what I cannot compute
I do not understand

fathoming heat (and charge) transport from the struggle to simulate it

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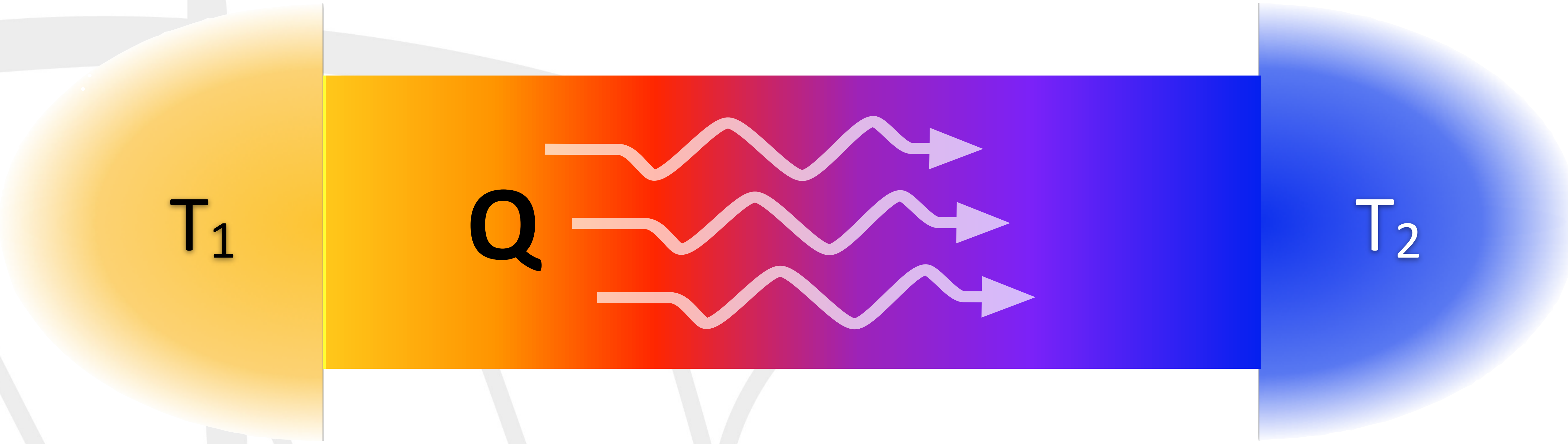
Scuola Internazionale Superiore di Studi Avanzati, Trieste

colloquium given at the Department of Physics of the Bilkent University, Ankara, May 9, 2018

what heat transport is all about



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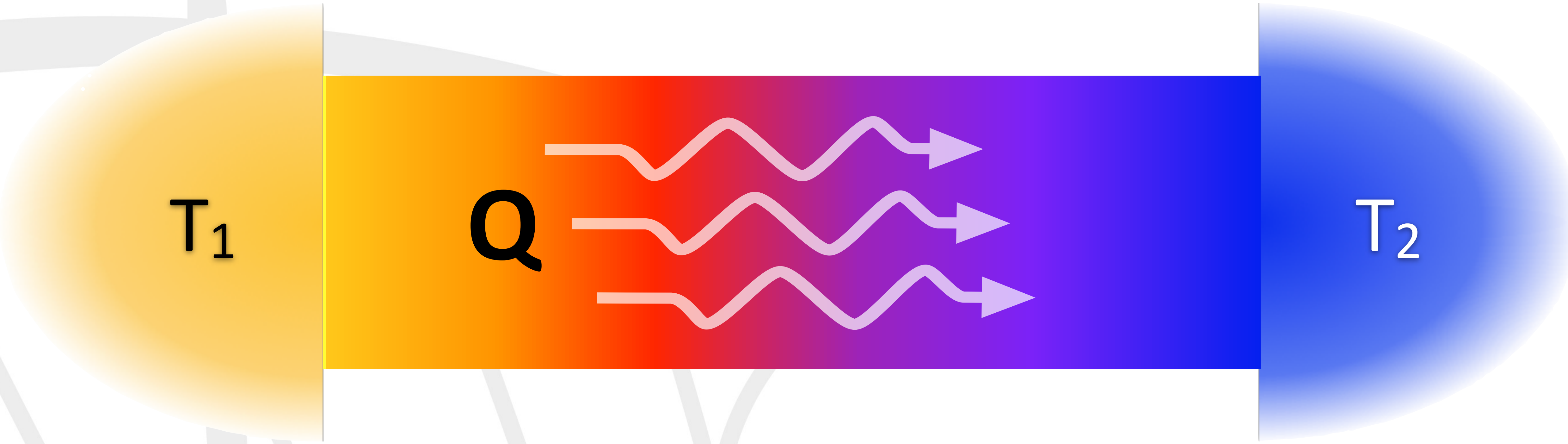
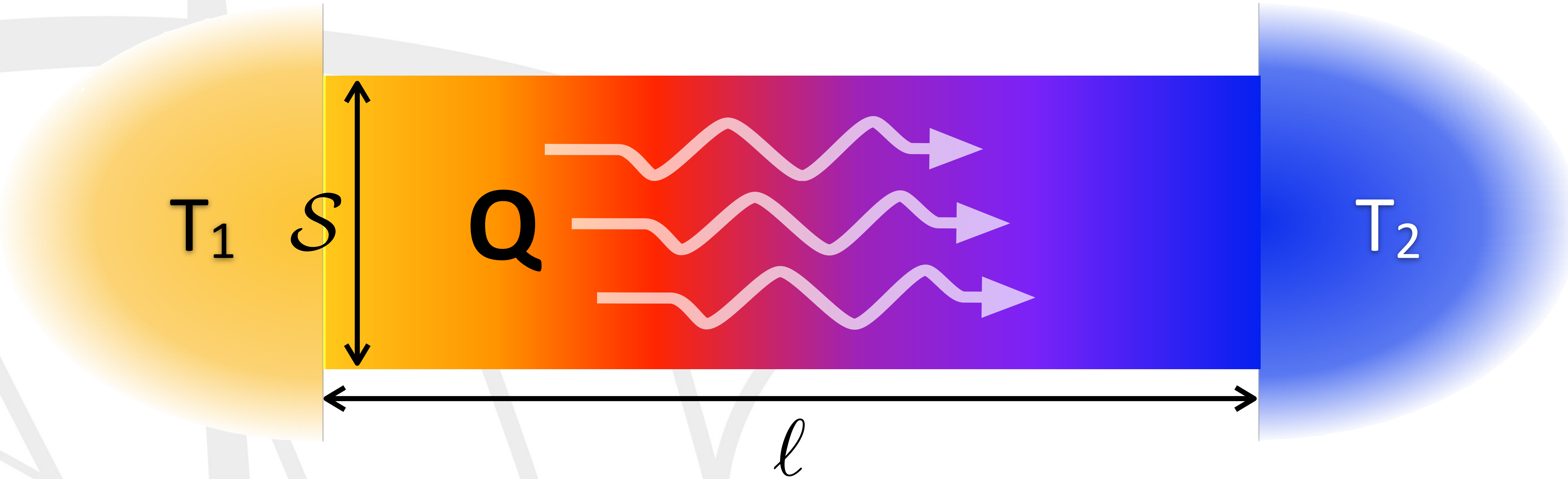


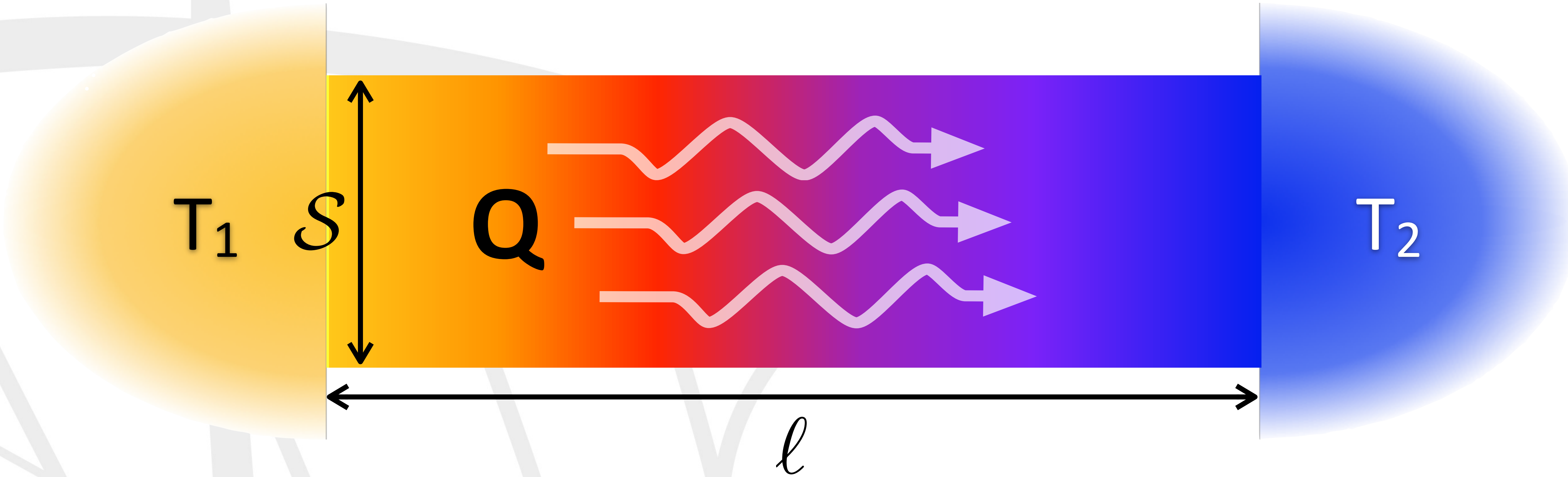
heat flows from the warm to the cool
as time flows from the past to the future

what heat transport is all about



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

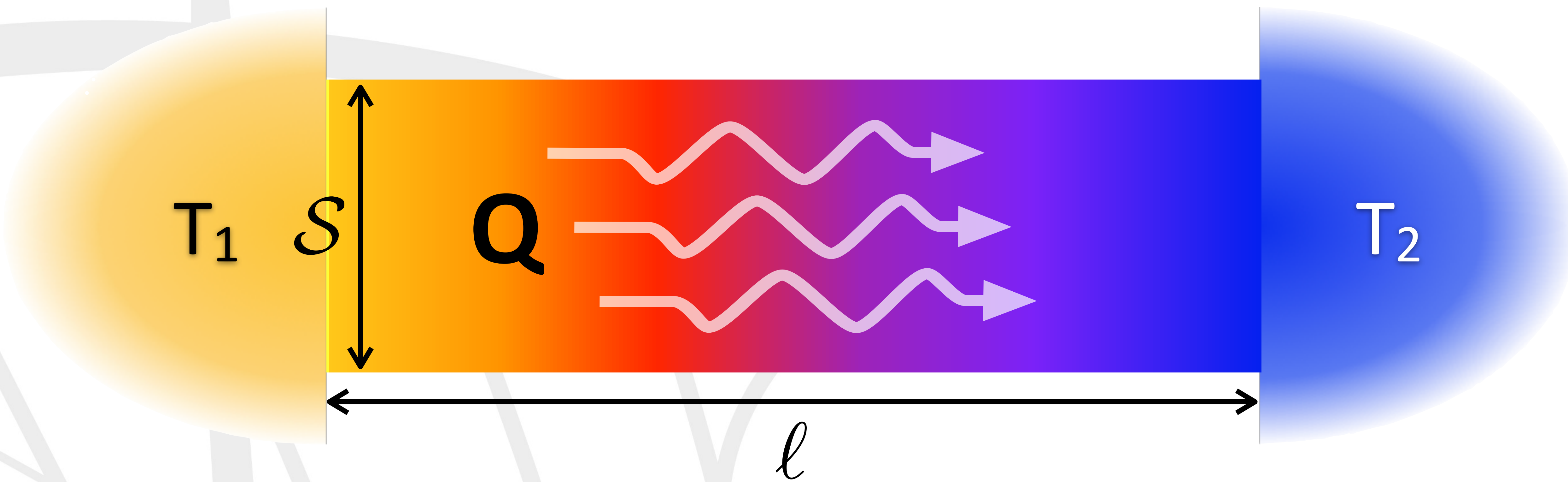
what heat transport is all about



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

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

what heat transport is all about



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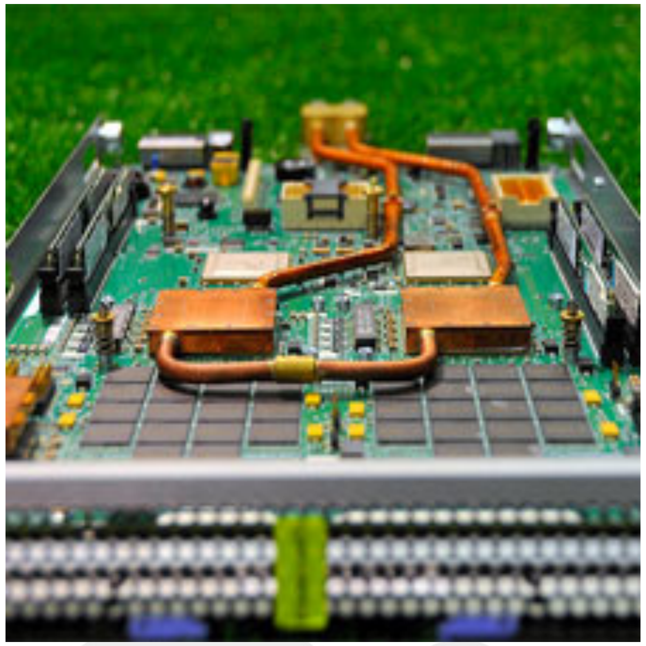
$$\mathbf{j}_Q(\mathbf{r},t) = -\kappa\nabla T(\mathbf{r},t)$$

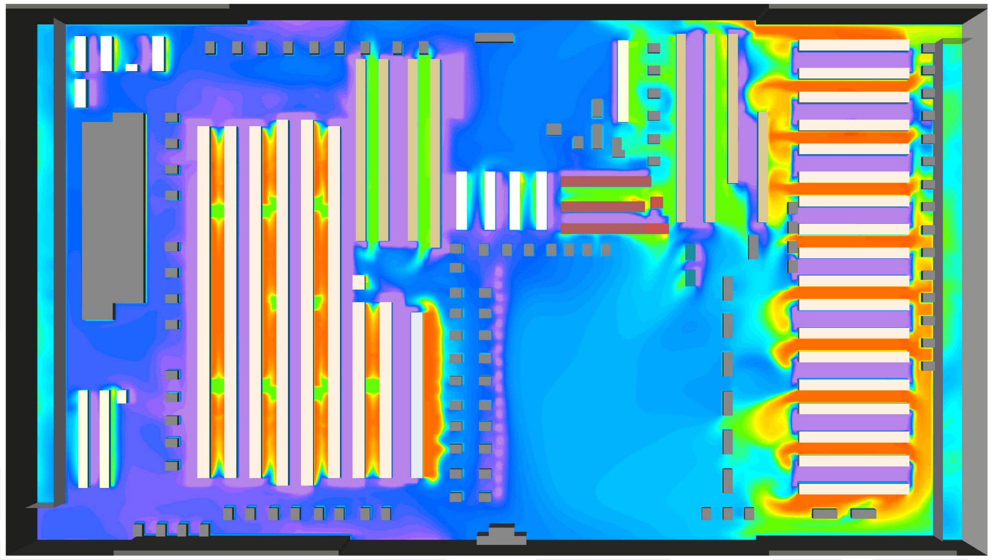
$$\frac{\partial T}{\partial t} = \frac{\kappa}{\rho c_p}\Delta T$$

why should we care?

