# ab initio simulation of heat transport in liquids and glasses

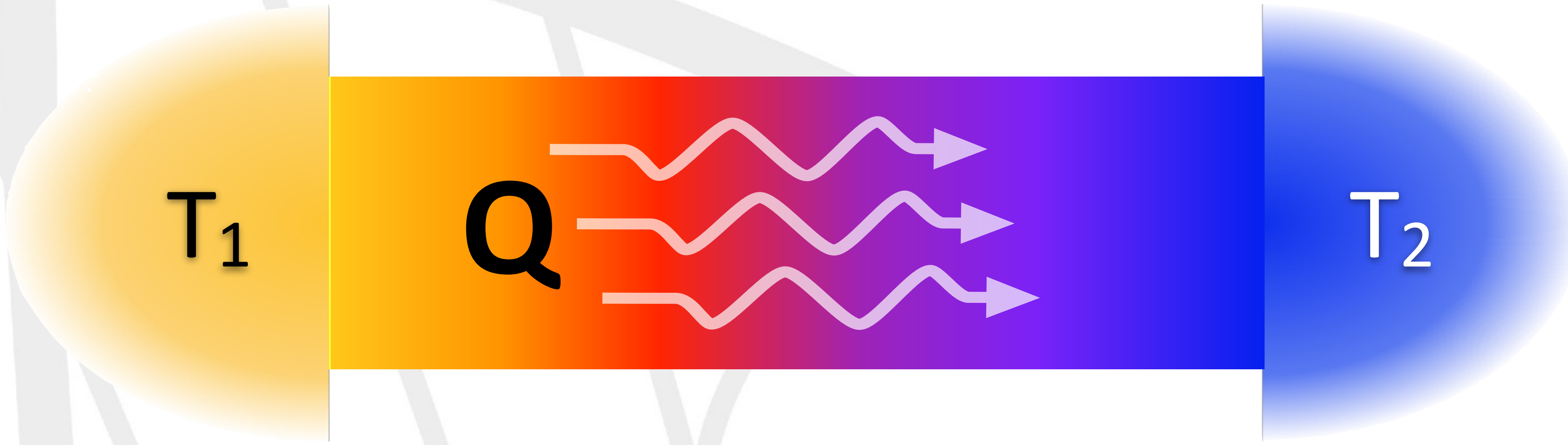
Stefano Baroni

Scuola Internazionale Superiore di Studi Avanzati, Trieste

talk given at the *2019 International Conference on Multi-Scale Modelling and Simulation of Materials (ICM3)*

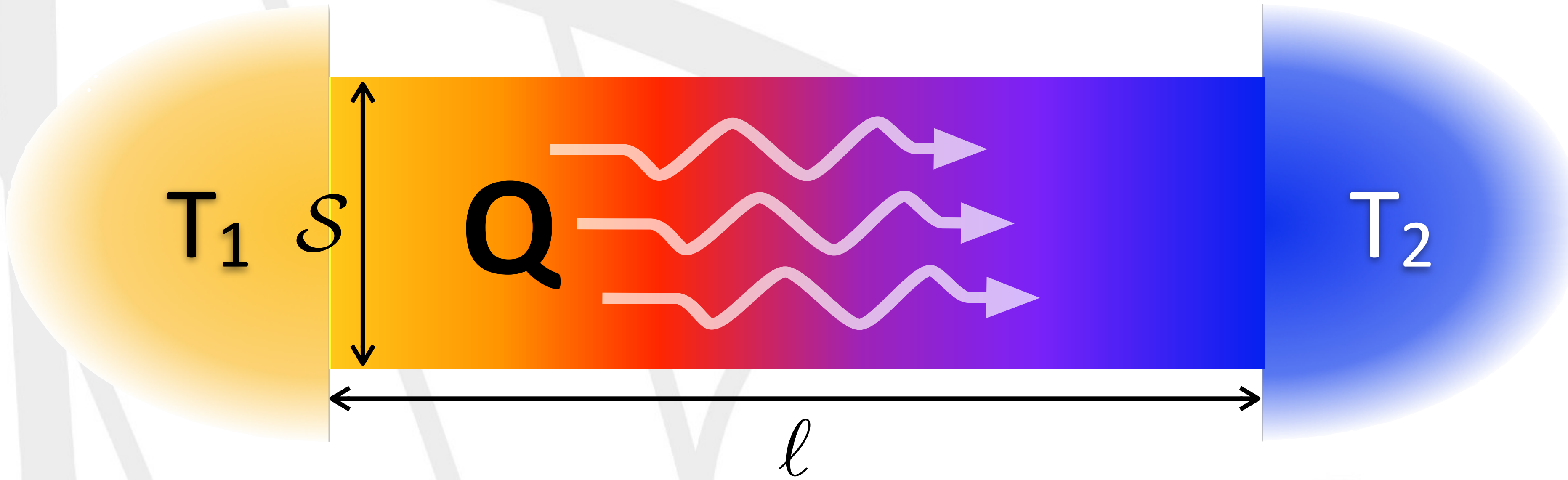
July 1-5, 2019, Ningbo, China

# 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




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

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

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

# why should we care?

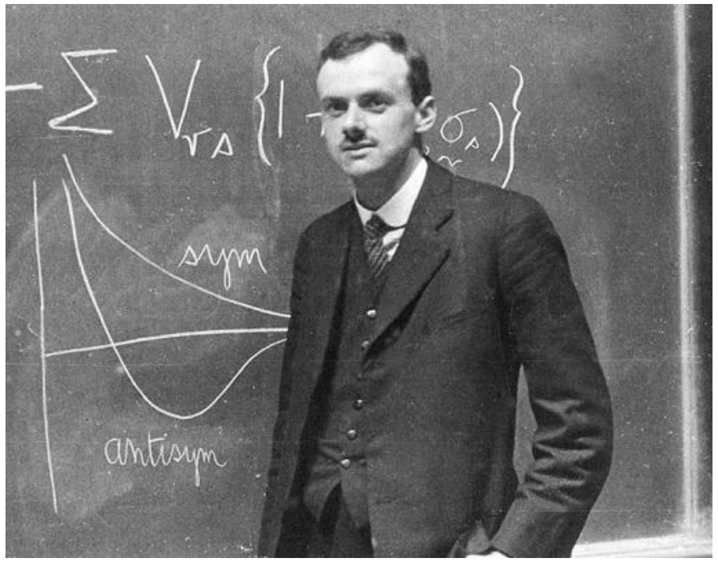
- energy saving and heat dissipation
- heat shielding
- energy harvesting and scavenging
- earth and planetary sciences
- …

# why should we care?

- … because it is important and still poorly understood

# 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

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

M.L. Cohen, 2015

# hurdles towards an ab initio theory of heat transport

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

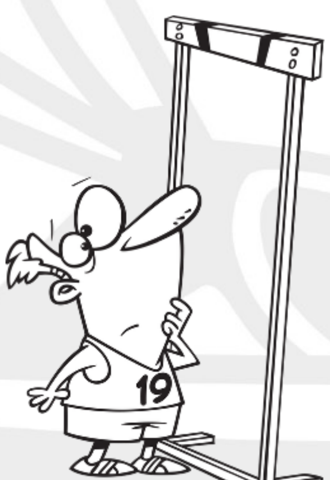
**Thermal Conductivity of Periclase (MgO) from First Principles**

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

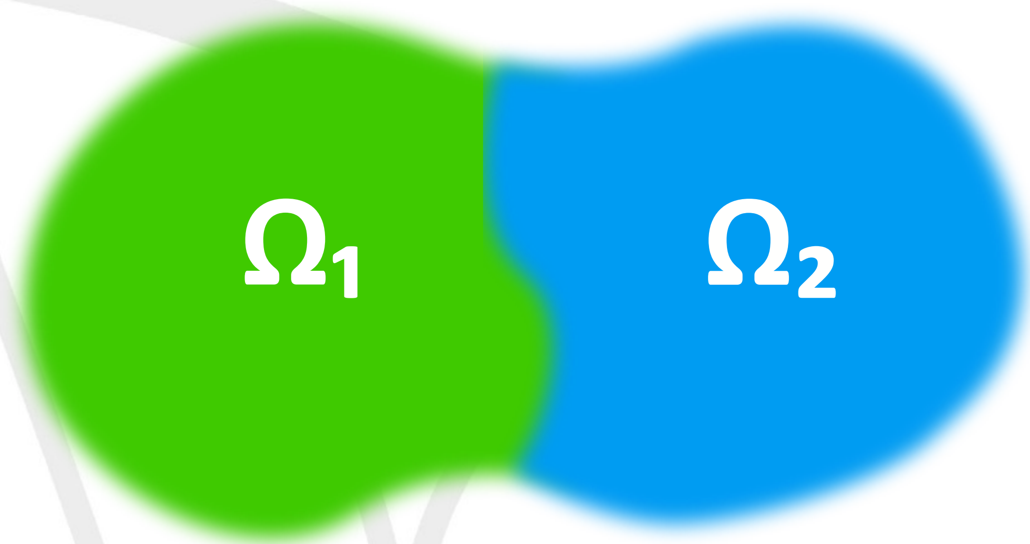
Lars Stixrude†
*Department of Earth Sciences, University College London, Gower Street, London WC1E 6BT, United Kingdom*

Bijaya B. Karki‡
*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.



