ab initio simulation of heat transport in liquids and glasses

Stefano Baroni

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talk given at the *Conference on Nanophononics: Bridging Statistical Physics, Molecular Modeling, and Experiments*,
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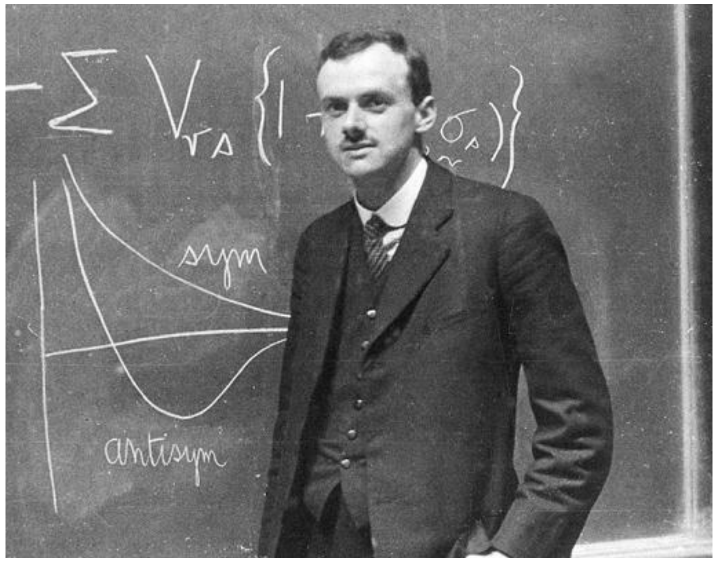
materials properties from first principles

The underlying physical laws necessary for a large part of physics and all of chemistry are completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble.



P.A.M. Dirac, 1929

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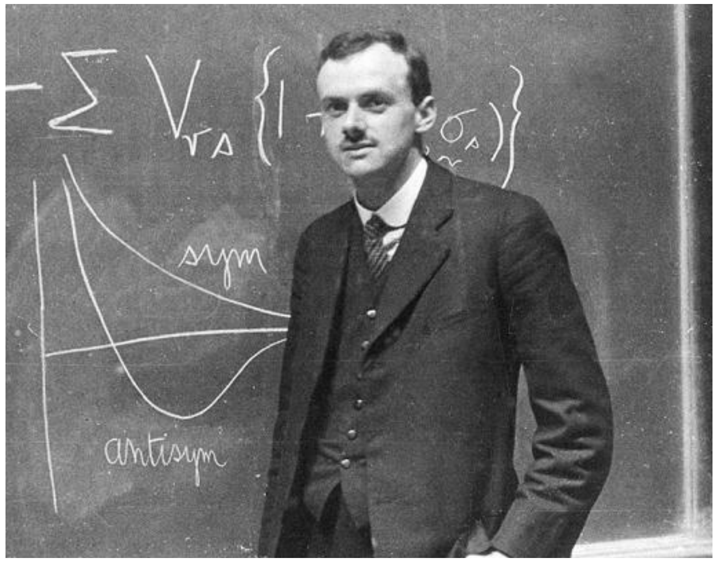

P.A.M. Dirac, 1929

Dirac's challenge has been answered in [our] field [… using] new physical models [… and] computers.

M.L. Cohen, 2015

why thermal transport?

- energy saving and heat dissipation
- heat shielding
- energy harvesting and scavenging
- earth and planetary sciences
- …

why thermal transport?

- … because it is important and still poorly understood

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

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

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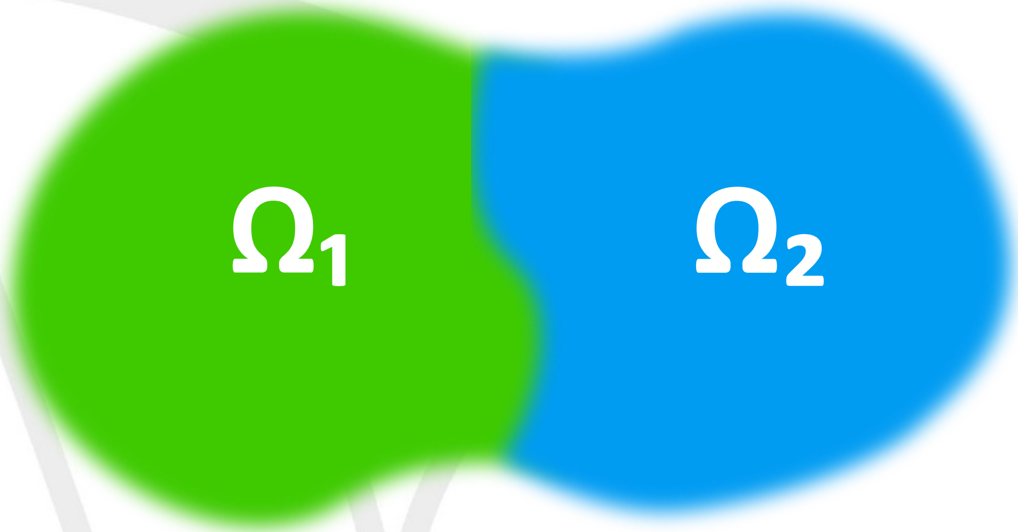
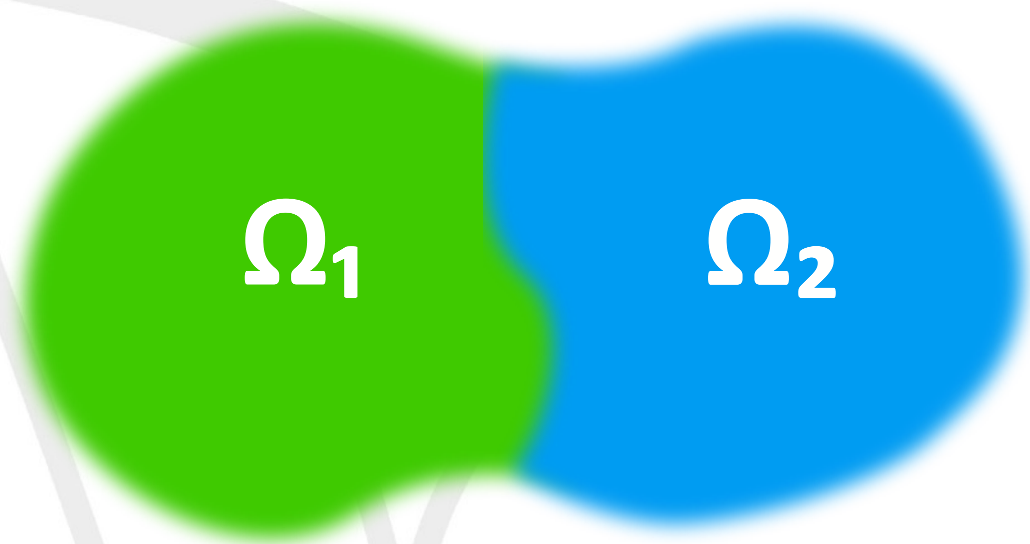
transport theory: extensive properties



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

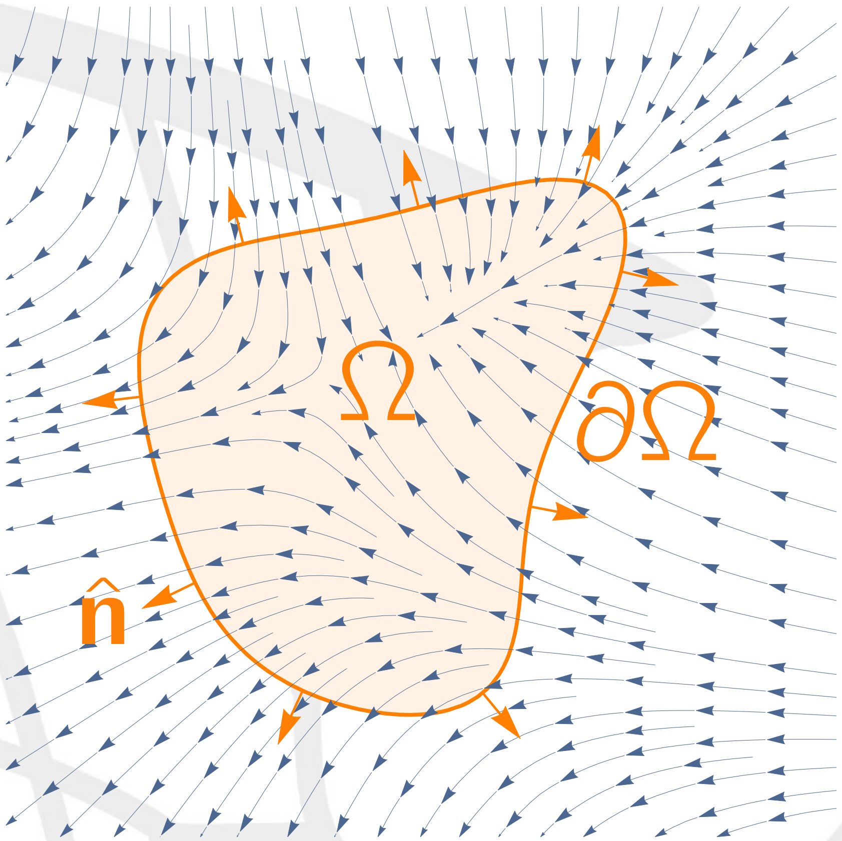
transport theory: extensive properties



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

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

transport theory: conservation laws



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

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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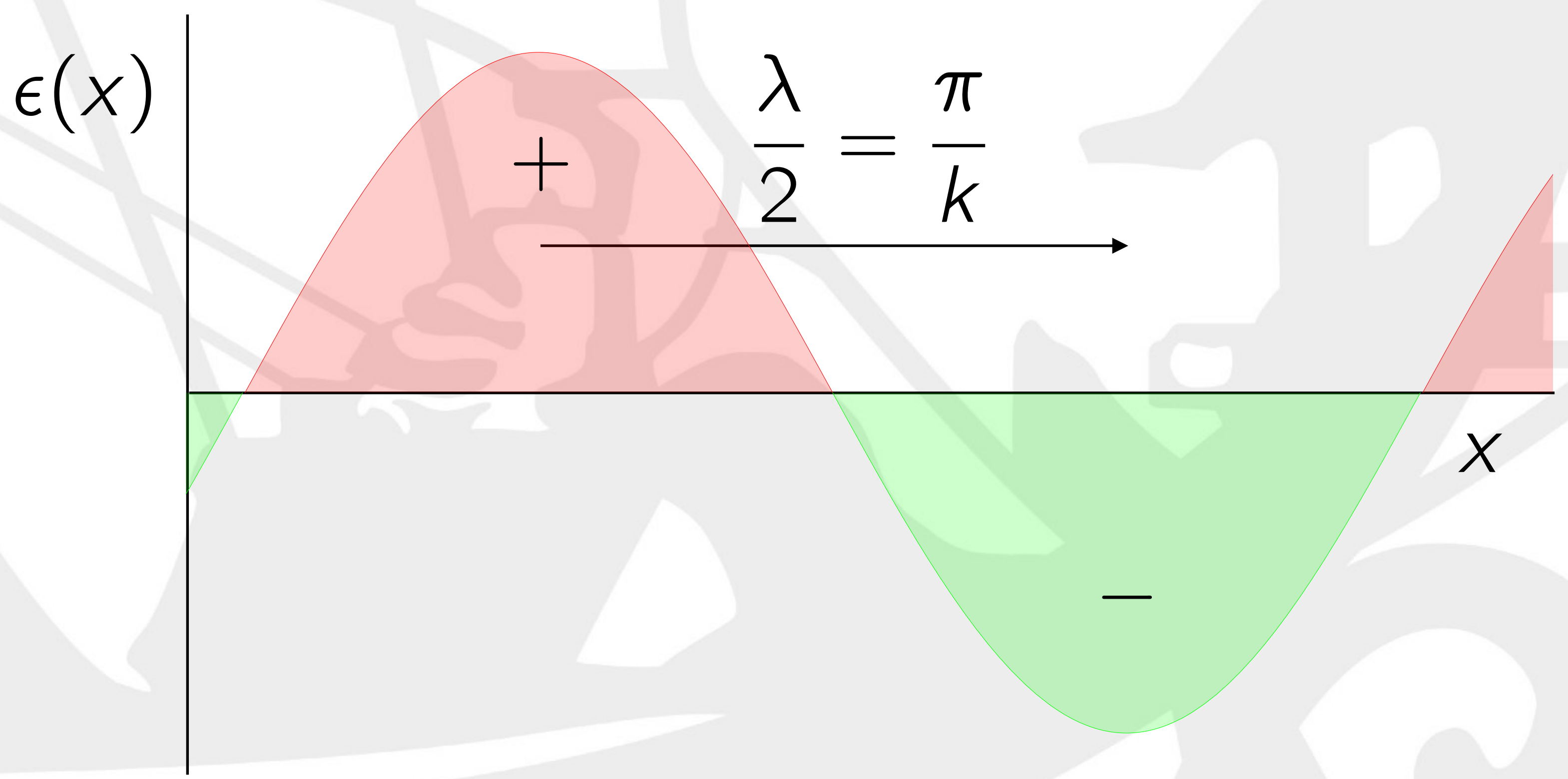

constitutive relations: Onsager's equations

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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at equilibrium:

$$\frac{\delta S}{\delta a_i(\mathbf{r})} = \mathrm{cnst}$$

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off equilibrium:

$$\mathbf{j}_i = \sum_j \Lambda_{ij} \mathbf{f}_j$$

$$\mathbf{f}_i(\mathbf{r}) = \nabla \frac{\delta S}{\delta a_i(\mathbf{r})}$$

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A	$\frac{\partial S}{\partial a}$
E	$\frac{1}{T}$
V	$\frac{p}{T}$
N_i	$-\frac{\mu_i}{T}$

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E	$\frac{1}{T}$
V	$\frac{p}{T}$
N_i	$-\frac{\mu_i}{T}$

$$\mathbf{j}_q = -\kappa \nabla T$$

$$\kappa = \frac{\Lambda_{EE}}{T^2}$$

Green-Kubo linear-response theory

$$\Lambda = \frac{\Omega}{k_B} \int_0^{\infty} \langle J(t) J(0) \rangle \, dt$$

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Einstein-Helfand relations

Einstein (1905)

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

$$\approx 2Dt$$

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

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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

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

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

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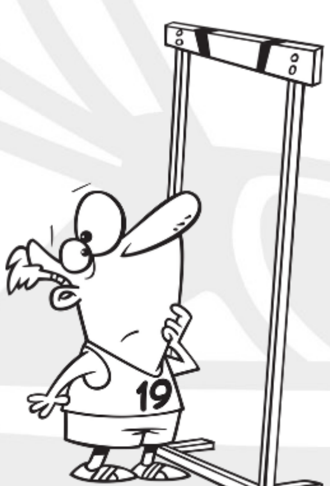

insights from classical mechanics

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

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

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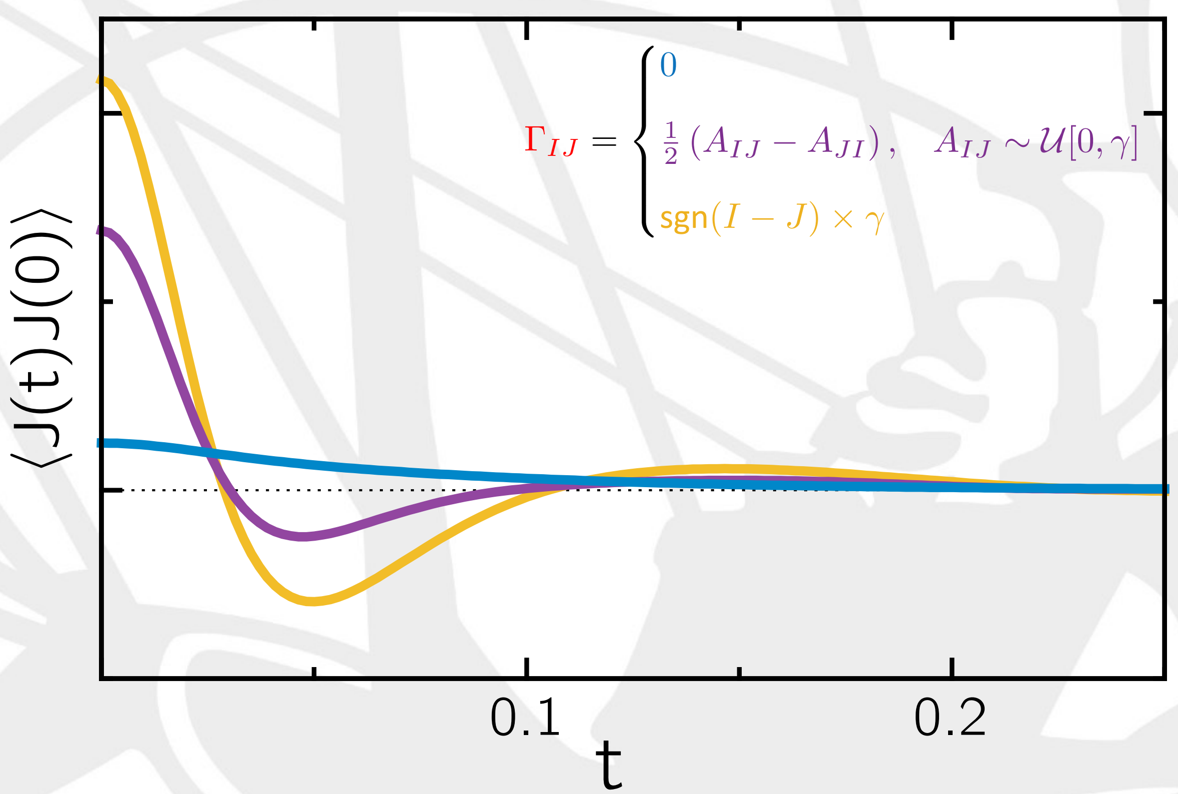