energy saving

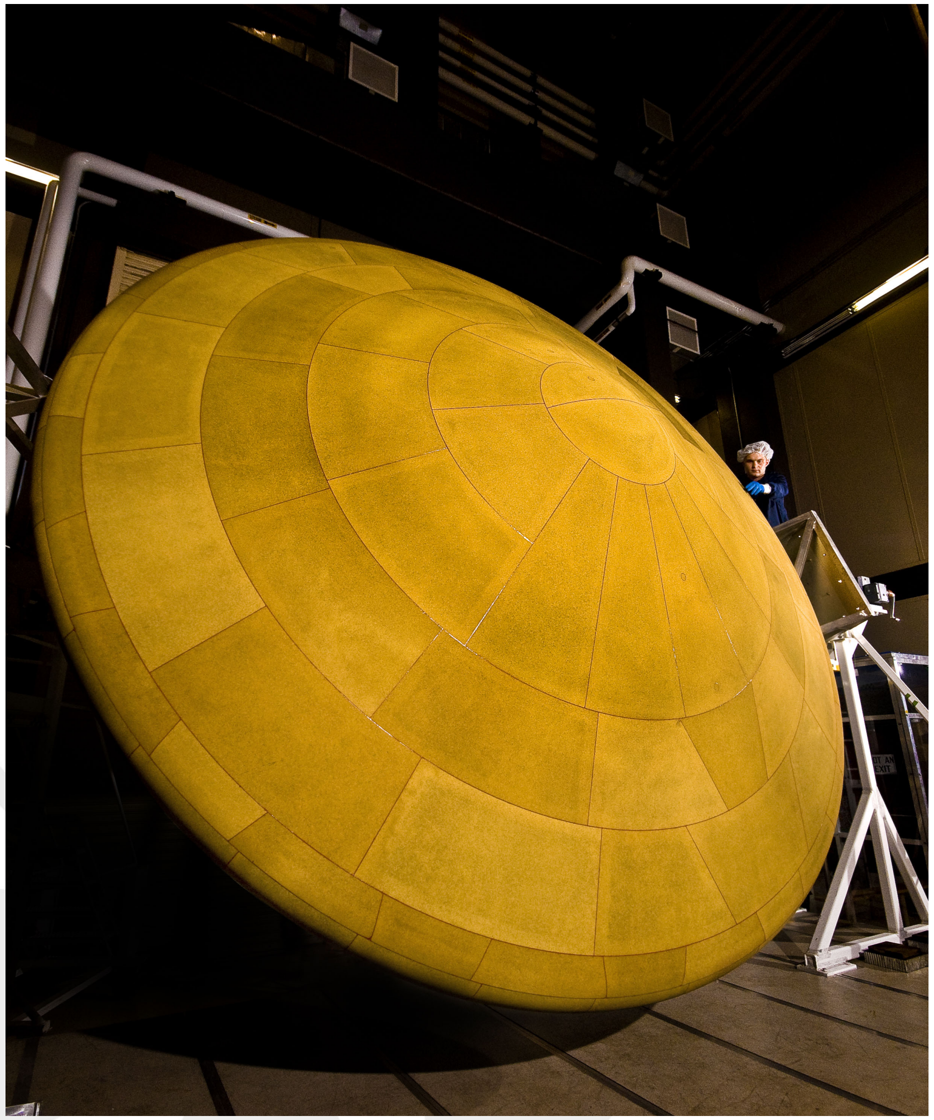
heat dissipation



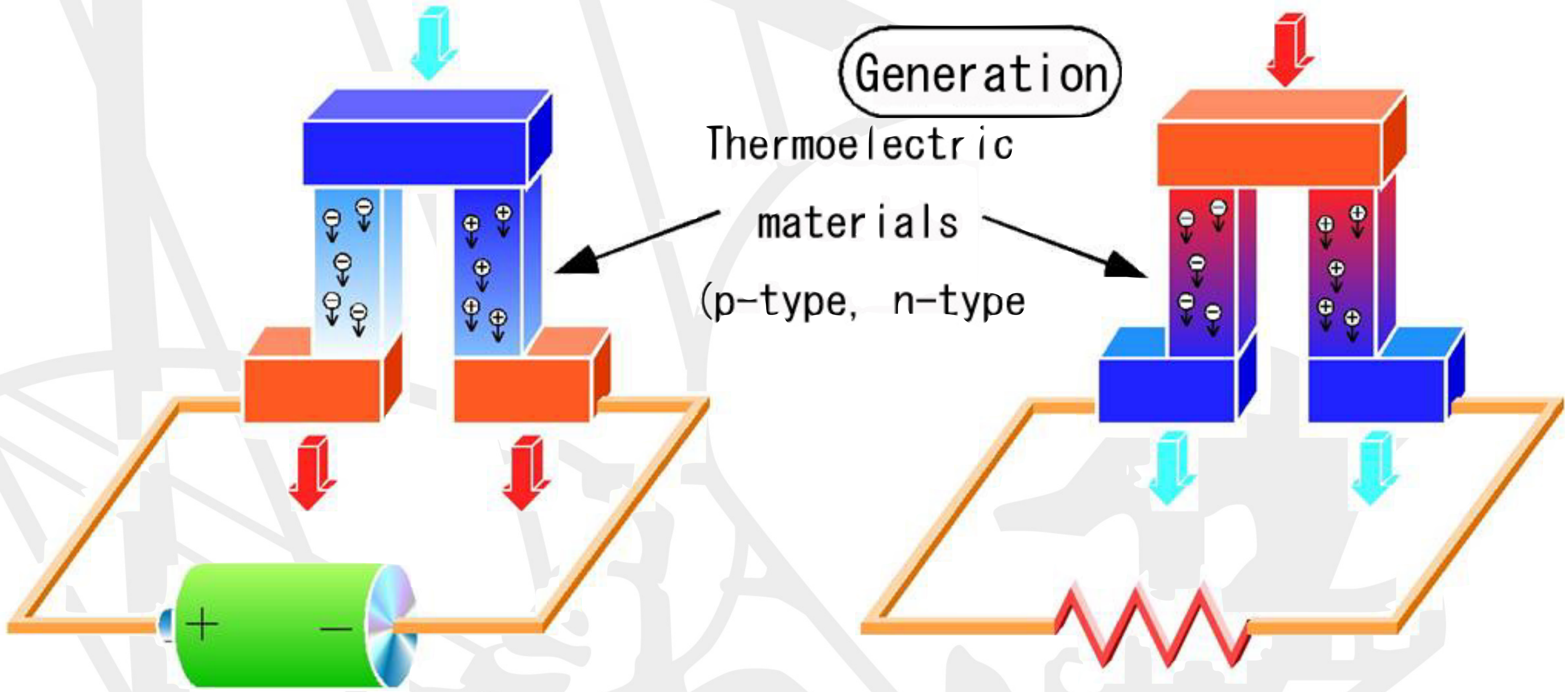


heat shielding

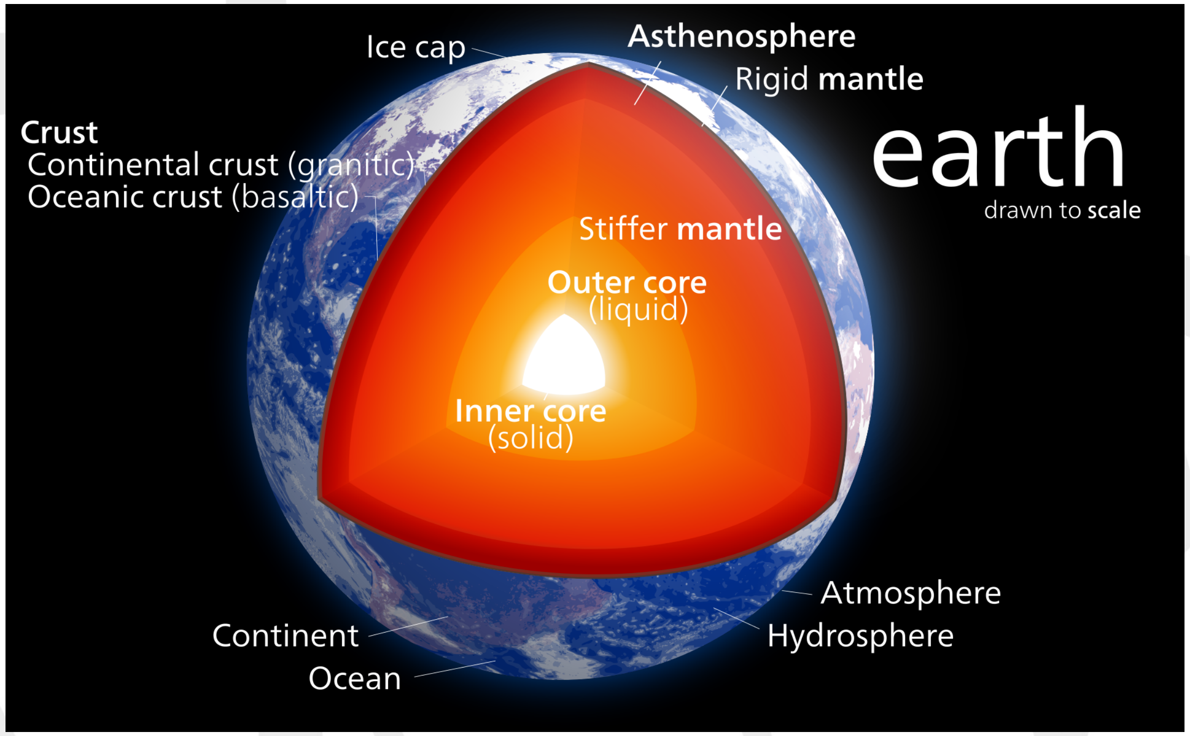
heat shielding

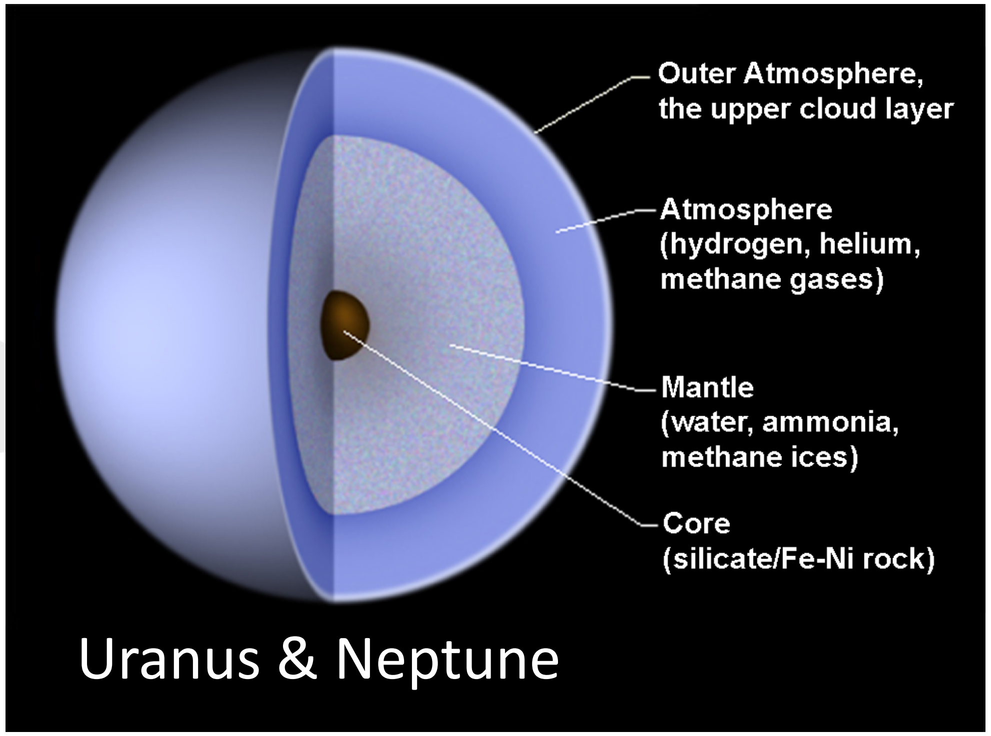


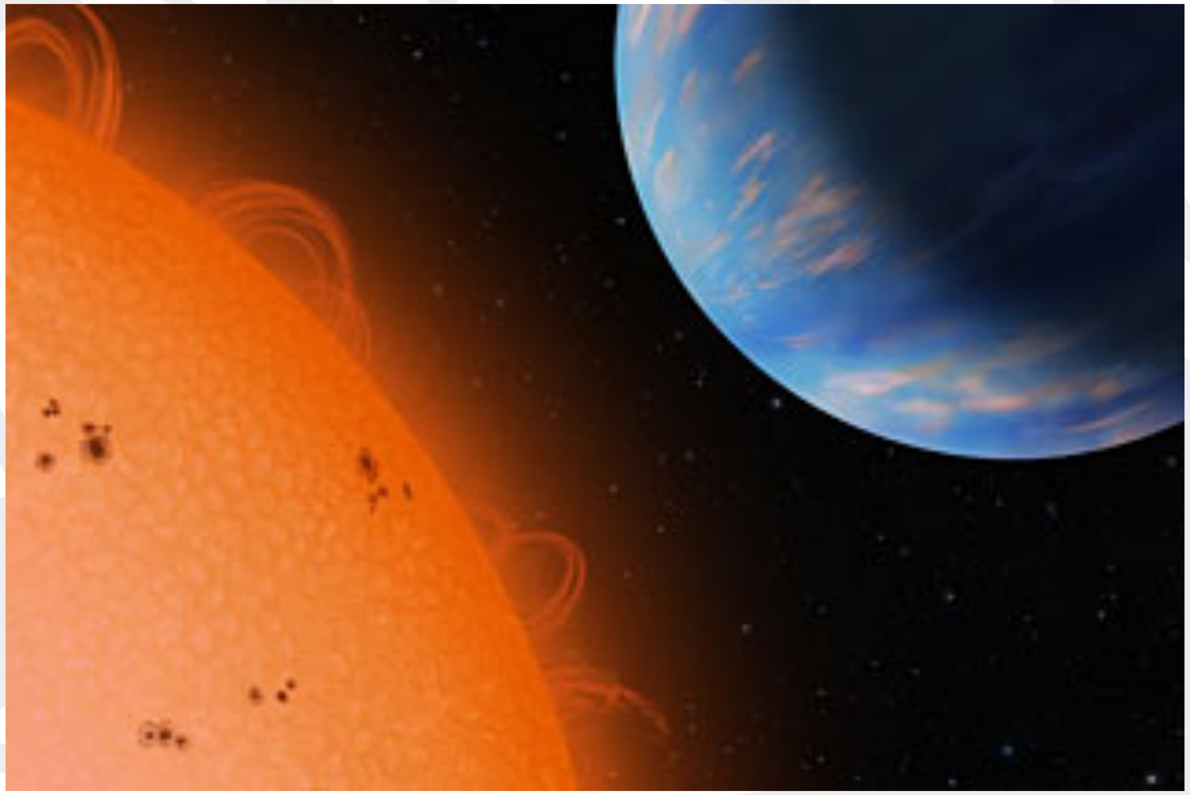
energy conversion

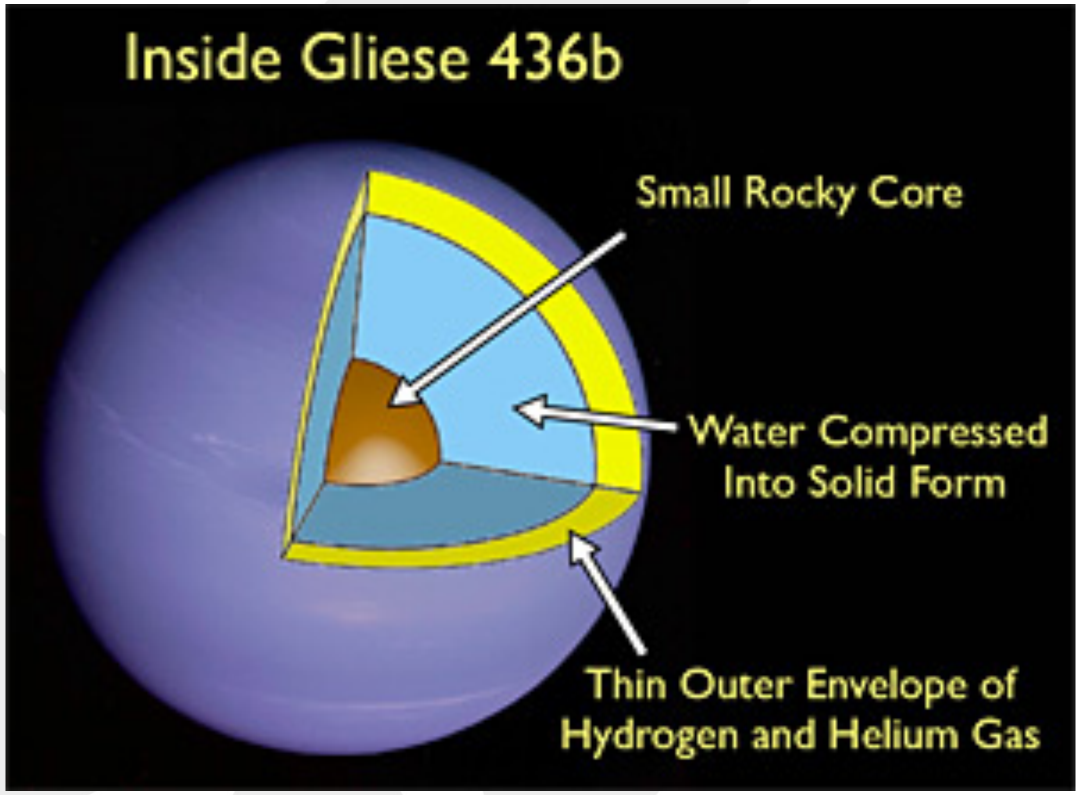


planetary sciences









why should we care?

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

why should we care?

why should we care?

- … because it is important and poorly understood

Green-Kubo theory

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

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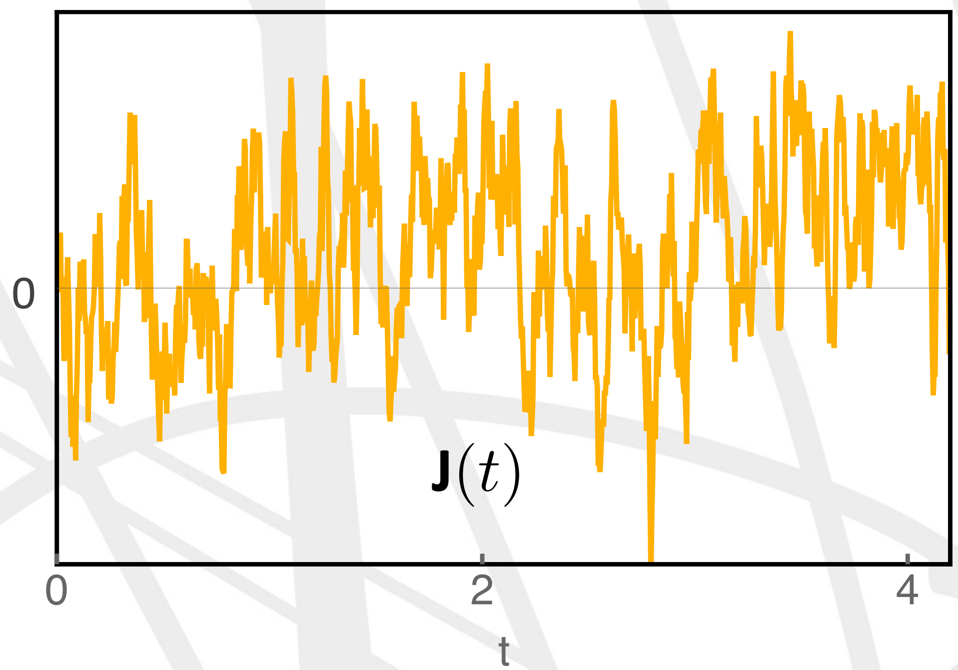

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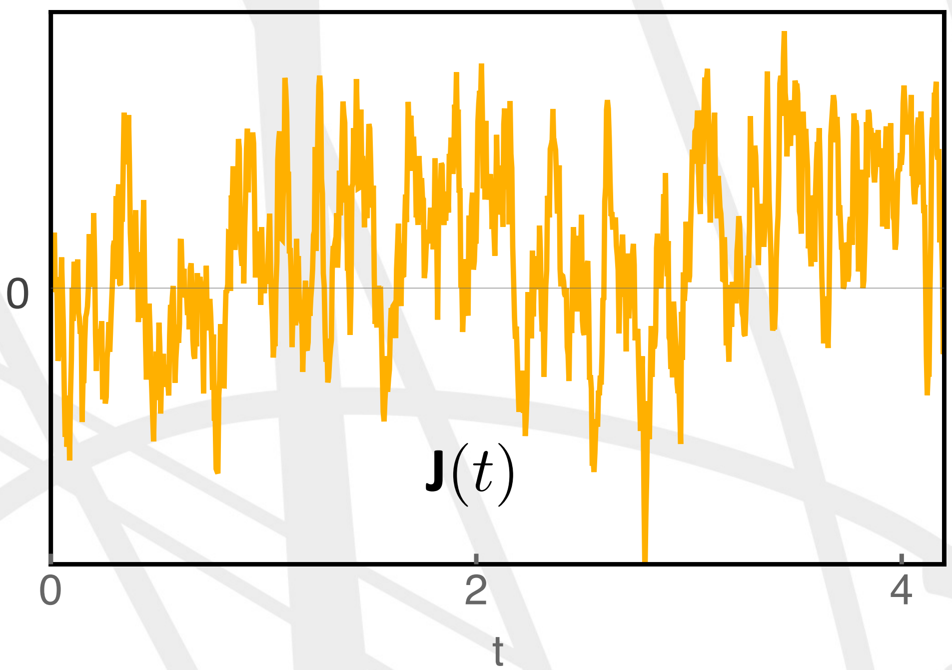

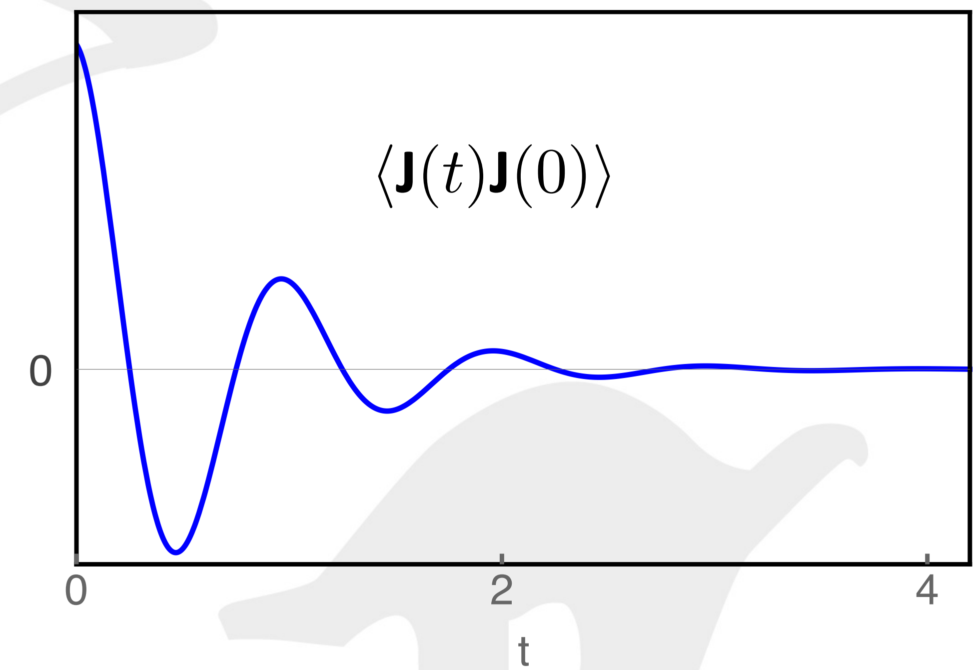

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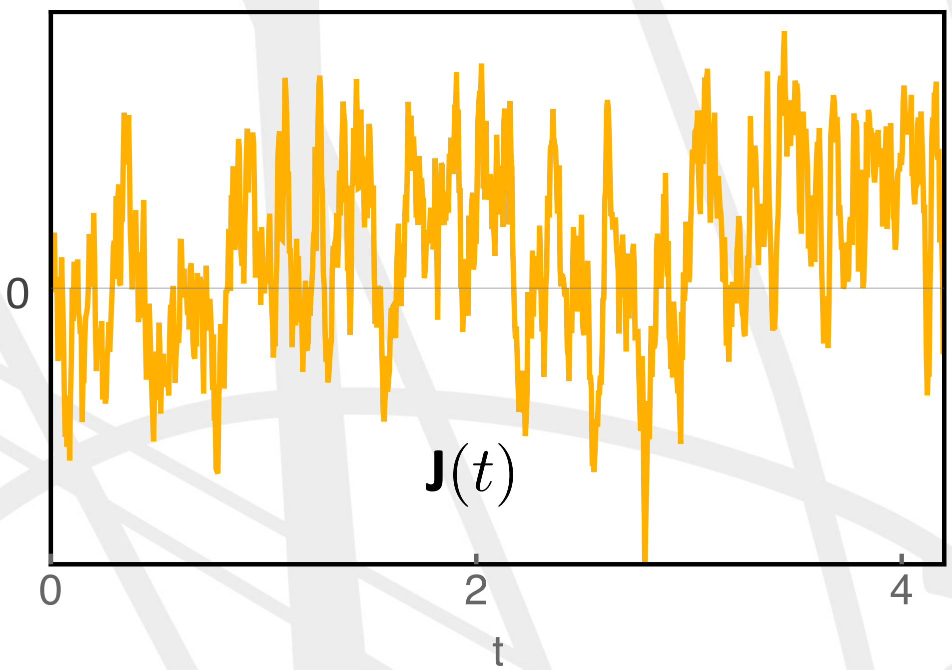

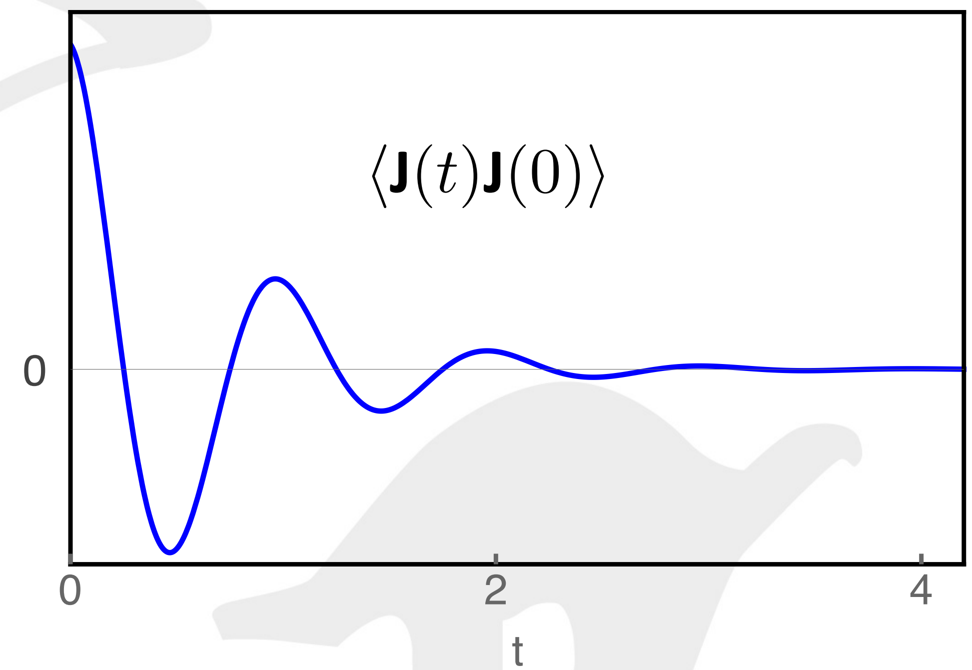

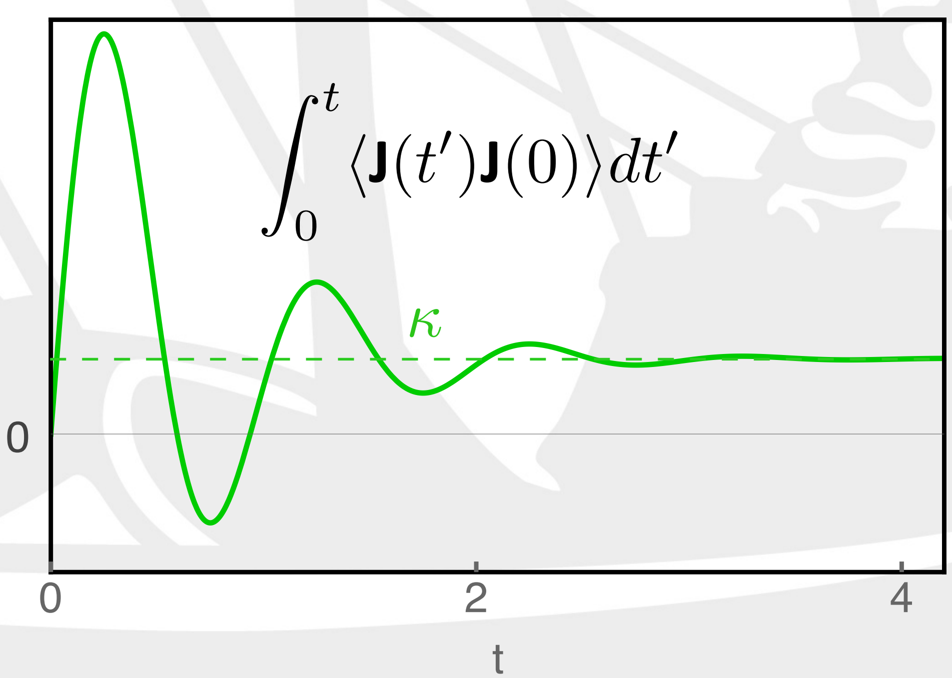

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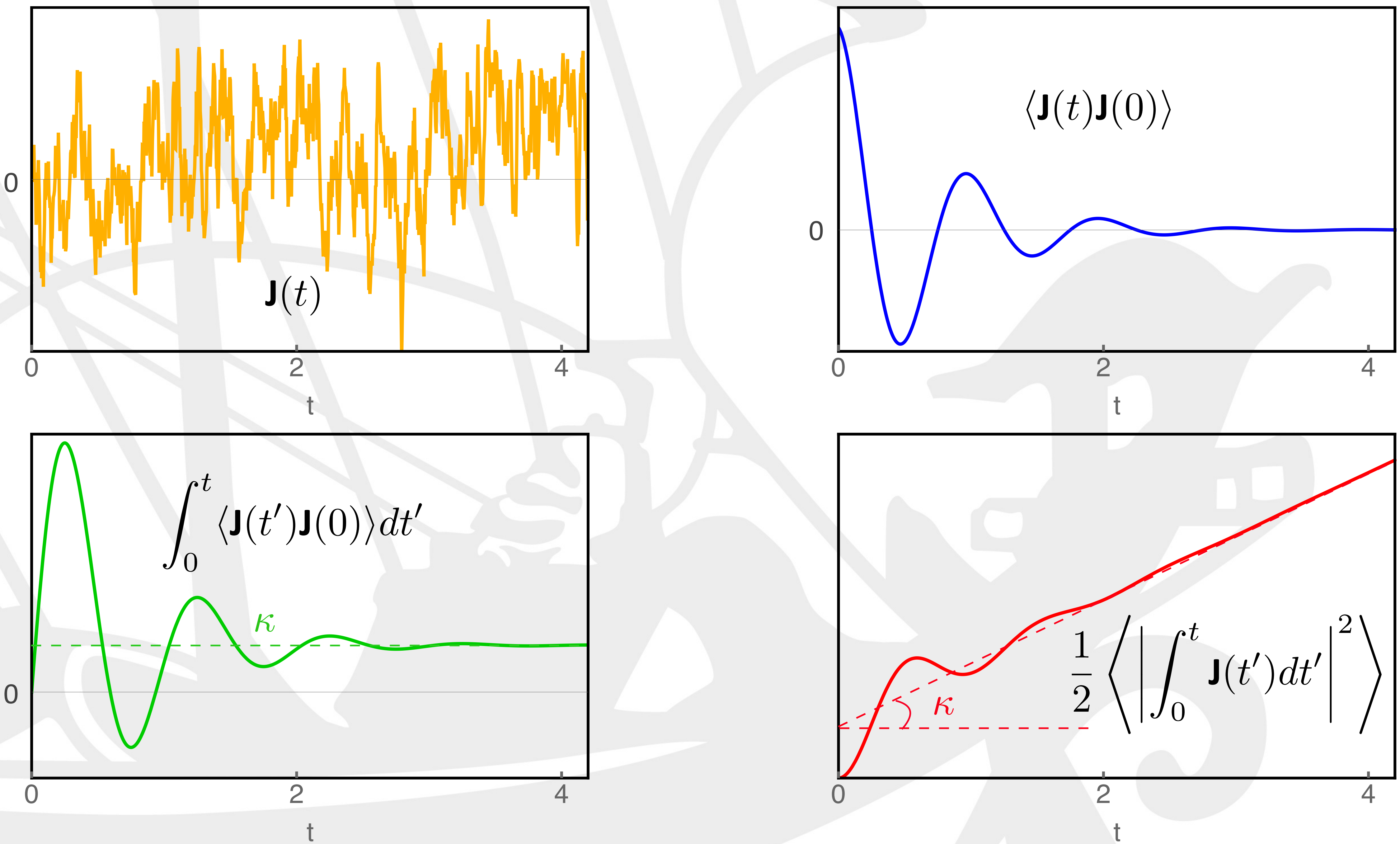

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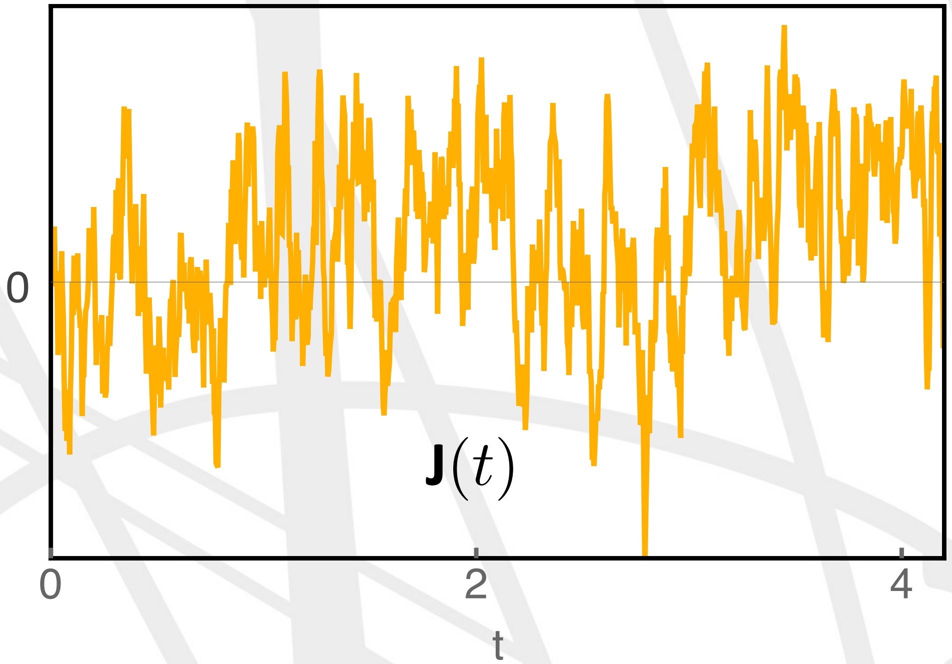