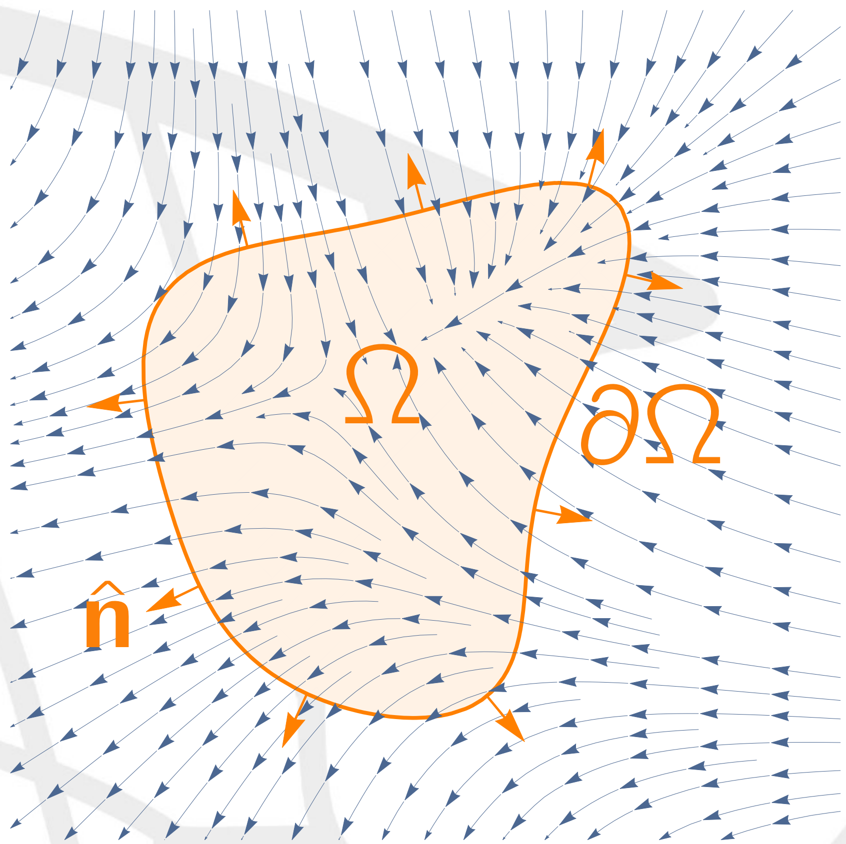
# transport theory: extensive properties




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

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

# transport theory: conservation laws



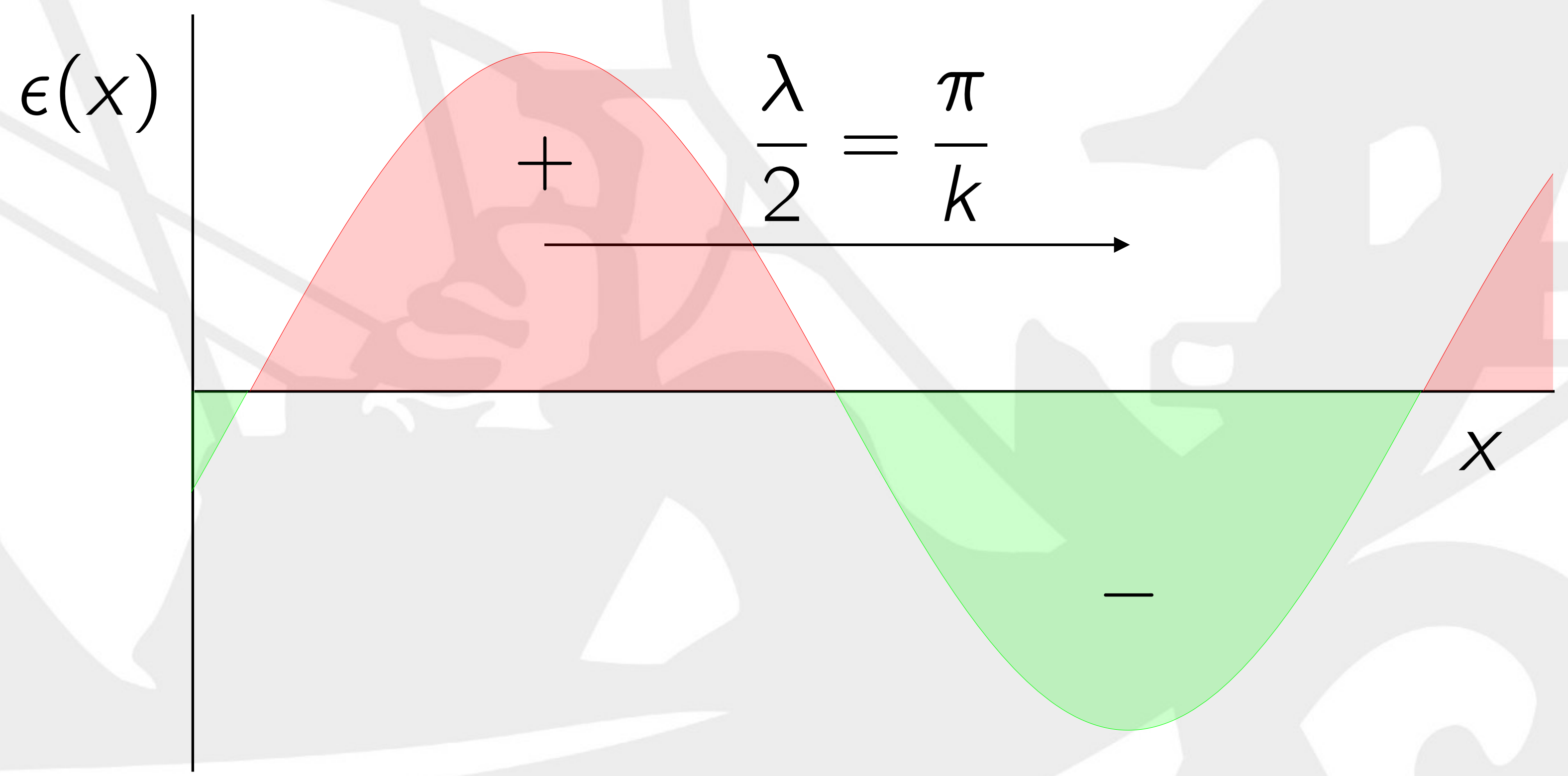

$$\dot{\epsilon}(\mathbf{r}, t) + \nabla \cdot \mathbf{j}(\mathbf{r}, t) = 0$$

# adiabatic decoupling of conserved densities

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

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

the smaller the wavevector, the slower the dynamics



# Green-Kubo linear-response theory

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

$$\boxed{\kappa = \frac{\Omega}{k_B T^2}\int_0^\infty \langle J(t)J(0)\rangle dt}$$

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

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

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

# Einstein-Helfand relations

## Einstein (1905)

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

$$\approx 2Dt$$

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

## 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

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

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

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

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

$$\boxed{\mathbf{J} = \frac{1}{\Omega} \int_\Omega \mathbf{r}\dot{\epsilon}(\mathbf{r}) d\mathbf{r}}$$

# the classical energy current

$$\boxed{\mathbf{J} = \frac{1}{\Omega}\int_\Omega \mathbf{r}\dot{\epsilon}(\mathbf{r})d\mathbf{r}}$$

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

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

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

# hurdles towards an ab initio theory of heat transport

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

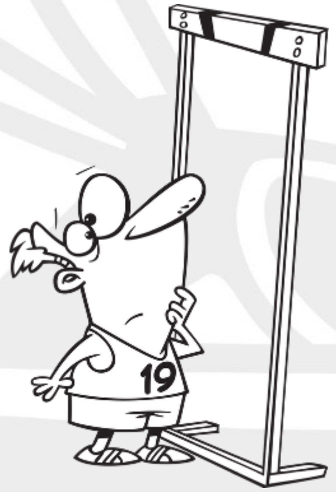
## Thermal Conductivity of Periclase (MgO) from First Principles

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

Lars Stixrude†
*Department of Earth Sciences, University College London, Gower Street, London WC1E 6BT, United Kingdom*