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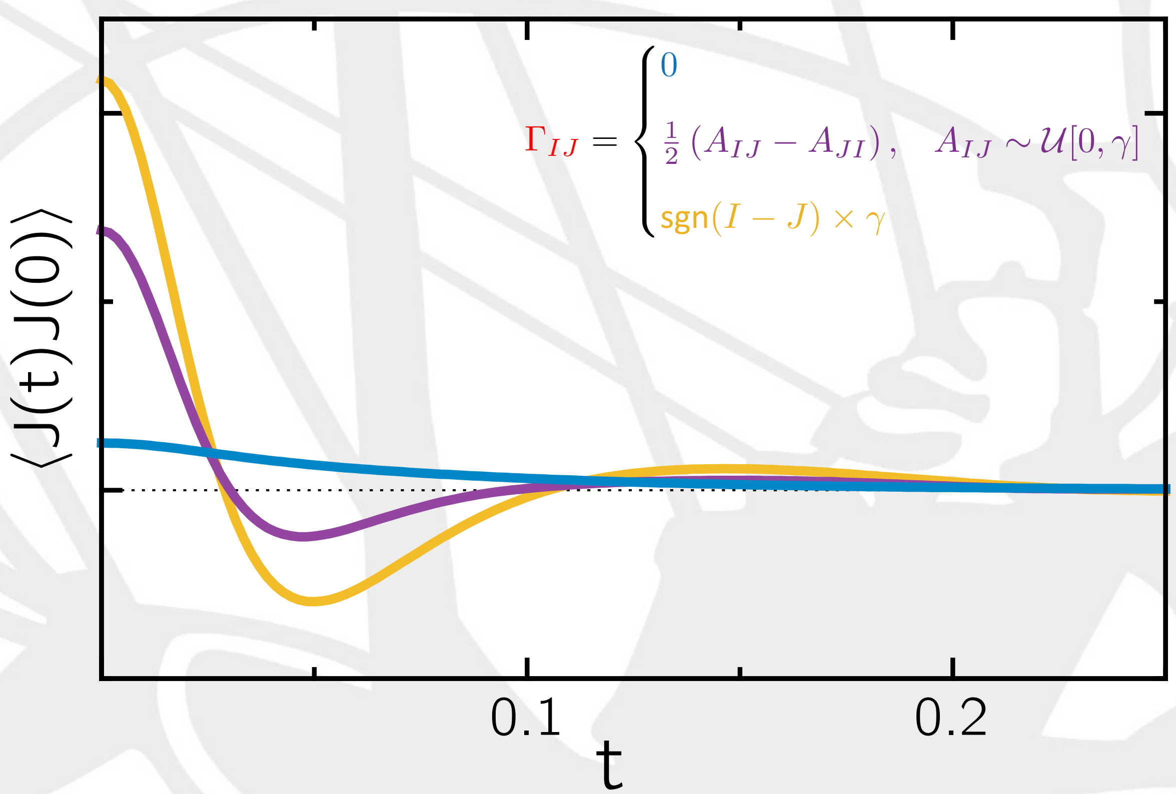

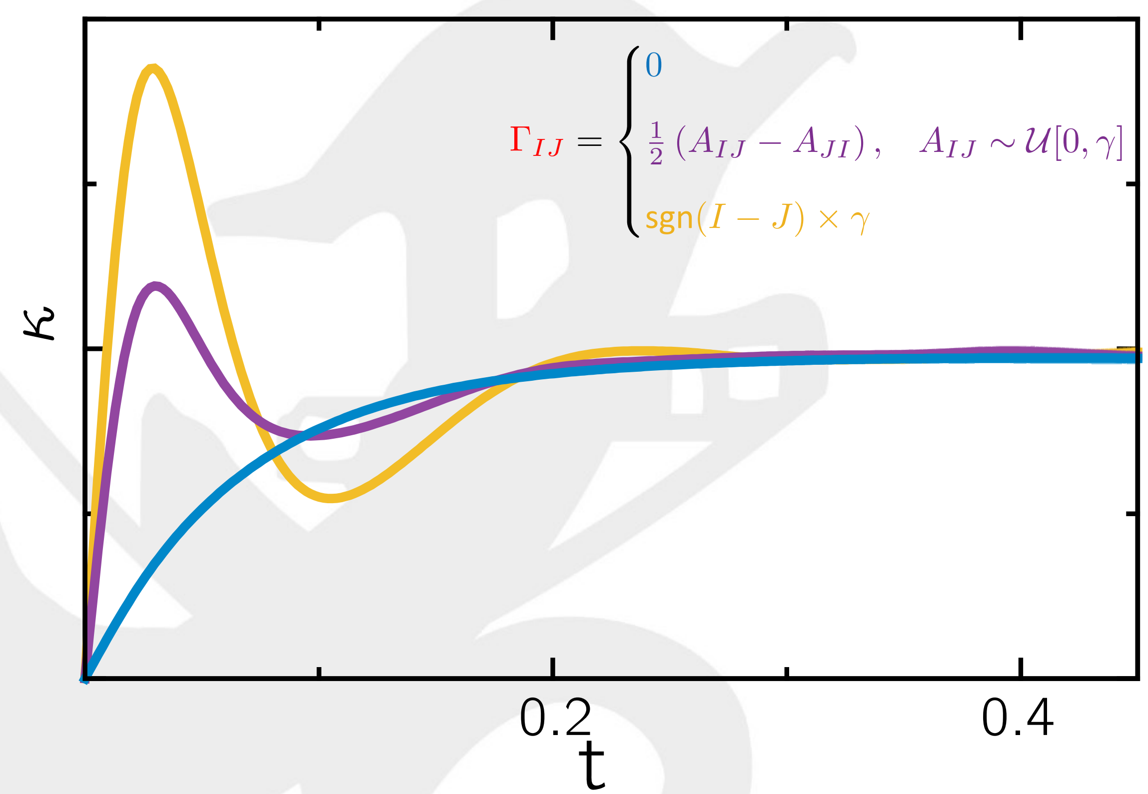

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$$\dot{\mathbf{P}} = \frac{\mathrm{d}}{\mathrm{dt}}\frac{1}{4}\sum_{I\neq J}\Gamma_{IJ}\, v(|\mathbf{R}_I-\mathbf{R}_J|)(\mathbf{R}_I-\mathbf{R}_I)$$

insights from classical mechanics

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

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$$\kappa' = \kappa$$

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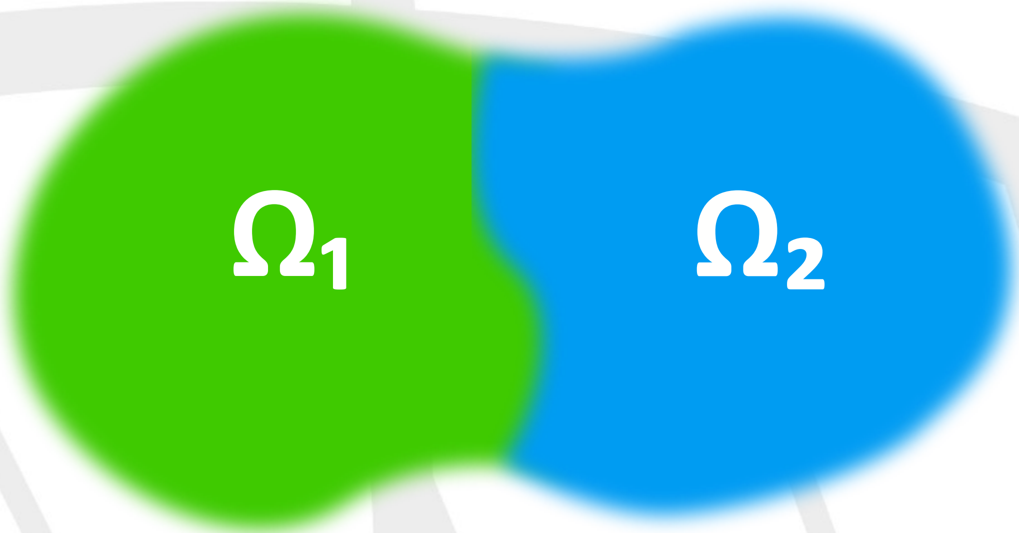
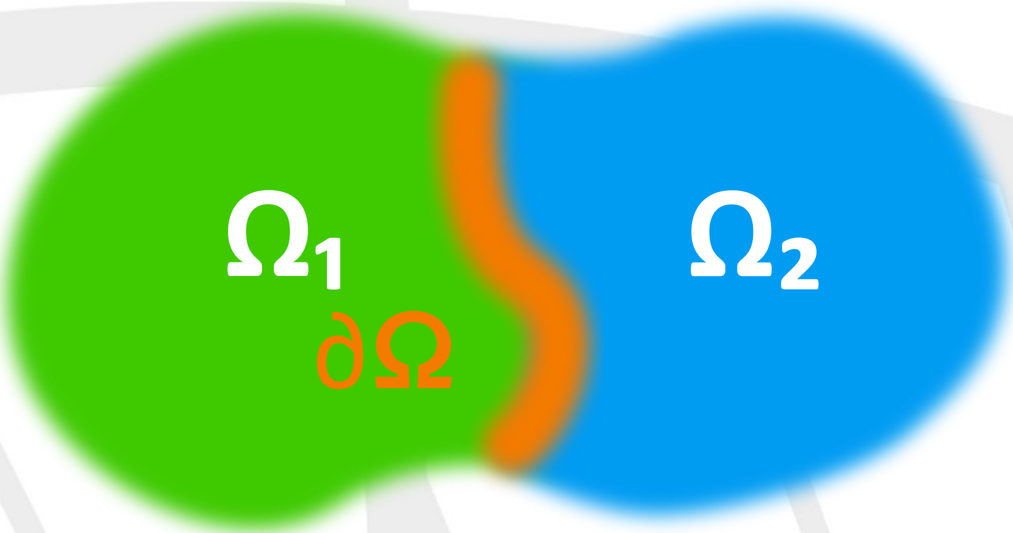
gauge invariance



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

gauge invariance



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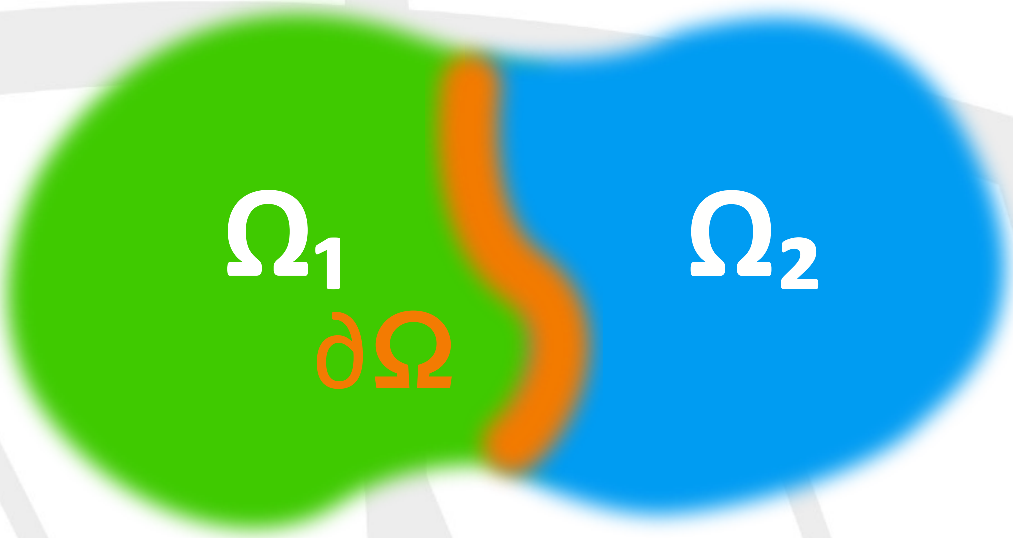

$$\mathsf{E}[\Omega_1 \cup \Omega_2] = \mathsf{E}[\Omega_1] + \mathsf{E}[\Omega_2] + \mathsf{W}[\partial\Omega]$$
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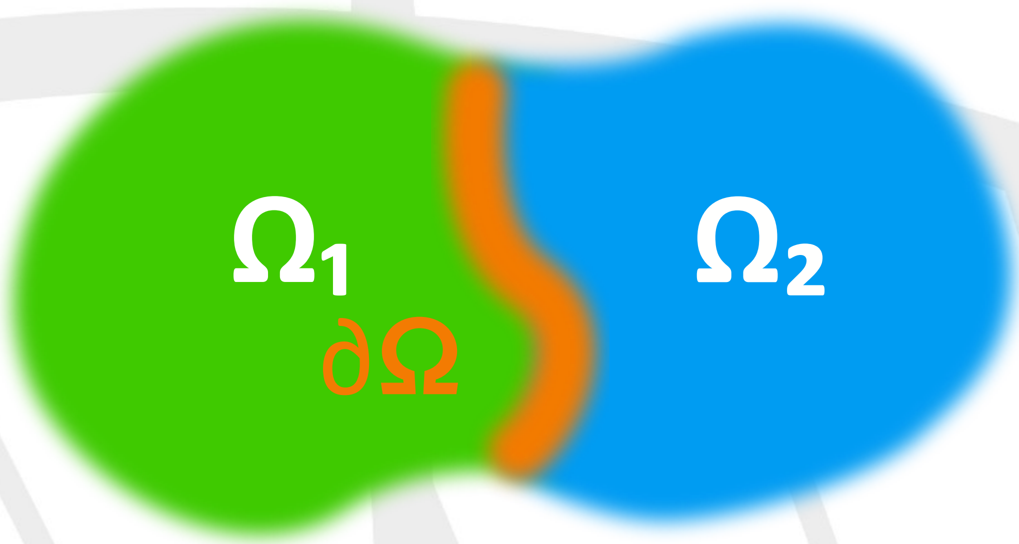

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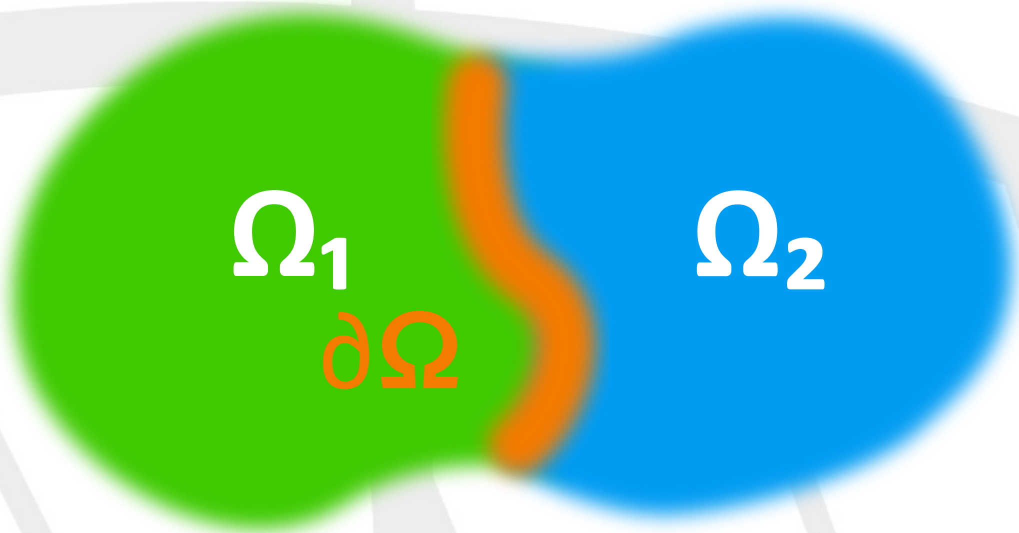
gauge invariance