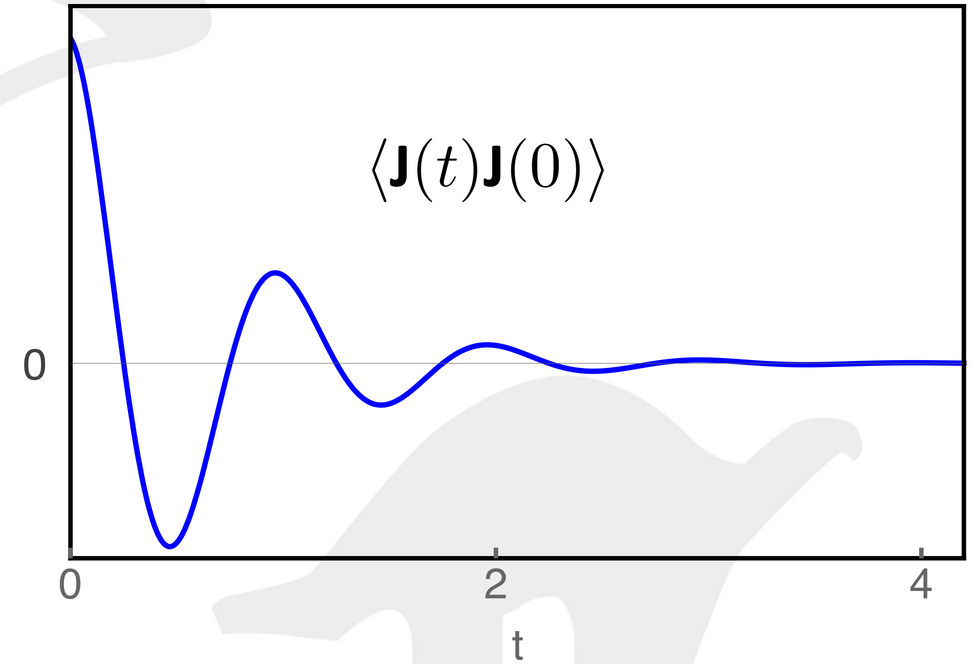

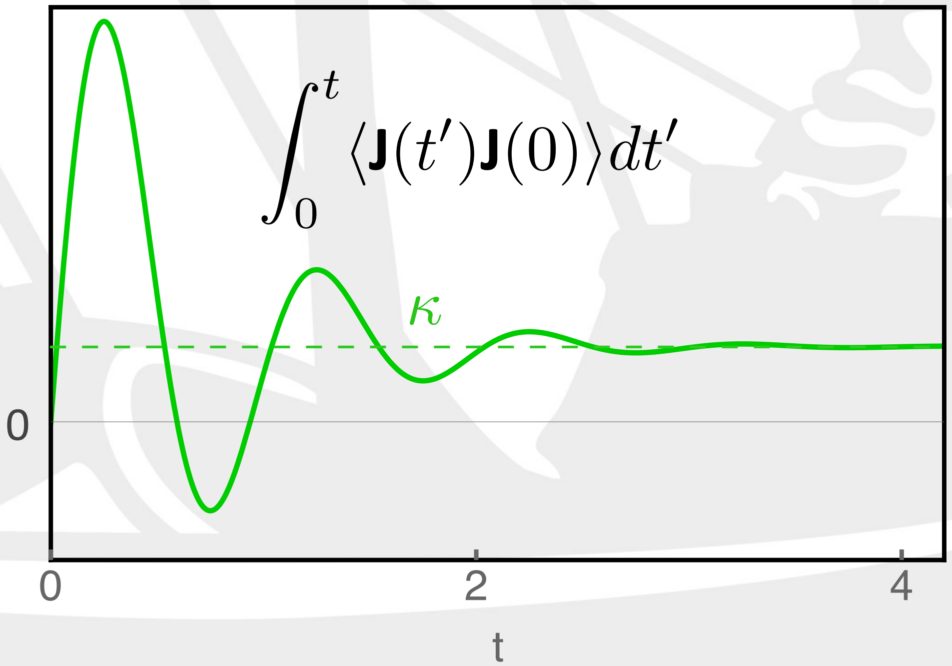

Einstein's relation
for the diffusion coefficients

$$\int_0^t \langle \mathbf{J}(t')\mathbf{J}(0)\rangle dt' = \frac{1}{2t}\left\langle \left| \int_0^t \mathbf{J}(t')dt' \right|^2 \right\rangle + \mathcal{O}\left(t^{-1}\right)$$

the classical MD ansatz

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

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

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ab initio simulations

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Thermal Conductivity of Periclase (MgO) from First Principles

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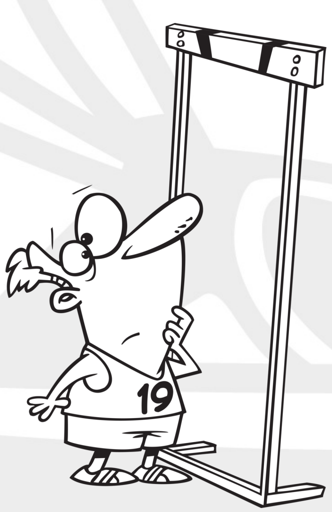
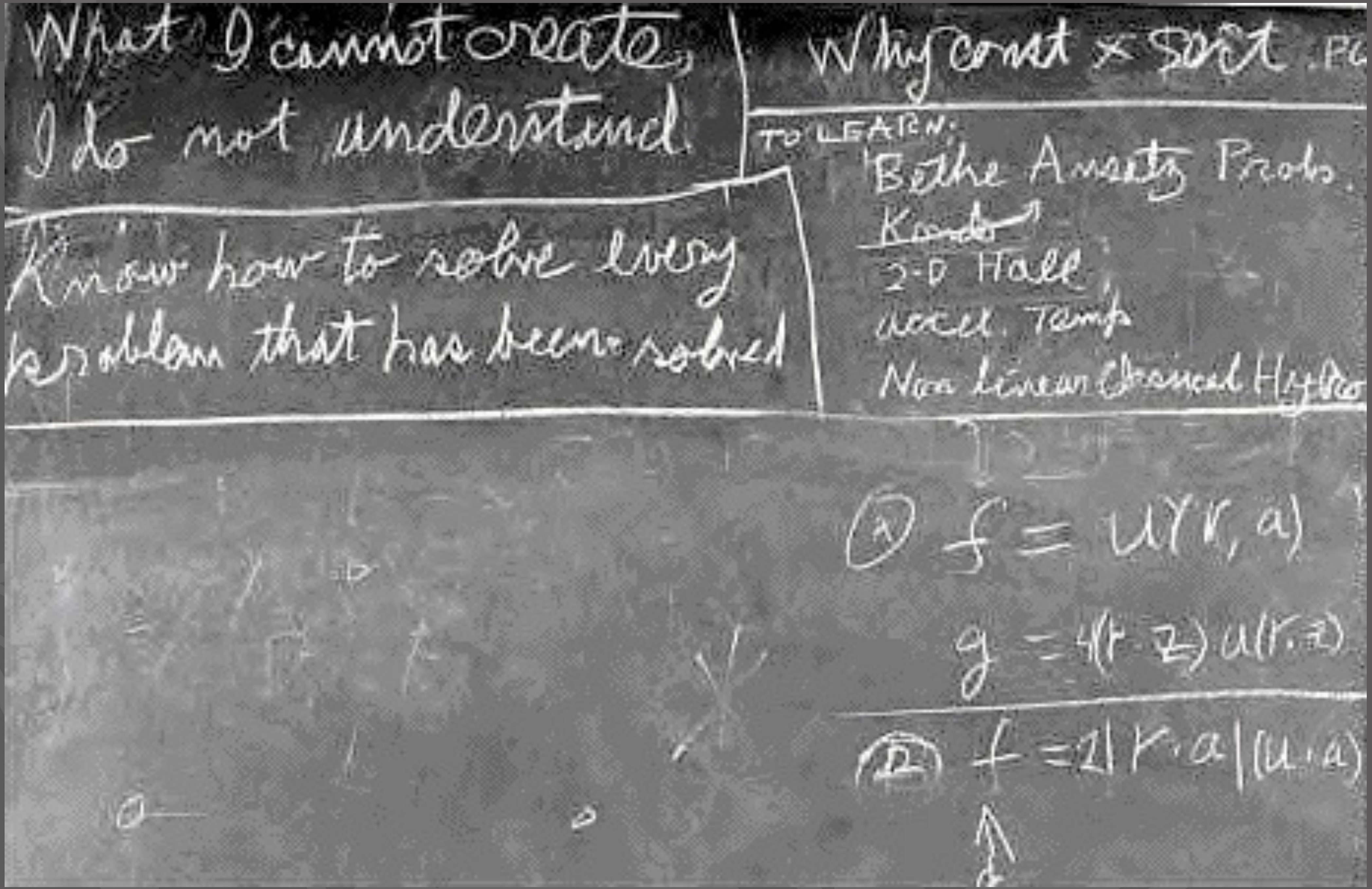
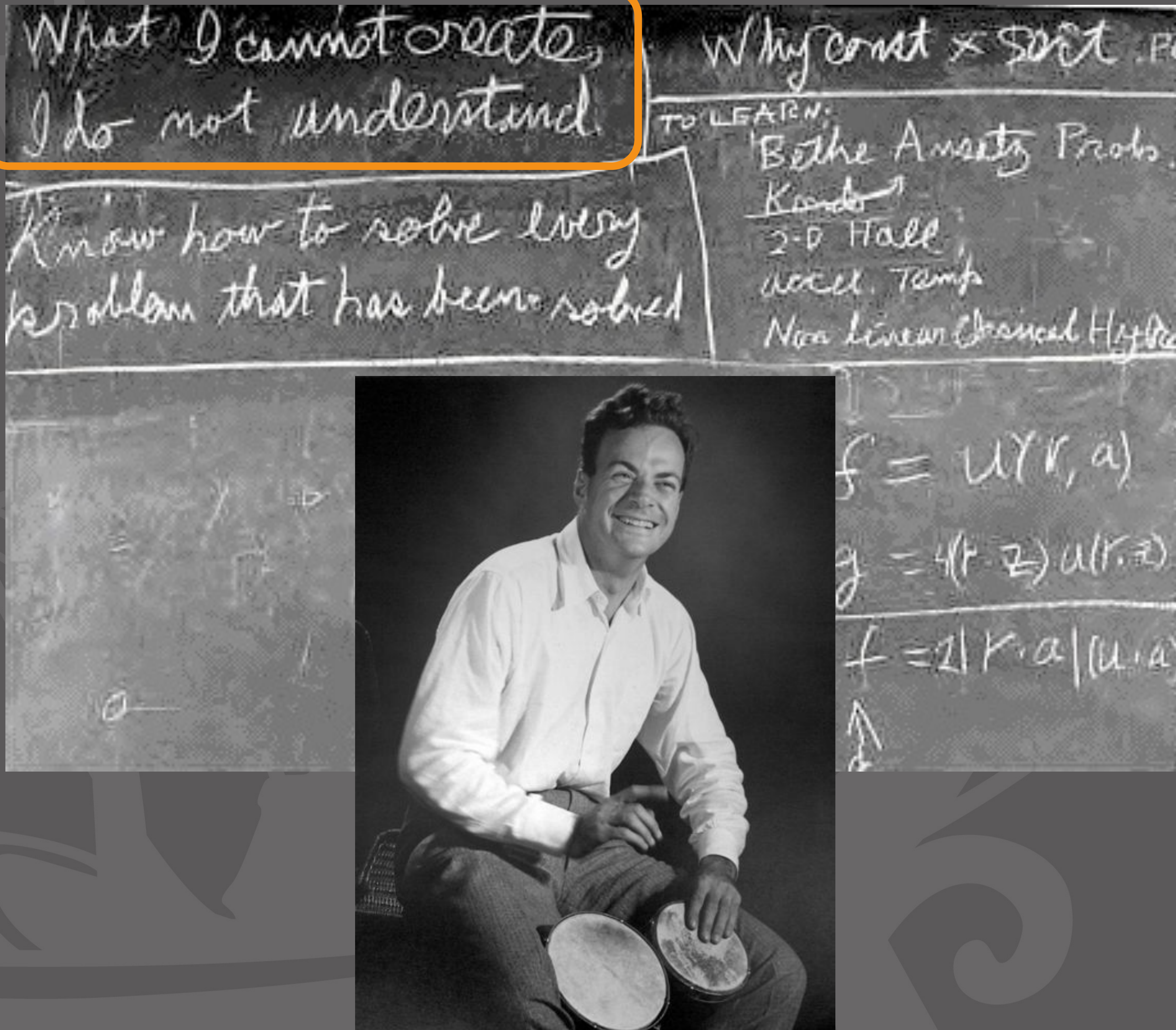
Department of Computer Science, Louisiana State University, Baton Rouge, Louisiana 70803, USA and Department of Geology and Geophysics, Louisiana State University, Baton Rouge, Louisiana 70803, USA

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.




What I cannot create,
I do not understand.
Know how to solve every
problem that has been solved
TO LEARN:
Bethe Ansatz Probs.
Kondo
2-D Hall
accel. Temp
Non Linear Classical Hydro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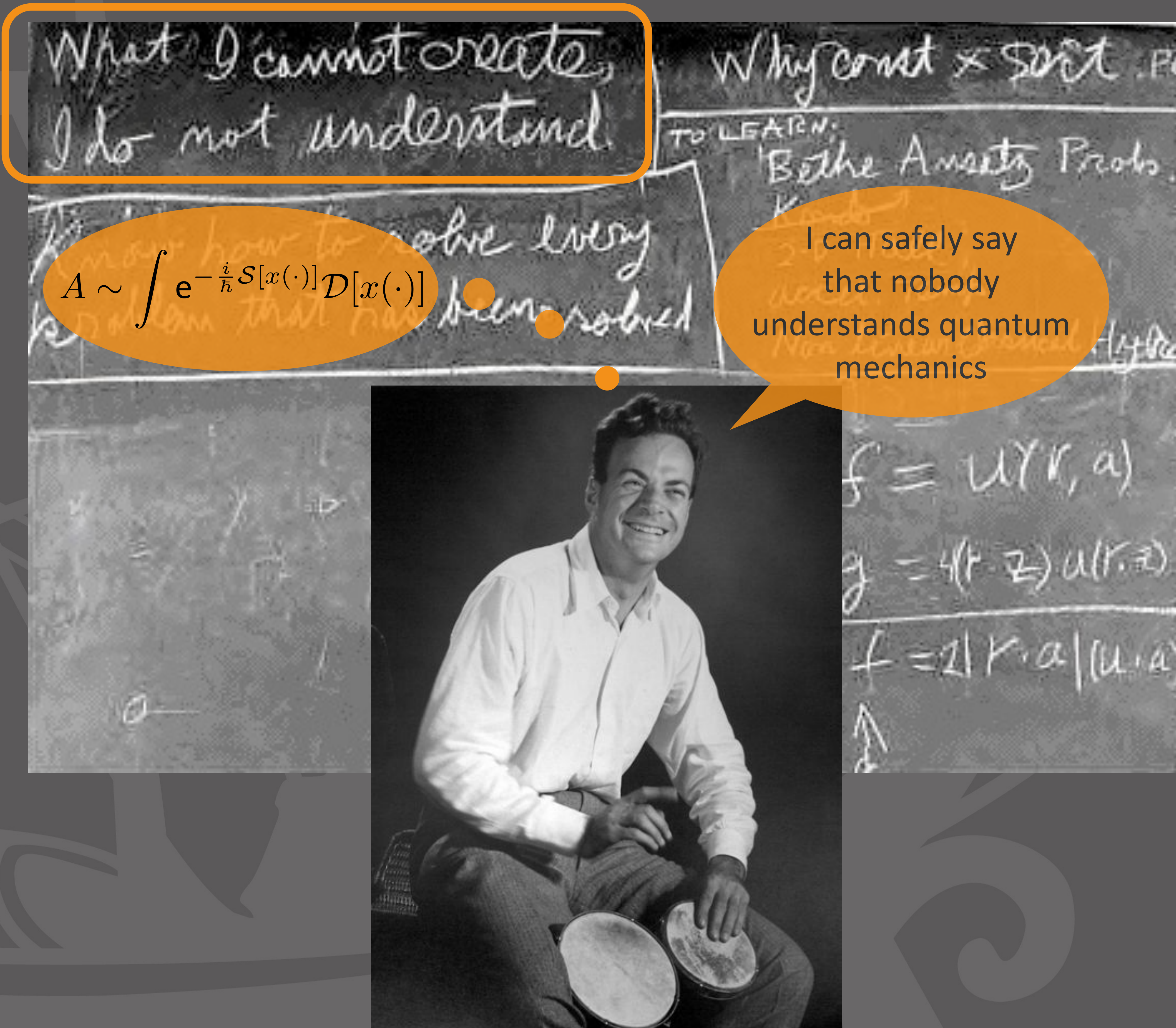
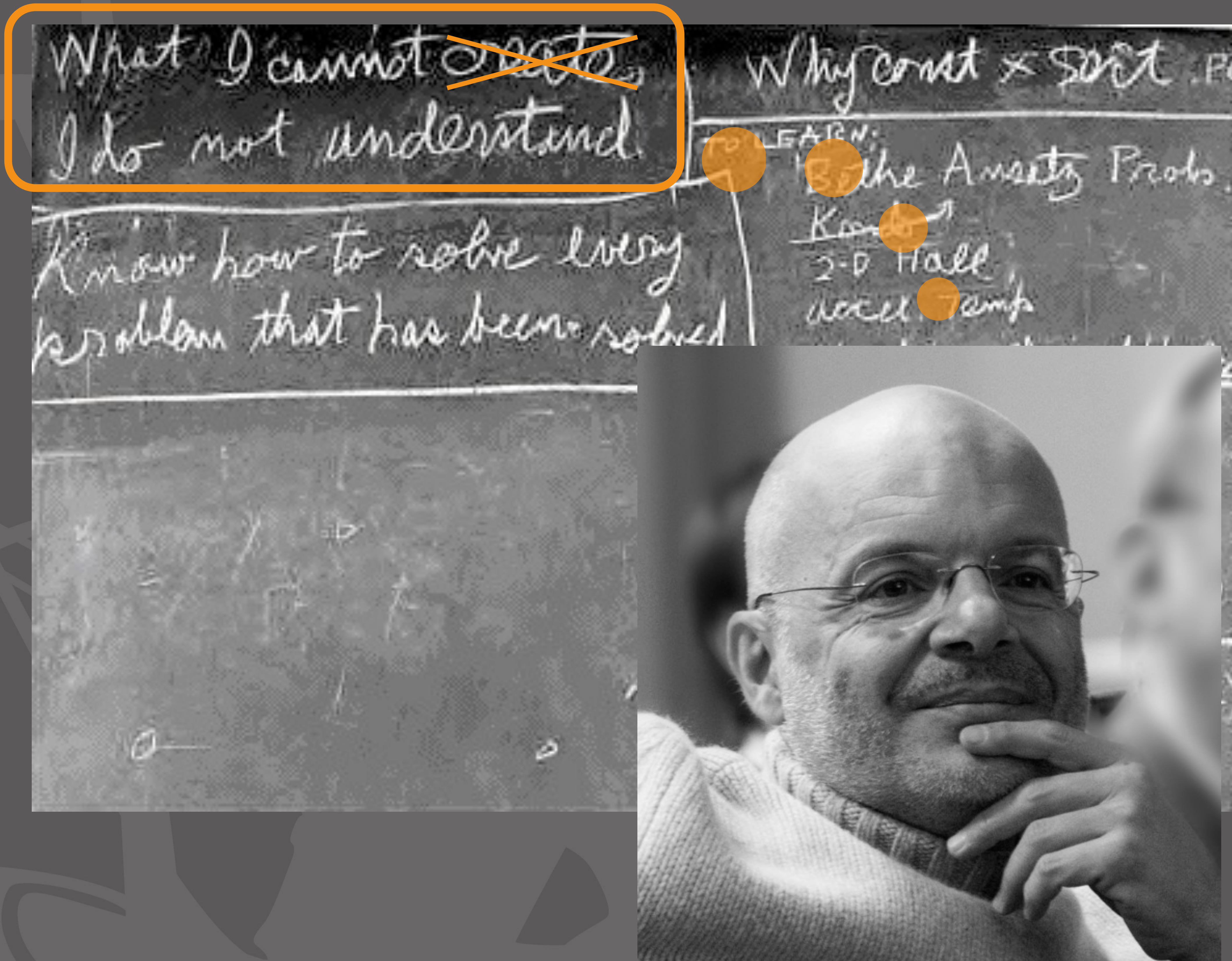

What I cannot create,
I do not understand
$A \sim \int e^{-\frac{i}{\hbar}\mathcal{S}[x(\cdot)]}\mathcal{D}[x(\cdot)]$
I can safely say that nobody understands quantum mechanics

compute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insights from classical mechanics

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$$= \text{cnst}$$

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insights from classical mechanics

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

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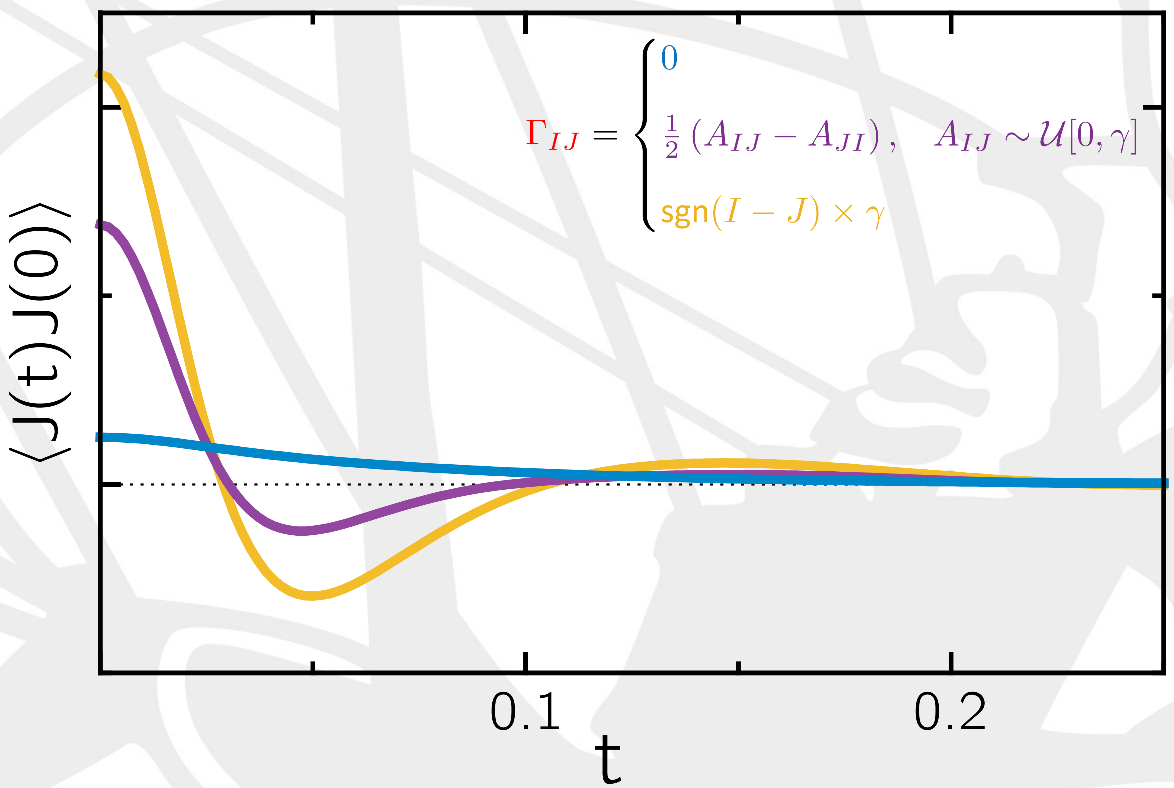

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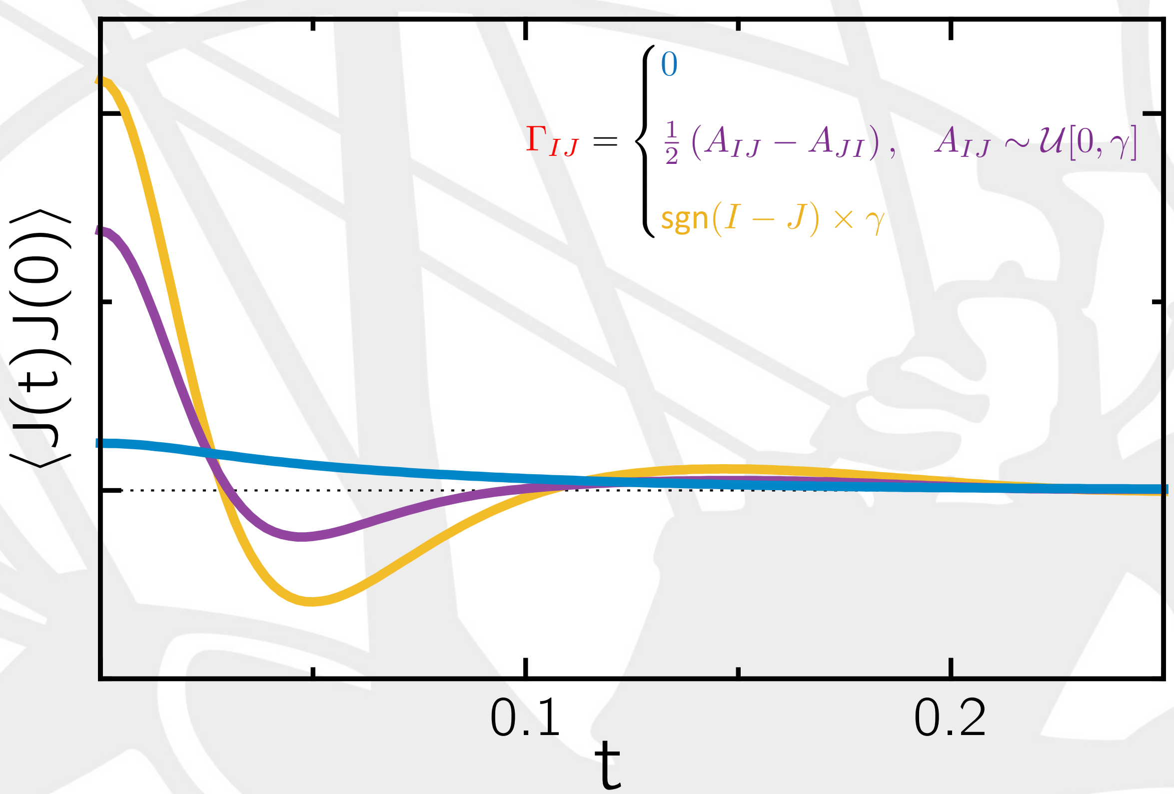

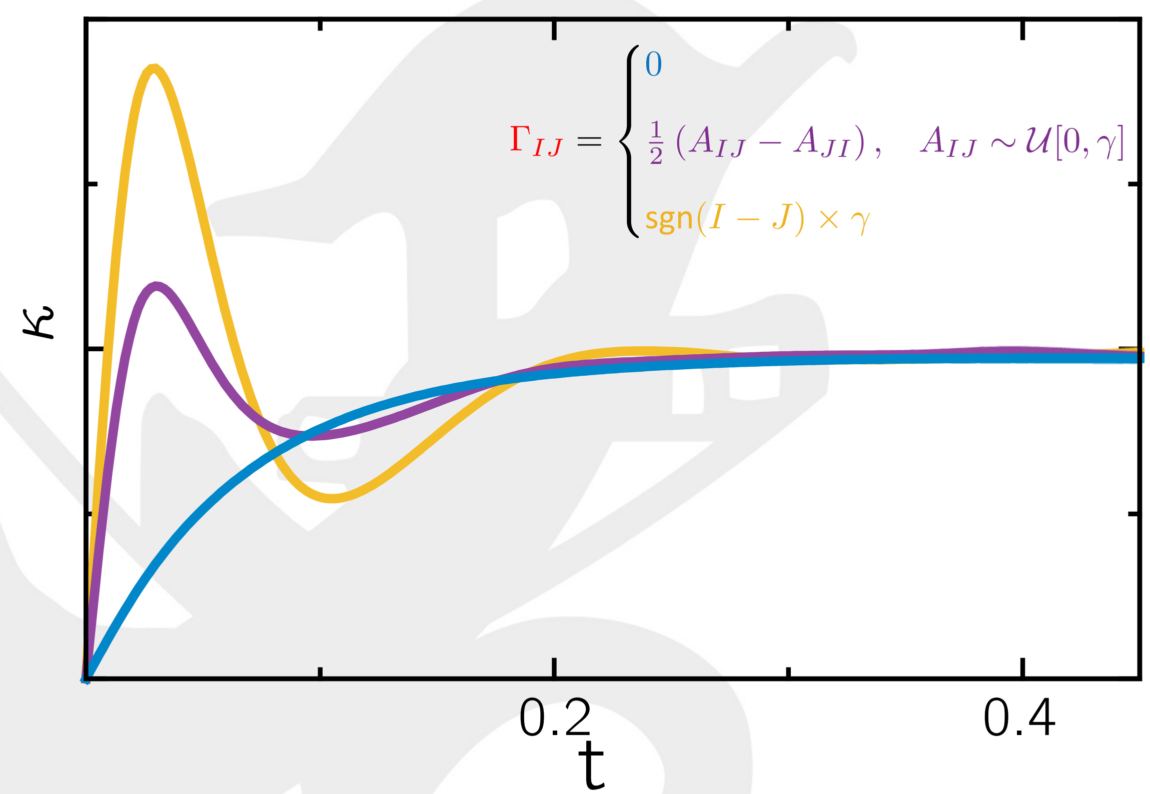

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$$\dot{\mathbf{P}} = \frac{\mathrm{d}}{\mathrm{dt}}\frac{1}{4}\sum_{I\neq J}\Gamma_{IJ}\, v(|\mathbf{R}_I - \mathbf{R}_J|)(\mathbf{R}_I - \mathbf{R}_I)$$

