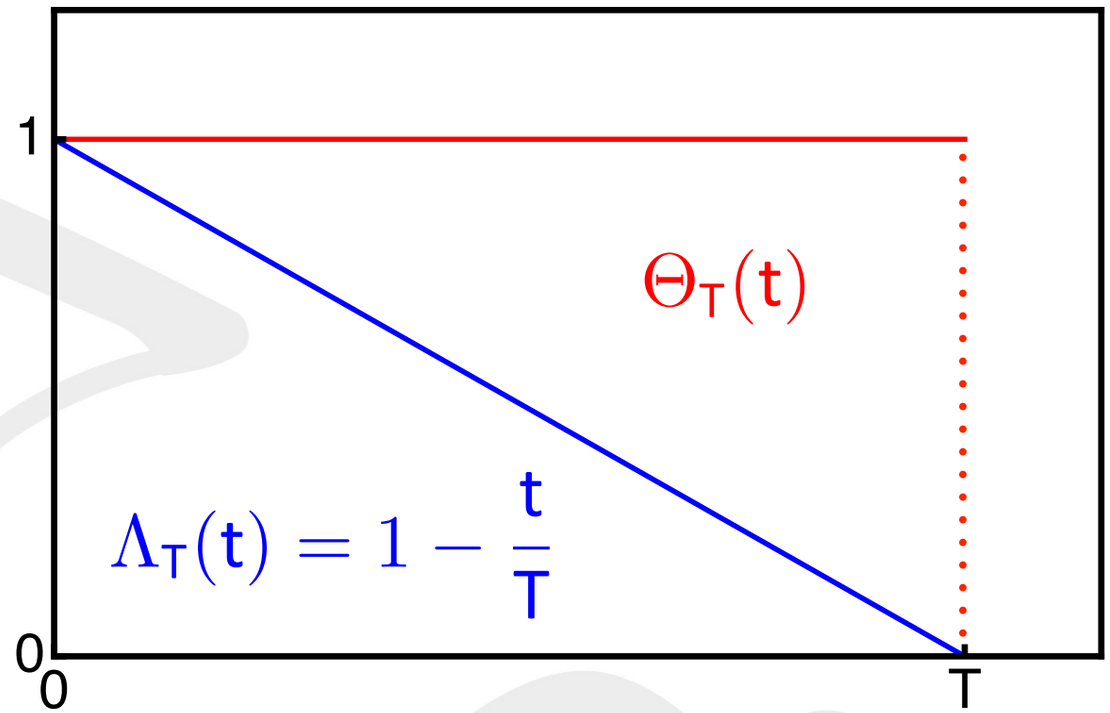


$$\kappa_E(T) = \frac{1}{2T}\left\langle \left| \int_0^T v(t)dt \right|^2 \right\rangle$$
$$= \int_0^\infty \langle v(t)v(0)\rangle \Lambda_T(t) dt$$

Einstein *vs.* Green-Kubo

$$\kappa_{GK}(T) = \int_0^T \langle v(t)v(0)\rangle dt$$
$$= \int_0^\infty \langle v(t)v(0)\rangle \Theta_T(t) dt$$
$$= \int_{-\infty}^\infty \tilde{C}_v(\omega)\tilde{\Theta}_T(\omega)\frac{d\omega}{2\pi}$$