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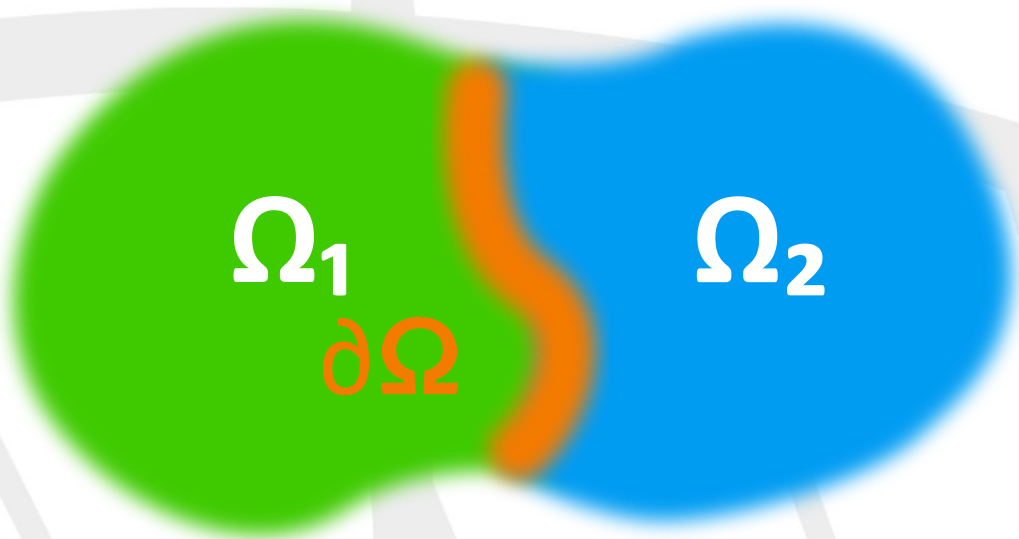

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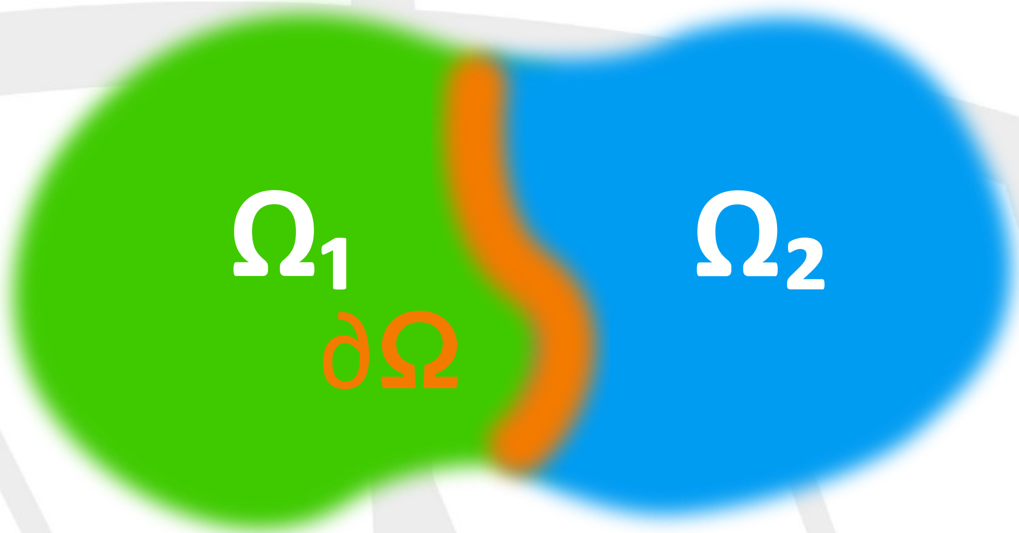

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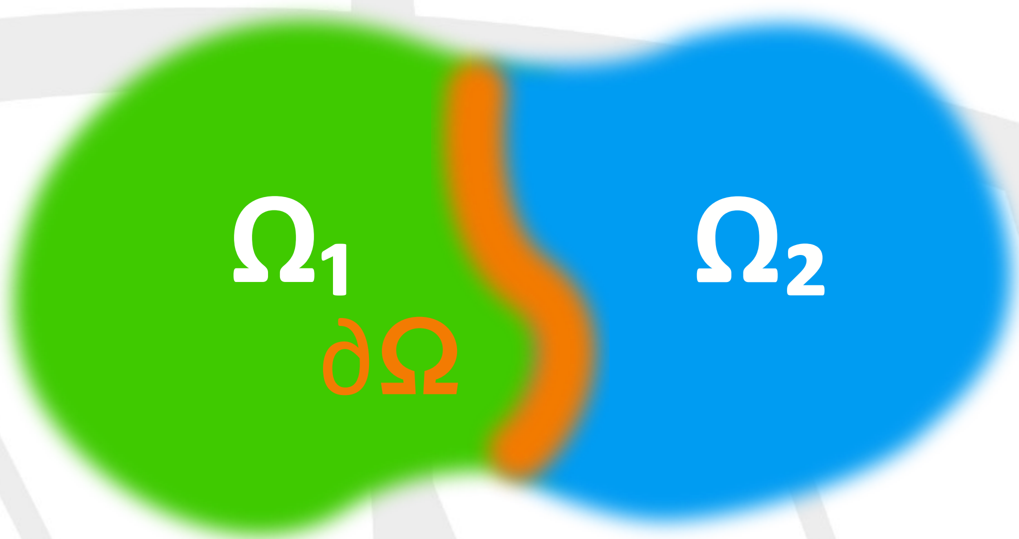

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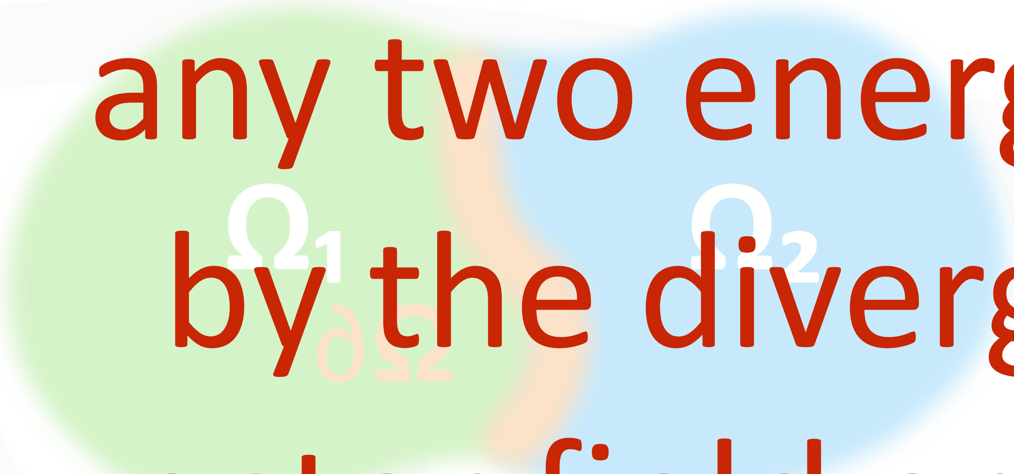
gauge invariance

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



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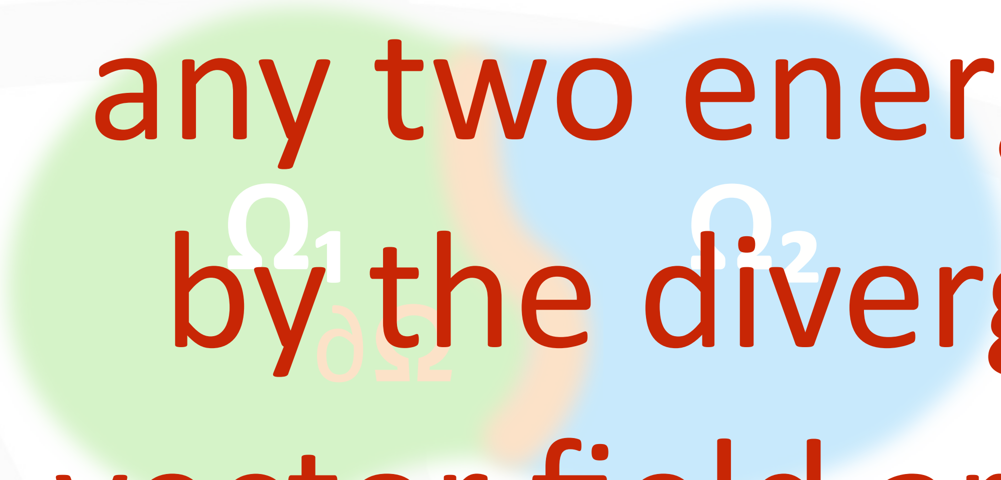

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the corresponding energy fluxes differ by a total time derivative, and the heat transport coefficients coincide

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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

$$
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$$

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

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

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

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

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

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

the DFT energy current

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

$$= \mathbf{J}_{KS} + \mathbf{J}_{H} + \mathbf{J}'_{0} + \mathbf{J}_{0} + \mathbf{J}_{XC}$$

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

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

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

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

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

the DFT energy current

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

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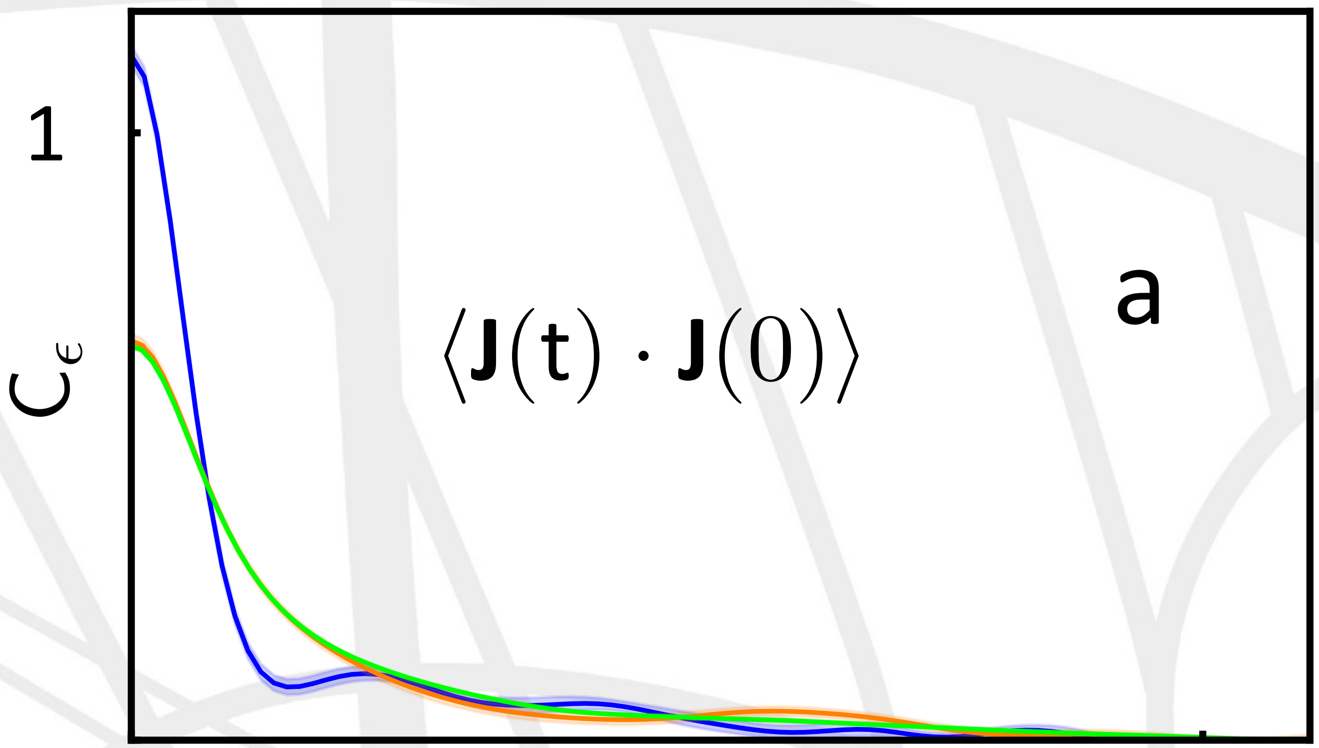
$$\mathbf{J}_{KS} = \sum_v \left(\langle \varphi_v | \mathbf{r}\hat{H}_{KS} | \dot{\varphi}_v \rangle + \varepsilon_v \langle \dot{\varphi}_v | \mathbf{r} | \varphi_v \rangle \right)$$