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

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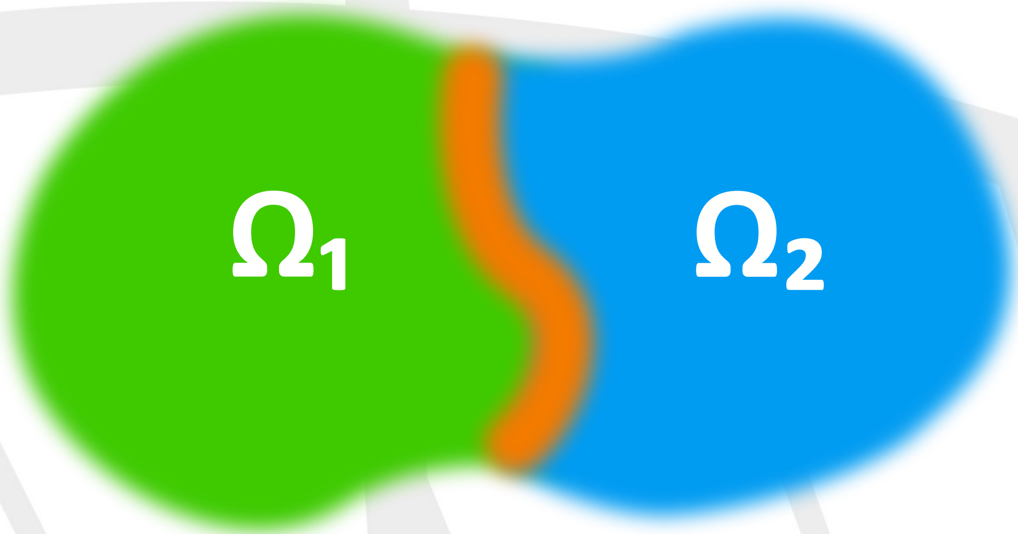
$$\mathbf{D}(t) = \mathbf{D}'(t) + \mathbf{P}(t) - \mathbf{P}(0)$$

$$\kappa' = \kappa$$

gauge invariance



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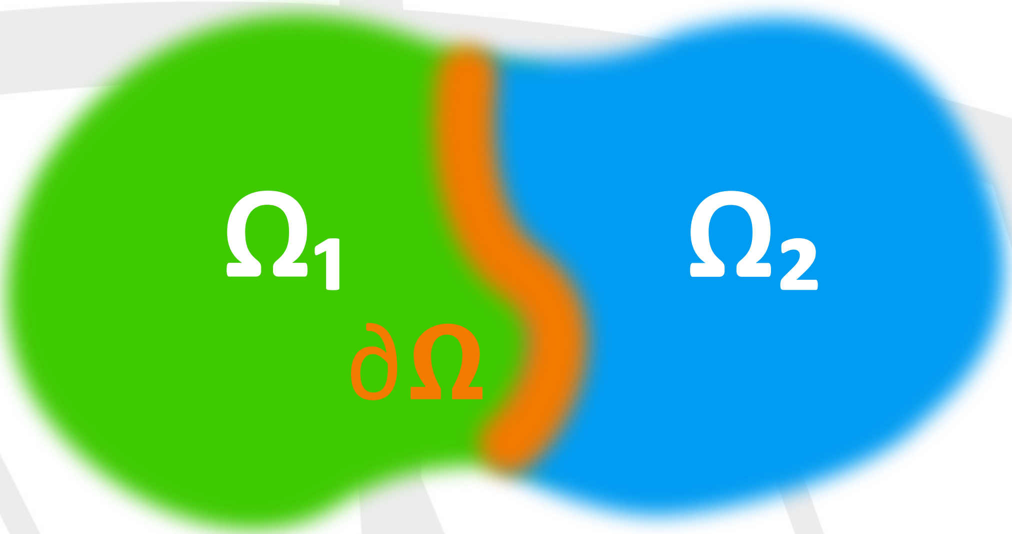
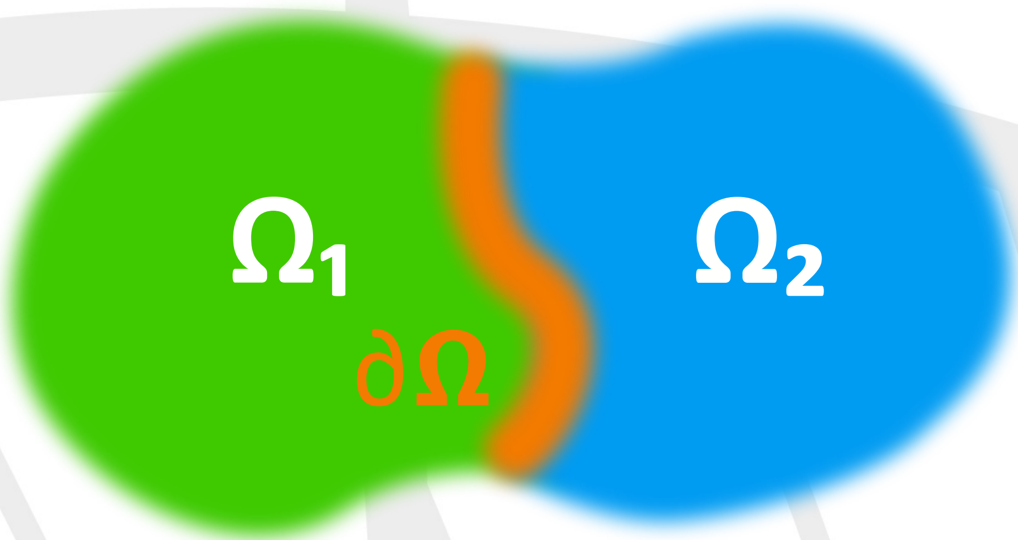


$$E[\Omega_1 \cup \Omega_2] = E[\Omega_1] + E[\Omega_2] + W[\partial\Omega]$$

gauge invariance



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

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

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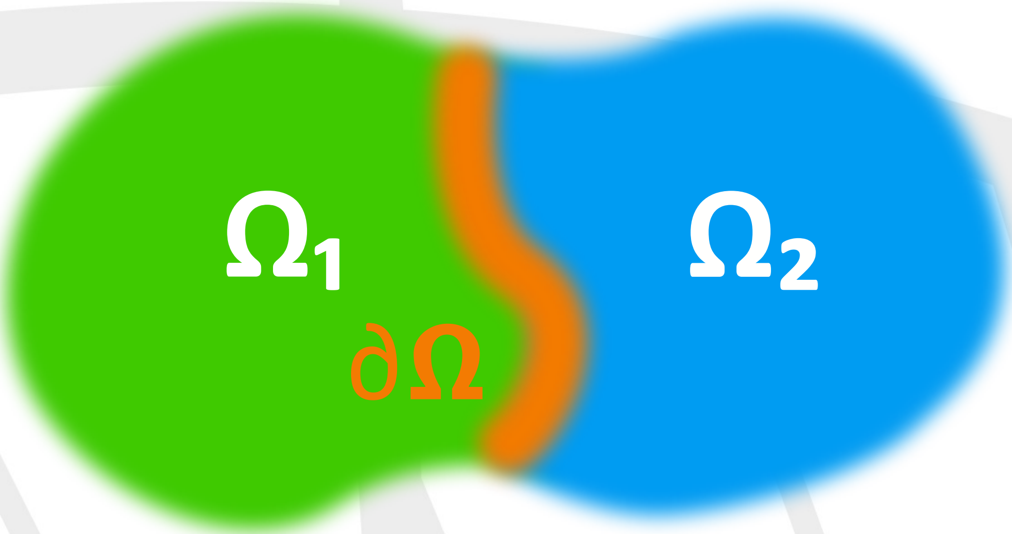
gauge invariance



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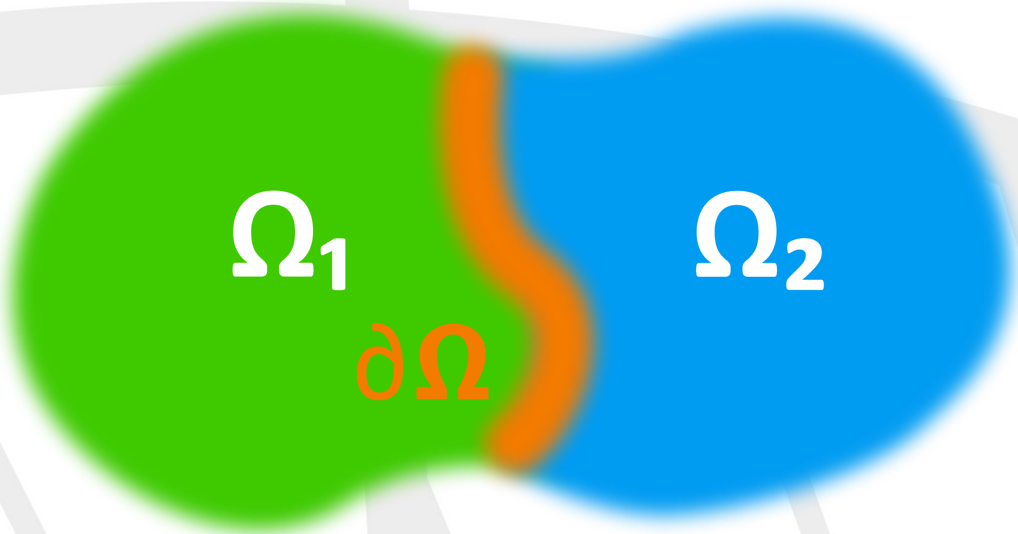

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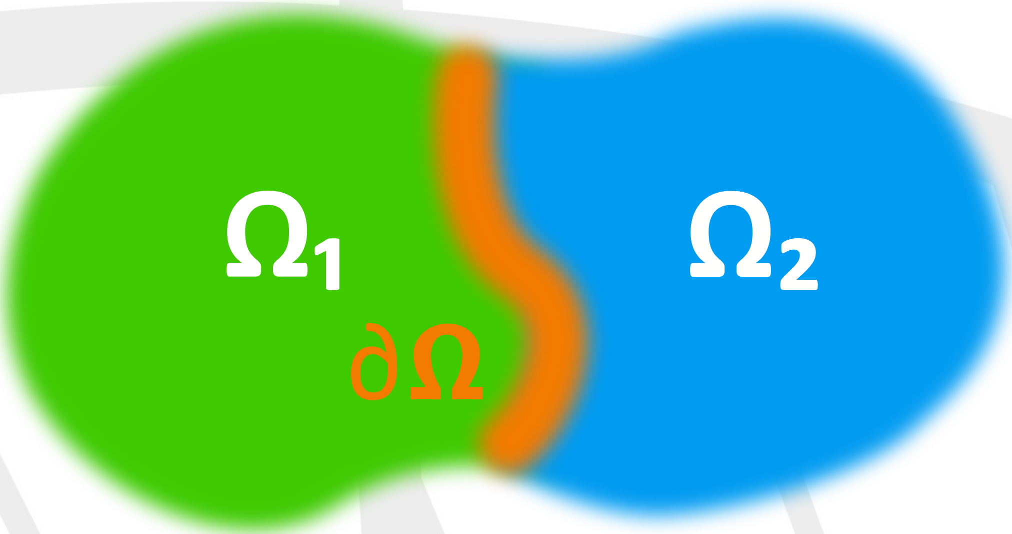

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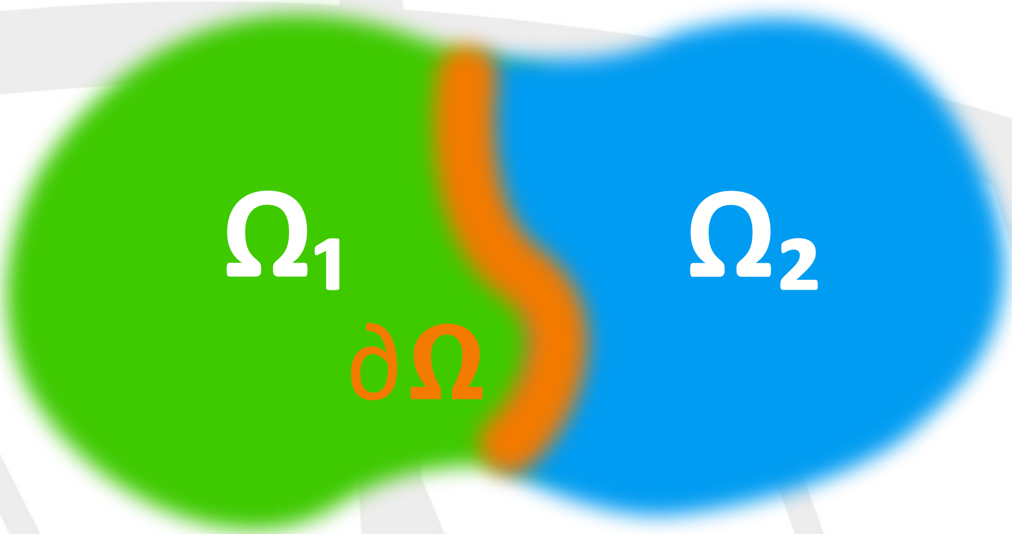

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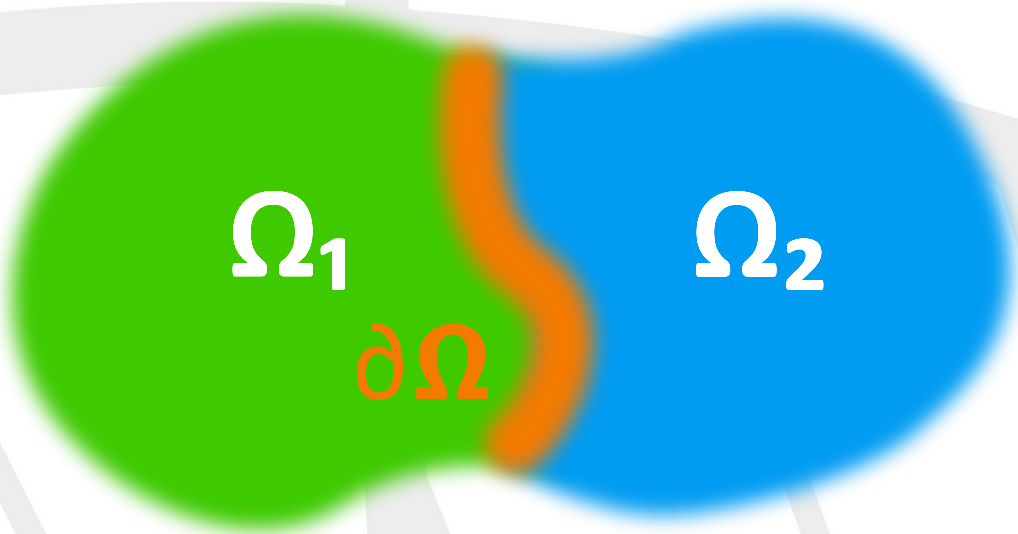

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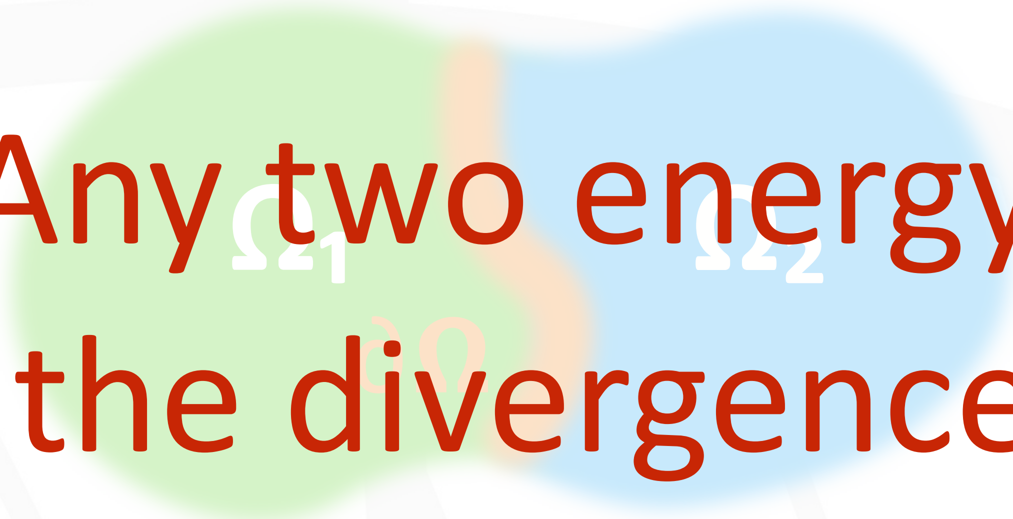

Any two energy densities that differ by the divergence of a (bounded) vector field are physically equivalent

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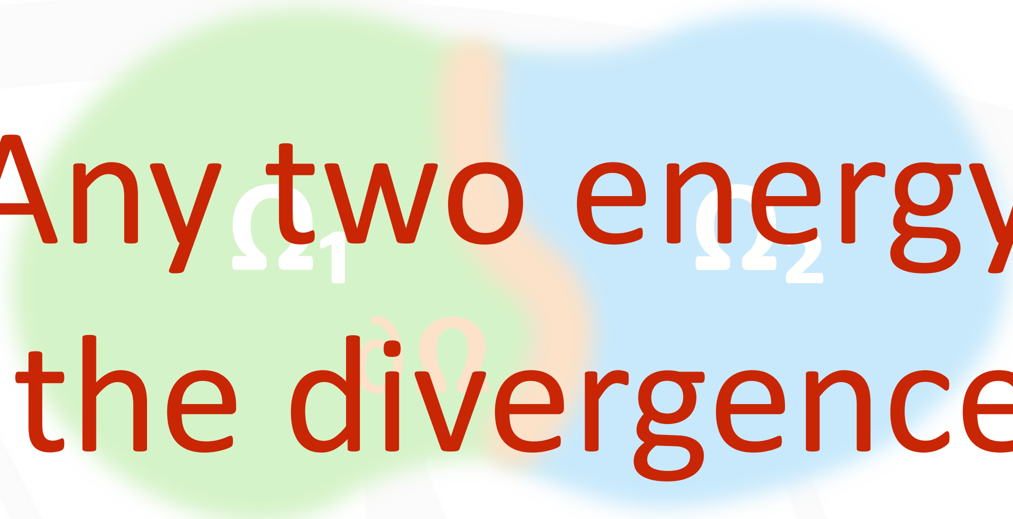

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The corresponding energy fluxes differ by a total time derivative, and the heat transport coefficients coincide

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

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density-functional theory

$$E_{DFT} = \frac{1}{2}\sum_I M_I V_I^2 + \frac{e^2}{2}\sum_{I\neq J}\frac{Z_I Z_J}{R_{IJ}}$$
$$+ \sum_v \epsilon_v - \frac{1}{2}E_H + \int \big(\epsilon_{XC}(\mathbf{r}) - \mu_{XC}(\mathbf{r})\big)\rho(\mathbf{r})d\mathbf{r}$$

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

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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

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

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

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

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

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

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

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

the DFT energy current

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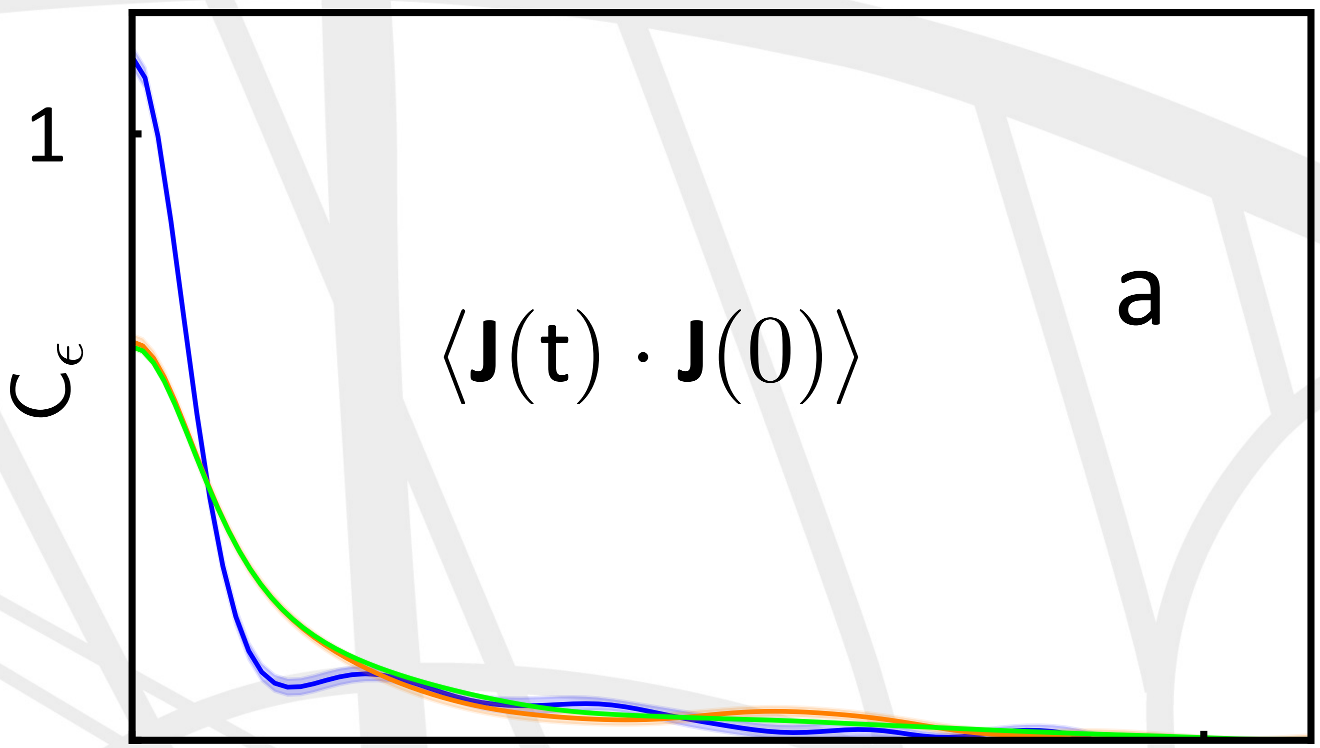
$$\mathbf{J}_H = \frac{1}{4\pi}\int \dot{v}_H(\mathbf{r})\nabla v_H(\mathbf{r})d\mathbf{r}$$