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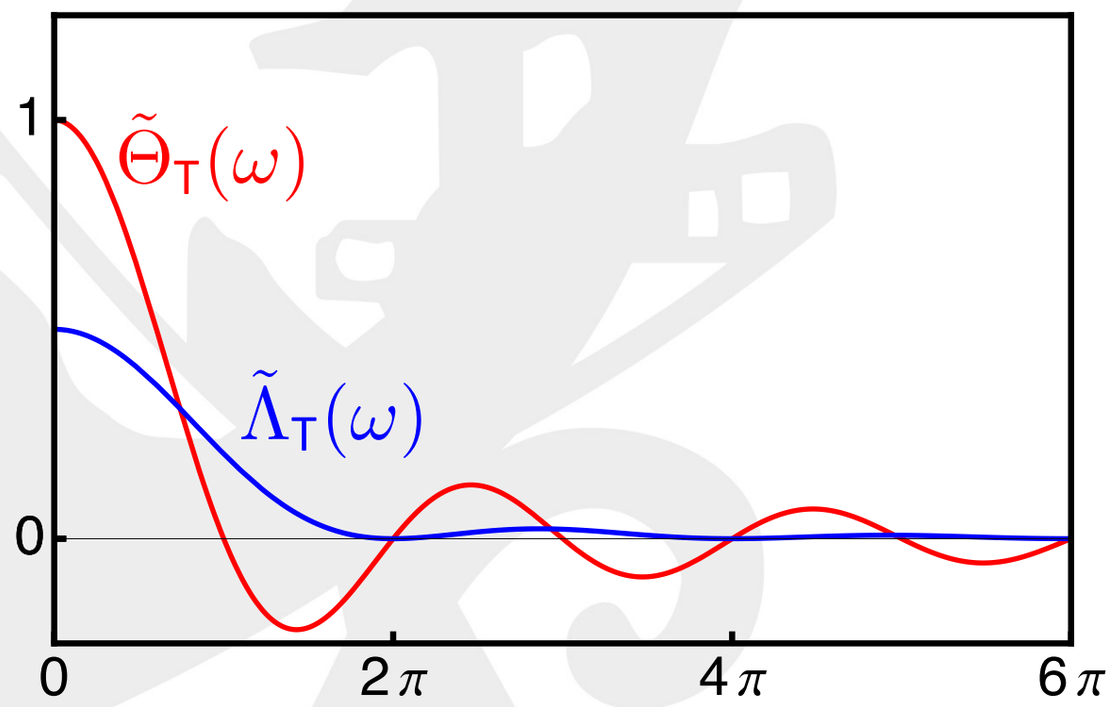
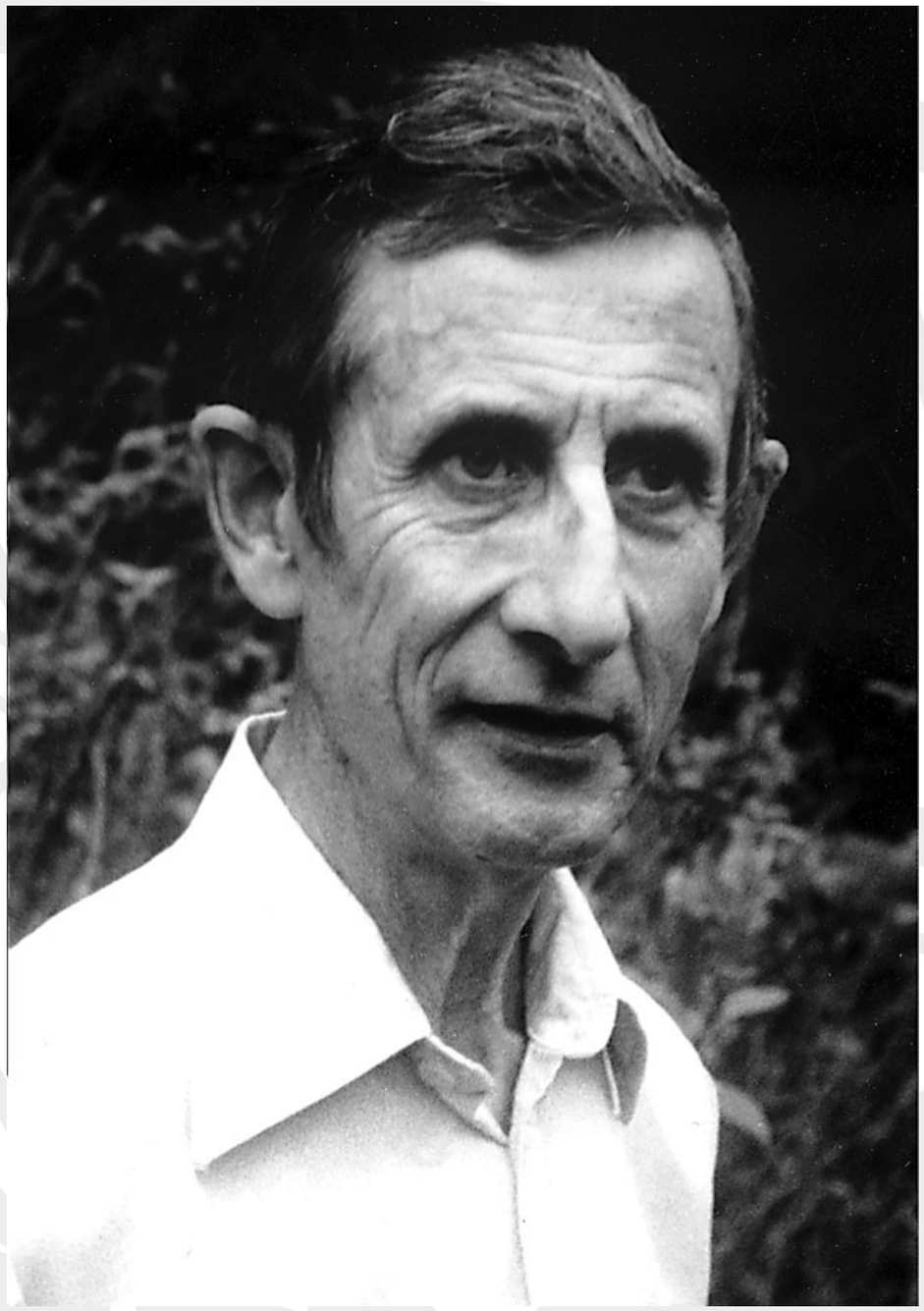


summary

- heat currents are intrinsically ill-defined at the atomic scale;
- energy conservation and extensivity make heat-transport coefficients independent of such an indeterminacy;
- this *gauge invariance* of thermal transport makes it possible to compute thermal transport coefficients from DFT using equilibrium AIMD and the Green-Kubo formalism;
- Einstein's relation is less sensitive to finite-frequency features of the spectrum than straight Green-Kubo;
- The statistical theory of time series can be leveraged to significantly improve the accuracy of the transport coefficients estimated from MD (in progress).



the computer is a tool for clear thinking

Freeman J. Dyson

thanks to:

Loris Ercole,
SISSA

Aris Marcolongo,
SISSA, now @EPFL

Paolo Umari,
University of Padua

thanks to:

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