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

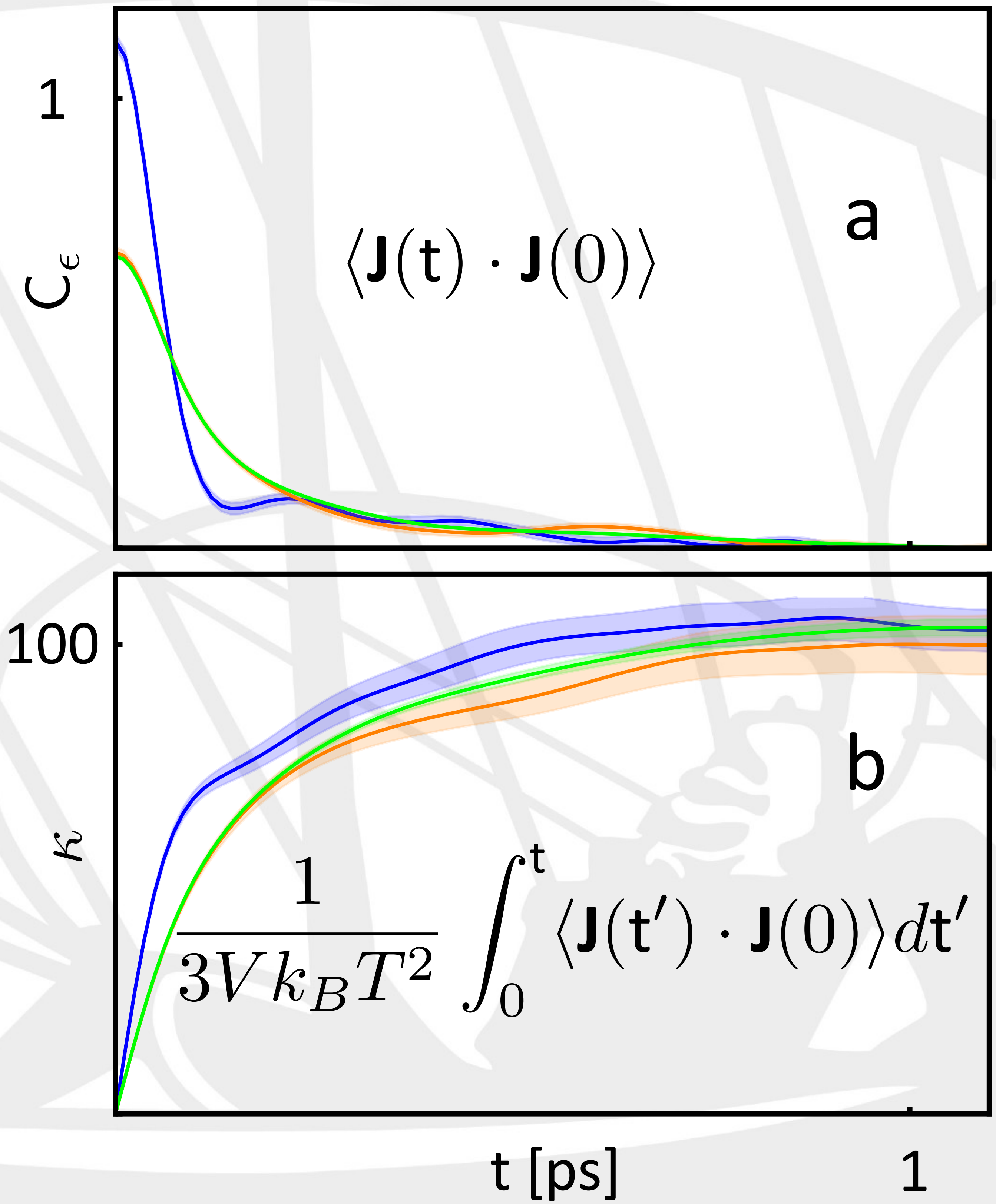
a benchmark



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

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

a benchmark



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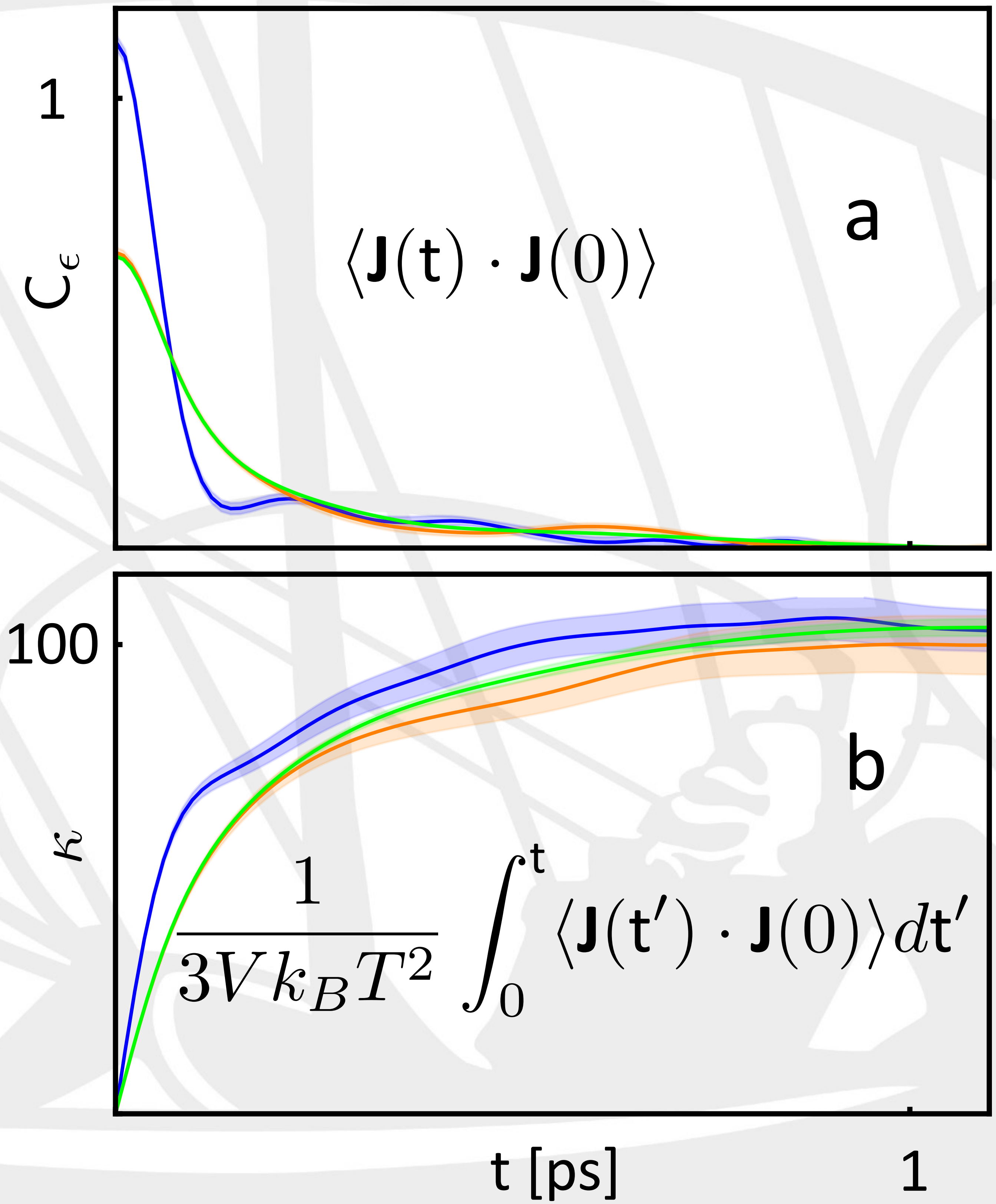

108 “LDA Ar” atoms
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100 ps CP trajectory
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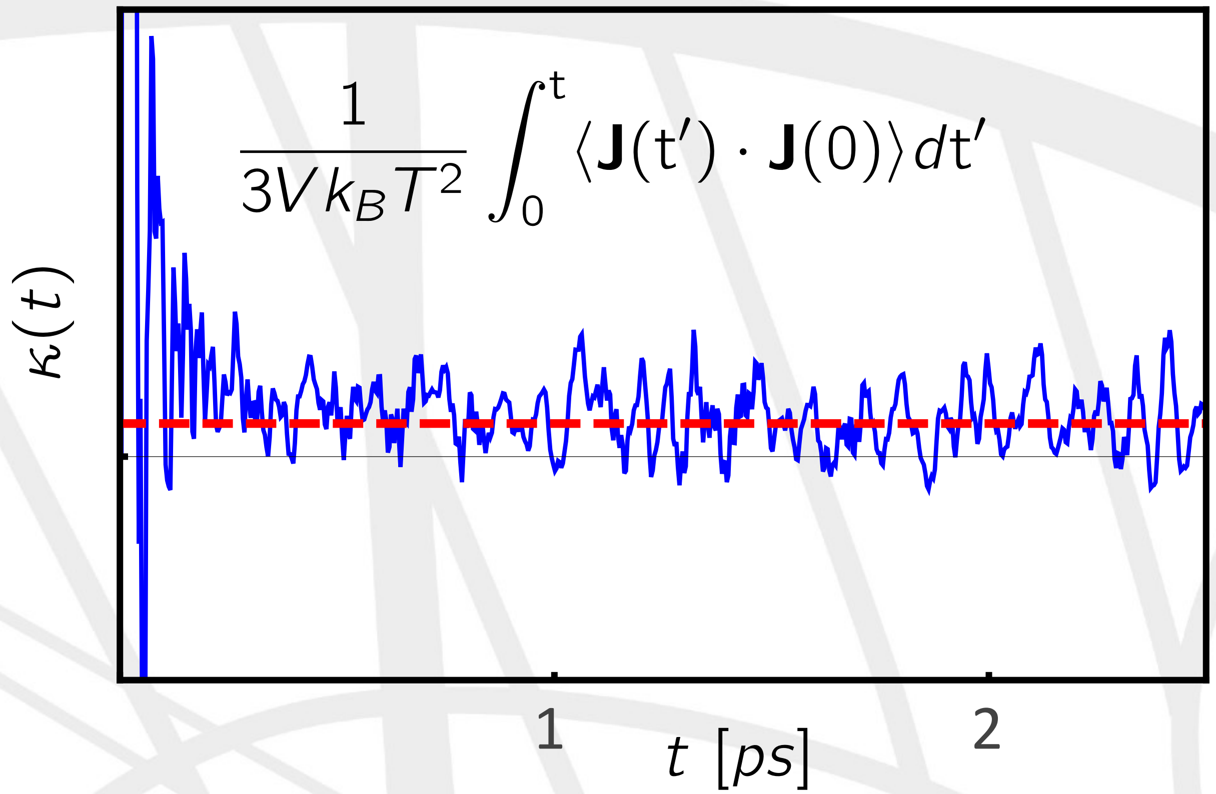
1 ns classical FF trajectory

same behavior at T=400 K

A. Marcolongo, P. Umari, and SB, Nat. Phys. **12**, 80 (2016)

liquid (heavy) water



64 molecules, T=385 K
expt density @ac

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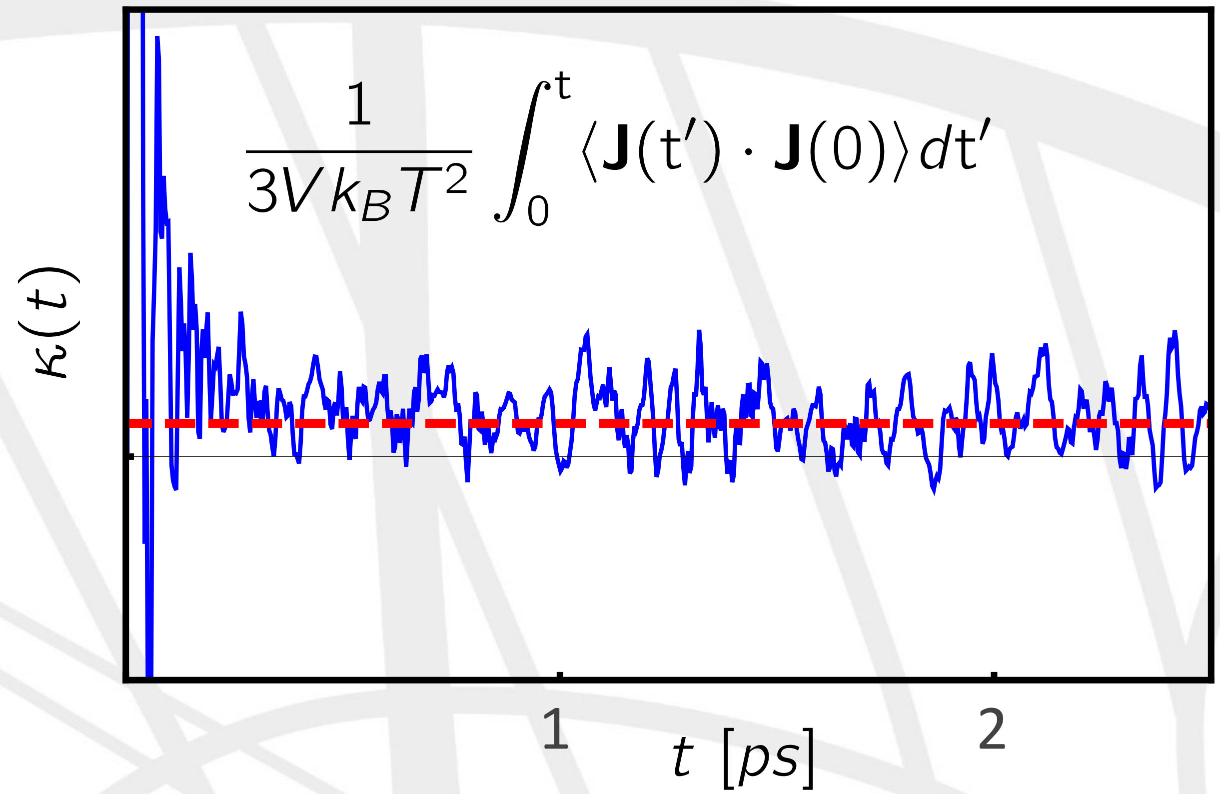

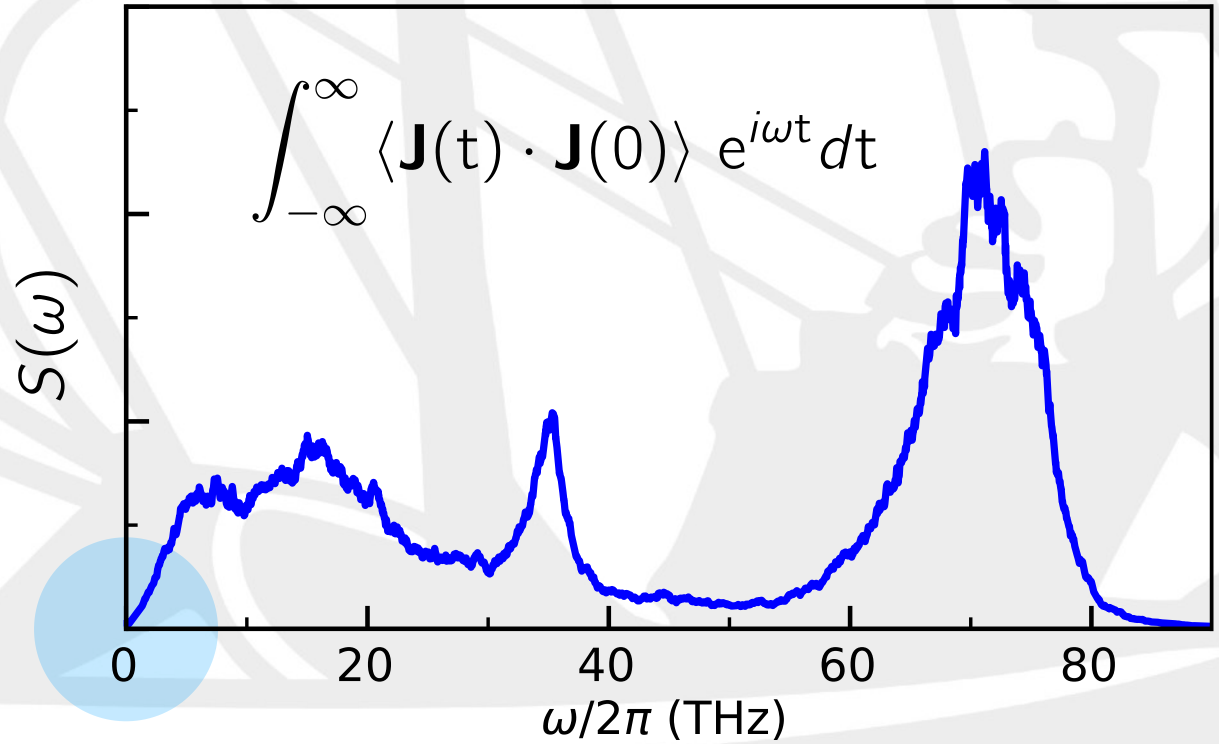

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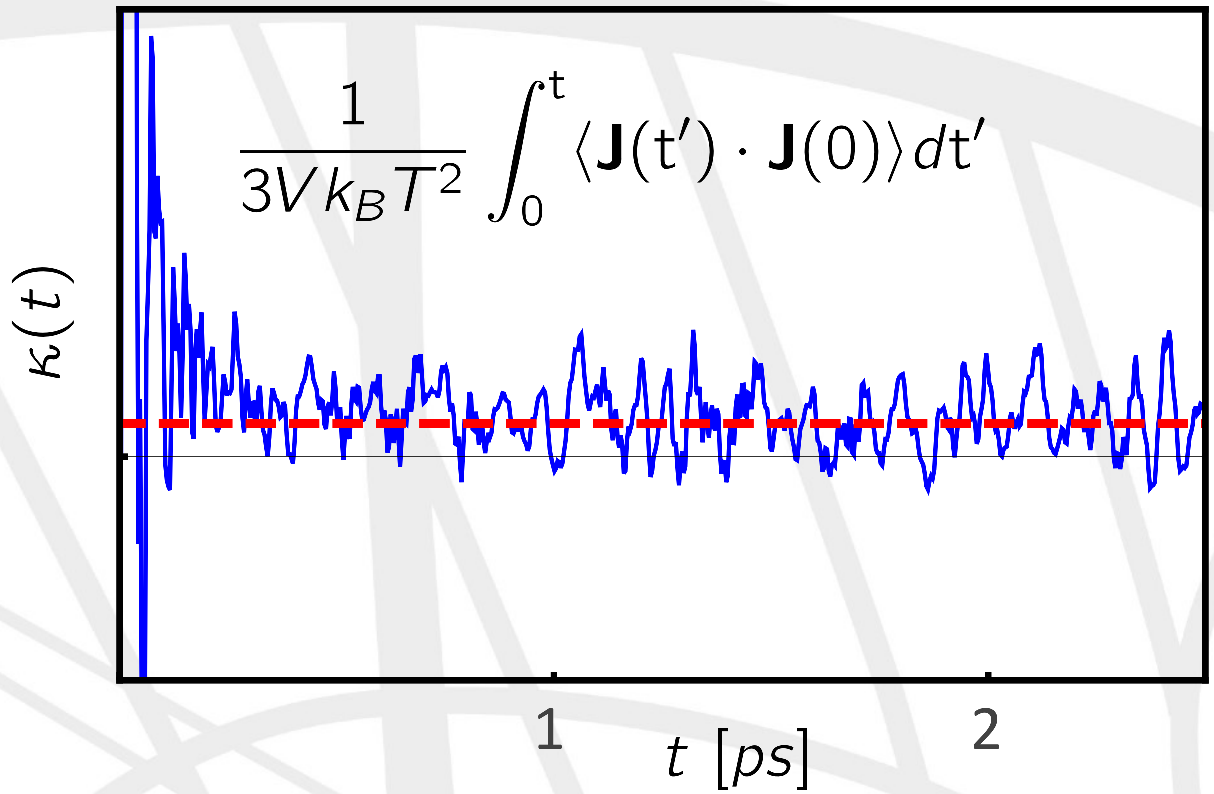