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

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

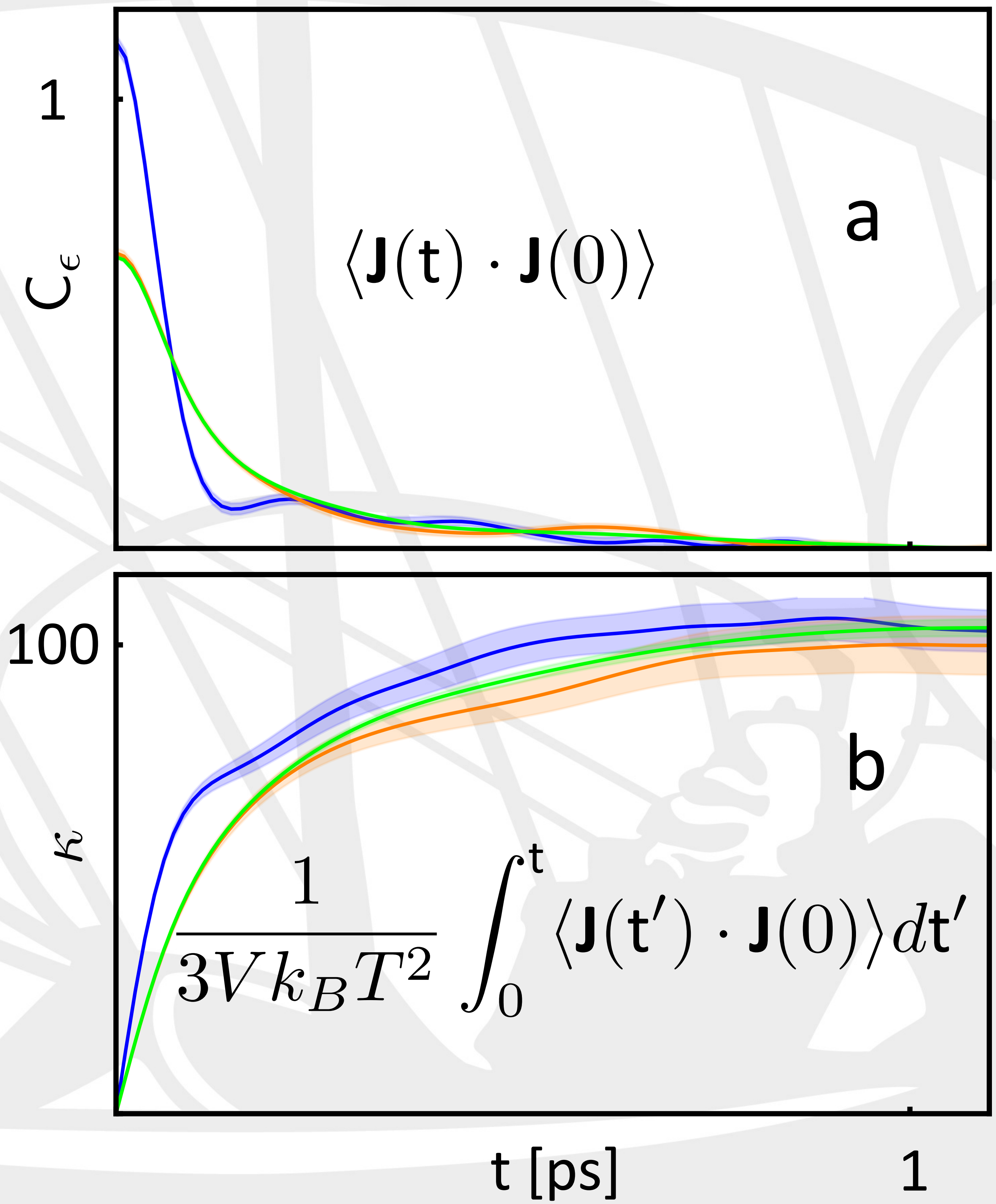
a benchmark



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



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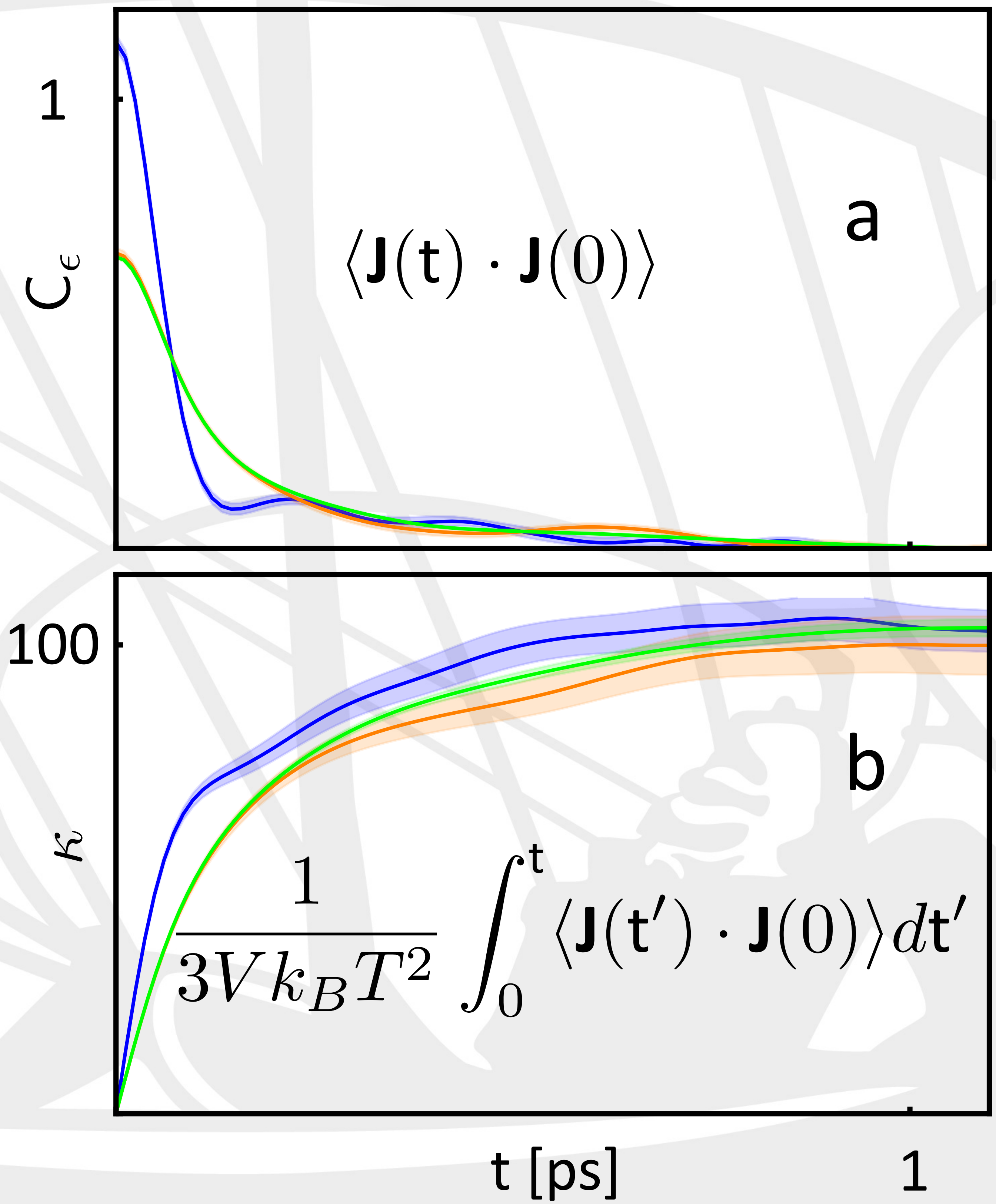

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100 ps CP trajectory
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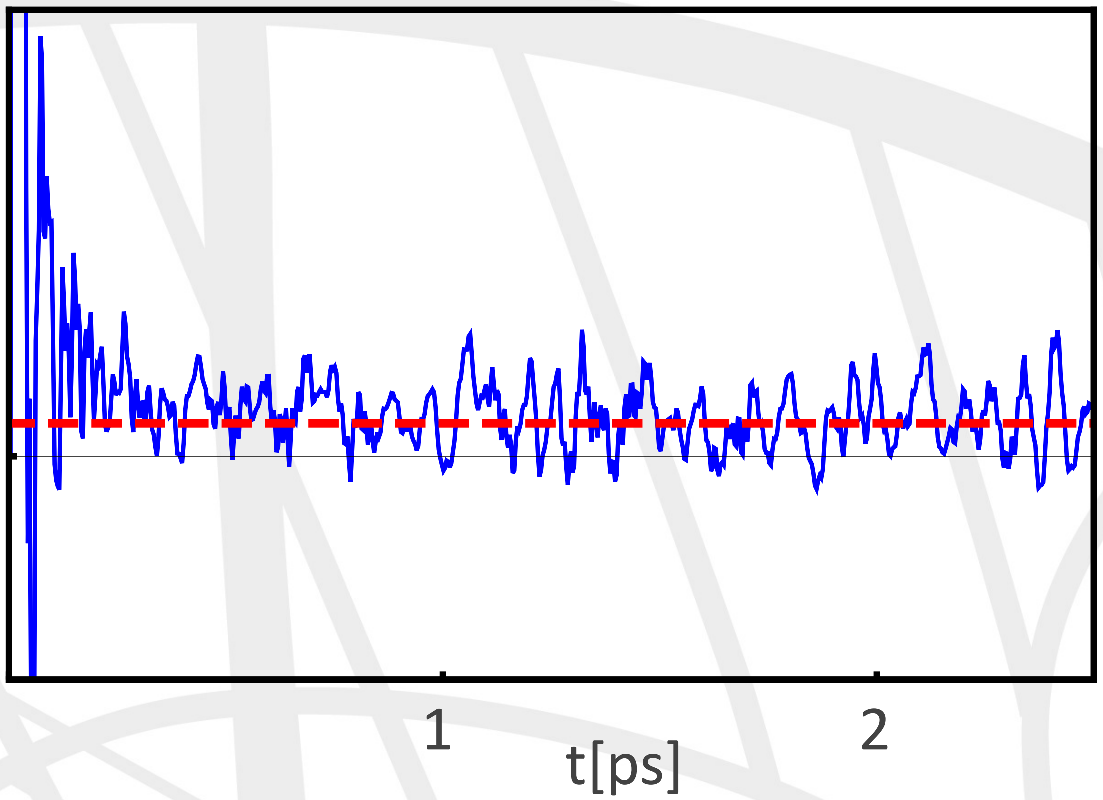
1 ns classical FF trajectory

same behavior at T=400 K

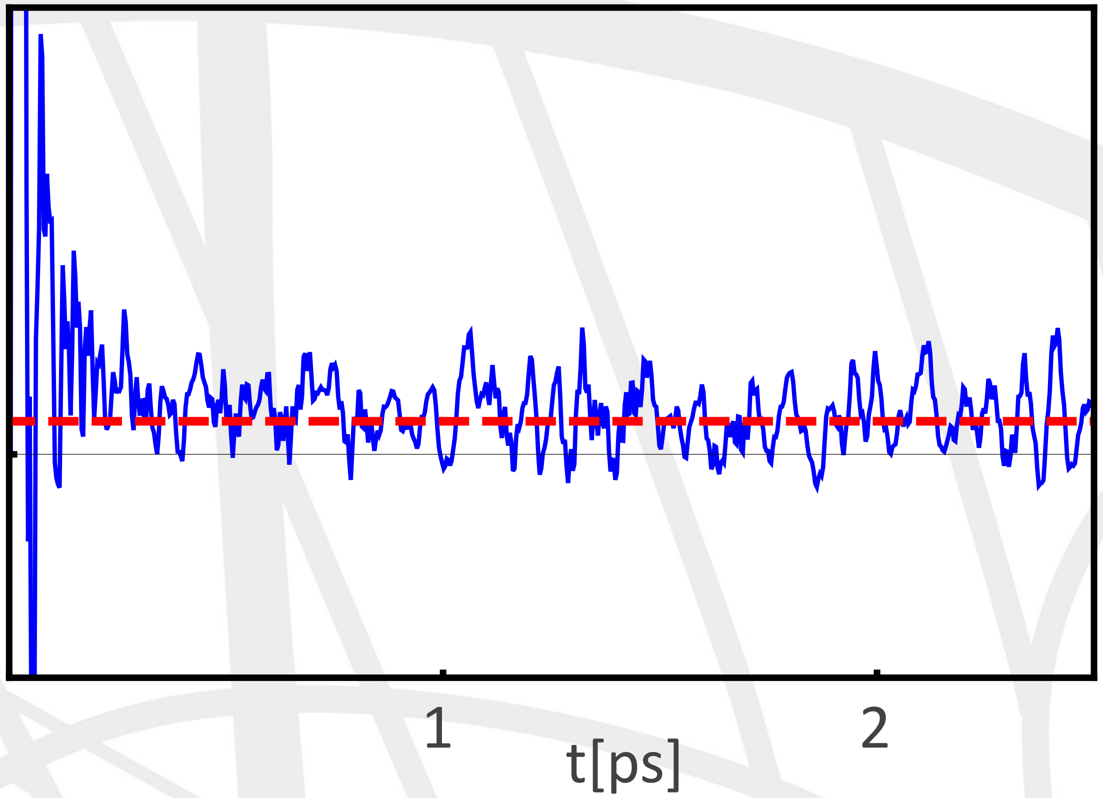
liquid (heavy) water



64 molecules, T=385 K
expt density @ac

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

liquid (heavy) water



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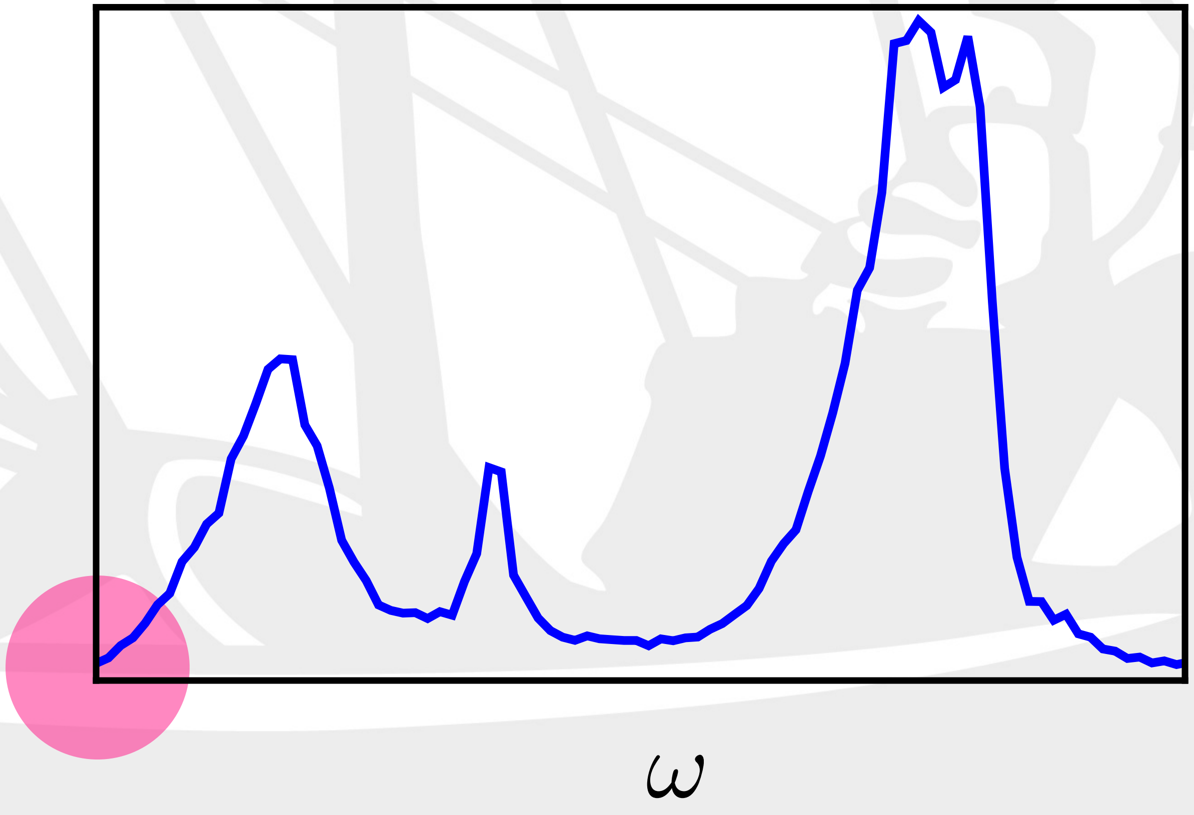
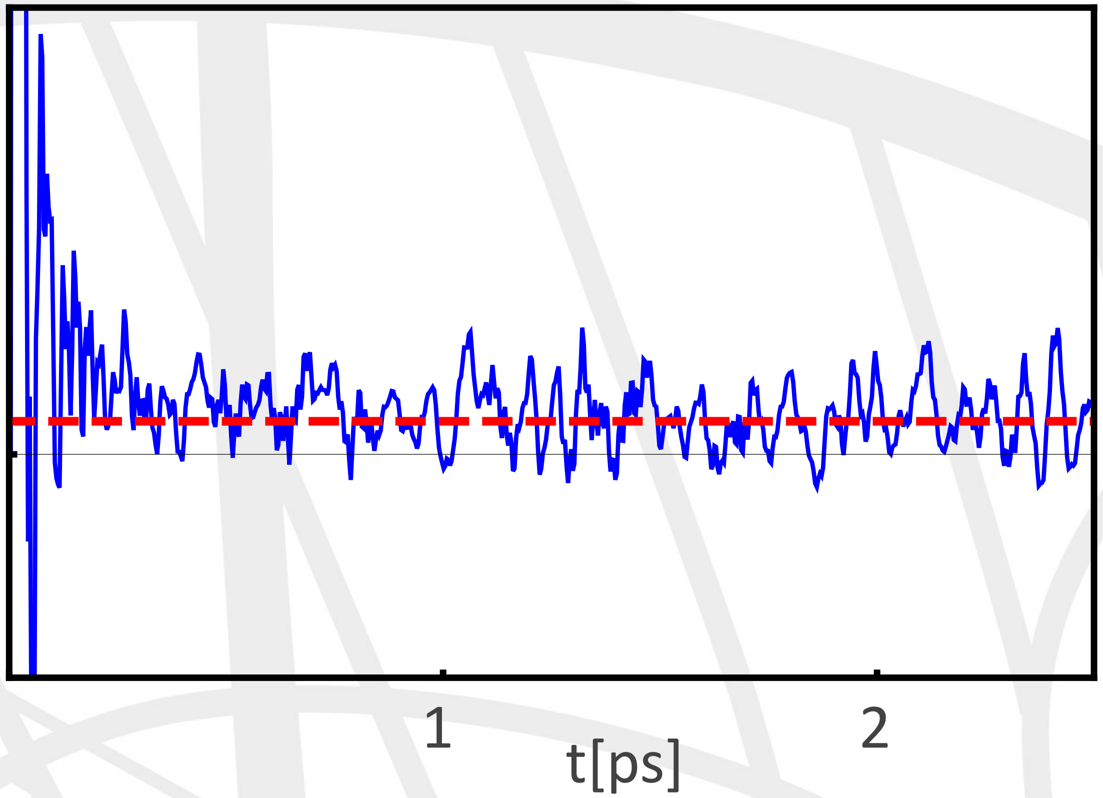


$$S(\omega) = \int_{-\infty}^{\infty} \langle \mathbf{J}(\mathsf{t}) \cdot \mathbf{J}(0)\rangle \, \mathsf{e}^{i\omega \mathsf{t}} dt$$

liquid (heavy) water



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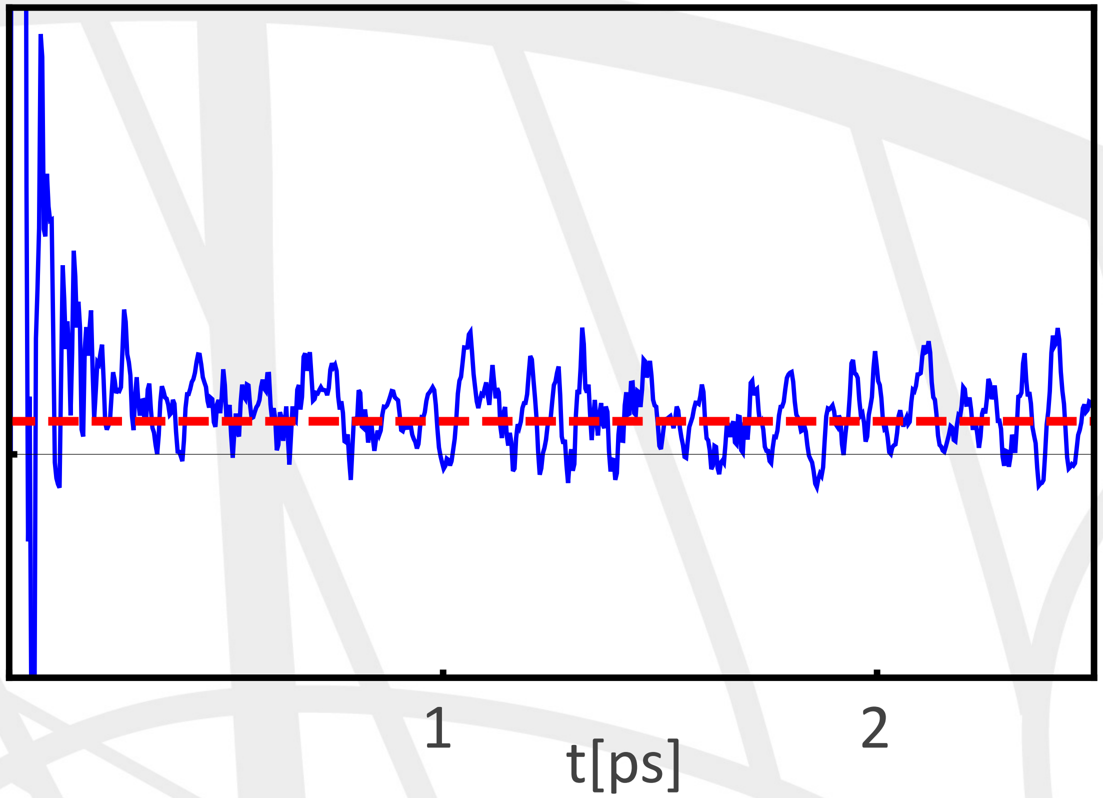
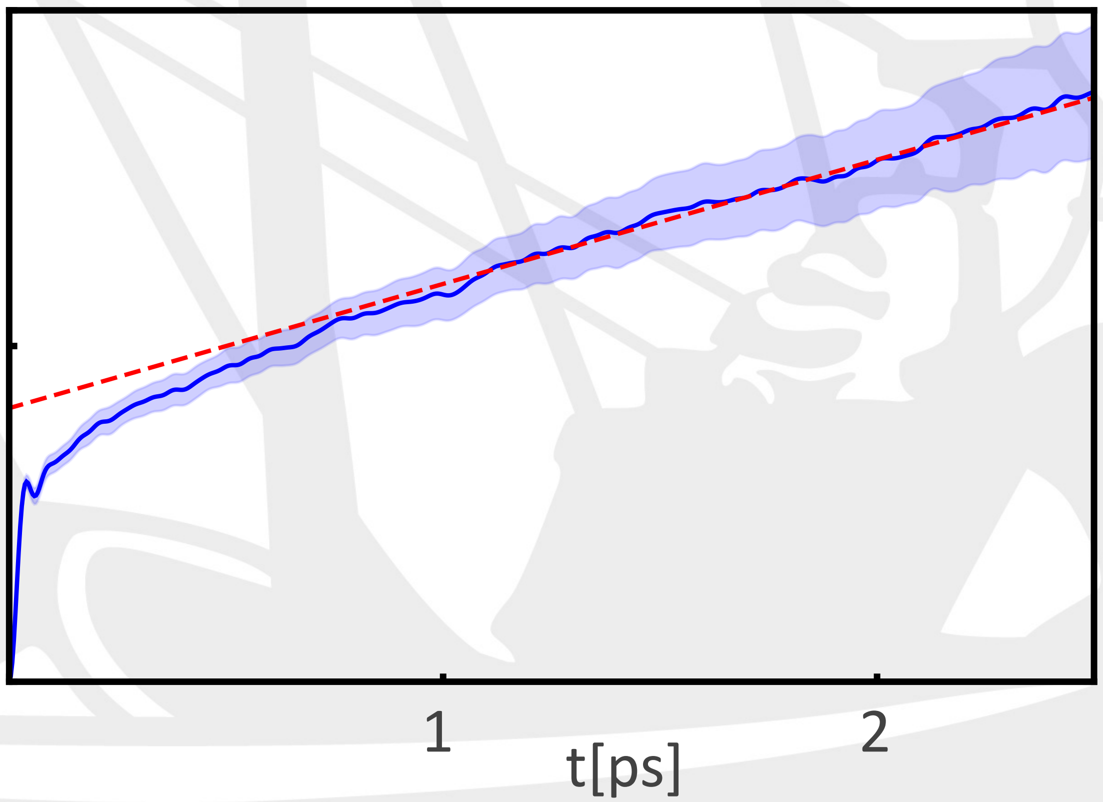
Einstein's relation

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

liquid (heavy) water





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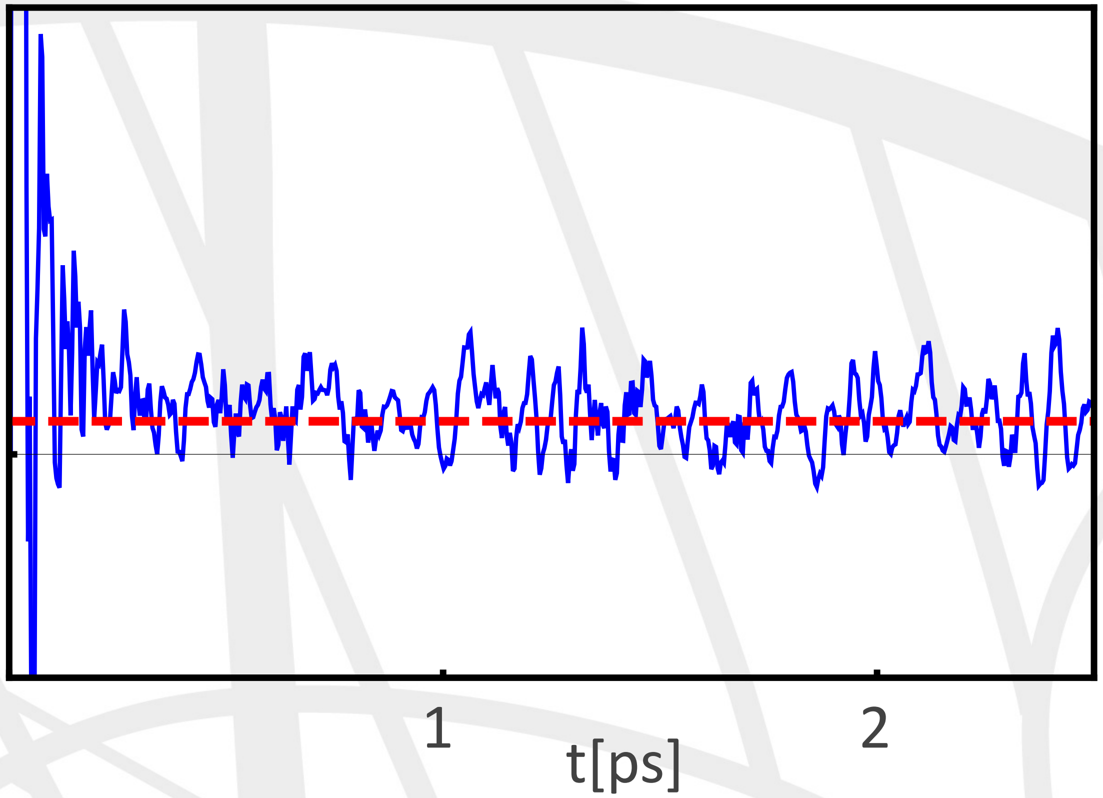

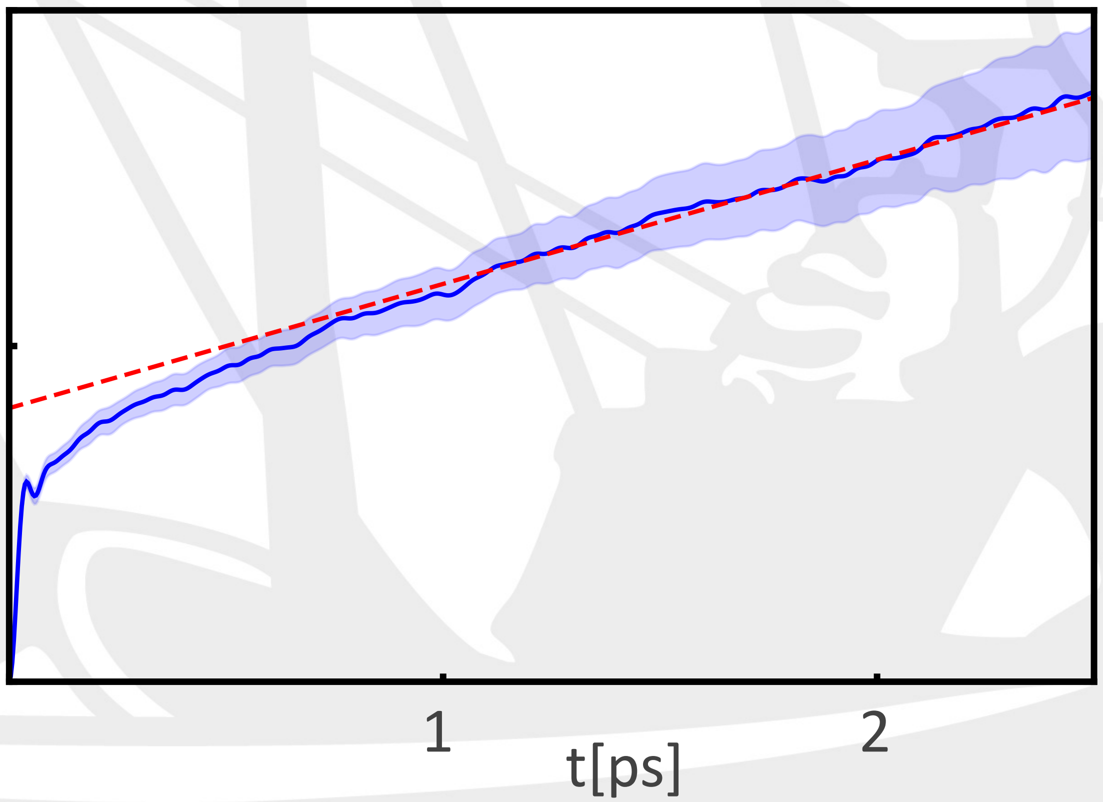

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$\kappa_{\mathrm{DFT}} = 0.74 \pm 0.12\ \mathrm{W/(mK)}$