Bijaya B. Karki‡
*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

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

$$= \mathsf{cnst}$$

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

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

# insights from classical mechanics

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

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

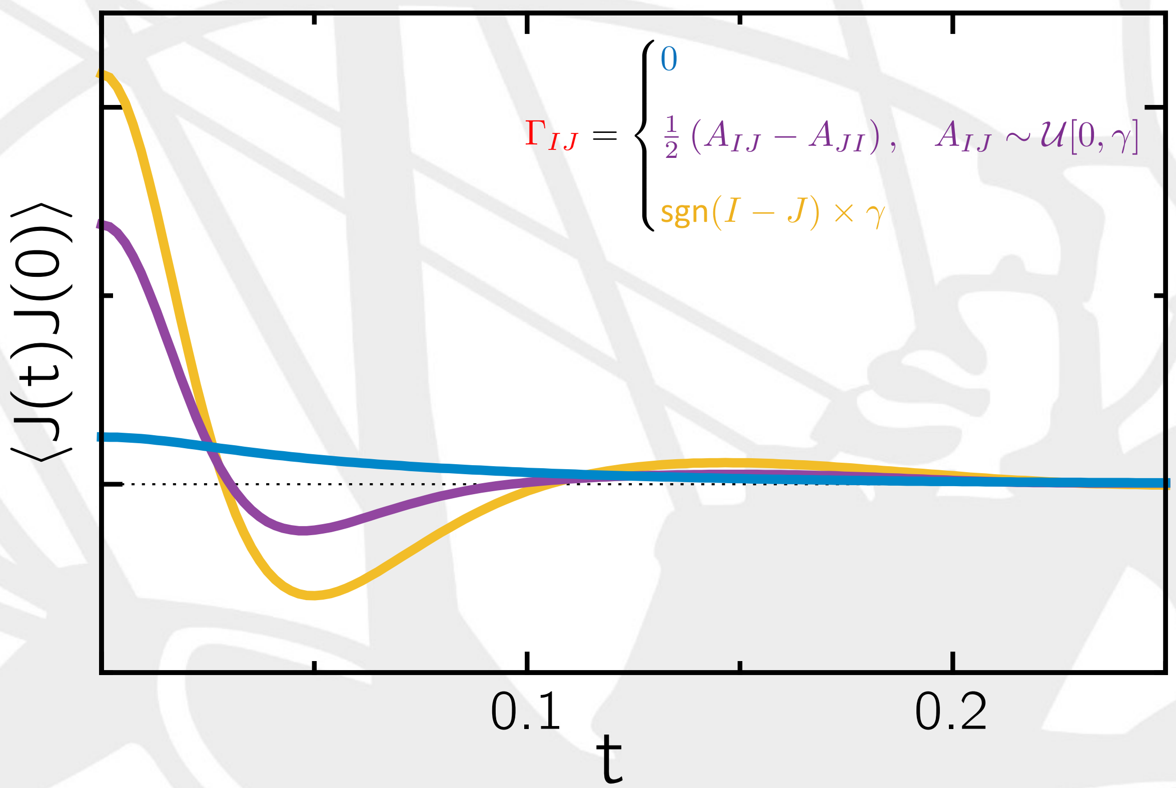
$$\mathbf{J}_e = \sum_I \epsilon_I \mathbf{V}_I + \frac{1}{2} \sum_{I \neq J} (\mathbf{V}_I \cdot \mathbf{F}_{IJ})(\mathbf{R}_I - \mathbf{R}_J)$$

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

# insights from classical mechanics

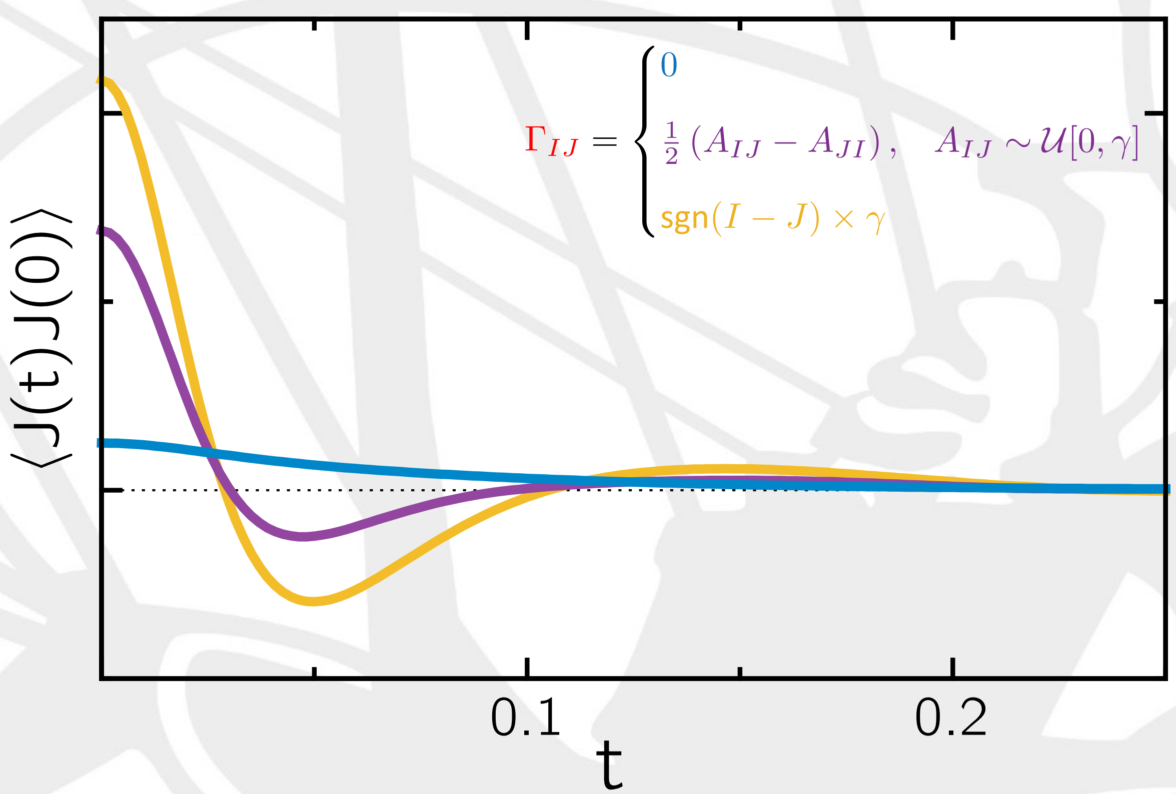
$$\mathbf{J}_e = \sum_I \epsilon_I \mathbf{V}_I + \frac{1}{2}\sum_{I\neq J}(\mathbf{V}_I \cdot \mathbf{F}_{IJ})(\mathbf{R}_I - \mathbf{R}_J)$$

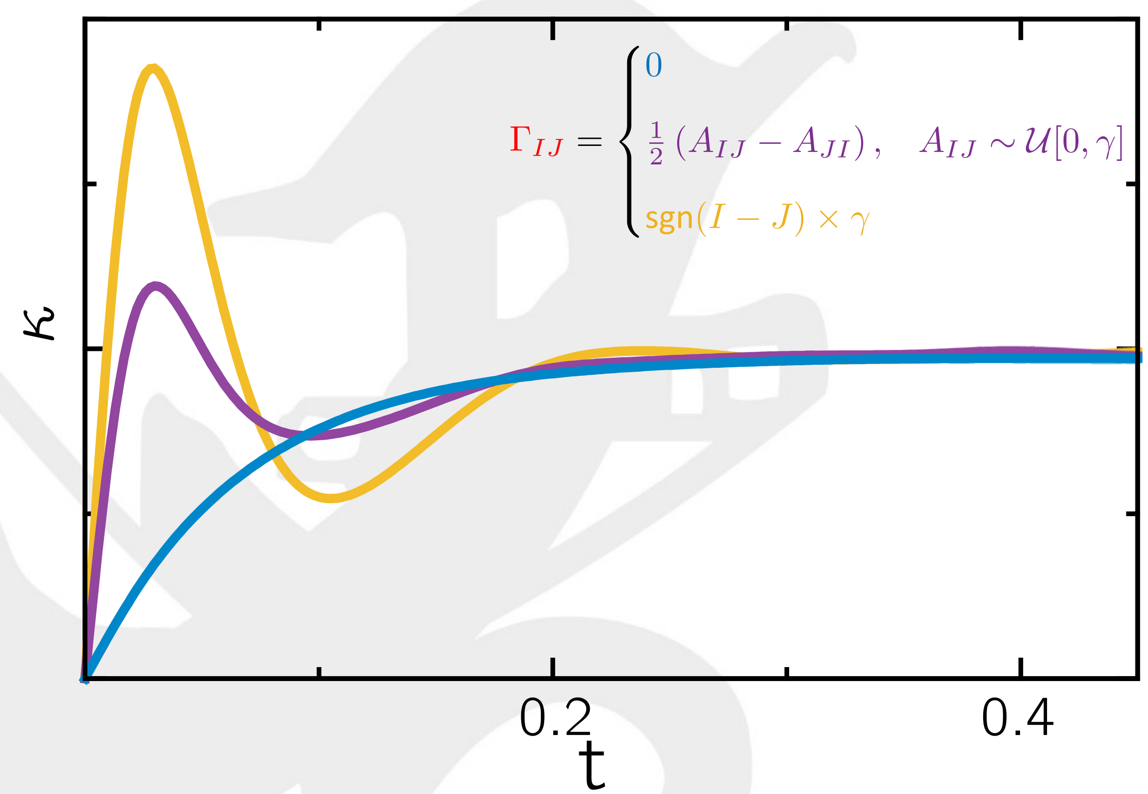
$$+ \frac{1}{2}\sum_{I\neq J}\Gamma_{IJ}\left[\mathbf{V}_I v(|\mathbf{R}_I - \mathbf{R}_J|) + (\mathbf{V}_I \cdot \mathbf{F}_{IJ})(\mathbf{R}_I - \mathbf{R}_I)\right]$$