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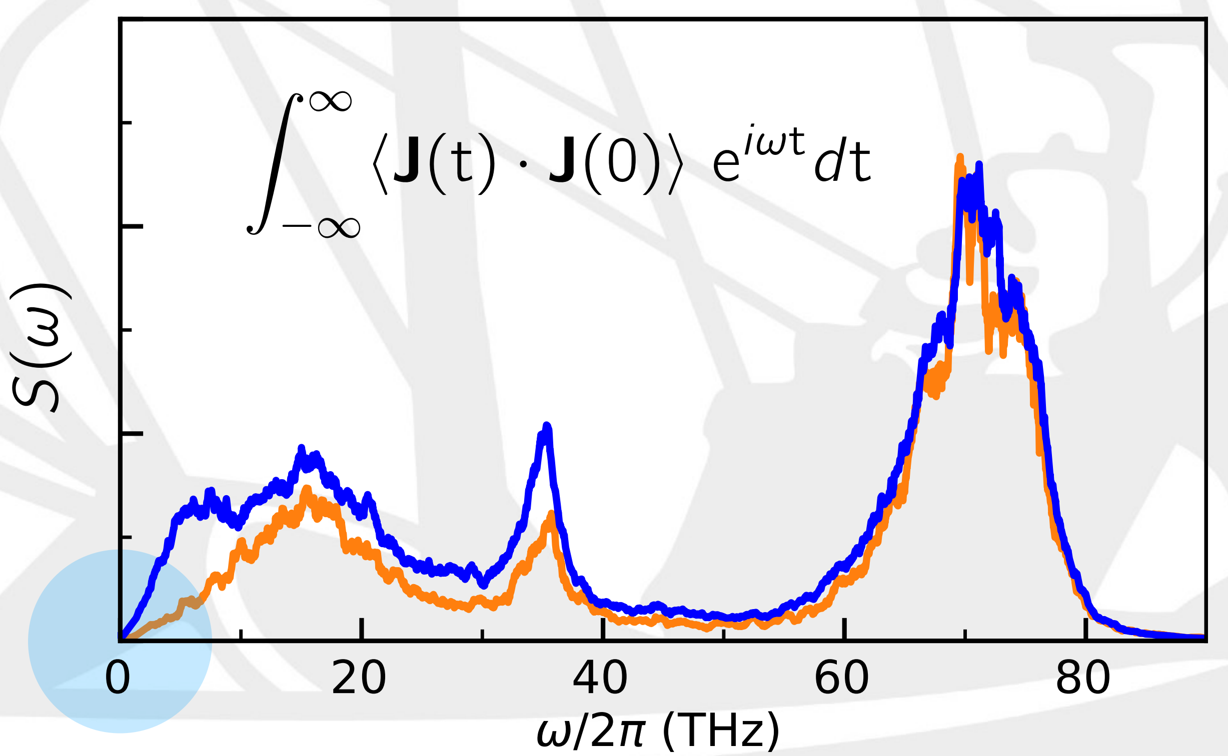

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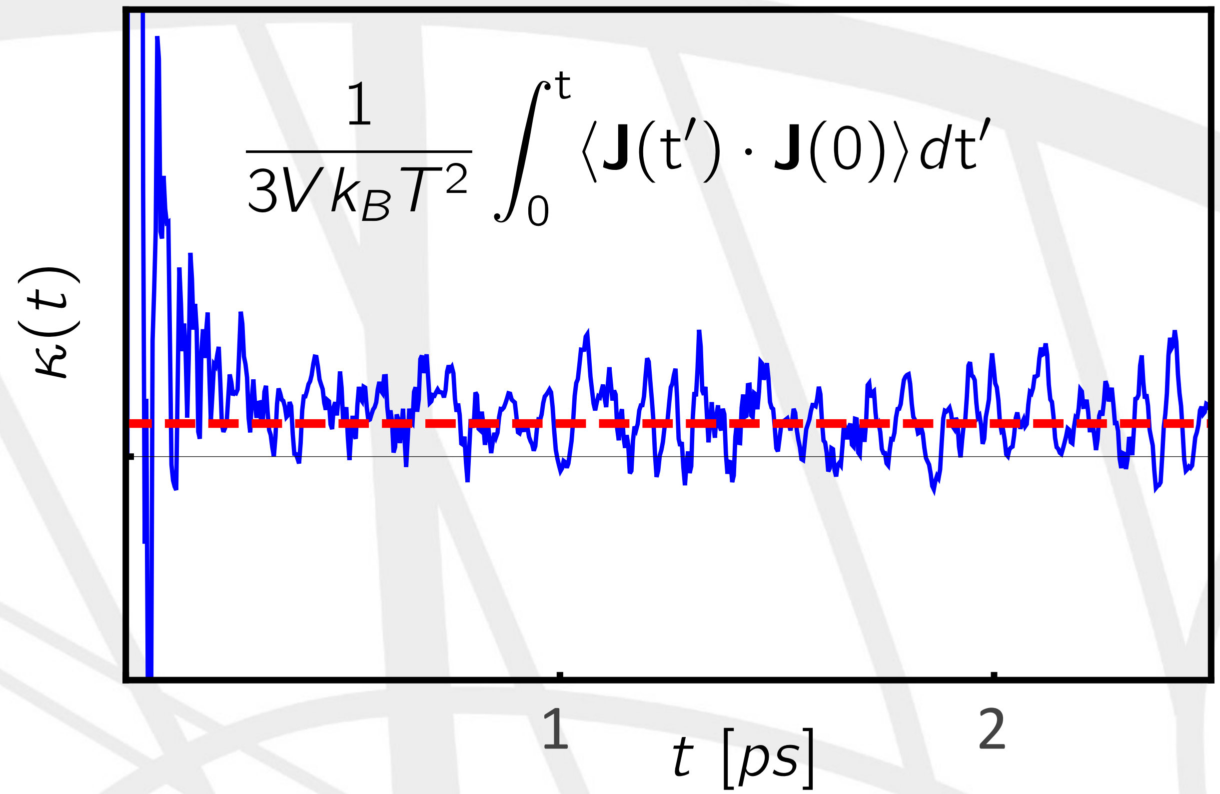

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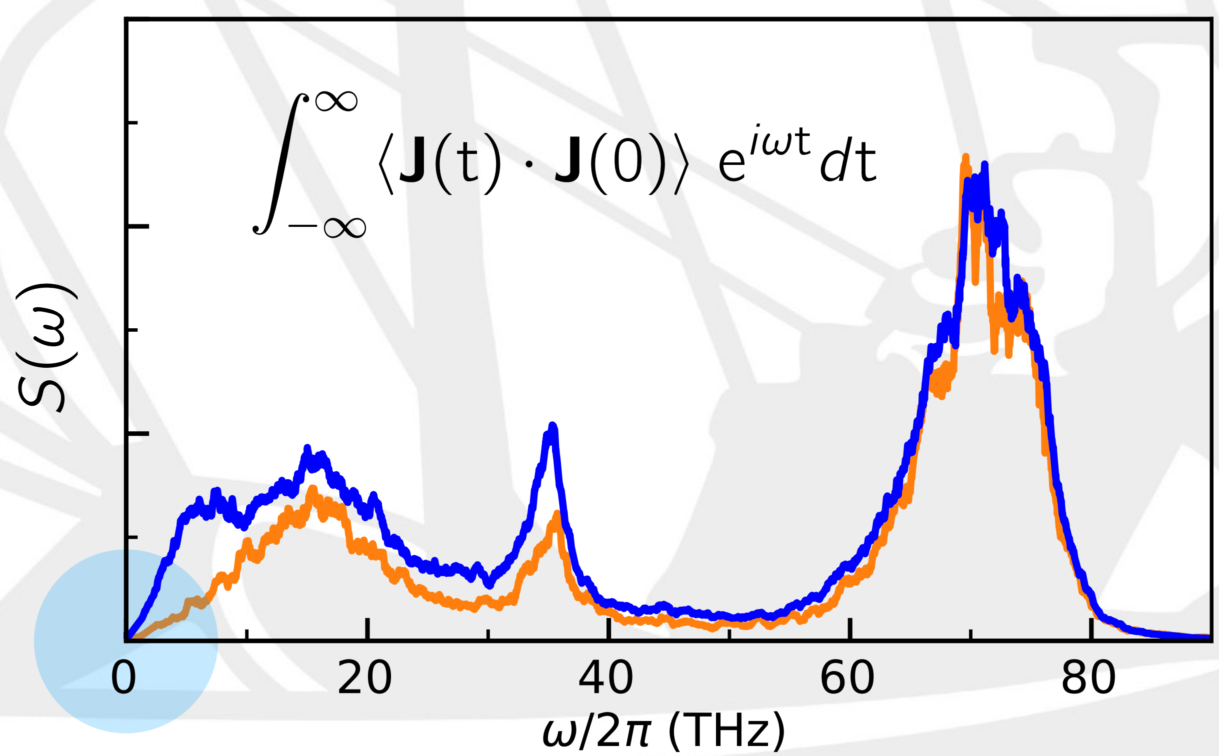
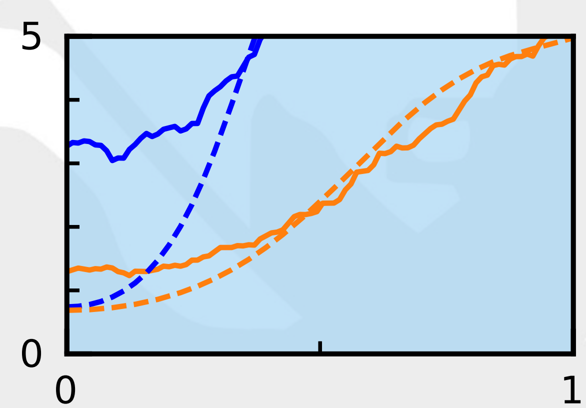


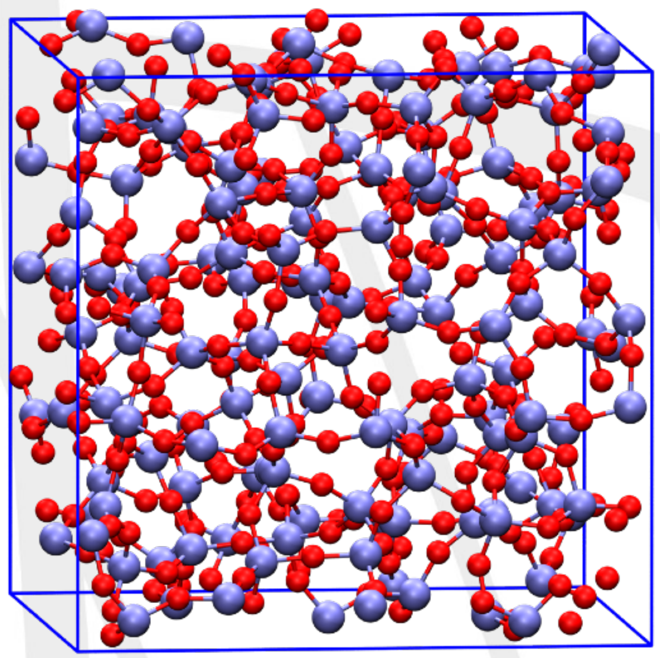


$\kappa_{DFT} = 0.70 \pm 0.17$ W/mK
$\kappa_{expt} = 0.61$ W/mK

A. Marcolongo, P. Umari, and SB, Nat. Phys. **12**, 80 (2016)

R. Bertossa, F. Grasselli, L. Ercole and SB, Phys. Rev. Lett. in press (2019)

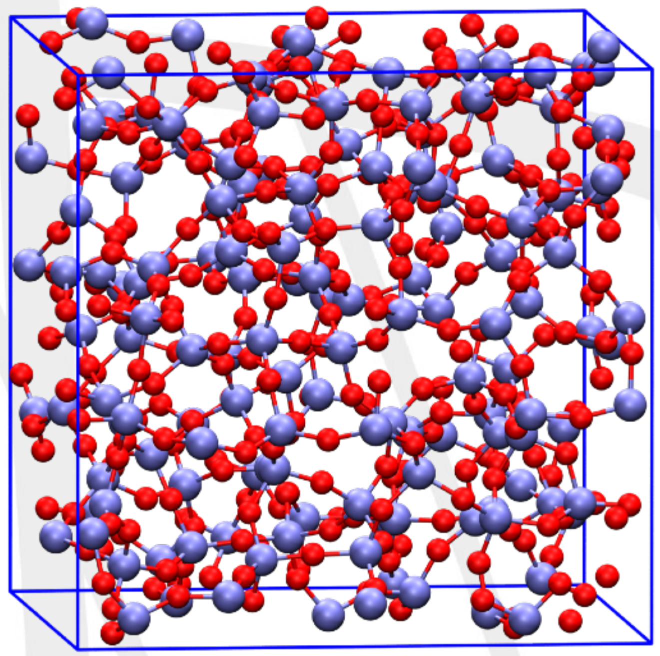
silica glass

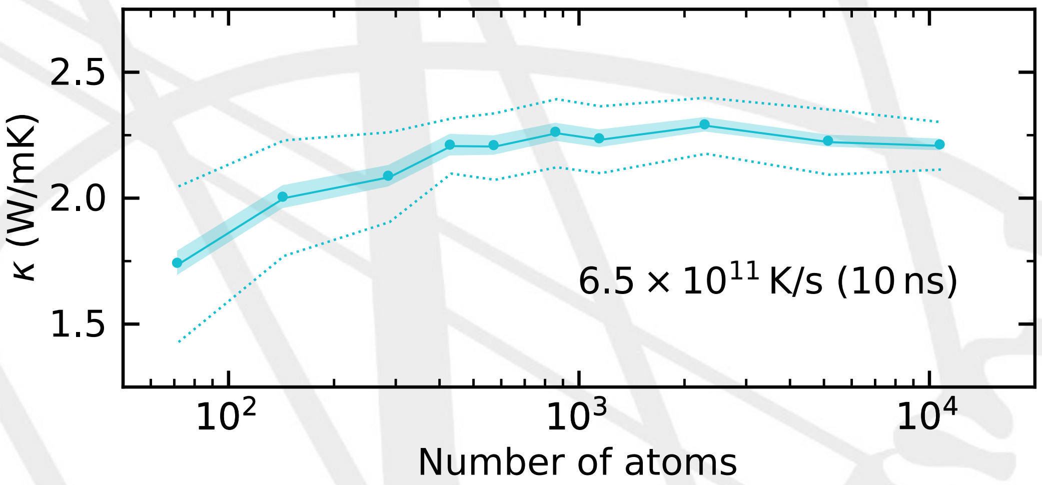


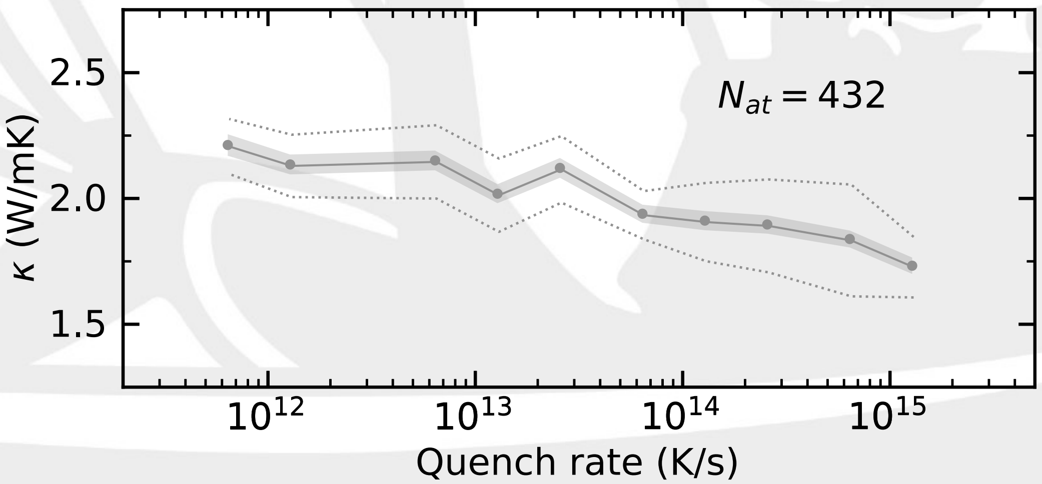
432 atoms
sample quenched from melt
@6.5×10^{11} K/sec