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

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

electric transport in ionic fluids

$$\mathbf{J} = \boldsymbol{\sigma} \cdot \mathbf{E}$$

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$$\mathbf{J} = \boldsymbol{\sigma} \cdot \mathbf{E}$$
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electric transport in ionic fluids

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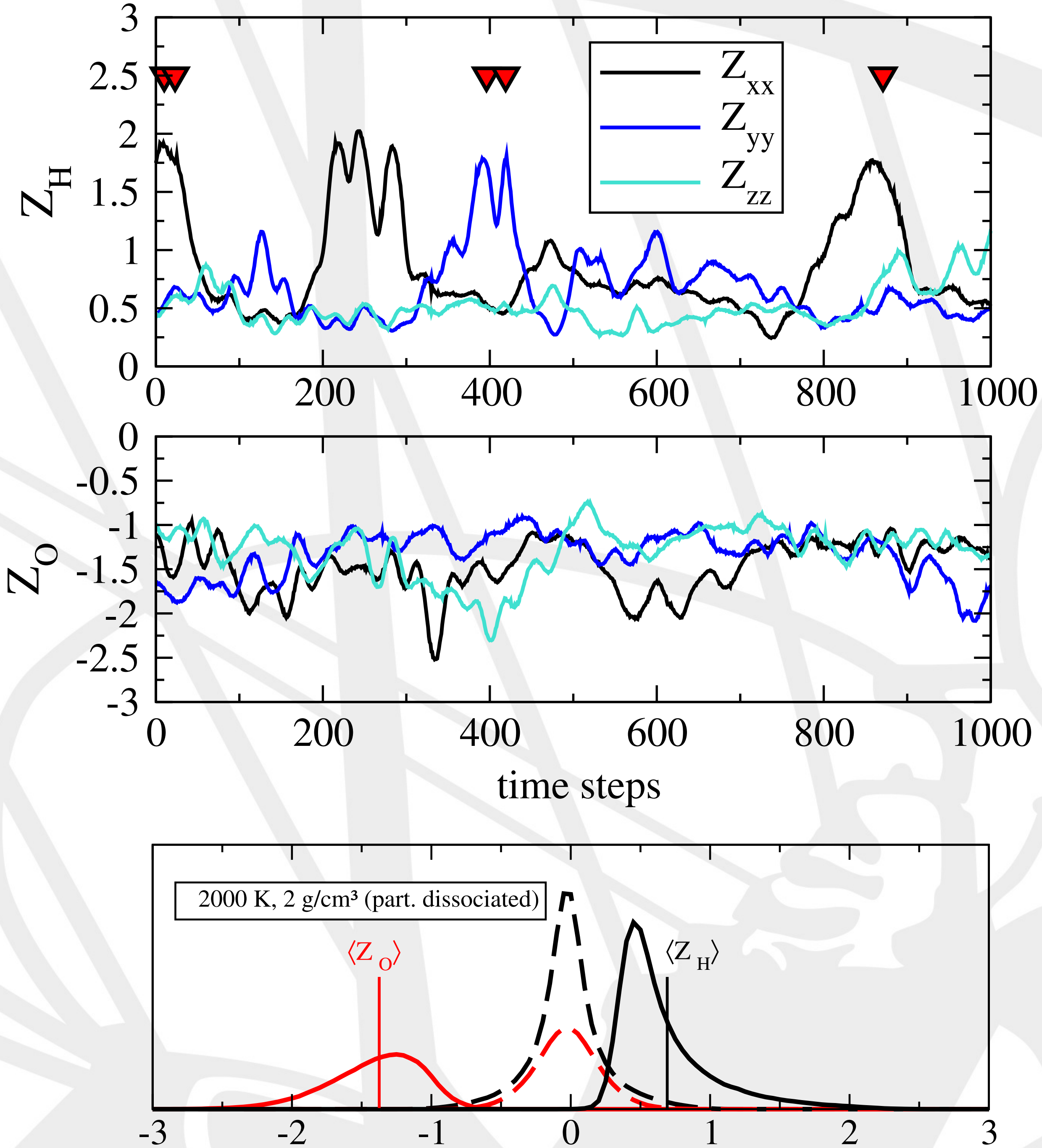
$$= \sum_I \mathbf{Z}_I \cdot \mathbf{V}_I$$

electric transport in ionic water

M. French, S. Hamel, and R. Redmer, Phys. Rev. Lett. **107** (2011)



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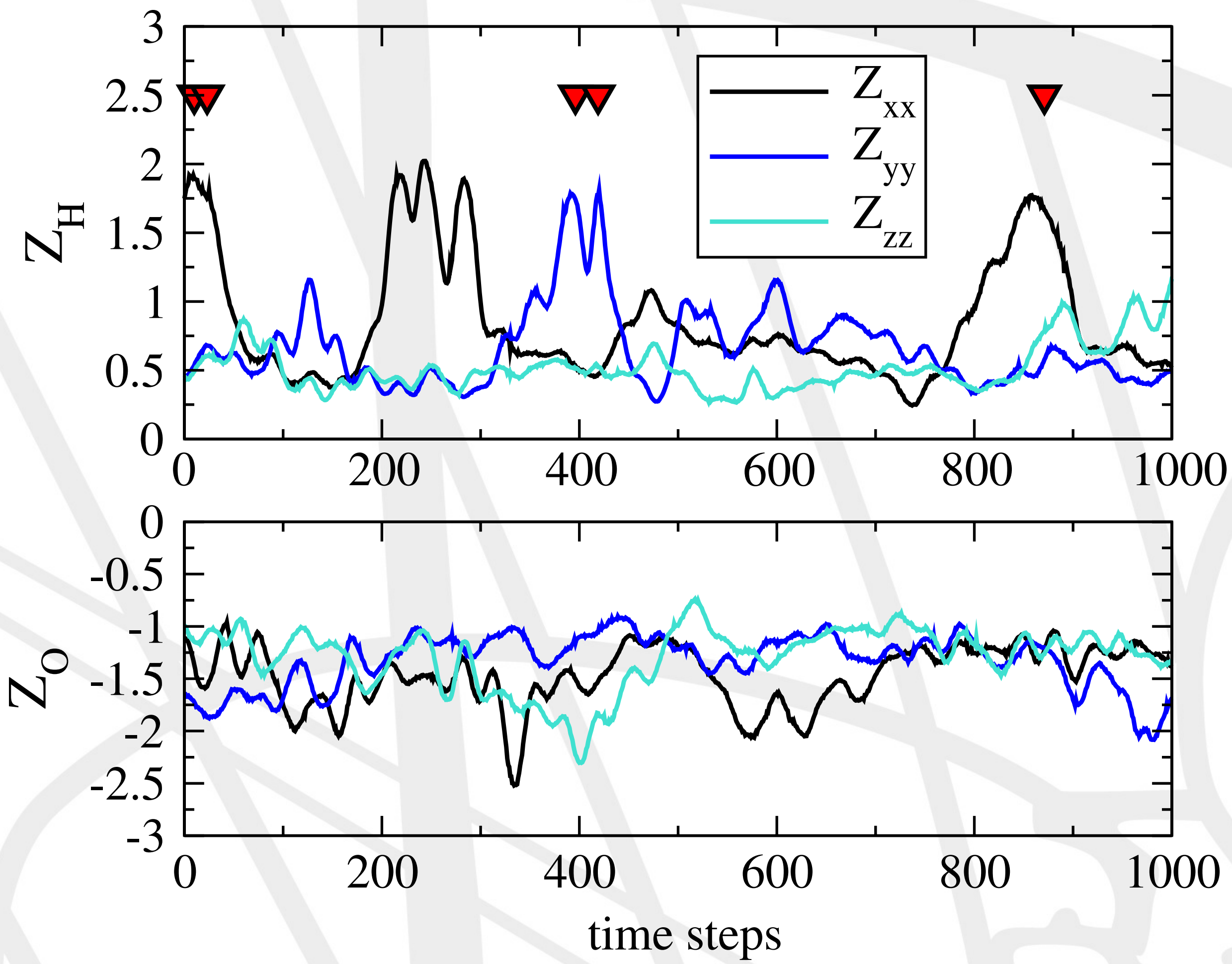

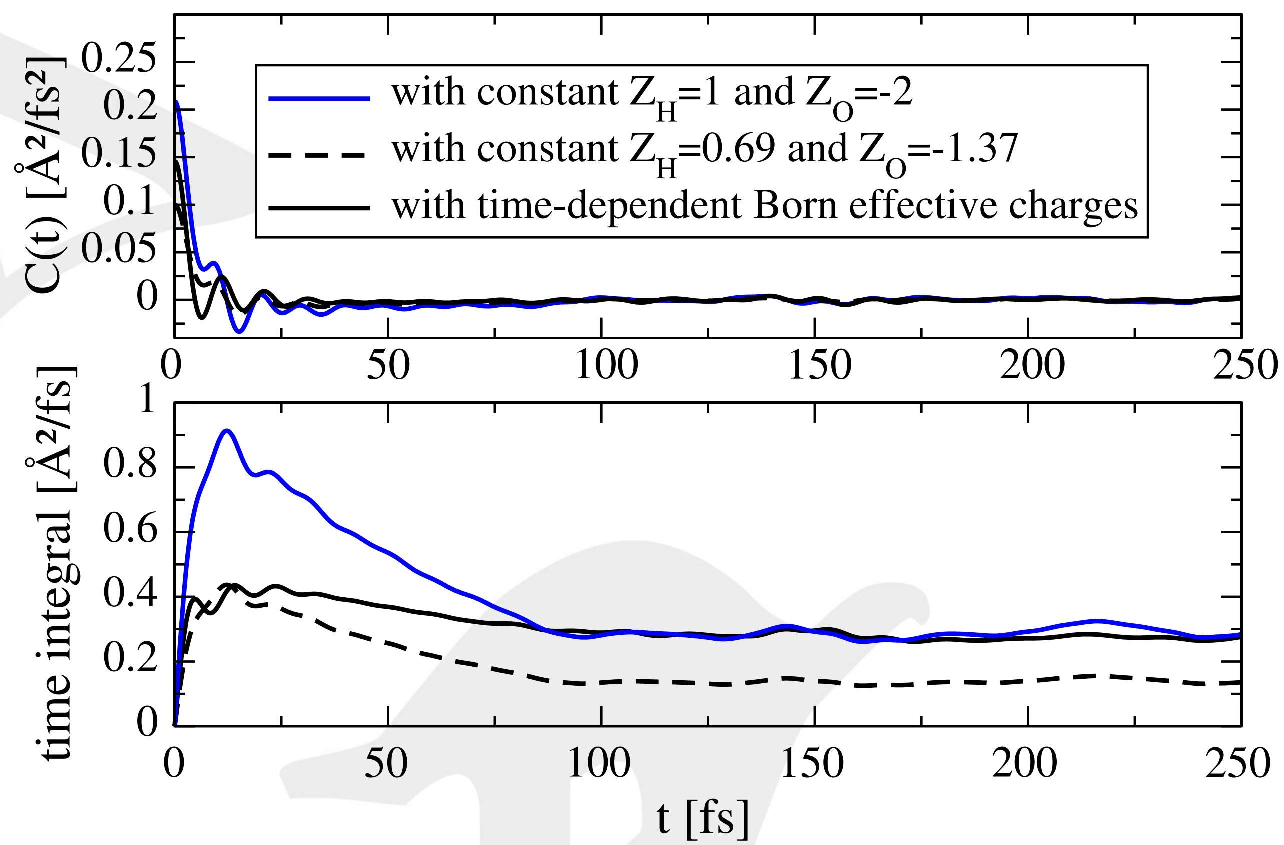

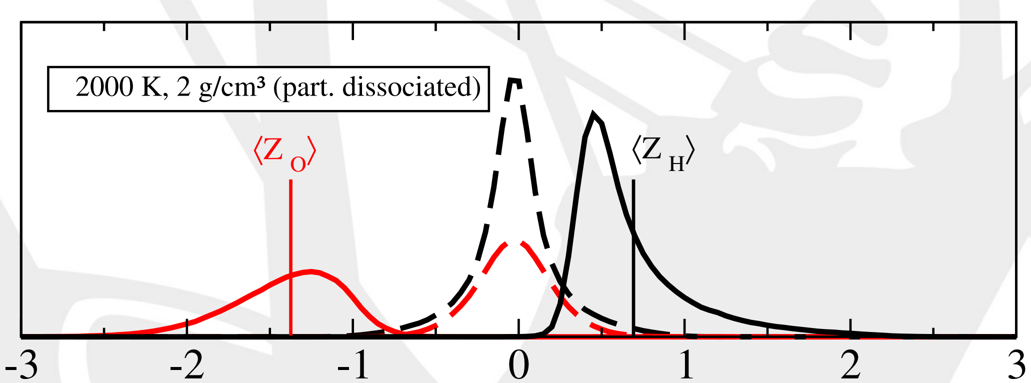

"Interestingly, the use of predefined constant charges can yield the same conductivity as is found with the fully time-dependent charge tensors." [op. cit.]

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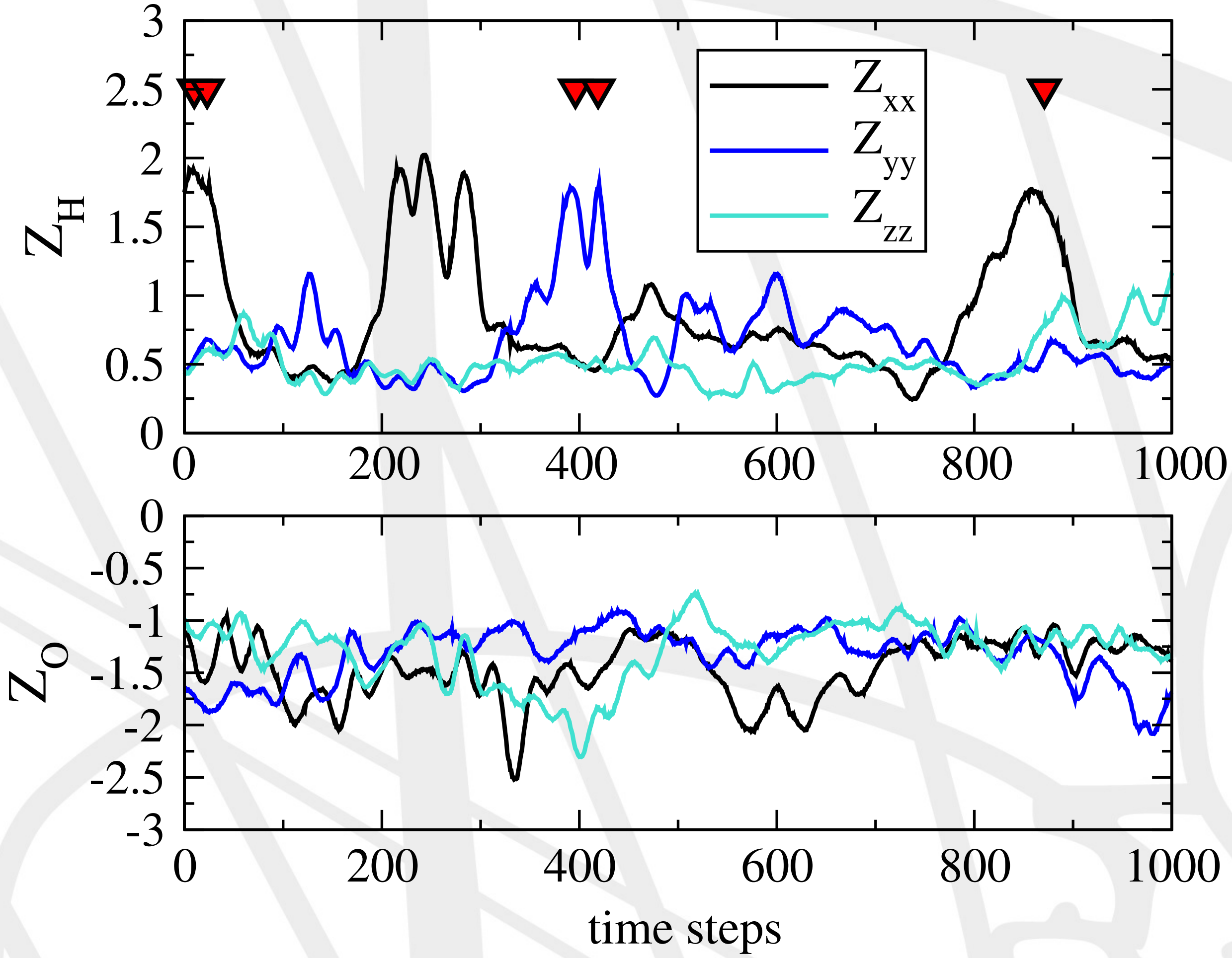

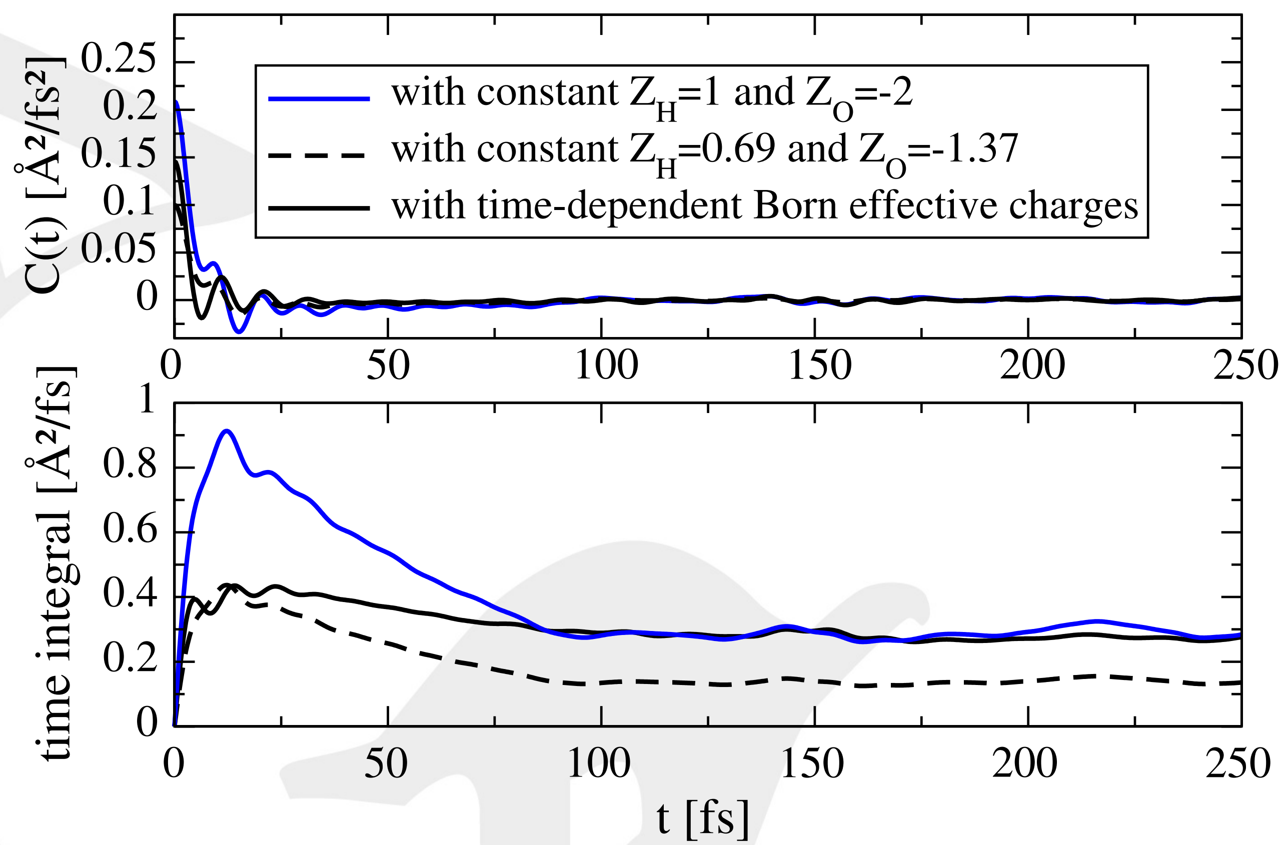

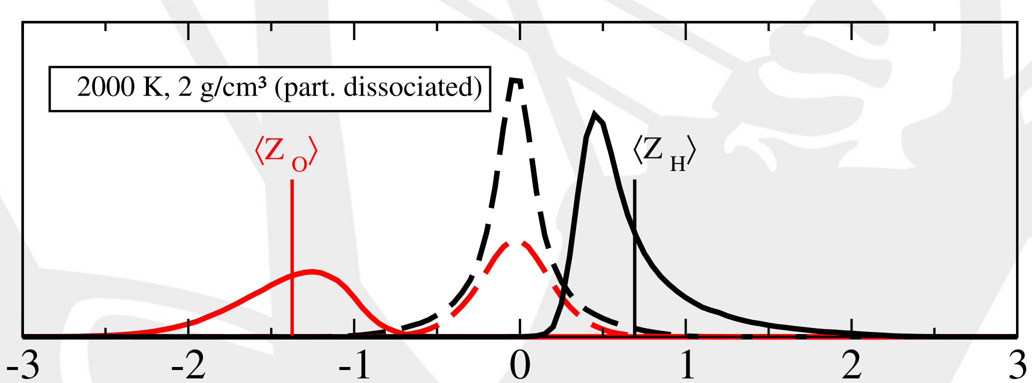

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even more interestingly, these constant charges are <u>integer</u> and coincide with the <u>formal oxidation numbers</u> of the ionic species

how come?