# insights from classical mechanics

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



# 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

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

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

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

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

# insights from classical mechanics

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

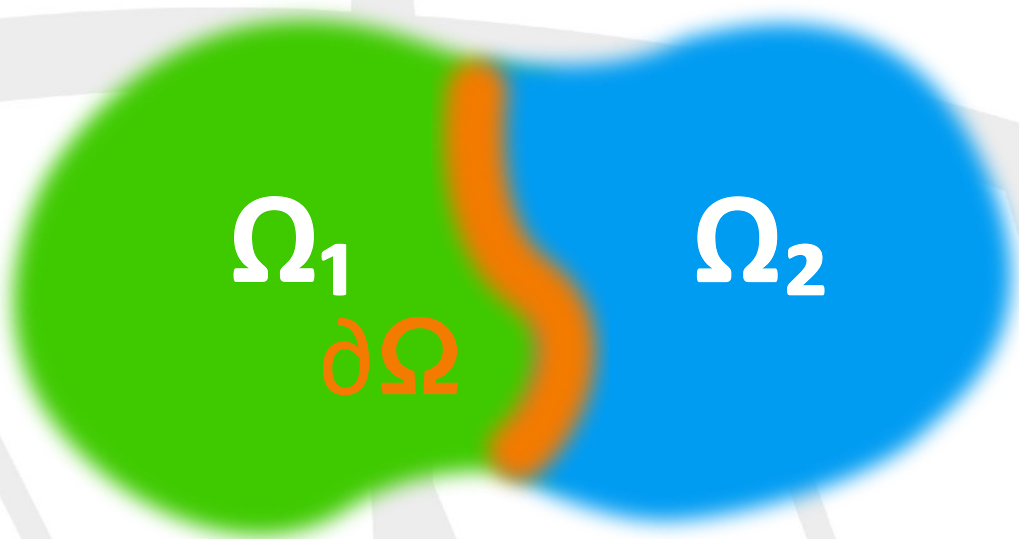
$$\kappa \sim \frac{1}{2t}\mathrm{var}\left[\mathbf{D}(t)\right] \qquad \mathbf{D}(t) = \int_0^t \mathbf{J}(t')dt'$$

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

$$\boxed{\kappa' = \kappa}$$

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

# gauge invariance




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

$$\mathcal{E}[\Omega] = \int_\Omega e(\mathbf{r})d\mathbf{r}$$

$$\mathcal{E}'[\Omega] = \mathcal{E}[\Omega] + \mathcal{O}[\partial\Omega]$$

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

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

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

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

# 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

$$E[\Omega_1 \cup \Omega_2] = E[\Omega_1] + E[\Omega_2] + W[\partial\Omega] \stackrel{?}{=} \mathcal{E}[\Omega_1] + \mathcal{E}[\Omega_2]$$

$$\mathcal{E}[\Omega] = \int_\Omega e(\mathbf{r})d\mathbf{r}$$

$$\mathcal{E}'[\Omega] = \mathcal{E}[\Omega] + \mathcal{O}[\partial\Omega]$$

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

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

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

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

# the DFT energy density

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

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

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

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

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

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

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

# the DFT energy current

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

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

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

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

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

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

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

# the DFT energy current

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

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

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

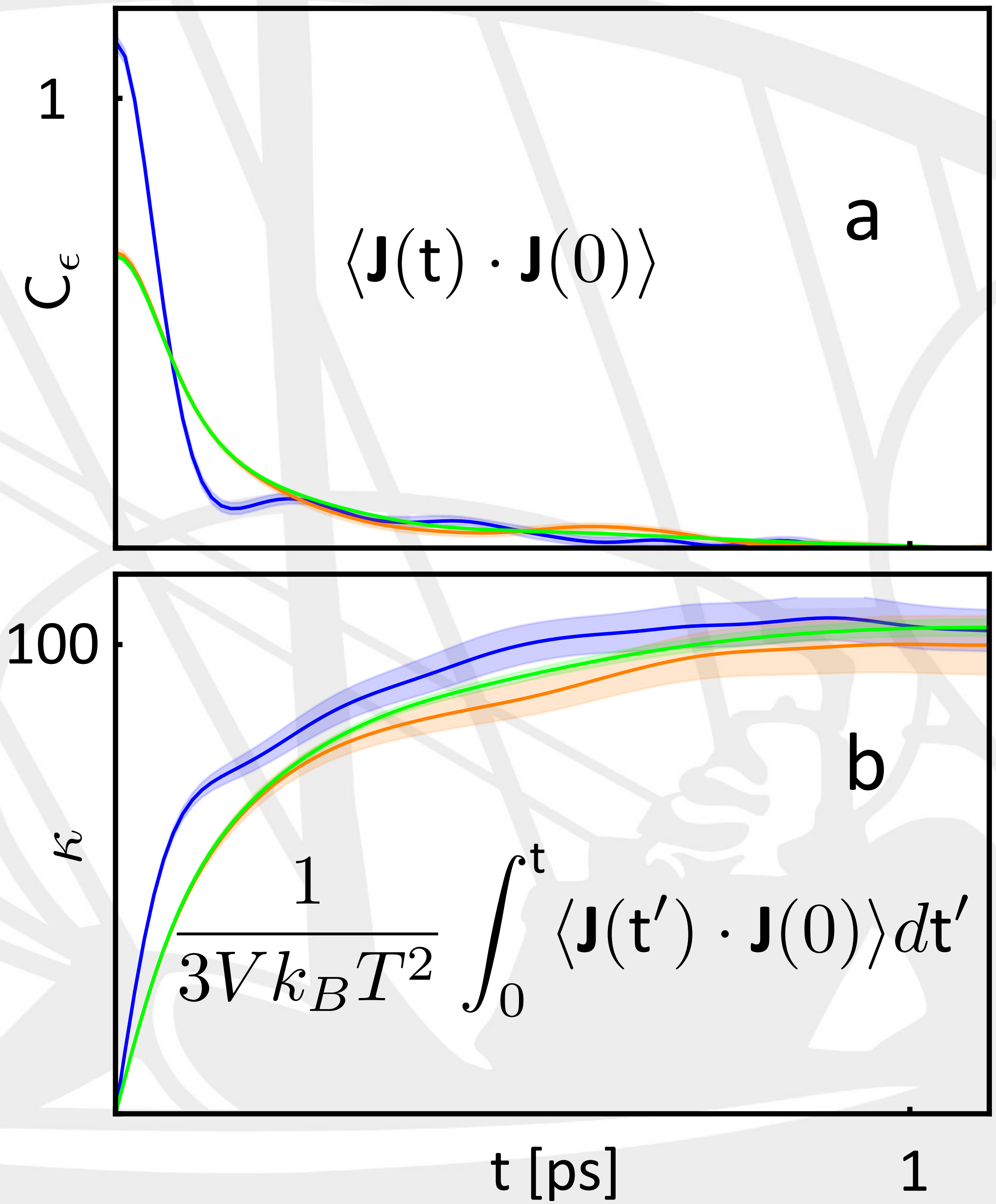
$$\mathbf{J}_H = \frac{1}{4\pi}\int \dot{v}_H(\mathbf{r})\nabla v_H(\mathbf{r})d\mathbf{r}$$