2304 electrons
2× 52 ps

silica glass







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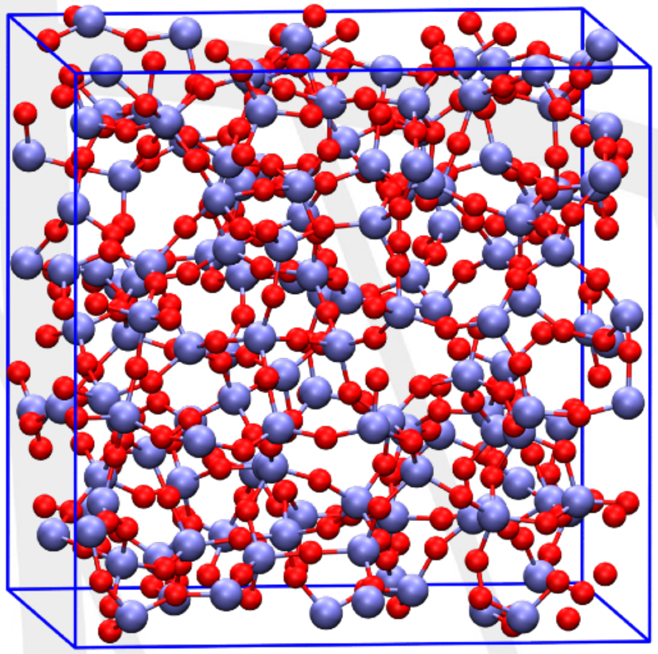

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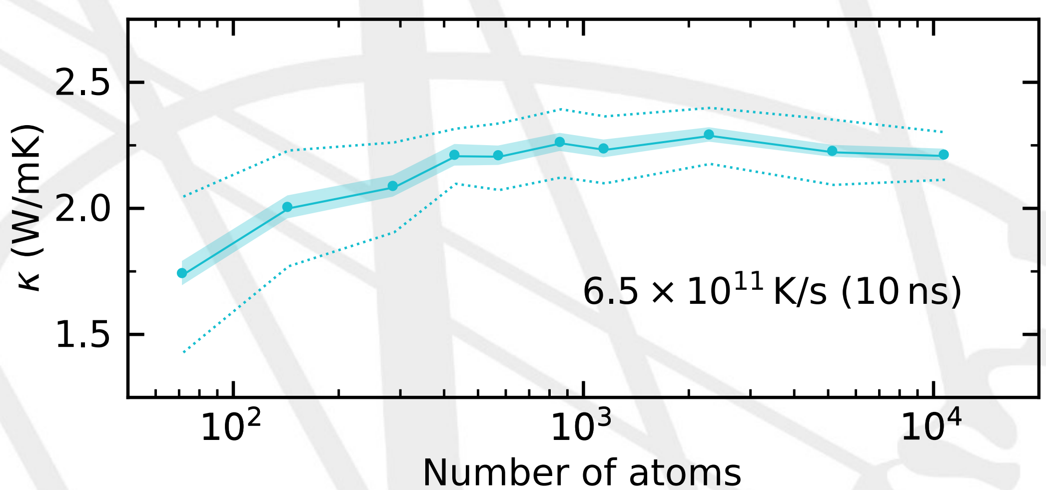

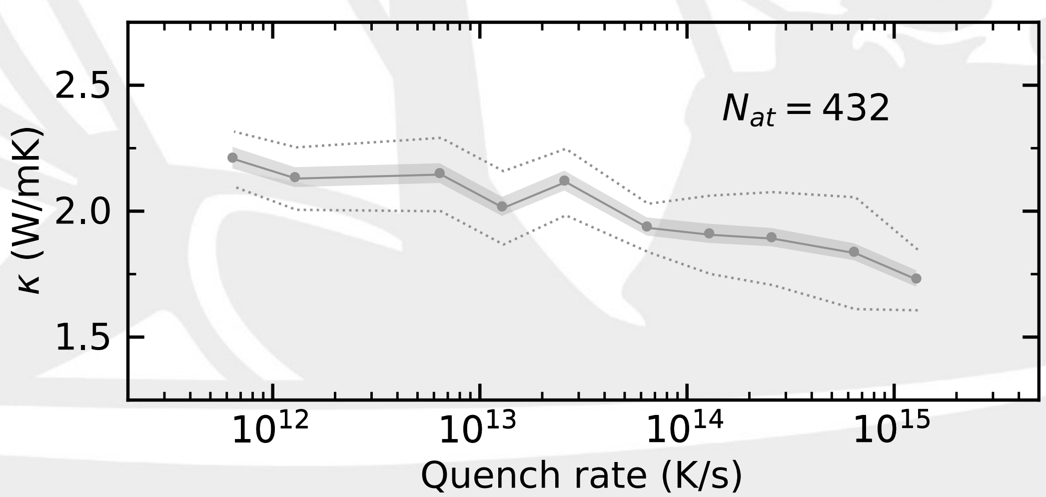

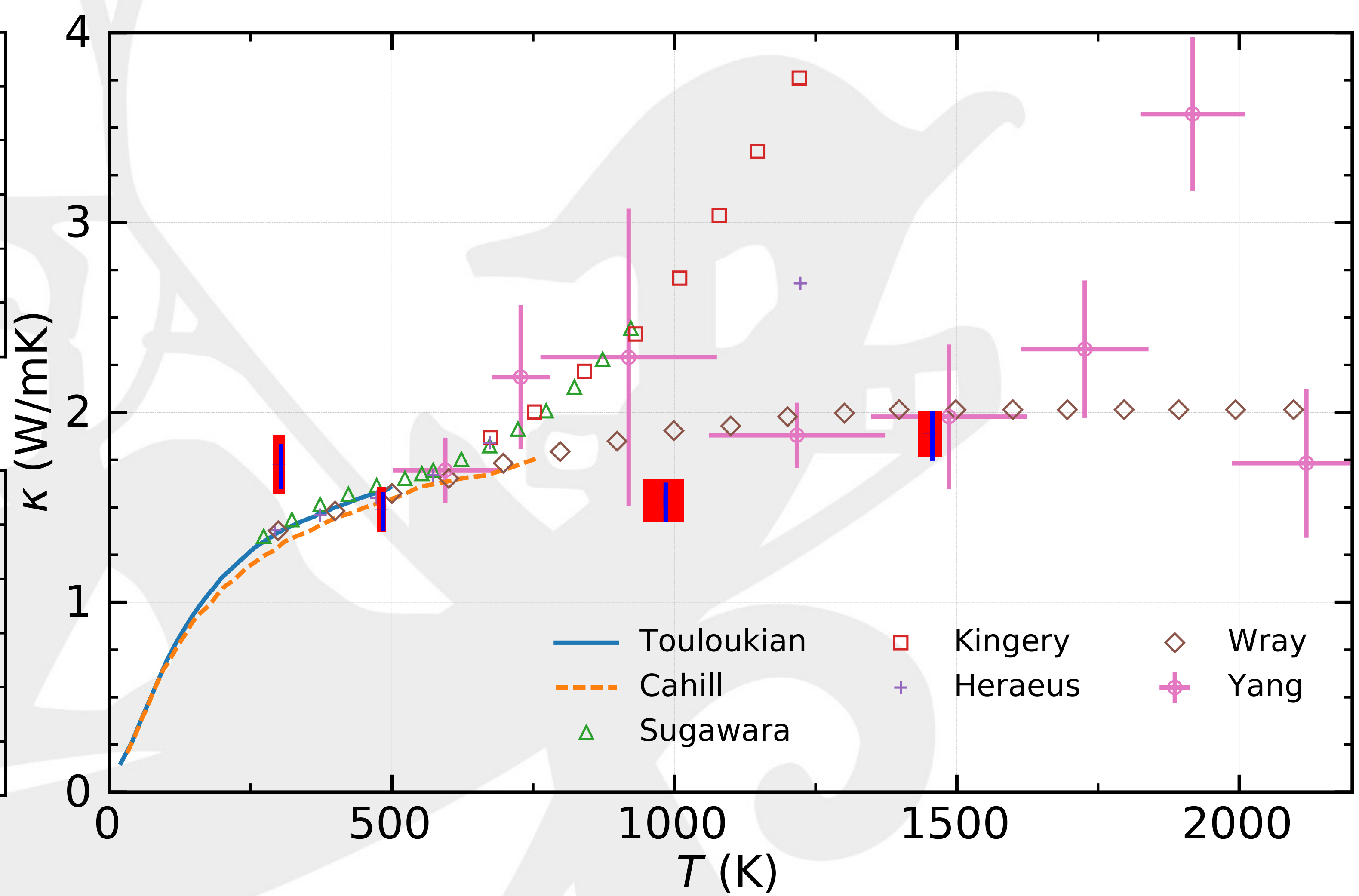

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do BTE!

$$\kappa = \sum_{\nu \mathrm{q}} c(\omega_\nu(\mathbf{q}))v_\nu(\mathbf{q})^2\tau_\nu(\mathbf{q})$$

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what about glasses and alloys?

Heat transport from lattice dynamics

$$\mathbf{J} = \sum_n \left(\dot{\mathbf{R}}_n e_n + \mathbf{R}_n \dot{e}_n \right)$$

Heat transport from lattice dynamics

$$\mathbf{R}_n = \mathbf{R}_n^\circ + \mathbf{u}_n$$

$$\begin{aligned}\mathbf{J} &= \sum_n \left(\dot{\mathbf{R}}_n e_n + \mathbf{R}_n \dot{e}_n\right) \\ &= \sum_n \mathbf{R}_n^\circ \dot{e}_n + \frac{d}{dt}\sum_n \mathbf{u}_n e_n\end{aligned}$$

Heat transport from lattice dynamics

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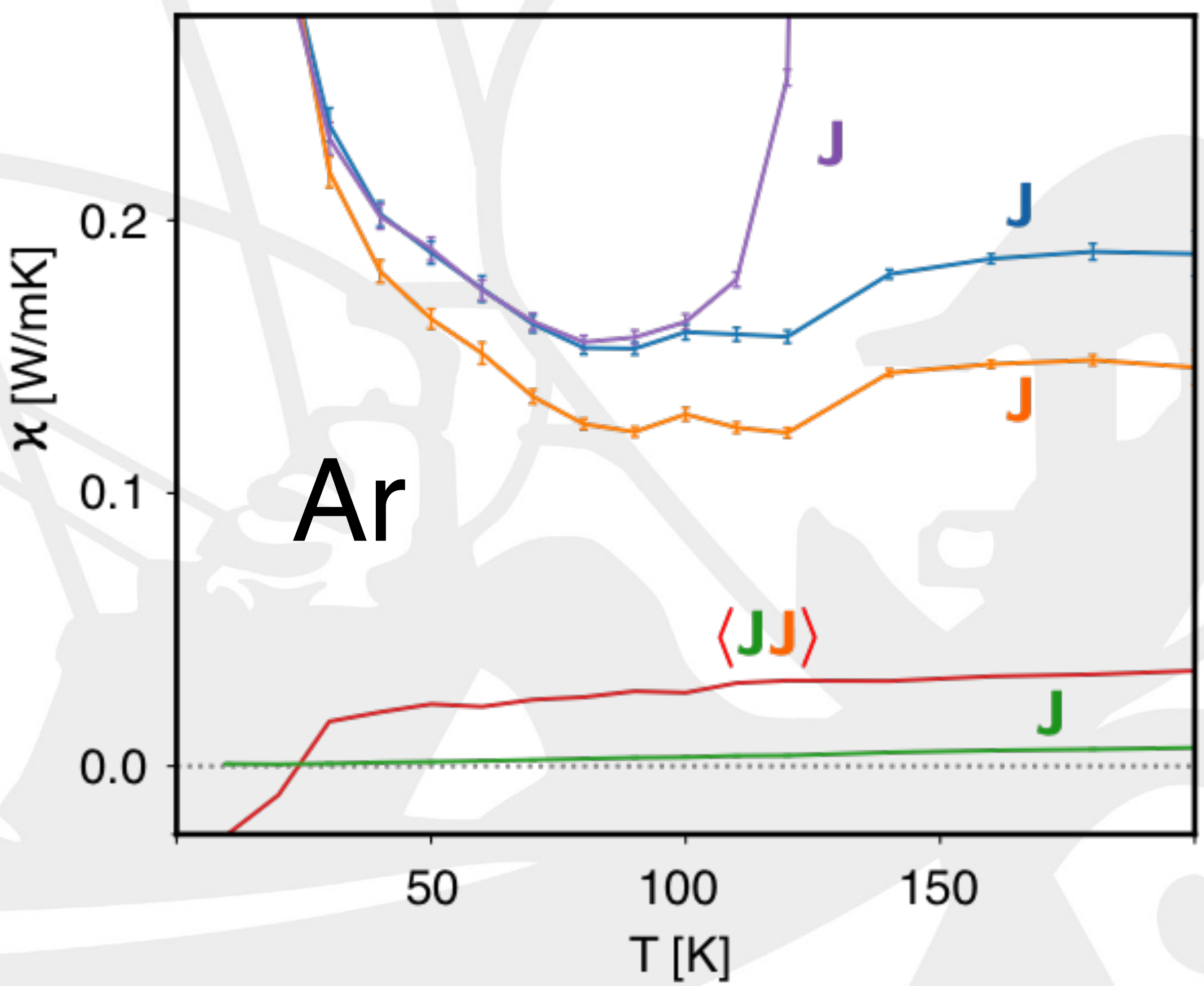

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$$\Phi_{i\beta}^{j\gamma} = \left.\frac{\partial^2 E}{\partial u_{i\beta} \partial u_{j\gamma}}\right|_{\mathrm{u}=0}$$

$$J_\alpha = \frac{1}{2} \sum_{ij\beta\gamma} \left(R_{i\alpha}^\circ - R_{j\alpha}^\circ\right) \Phi_{i\beta}^{j\gamma} u_{i\beta} \dot{u}_{j\gamma},$$

Heat transport from lattice dynamics

$$J_\alpha = \frac{1}{2}\sum_{ij\beta\gamma}(R^\circ_{i\alpha} - R^\circ_{j\alpha})\Phi^{j\gamma}_{i\beta} u_{i\beta}\dot{u}_{j\gamma},$$

$$\kappa \propto \int_0^\infty dt \int du_\circ d\dot{u}_\circ \underbrace{J(u_t\dot{u}_t)J(u_\circ\dot{u}_\circ)}_{\text{4-th order polynomial}} \underbrace{\mathrm{e}^{-\beta H(u_\circ \dot{u}_\circ)}}_{\text{Gaussian}}$$