Thouless' quantisation of particle transport

D.J. Thouless, Phys. Rev. B **27**, 6083 (2011)

R. Resta and D. Vanderbilt, Top. Appl. Phys. **105**, 31 (2007)

$$\hat{H}(t+T) = \hat{H}(t)$$

$$Q_\alpha = \frac{1}{L_\alpha} \int_0^T J_\alpha(t) dt \in \mathbb{Z}$$

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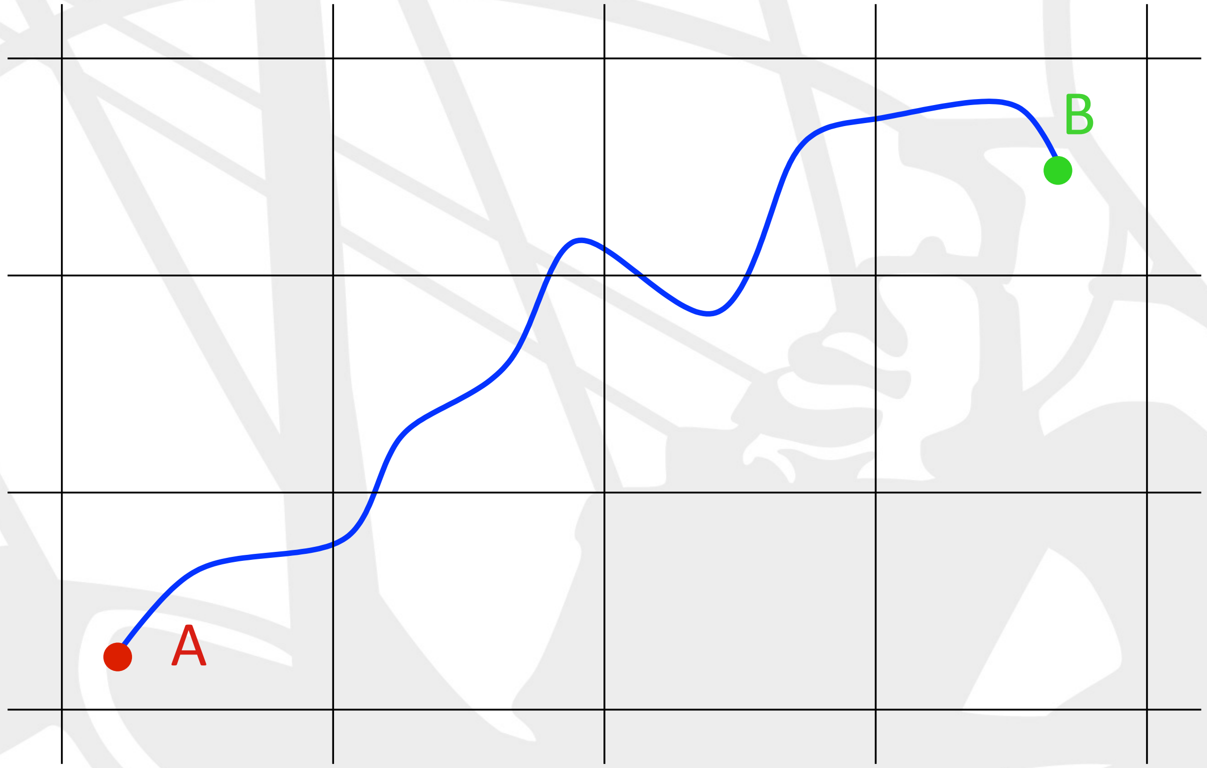

$$\sigma \propto \frac{1}{T}\left\langle Q\big(A(0), B(T)\big)^2 \right\rangle$$

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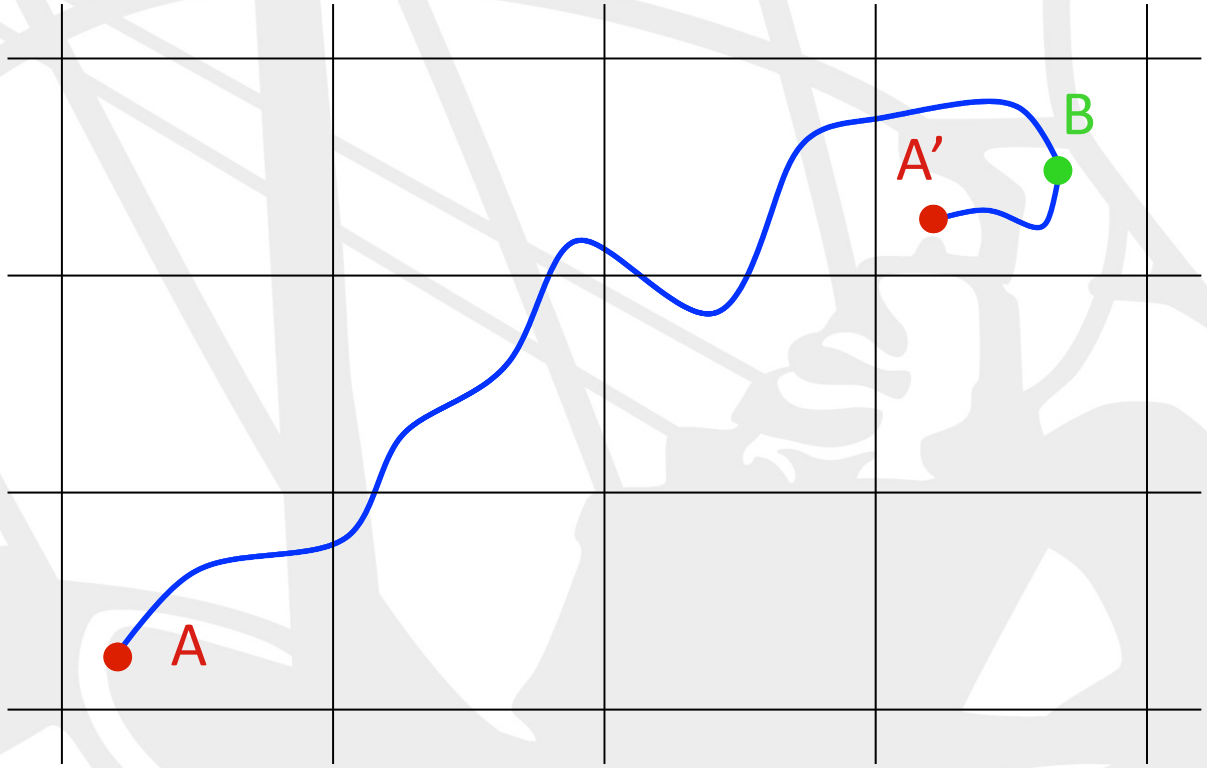
$$\hat{H}(A') = \hat{H}(A)$$



$$\sigma \propto \frac{1}{T}\left\langle Q\big(A(0), B(T)\big)^2 \right\rangle$$

$$Q\big(A, B\big) = Q(A, A') - Q(B, A')$$

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$$\hat{H}(B) \neq \hat{H}(A)$$
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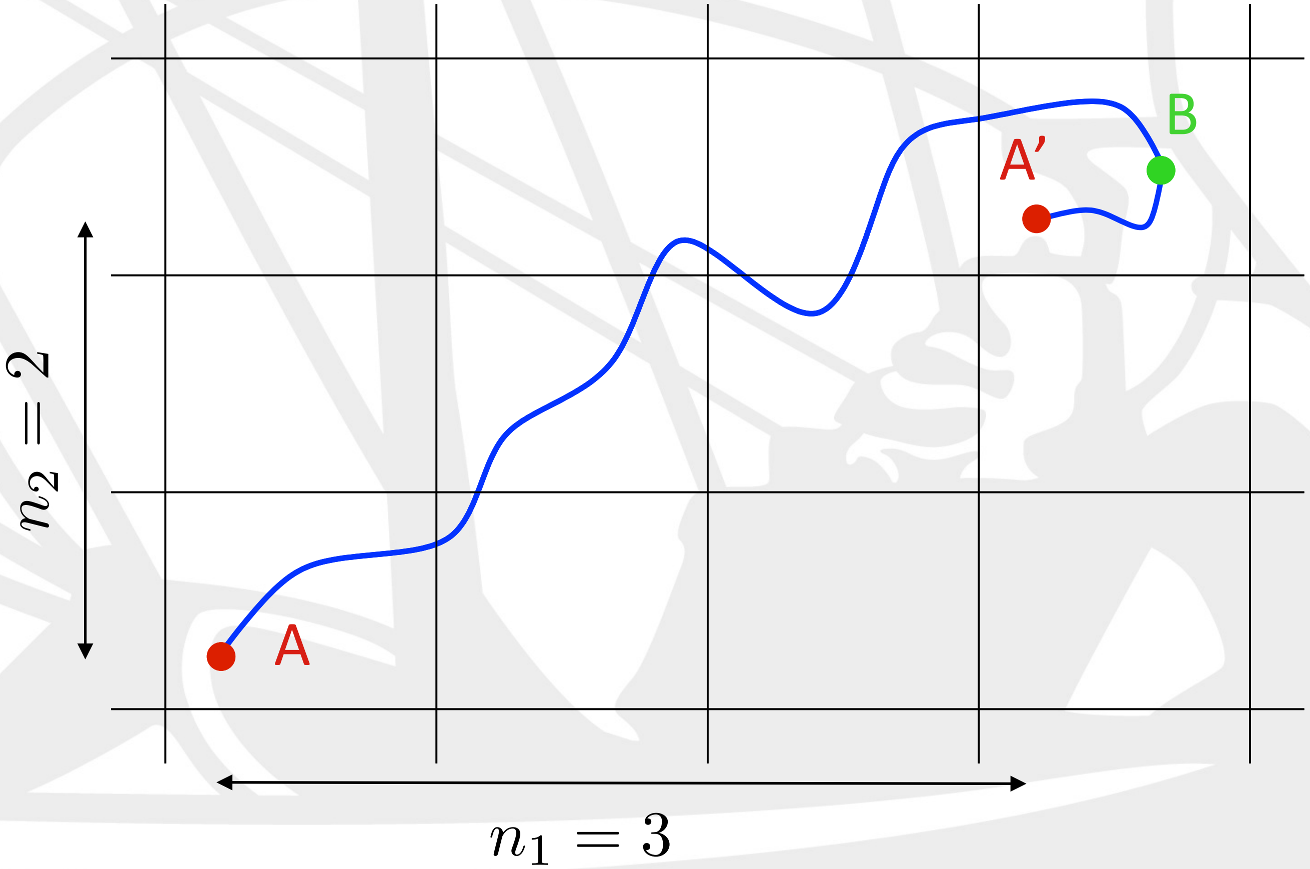

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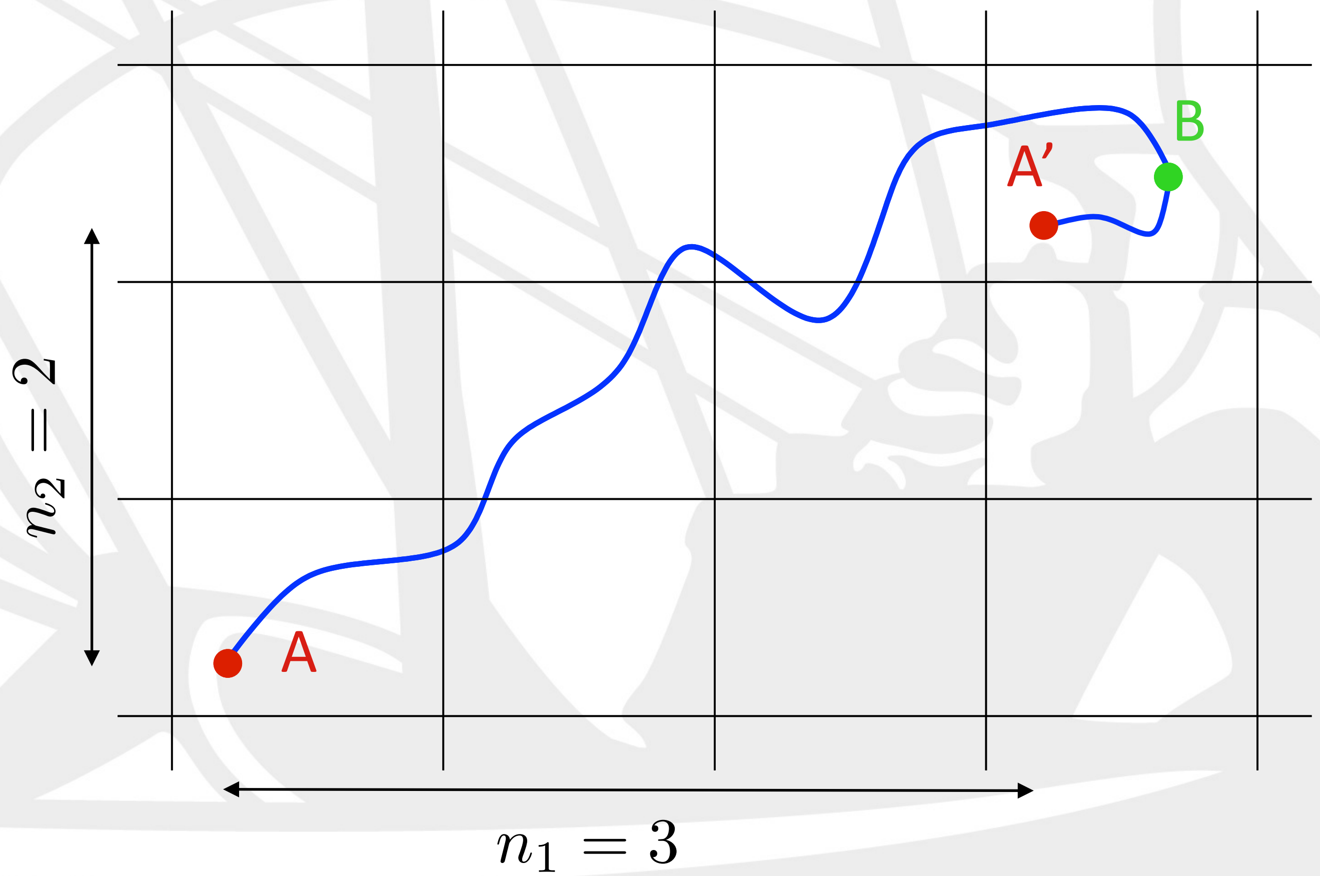

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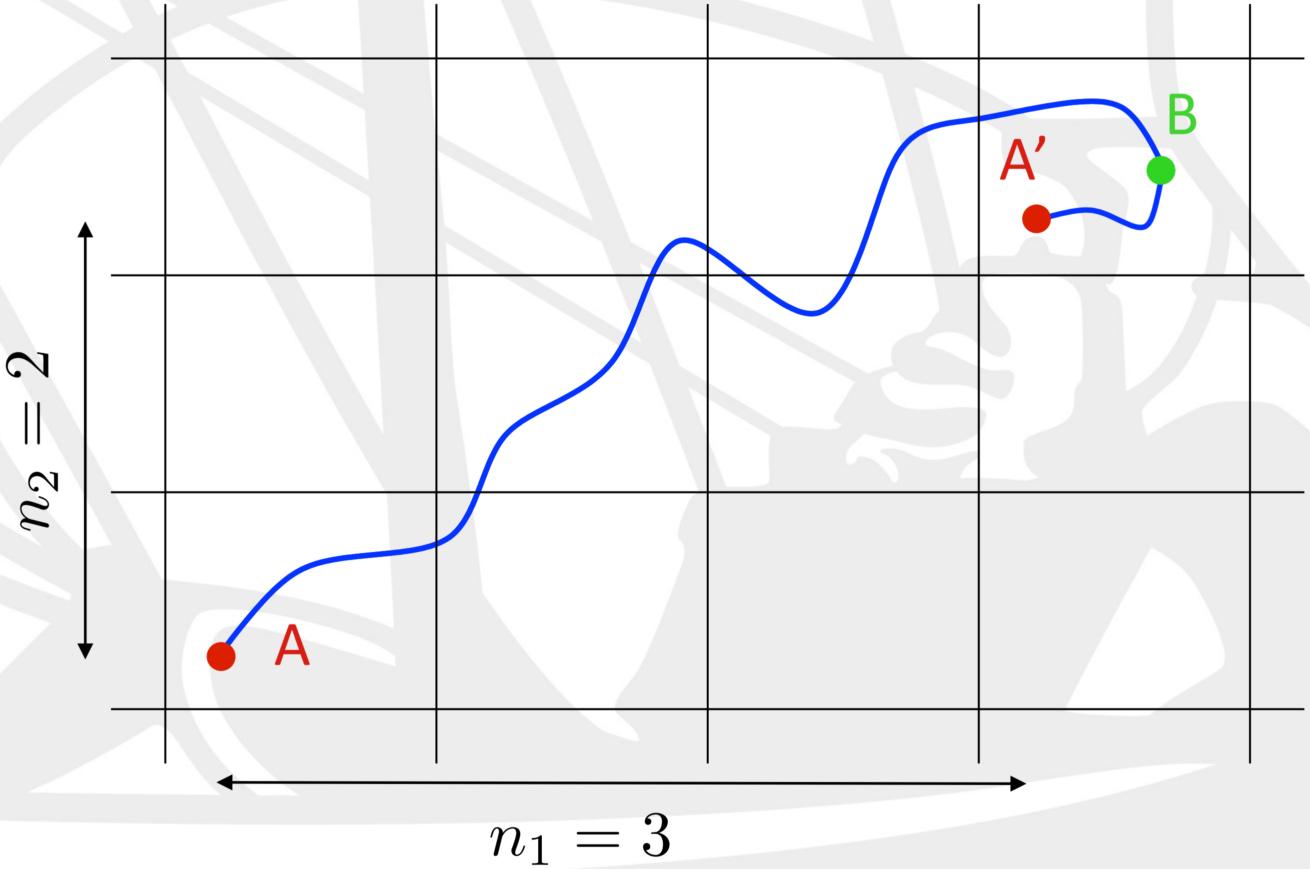

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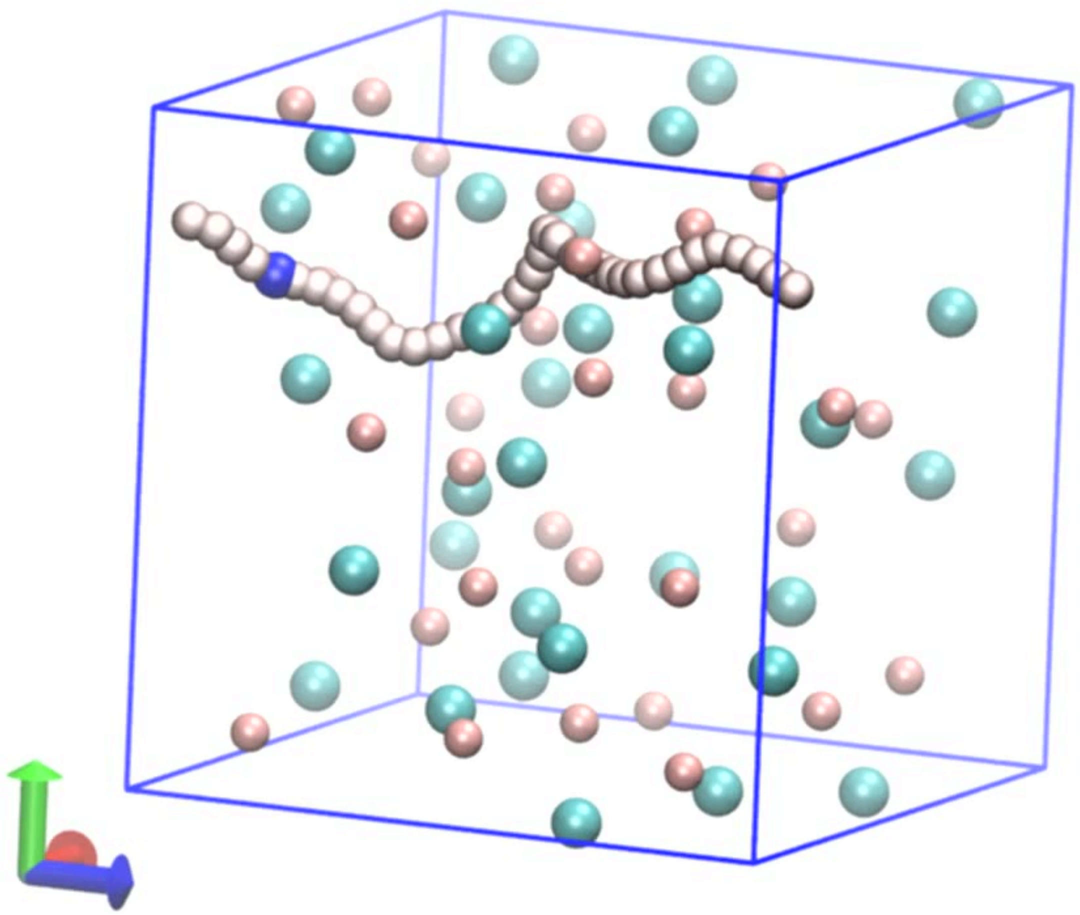
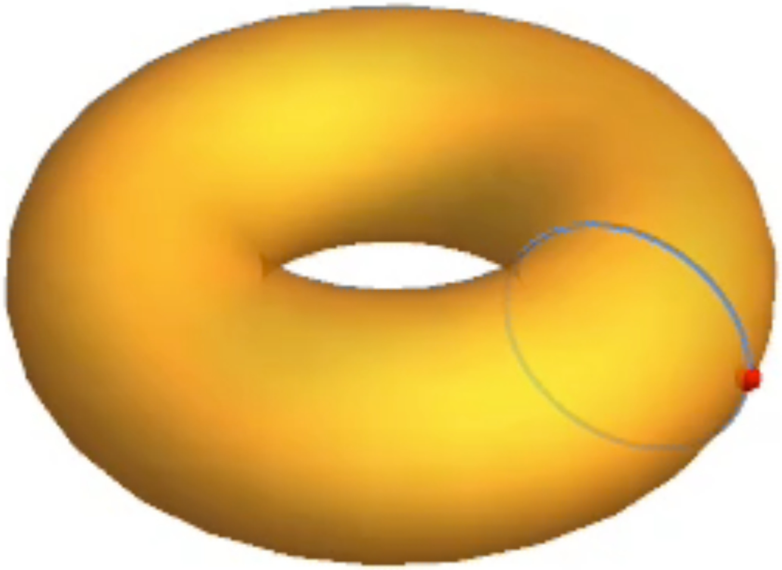
a numerical experiment on molten KCl





a topologically non-trivial minimum-energy path
connecting two identical configurations of a ionic fluid

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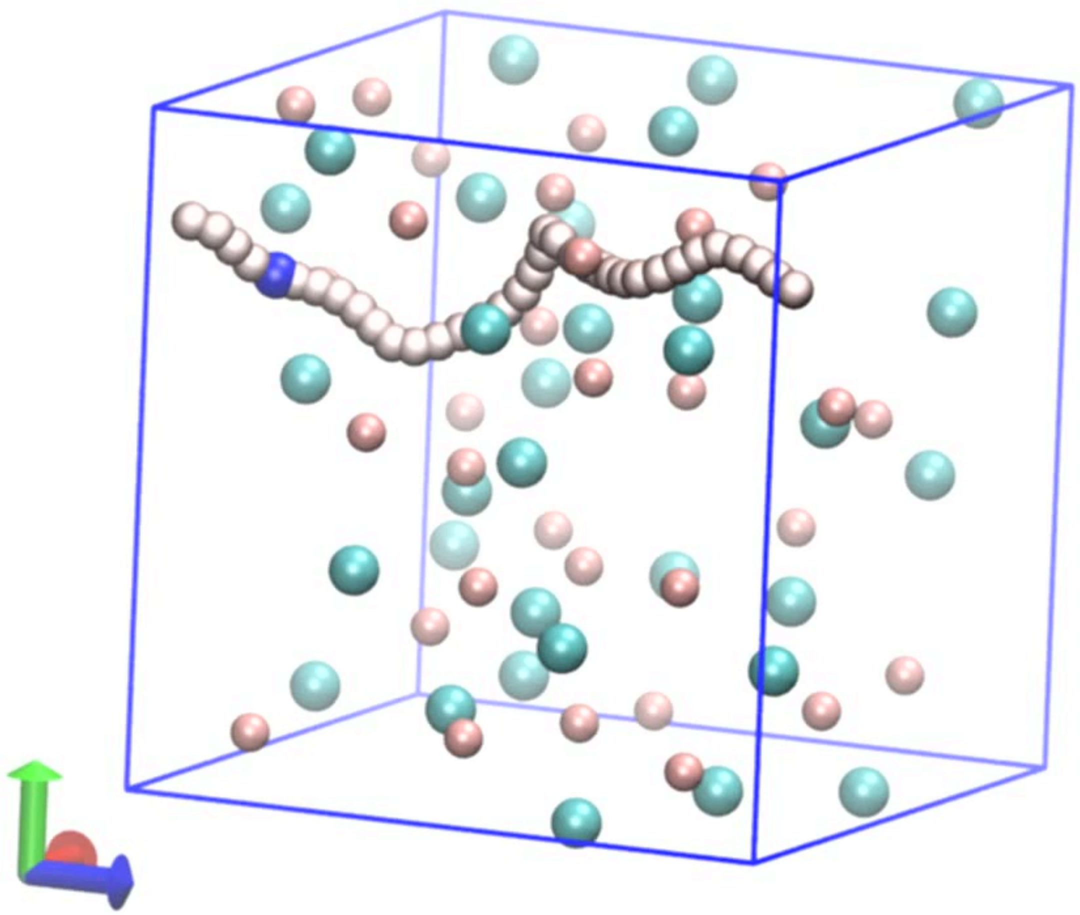