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



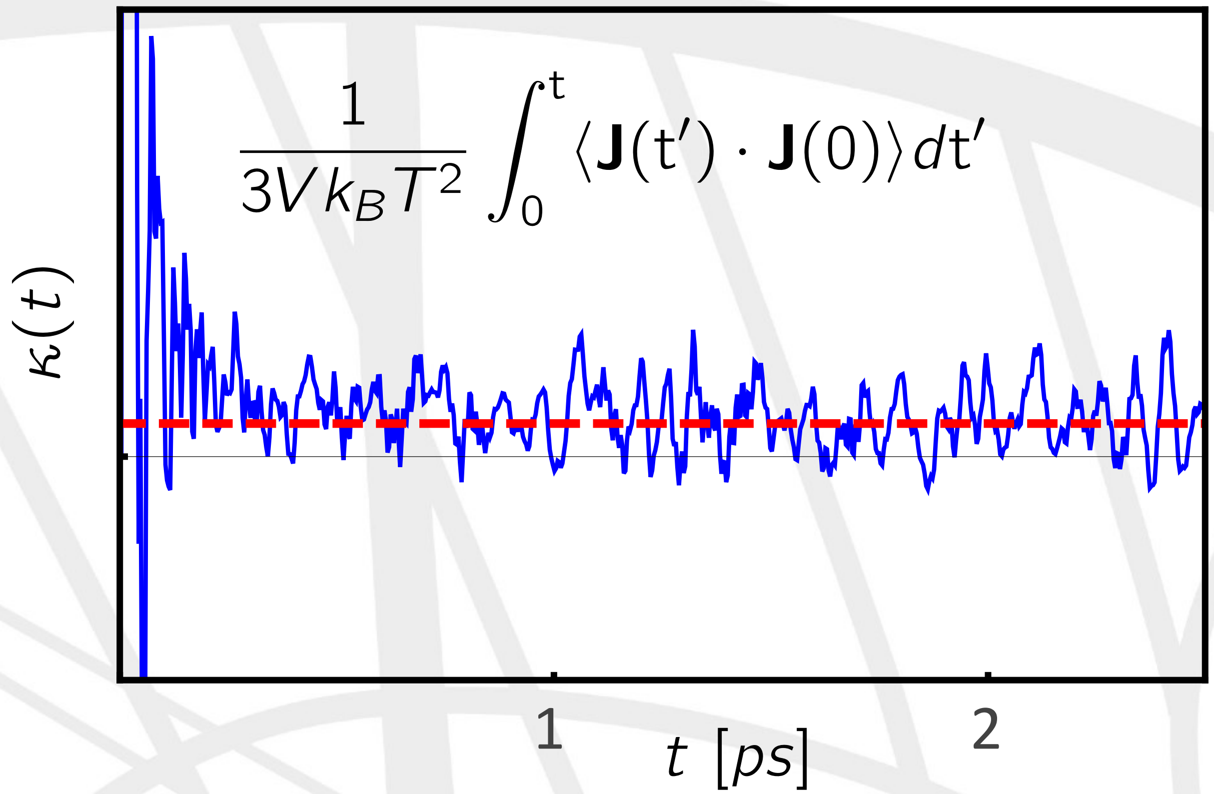

108 “LDA Ar” atoms
@bp density, T= 250 K

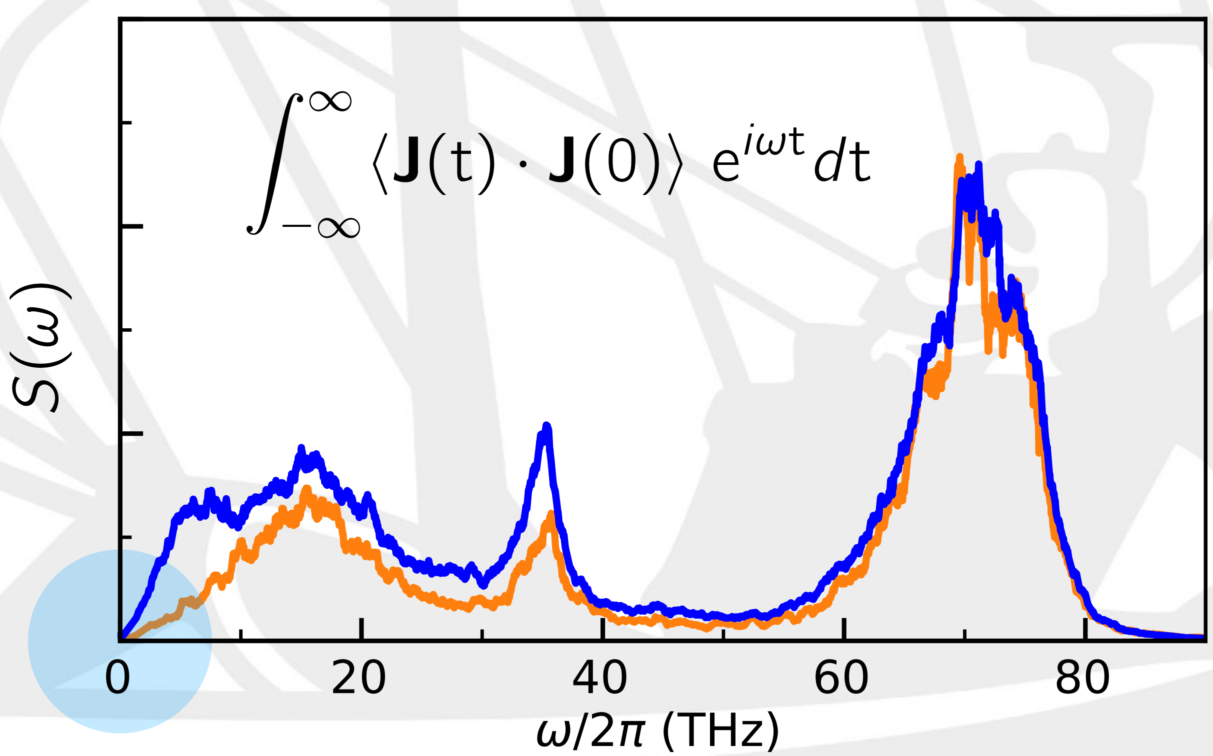
100 ps CP trajectory
100 ps classical FF trajectory
1 ns classical FF trajectory

same behavior at T=400 K

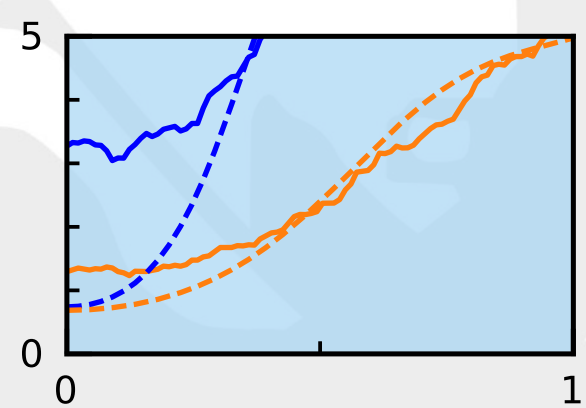
A. Marcolongo, P. Umari, and SB,
Nat. Phys. **12**, 80 (2016)

# liquid (heavy) water




64 molecules, T=385 K
expt density @ac

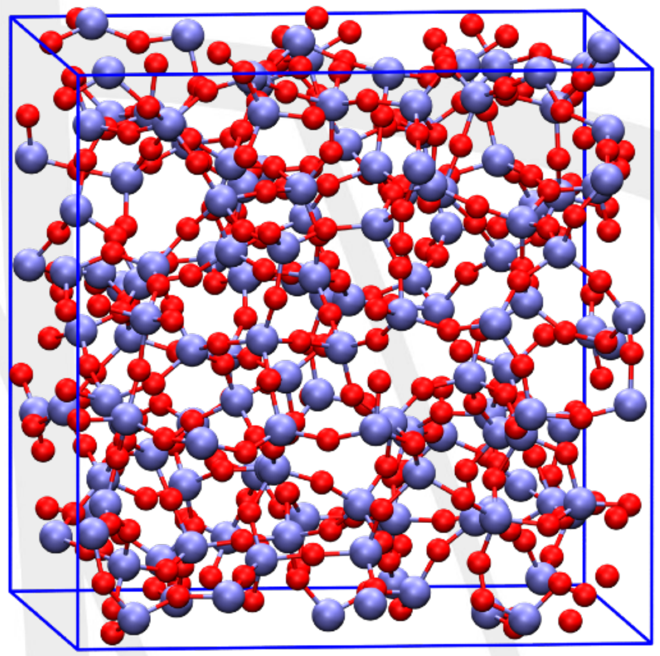



$\varkappa_{DFT} = 0.70 \pm 0.17$ W/mK
$\varkappa_{expt} = 0.61$ W/mK

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

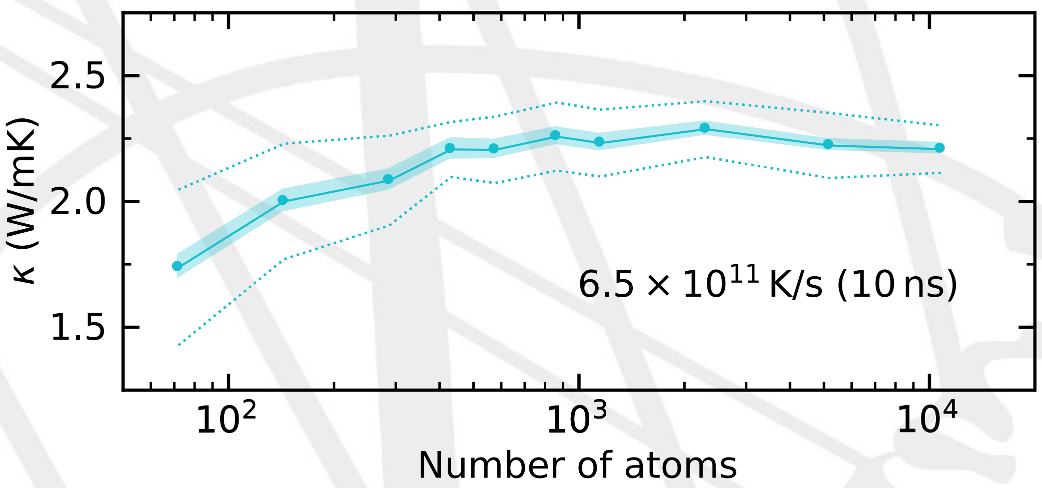
R. Bertossa, F. Grasselli, L. Ercole and SB, Phys. Rev. Lett. in press (2019)