Heat transport from lattice dynamics

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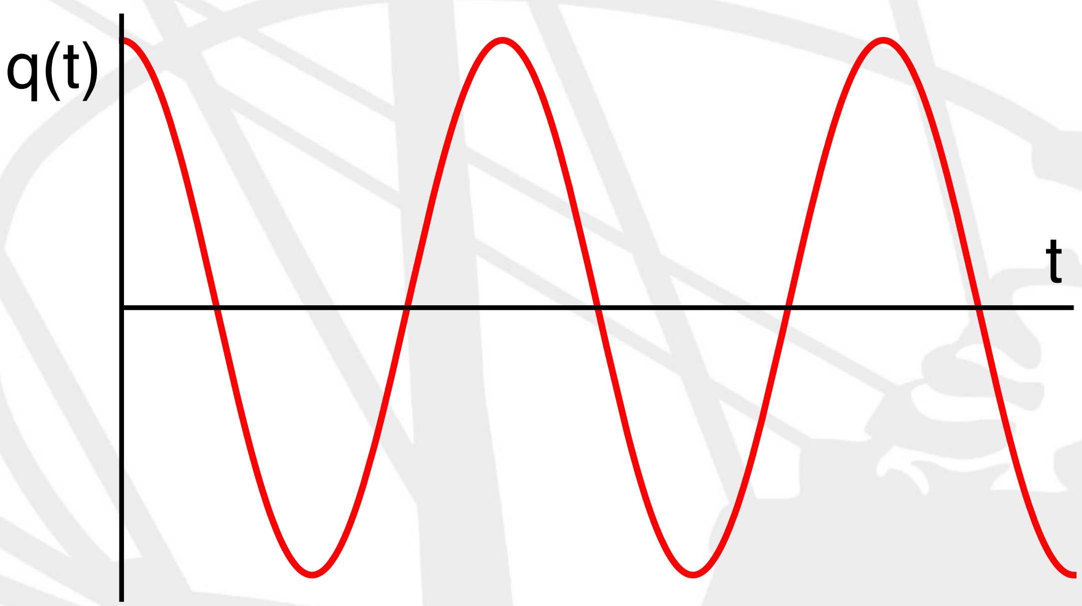

$$\kappa = \infty$$

Heat transport from lattice dynamics

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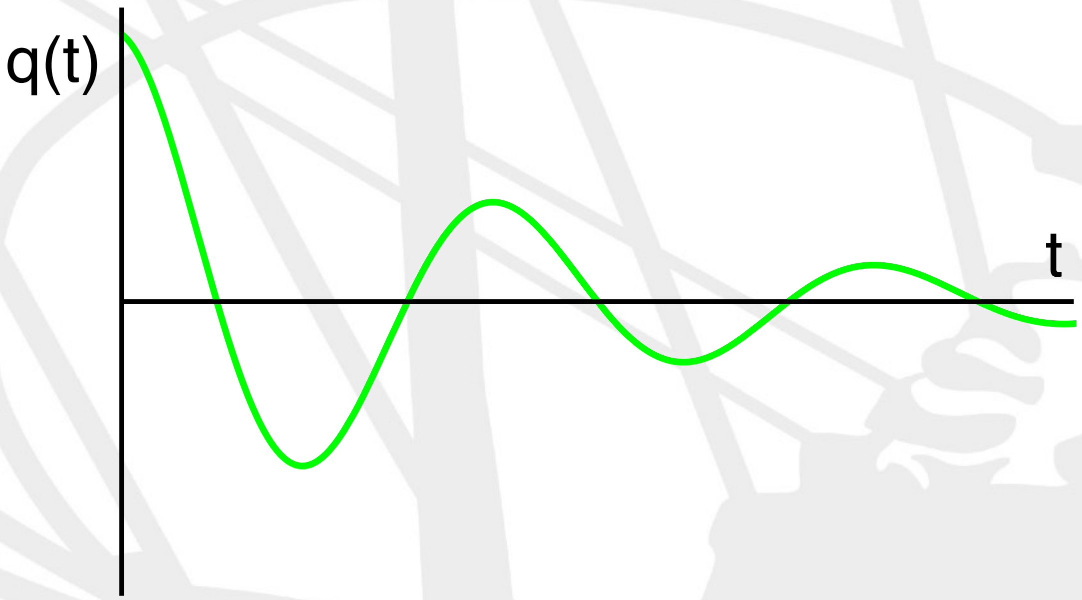

$$\xrightarrow{\omega \mapsto \omega + i\gamma}$$

$$\kappa < \infty$$

Heat transport from lattice dynamics

$$J_\alpha = \frac{1}{2}\sum_{ij\beta\gamma}\left(R^\circ_{i\alpha} - R^\circ_{j\alpha}\right)\Phi^{j\gamma}_{i\beta} u_{i\beta}\dot{u}_{j\gamma}$$

$$= \sum_{nm} v^\alpha_{nm}\sqrt{\omega_n\omega_m}\xi_n\pi_m$$

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

Heat transport from lattice dynamics

$$J_\alpha = \frac{1}{2}\sum_{ij\beta\gamma}\left(R^\circ_{i\alpha} - R^\circ_{j\alpha}\right)\Phi^{j\gamma}_{i\beta}u_{i\beta}\dot{u}_{j\gamma}$$

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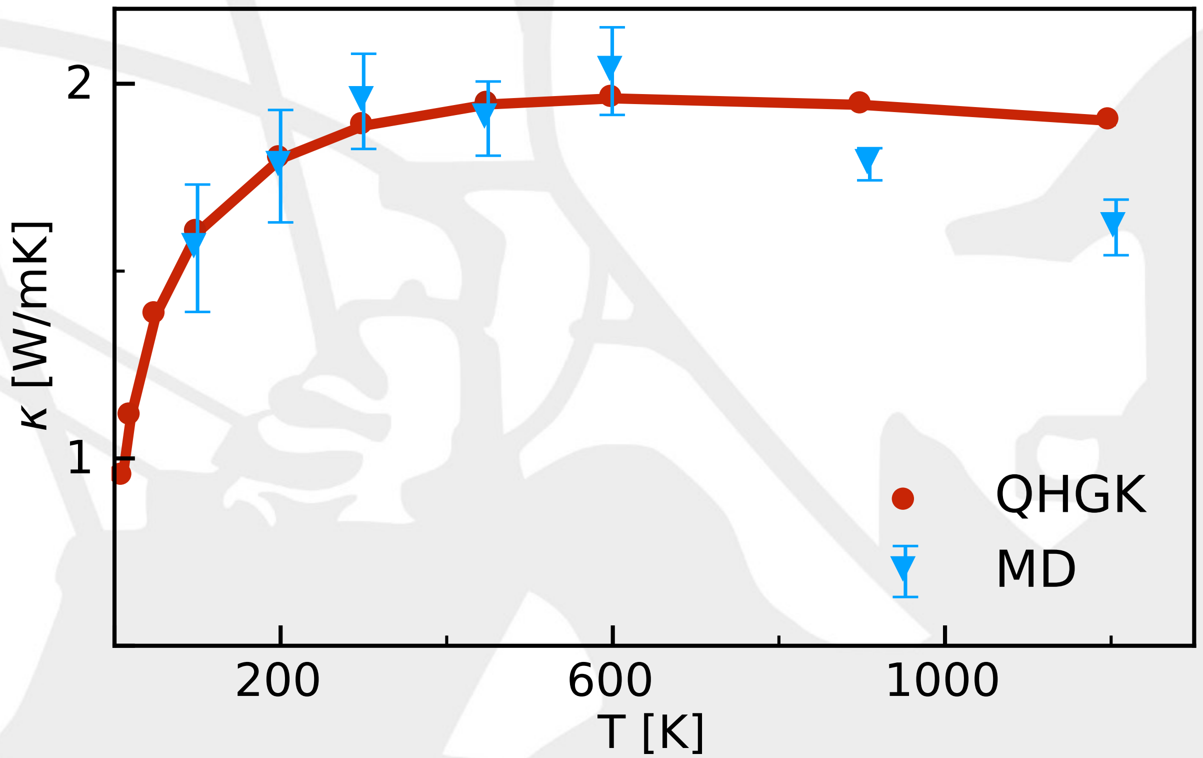

classical

$c_{nm} = k_B$

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

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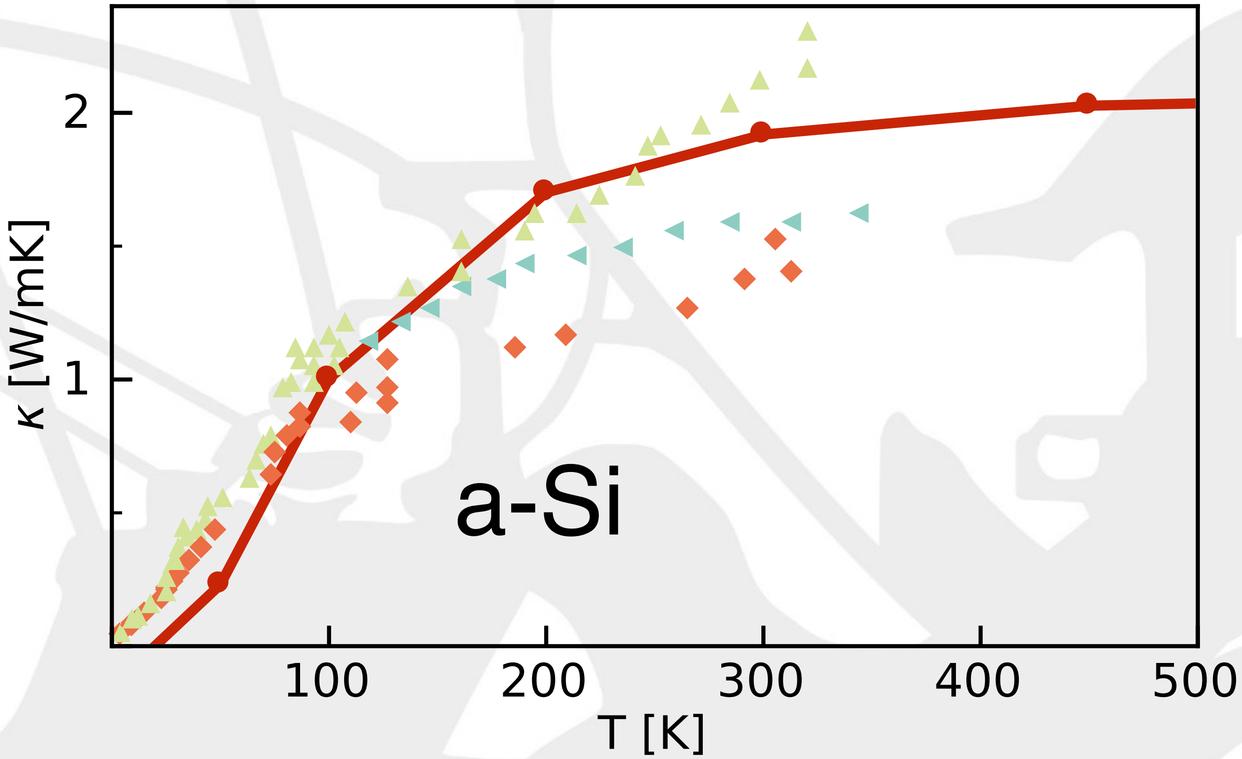

quantum QHGK

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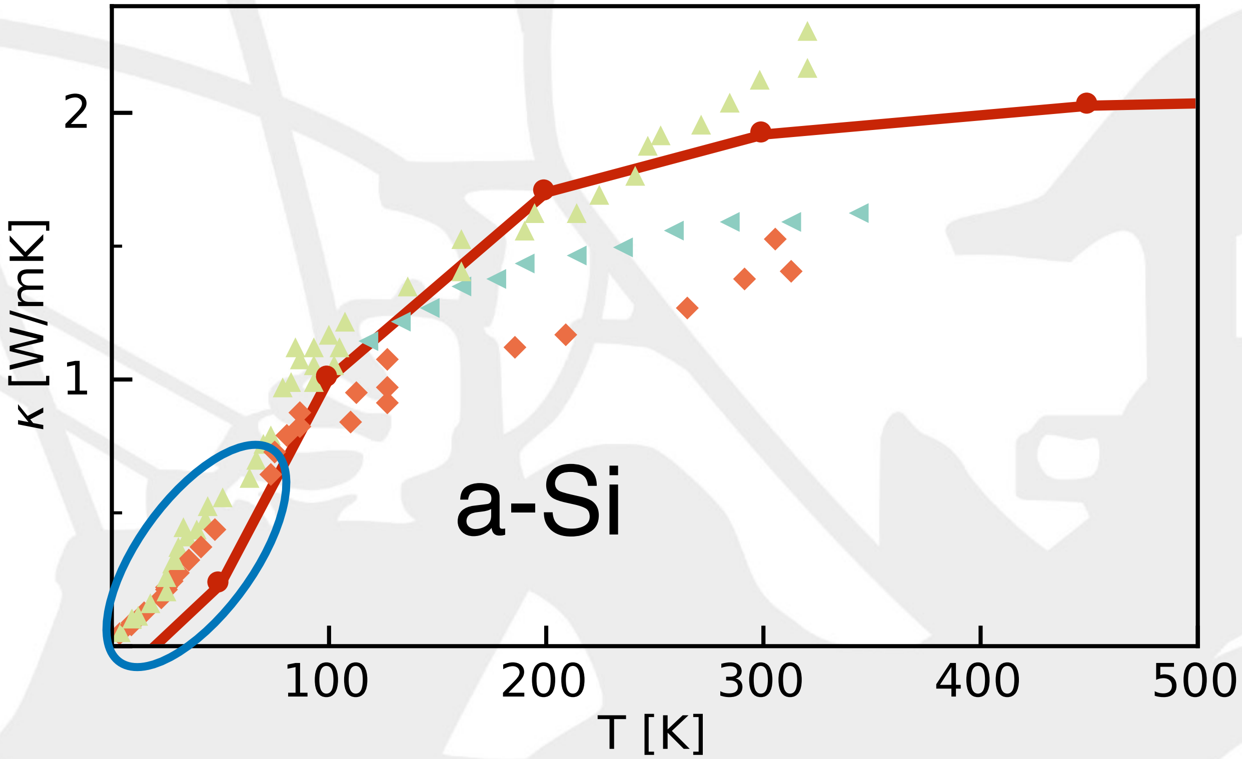

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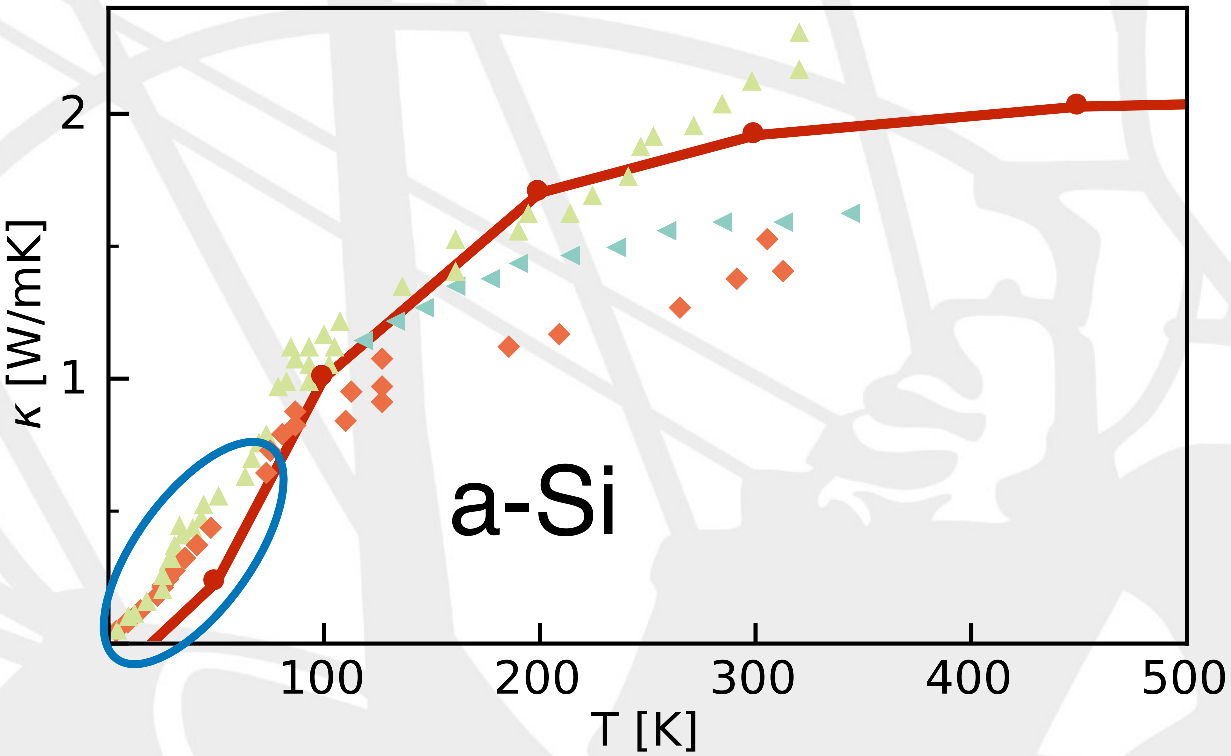