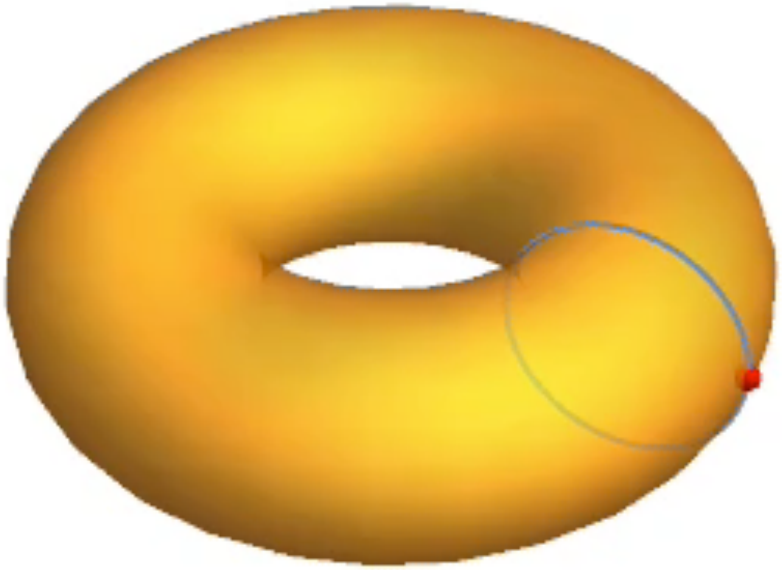

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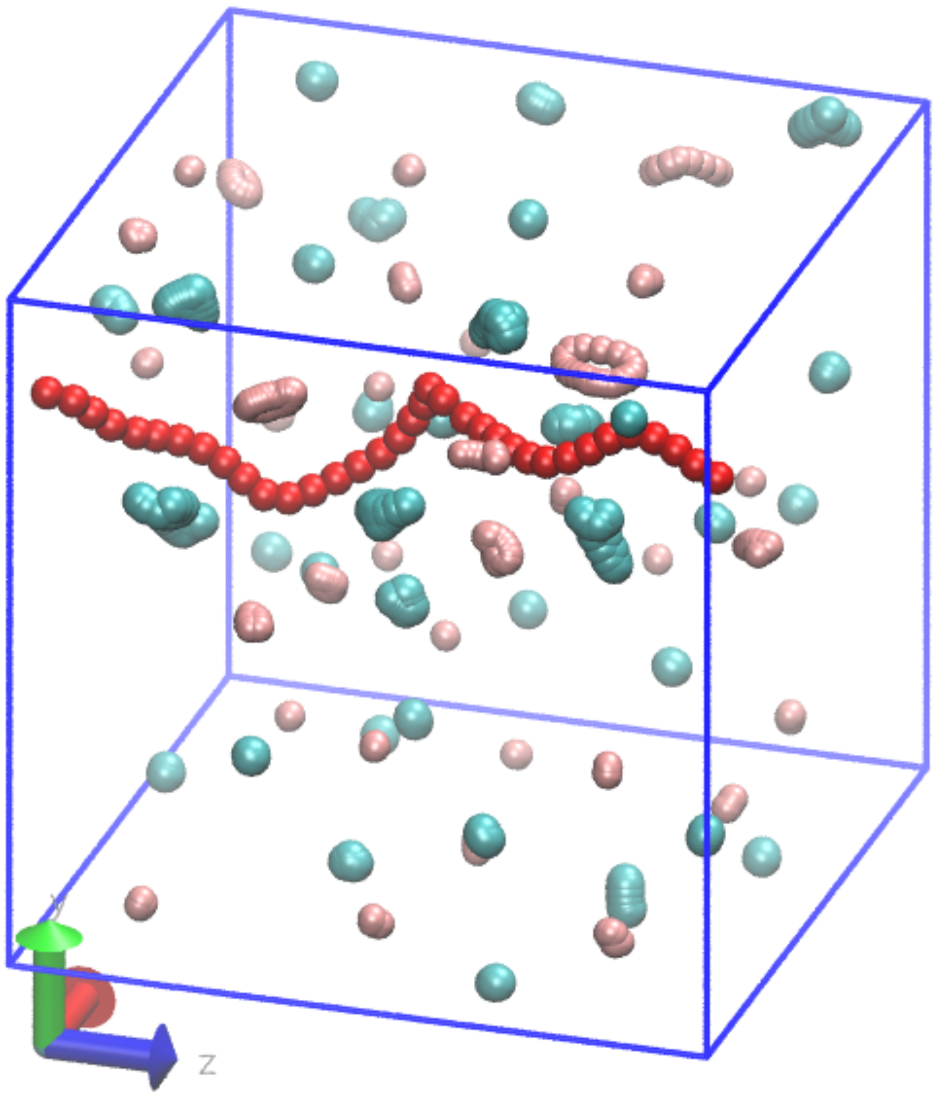
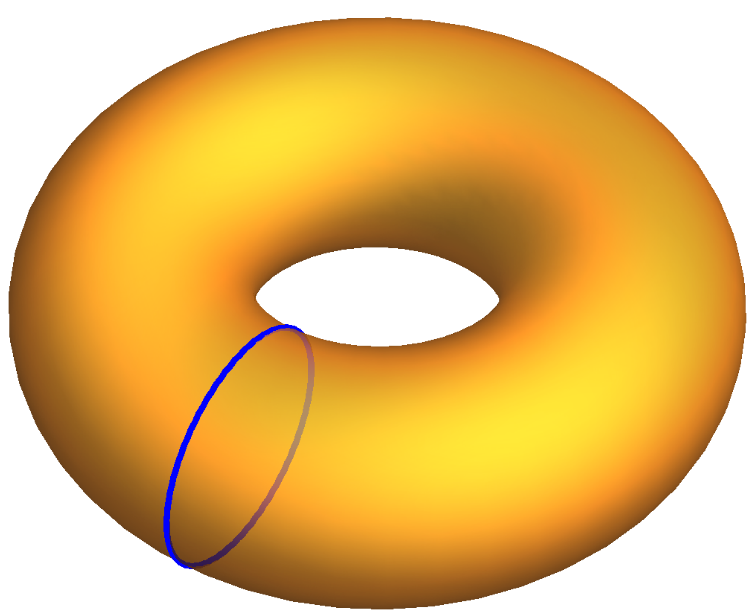
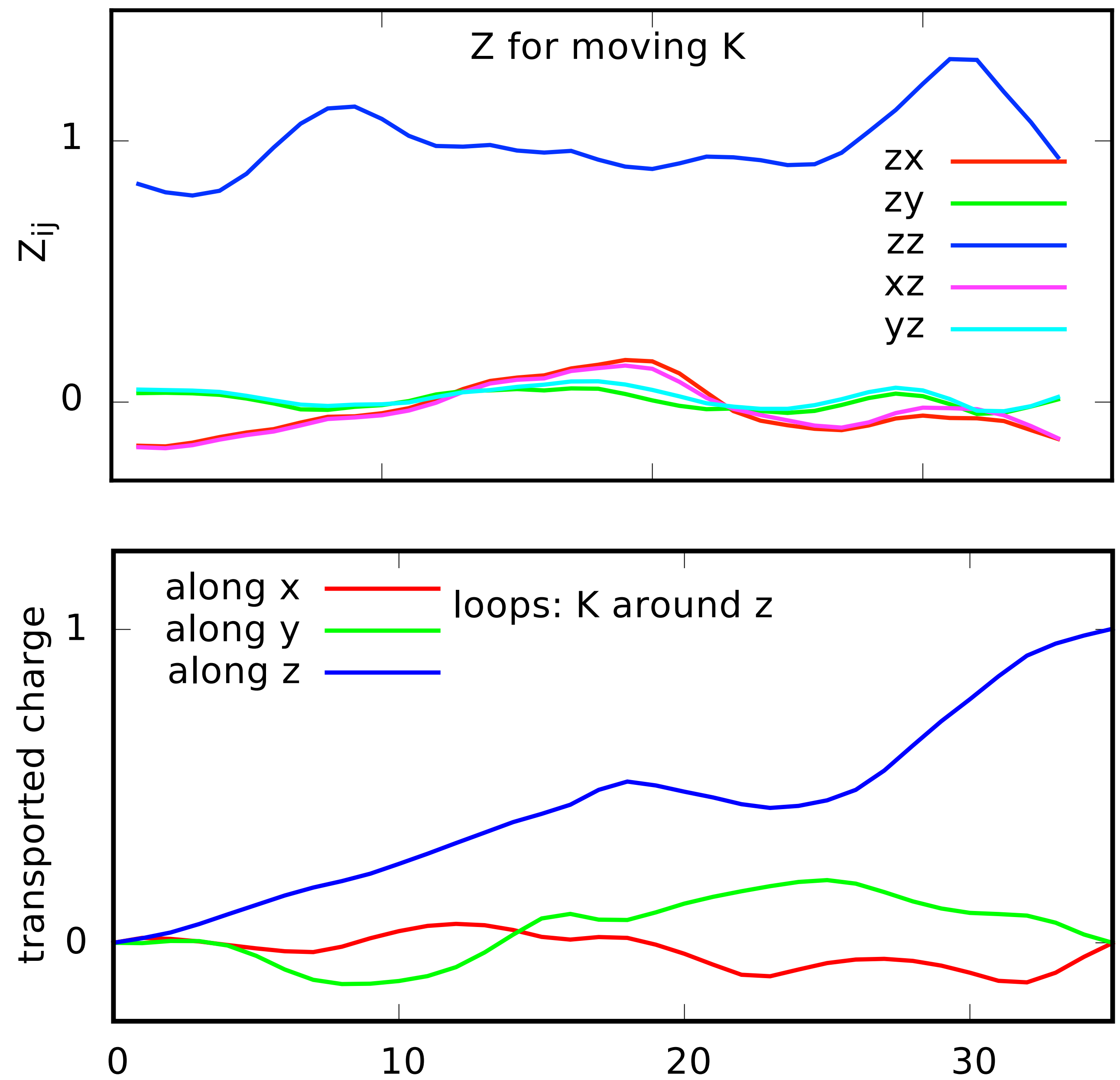
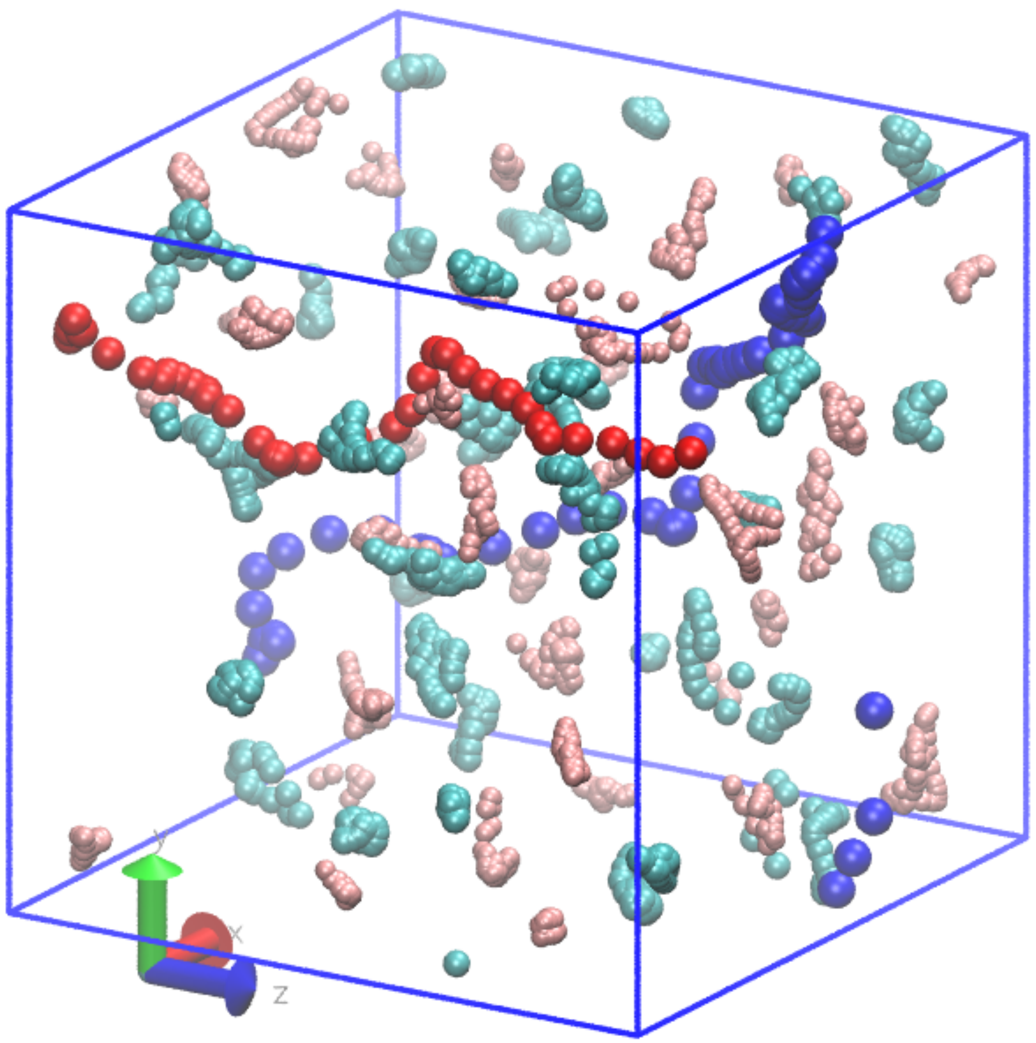


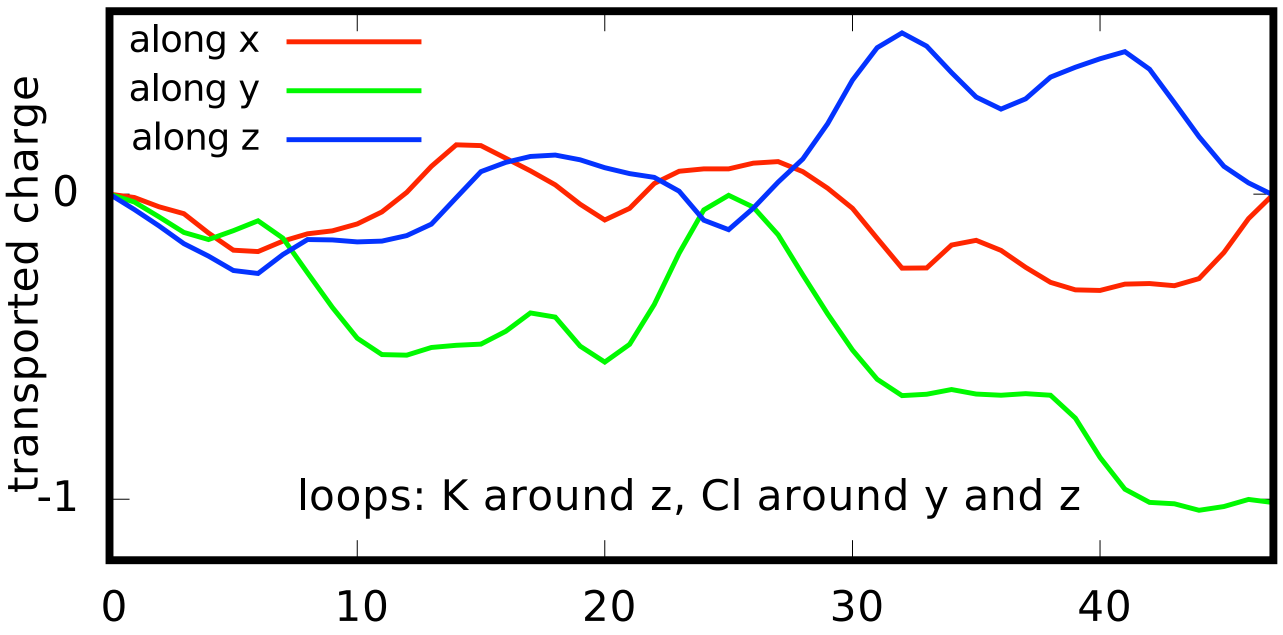


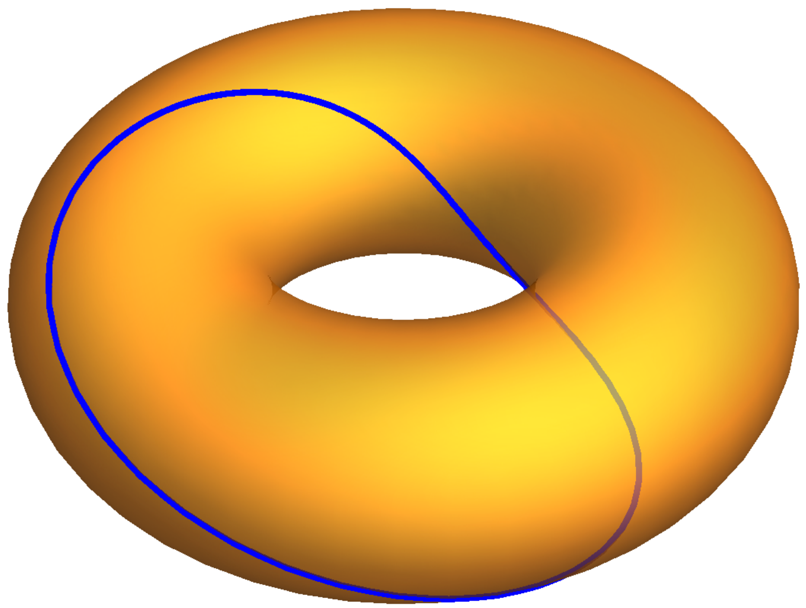


qx = =-0.000(6); qy = 0.000(2); qz = 1.00(18)

a numerical experiment on molten KCl

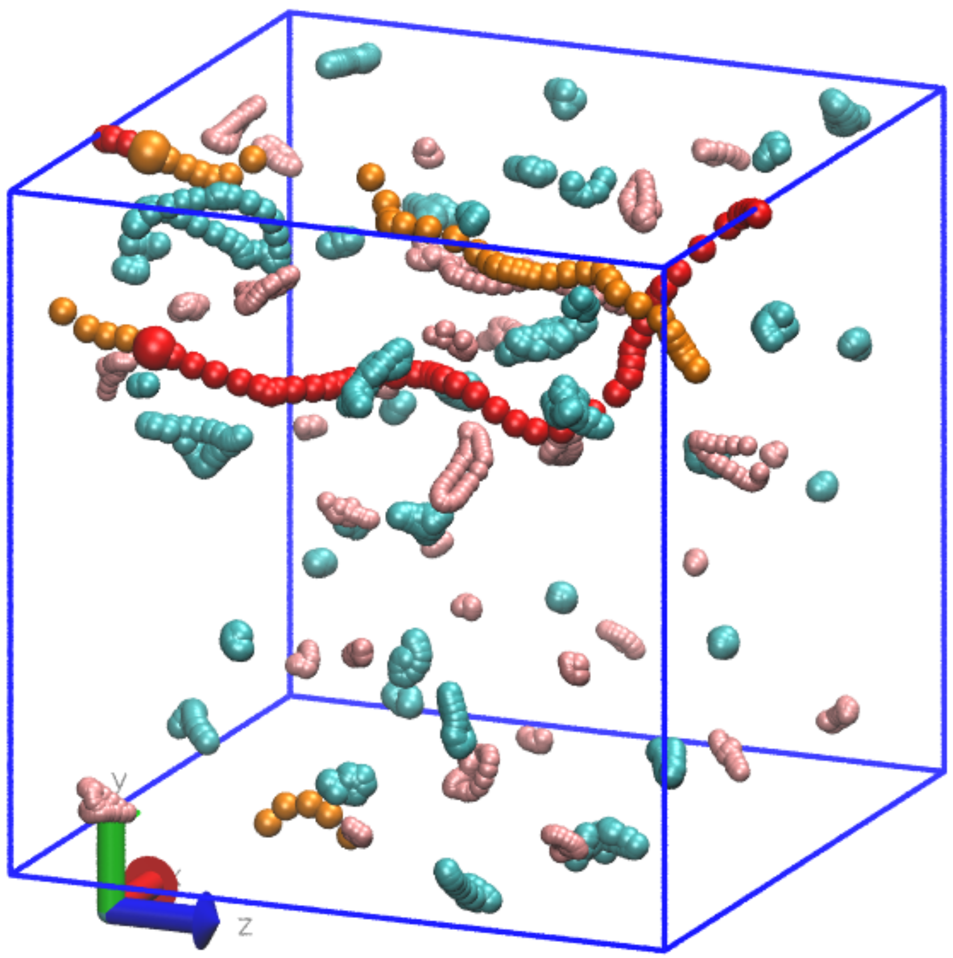


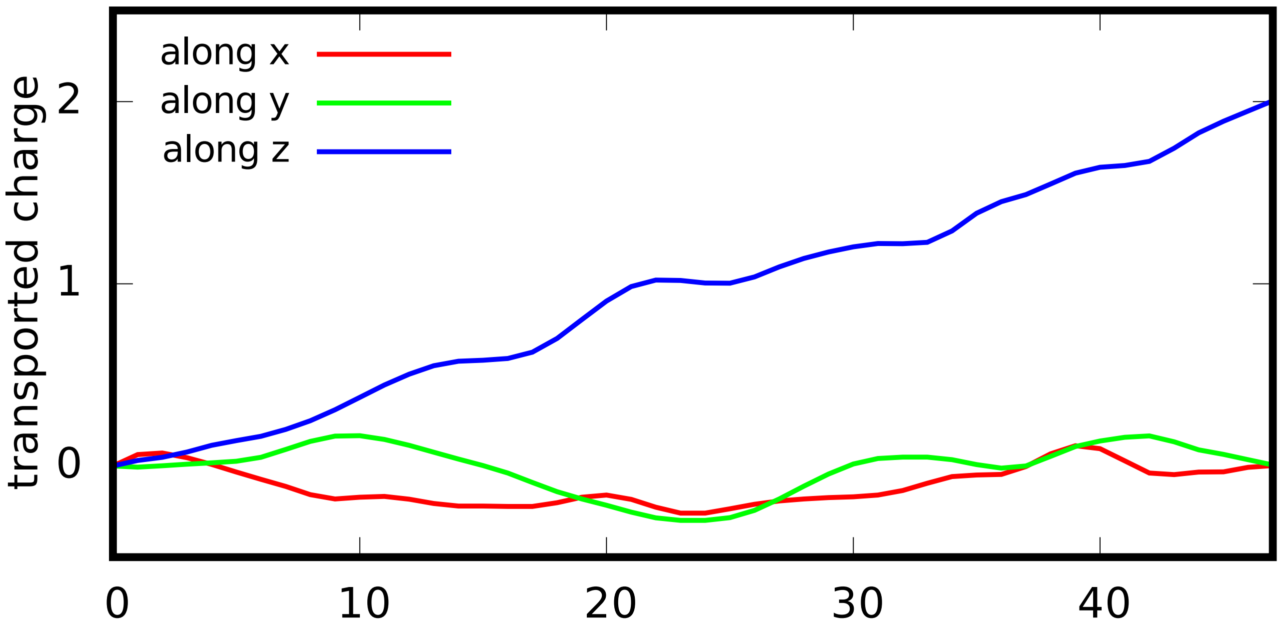




the charges transported by K and Cl around z cancel exactly

a numerical experiment on molten KCl





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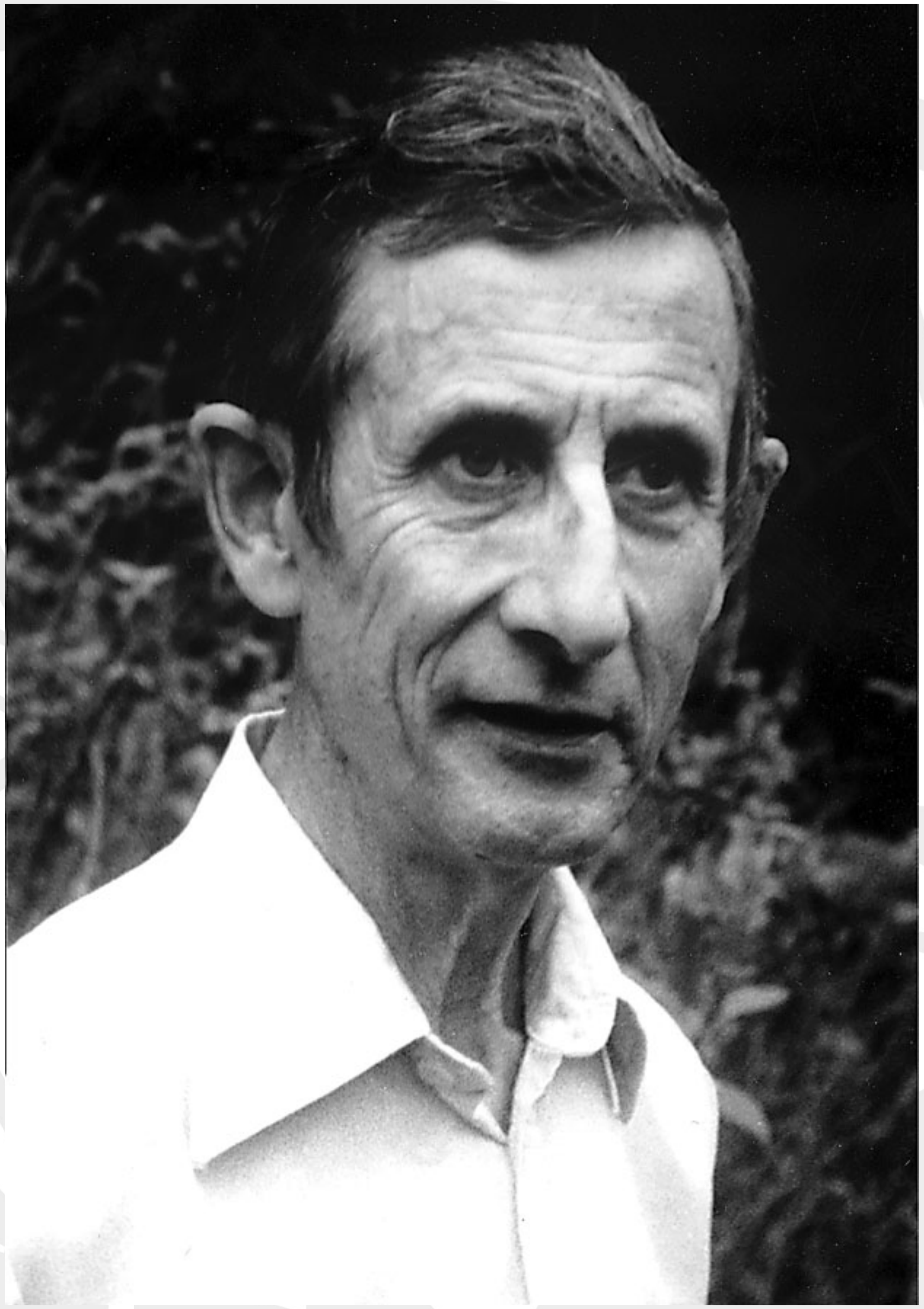
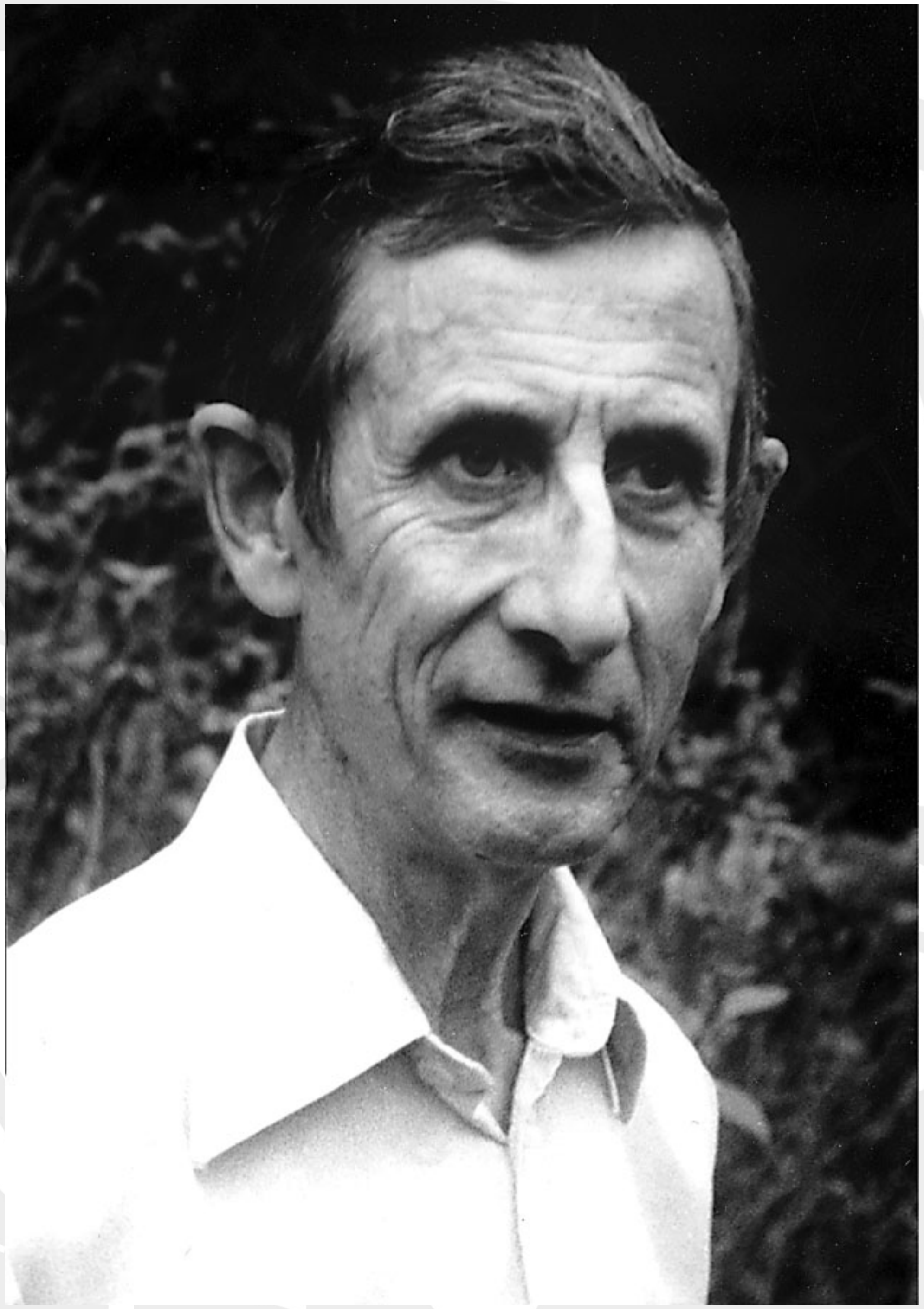
- this *gauge invariance* of thermal transport makes it possible to compute thermal transport coefficients from DFT using equilibrium AIMD and the Green-Kubo formalism;
- gauge invariance and topological quantization of charge transport make the electric conductivity of ionic fluids depend on the formal oxidation numbers of the ionic species, via the Green-Kubo formula.



Freeman J. Dyson



the computer is a tool for clear thinking

Freeman J. Dyson

thanks to:

Loris Ercole, SISSA

Aris Marcolongo, SISSA
now @EPFL

Federico Grasselli, SISSA

Riccardo Bertossa, SISSA

thanks to:

QUANTUMESPRESSO

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FOUNDATION

MAX

thank you for having me with you today

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