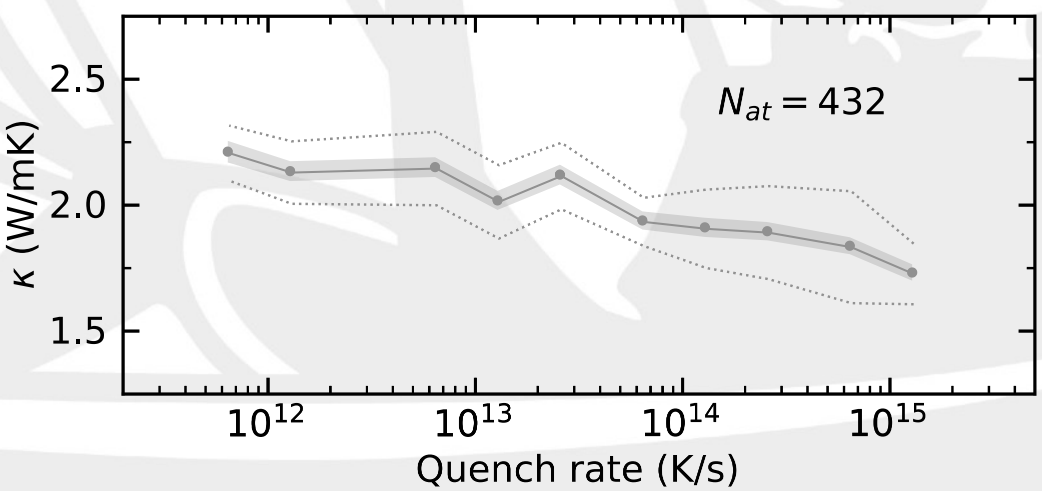
# silica glass

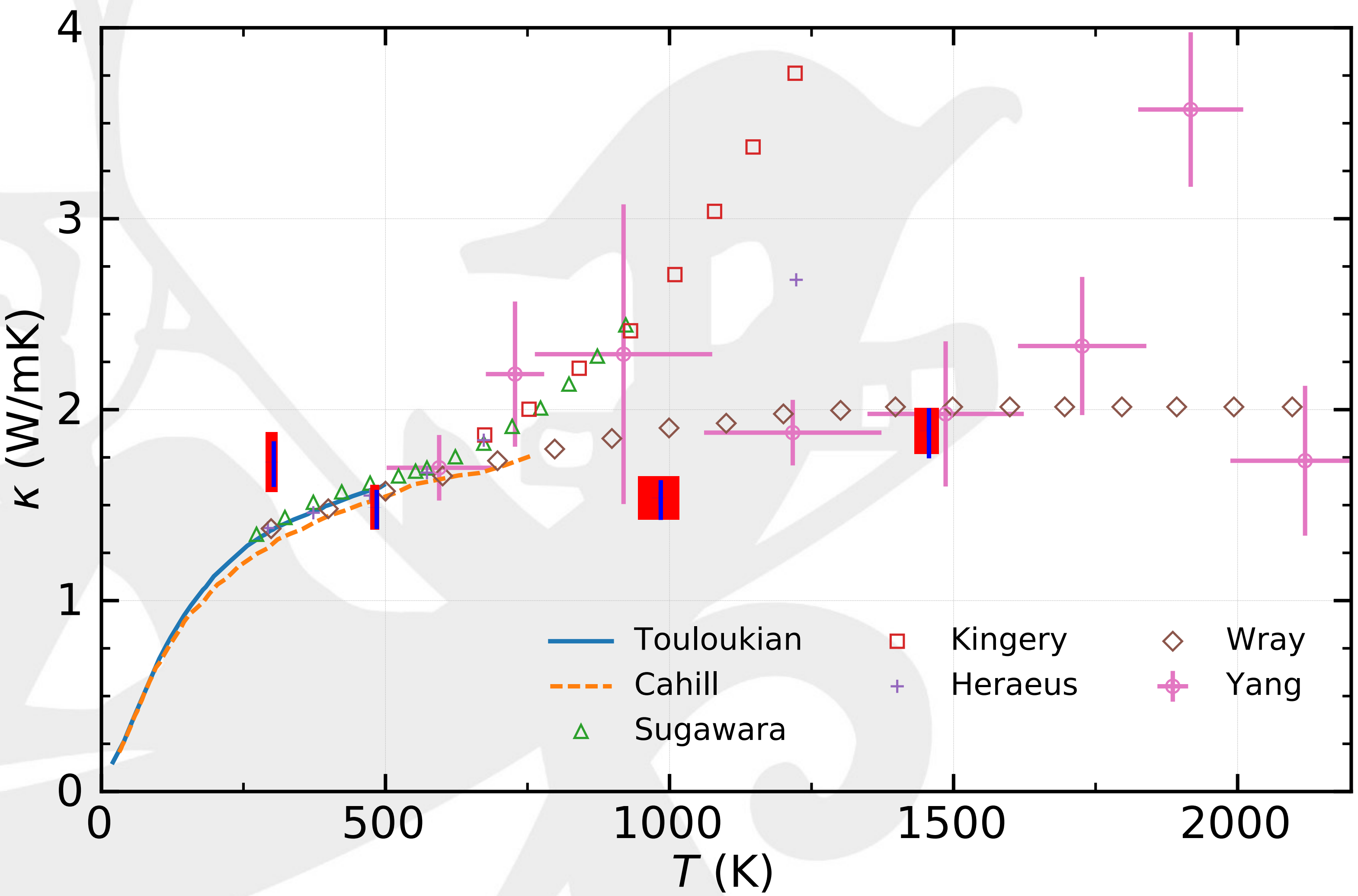


432 atoms
sample quenched from melt
@$6.5 \times 10^{11}$ K/sec

2304 electrons
2× 52 ps



molecular dynamics is less and less ergodic as temperature decreases

molecular dynamics cannot account for quantum effects, which are increasingly important as temperature decreases