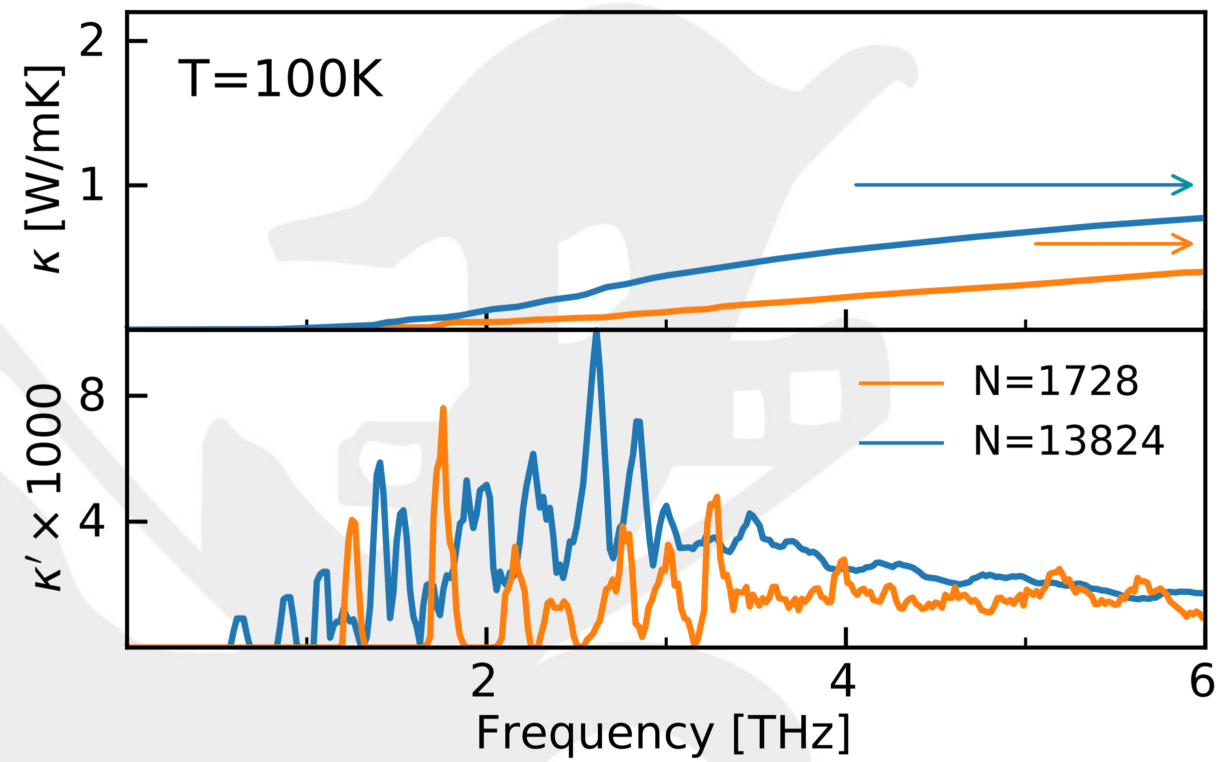

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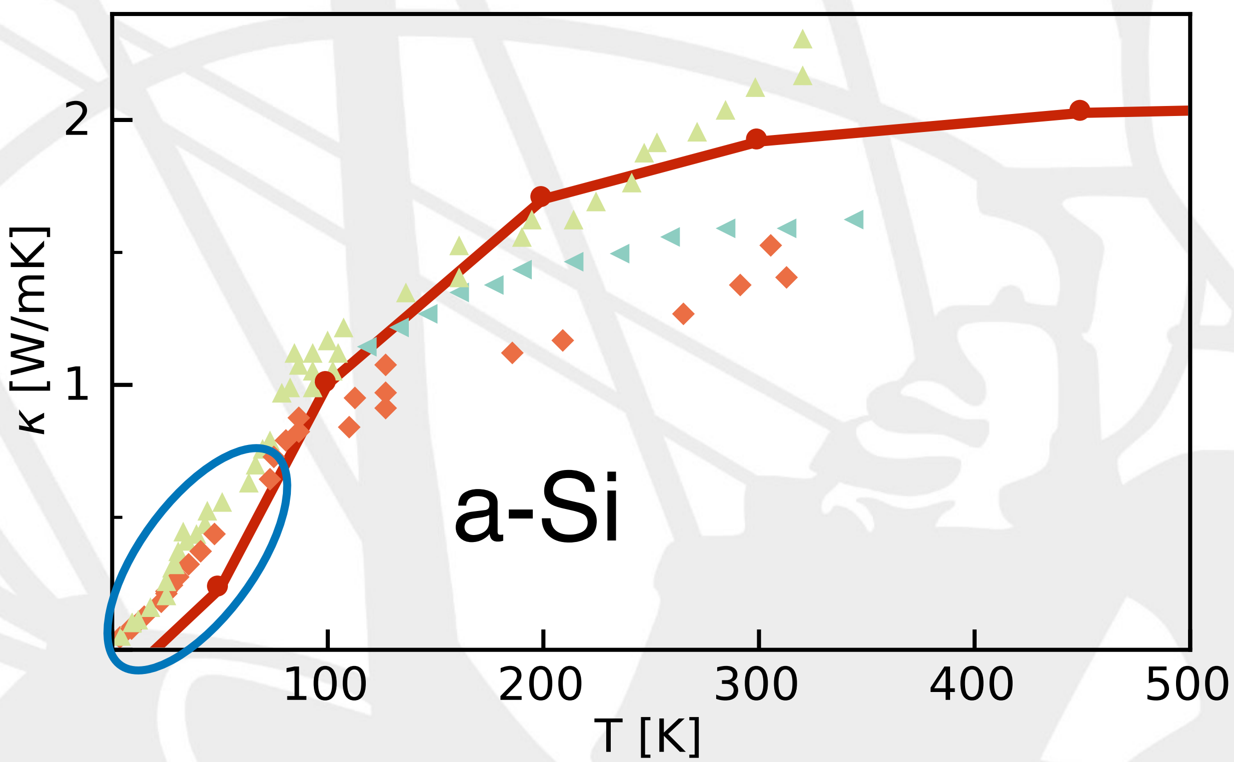

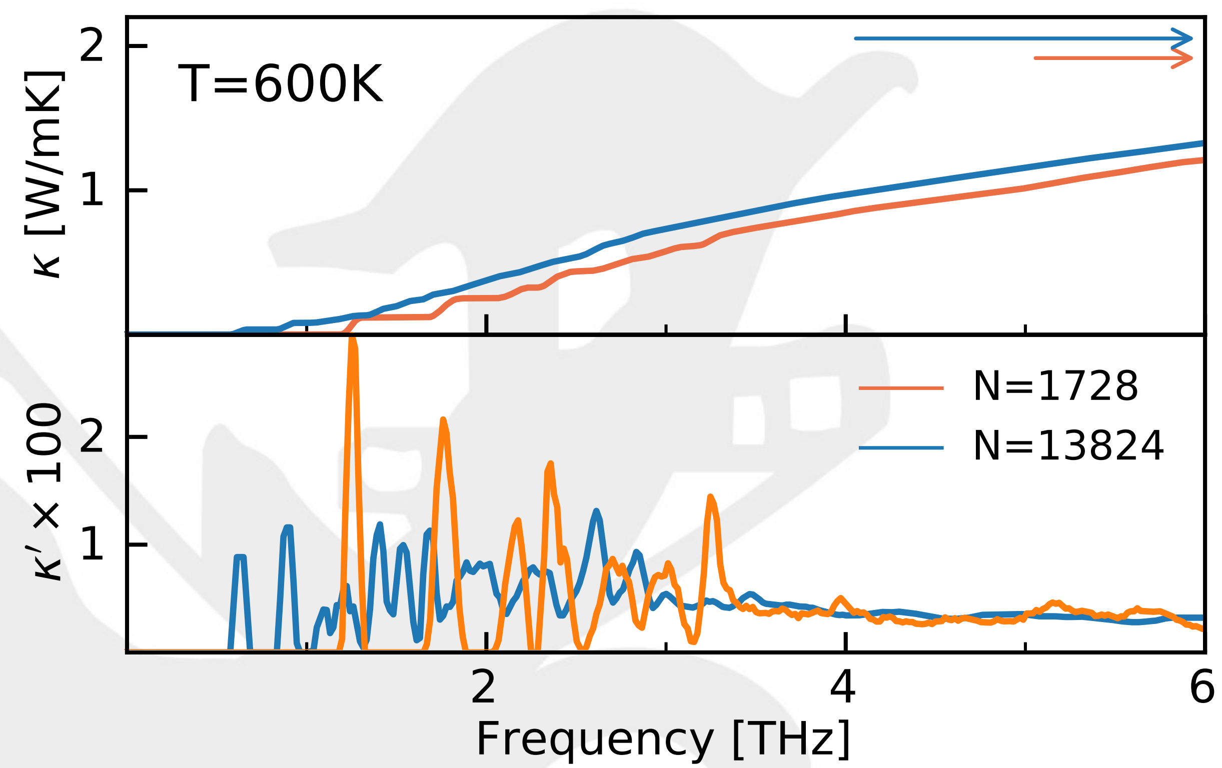

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In a periodic system

$$v_{nn'} = \delta_{\nu\nu'} \delta_{\mathrm{qq}'}$$

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BTE

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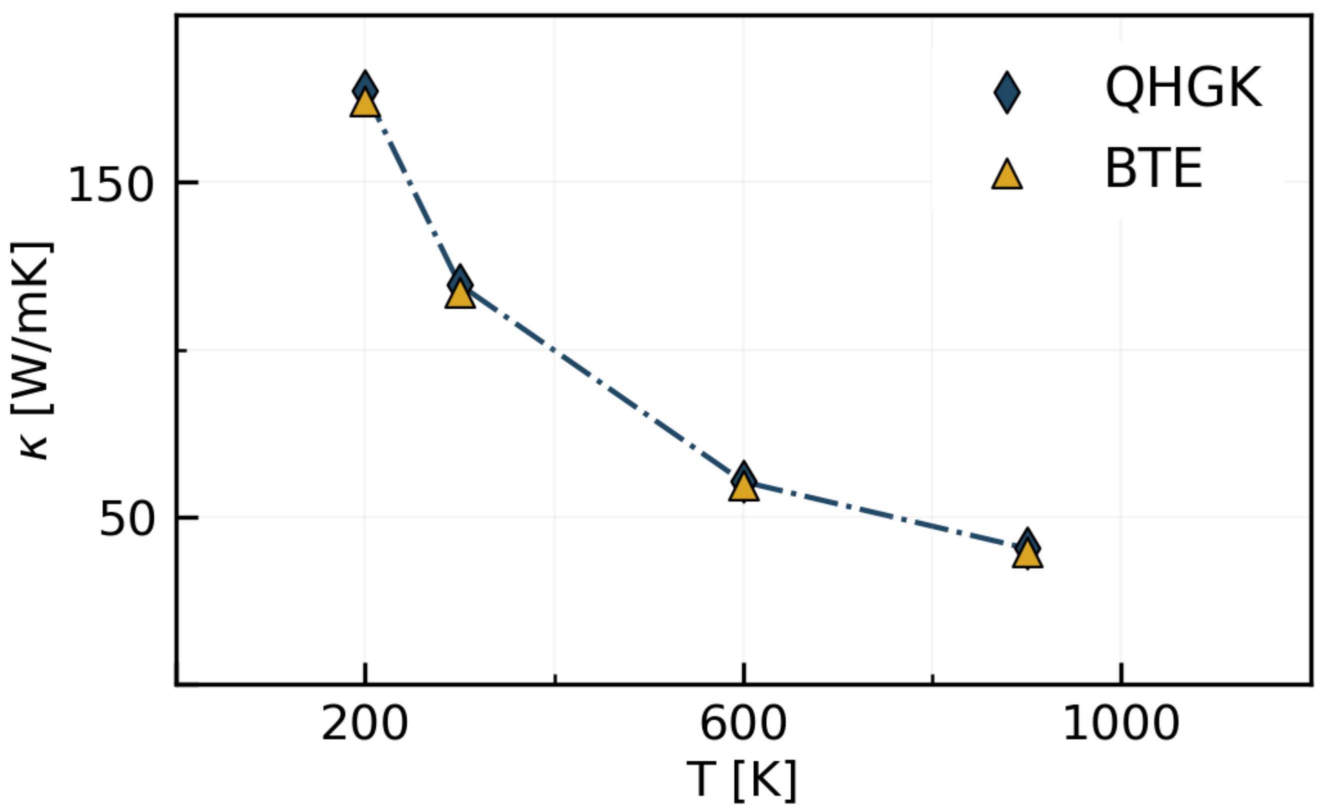

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QUANTUM ESPRESSO

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FOUNDATION

MAX

thanks to:

thanks to:

Aris Marcolongo

with whom it all started

thanks to:

Aris Marcolongo

Loris Ercole

the master of data analysis

thanks to:

Aris Marcolongo

Loris Ercole

Riccardo Bertossa

multicomponent systems

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Aris Marcolongo


Loris Ercole


Riccardo Bertossa


Leyla Isaeva


Giuseppe Barbalinardo


Davide Donadio

quasi-harmonic lattice dynamics

thanks to:

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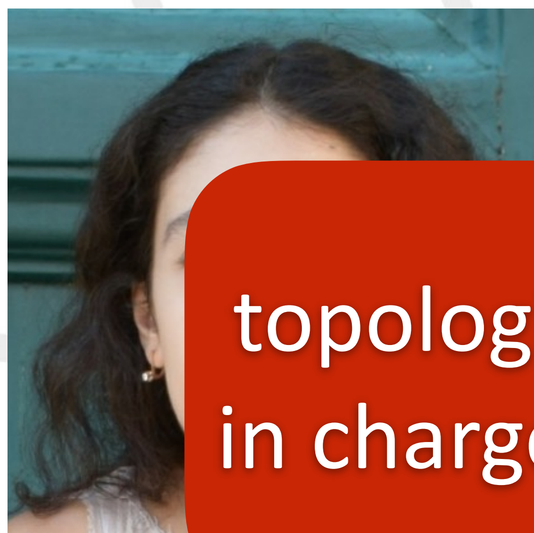

Leyla Isaeva

Giuseppe Barbalinardo

Davide Donadio

Federico Grasselli

Paolo Pegolo

topological effects in charge transport

thanks to:


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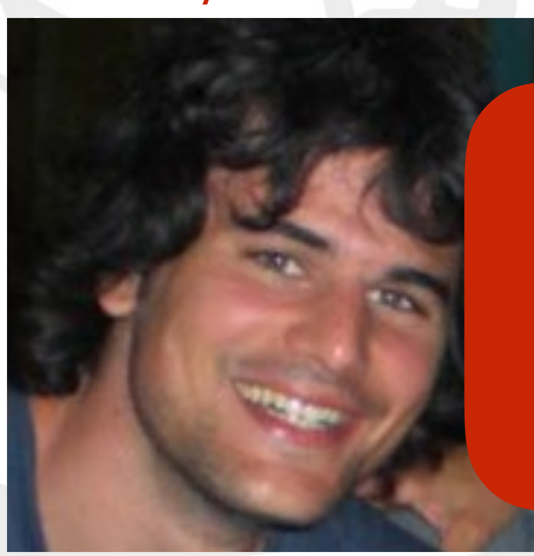
Federico Grasselli


Paolo Pegolo


Davide Tisi

transport from neural networks

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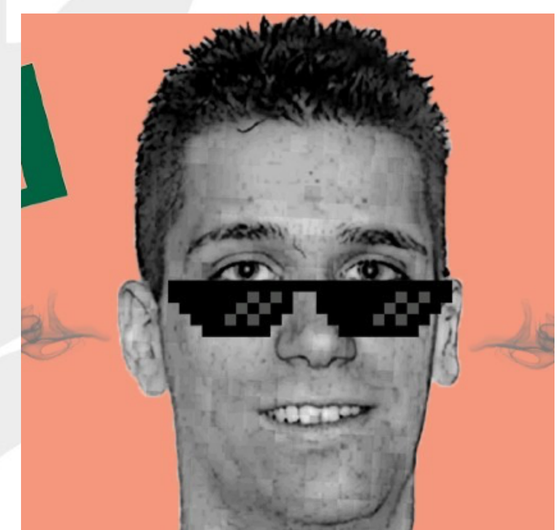
Davide Tisi

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