at lower temperatures the harmonic approximation is more and more accurate

# do BTE!

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

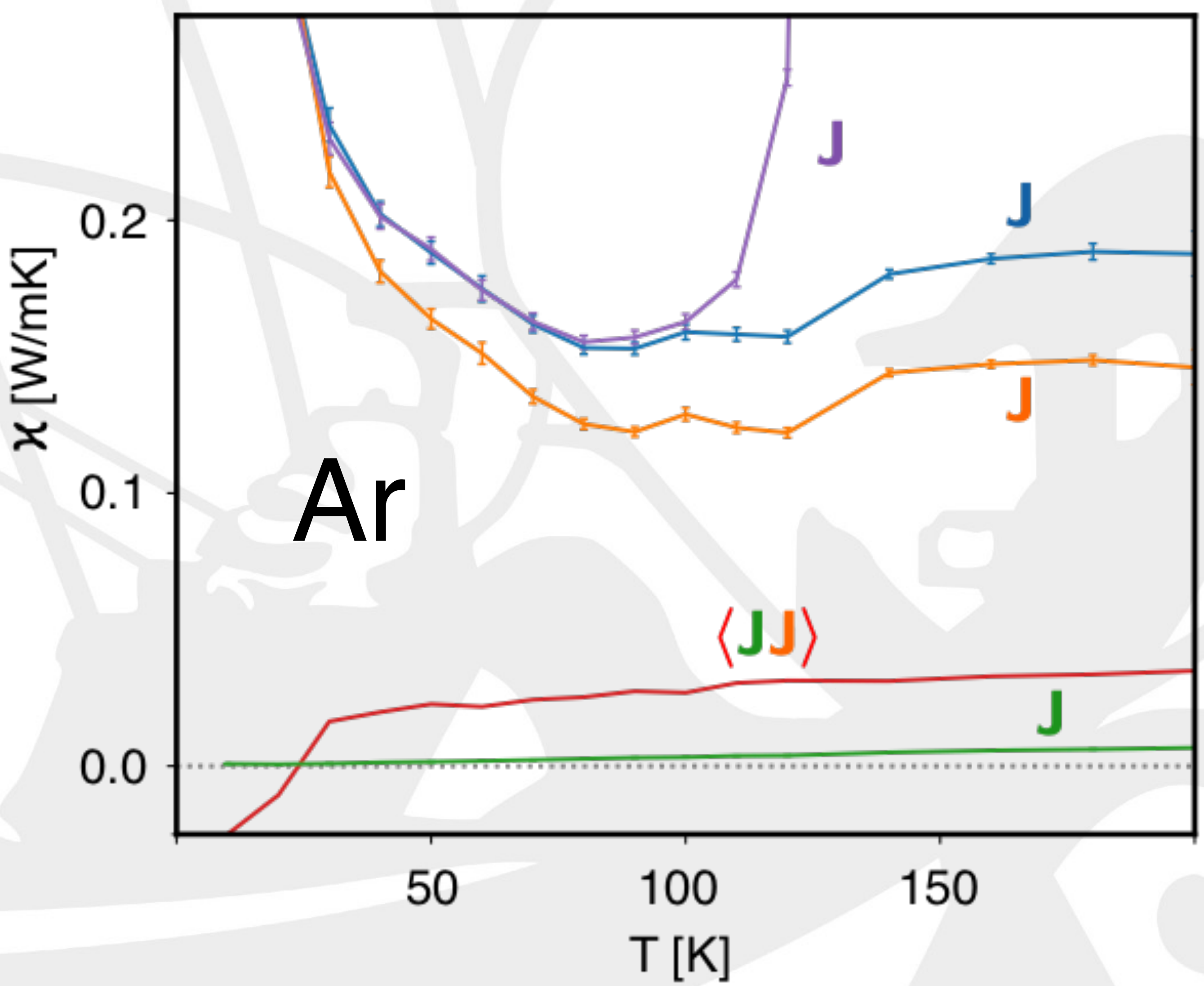
## what about glasses and alloys?

# heat transport from lattice dynamics

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

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

$$= \sum_n \mathbf{R}_n^\circ \dot{e}_n + \cancel{\frac{d}{dt} \sum_n \mathbf{u}_n e_n}$$



# heat transport from lattice dynamics

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

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

$$= \sum_n \mathbf{R}^\circ_n \dot{e}_n + \cancel{\frac{d}{dt} \sum_n \mathbf{u}_n e_n}$$

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

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

# heat transport from lattice dynamics

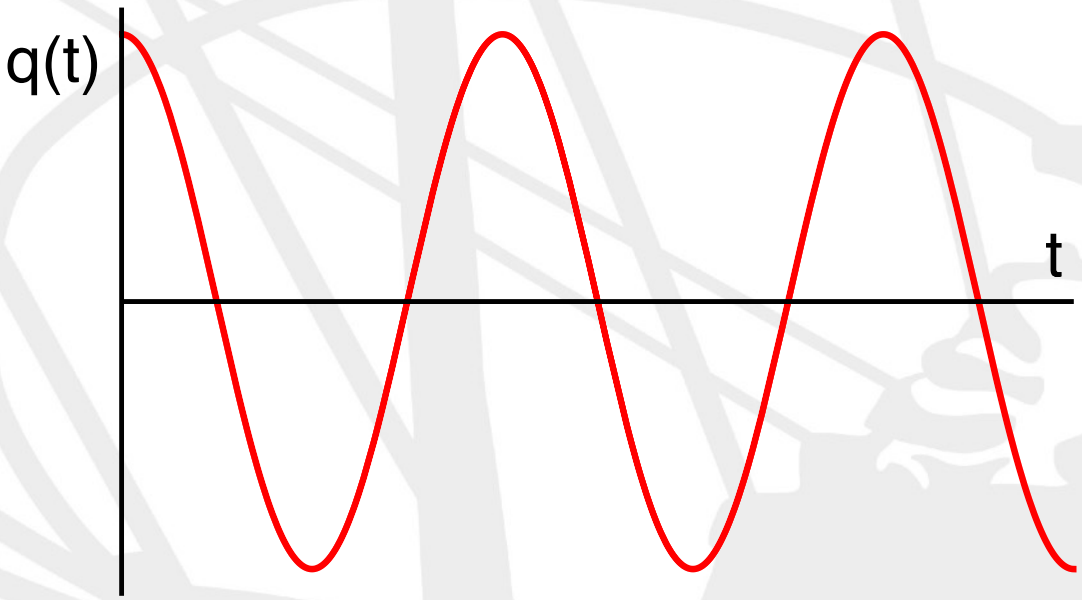
$$J_\alpha = \frac{1}{2}\sum_{ij\beta\gamma}(R^\circ_{i\alpha} - R^\circ_{j\alpha})\Phi^{j\gamma}_{i\beta} u_{i\beta}\dot{u}_{j\gamma},$$

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

# heat transport from lattice dynamics

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

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

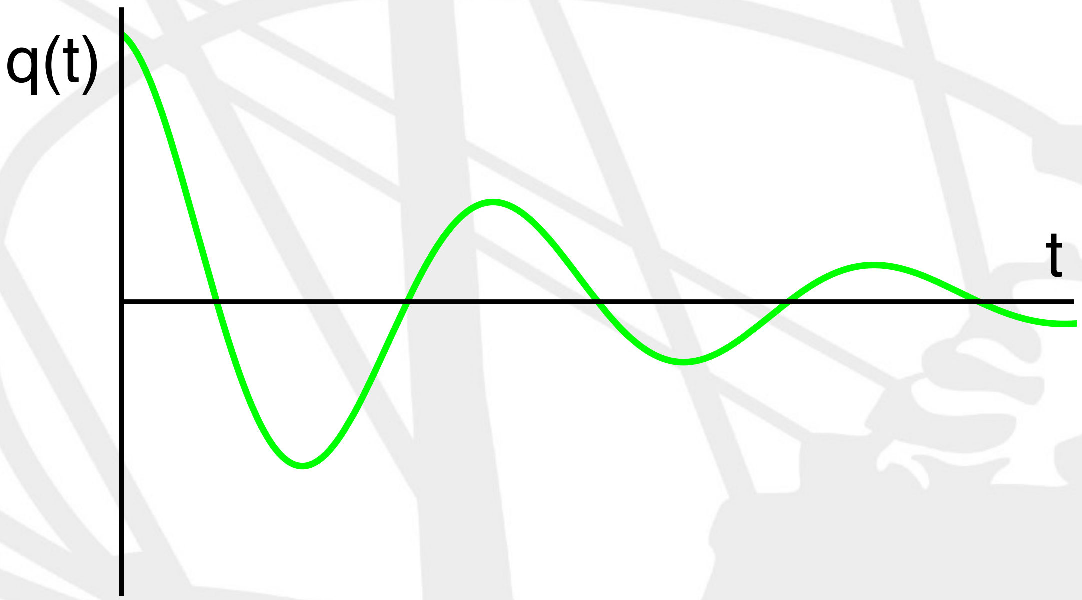



$$\longrightarrow \quad \boxed{\kappa = \infty}$$

# heat transport from lattice dynamics

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

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




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

$$\boxed{\kappa < \infty}$$

# 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

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

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

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

$$\boxed{\kappa = \frac{1}{V}\sum_{nm} c_{nm}\left(v_{nm}\right)^2 \tau^\circ_{nm}}$$

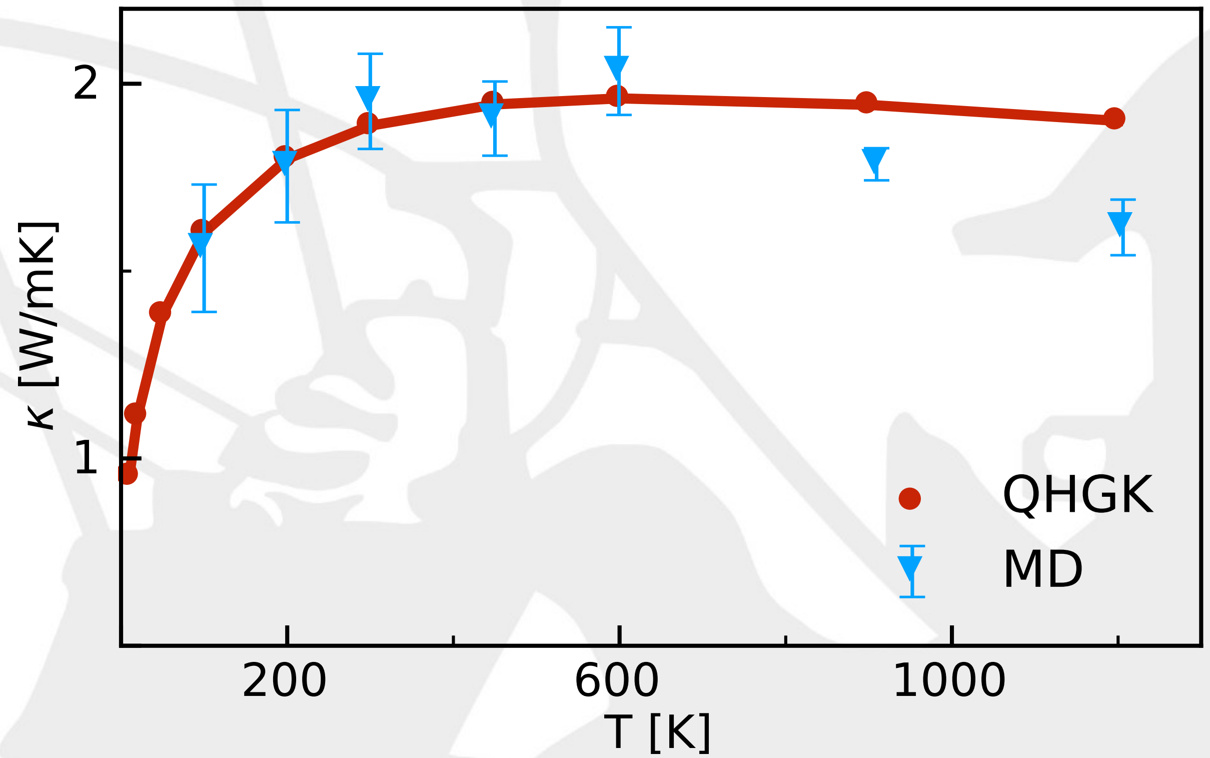
$$\tau^\circ_{nm} = \frac{\gamma_n + \gamma_m}{(\gamma_n + \gamma_m)^2 + (\omega_n - \omega_m)^2}$$

$$c_{nm} = \frac{\hbar\omega_m\omega_n}{T}\frac{n(\omega_n) - n(\omega_m)}{\omega_m - \omega_n} \approx k_B\left(\frac{\hbar\omega}{k_B T}\right)^2 \frac{1}{\left(e^{\frac{\hbar\omega}{k_B T}} - 1\right)^2}$$

# heat transport from lattice dynamics

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

$$\boxed{\kappa = \frac{1}{V} \sum_{nm} c_{nm} \left( v_{nm} \right)^2 \tau^\circ_{nm}}$$



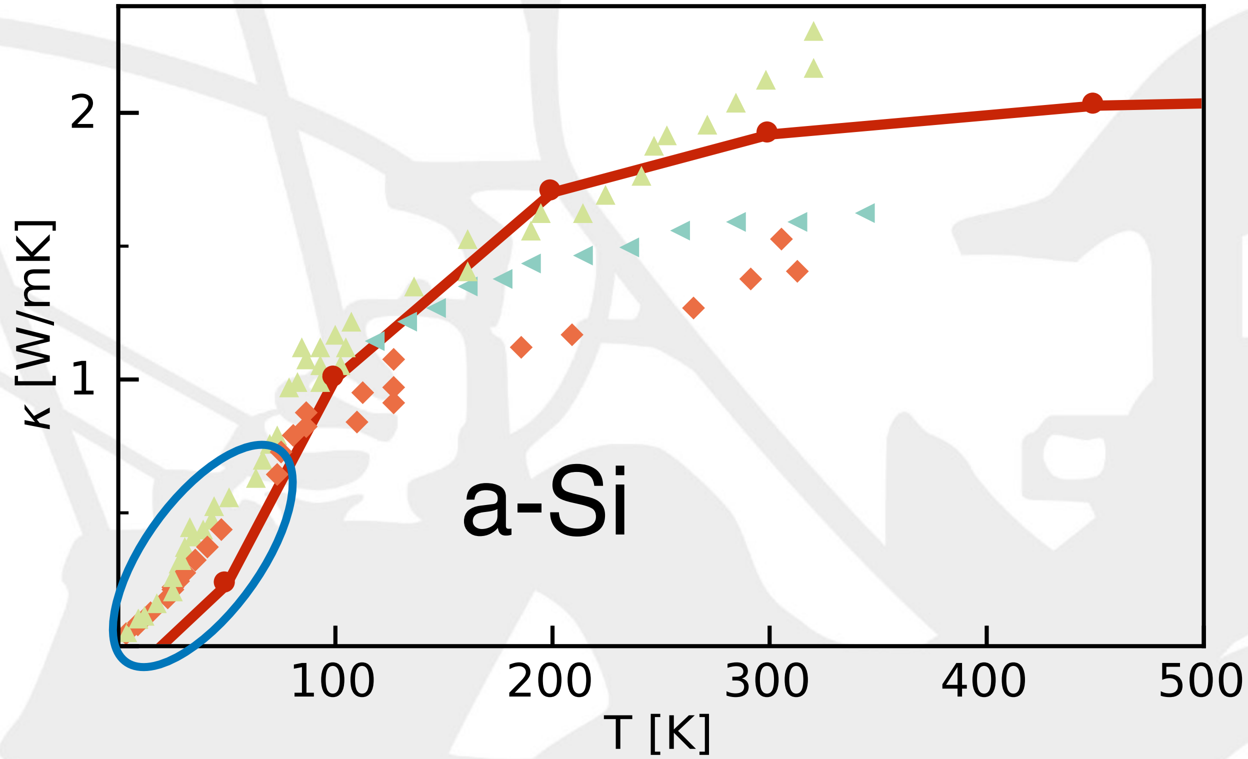

classical
$c_{nm} = k_B$

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

# heat transport from lattice dynamics

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

$$\boxed{\kappa = \frac{1}{V}\sum_{nm} c_{nm}\left(v_{nm}\right)^2 \tau^\circ_{nm}}$$



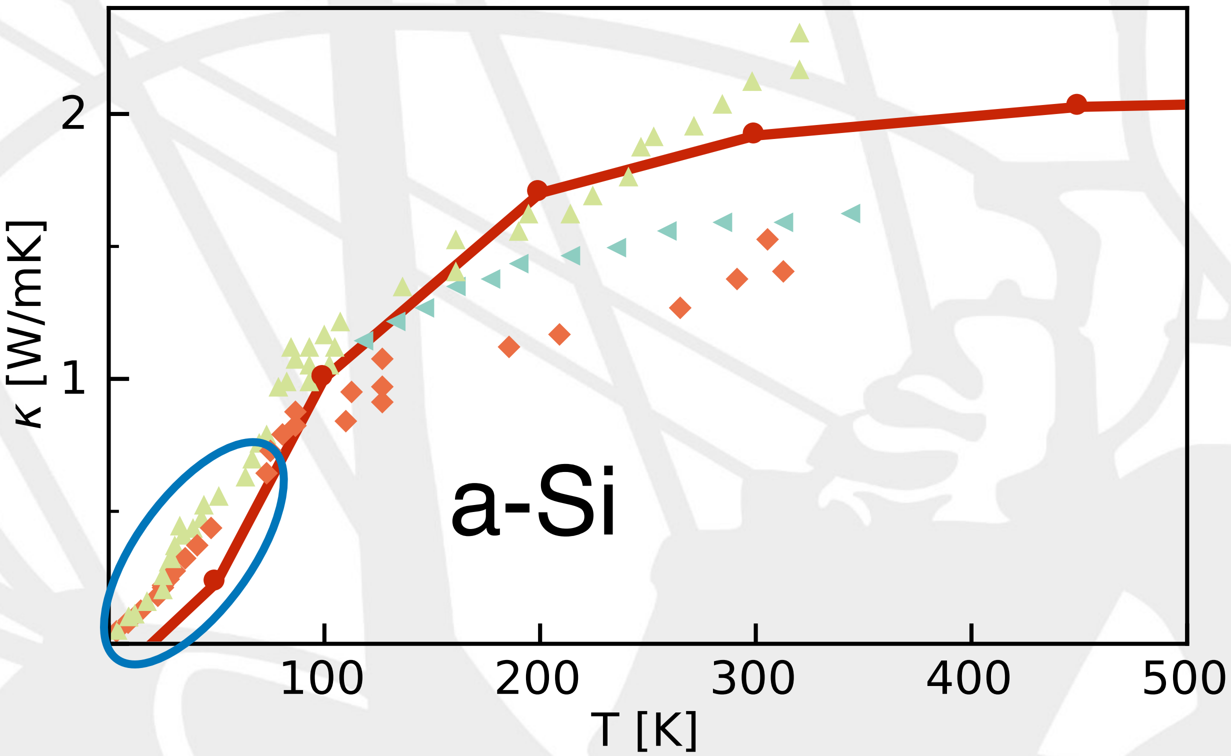

quantum
QHGK

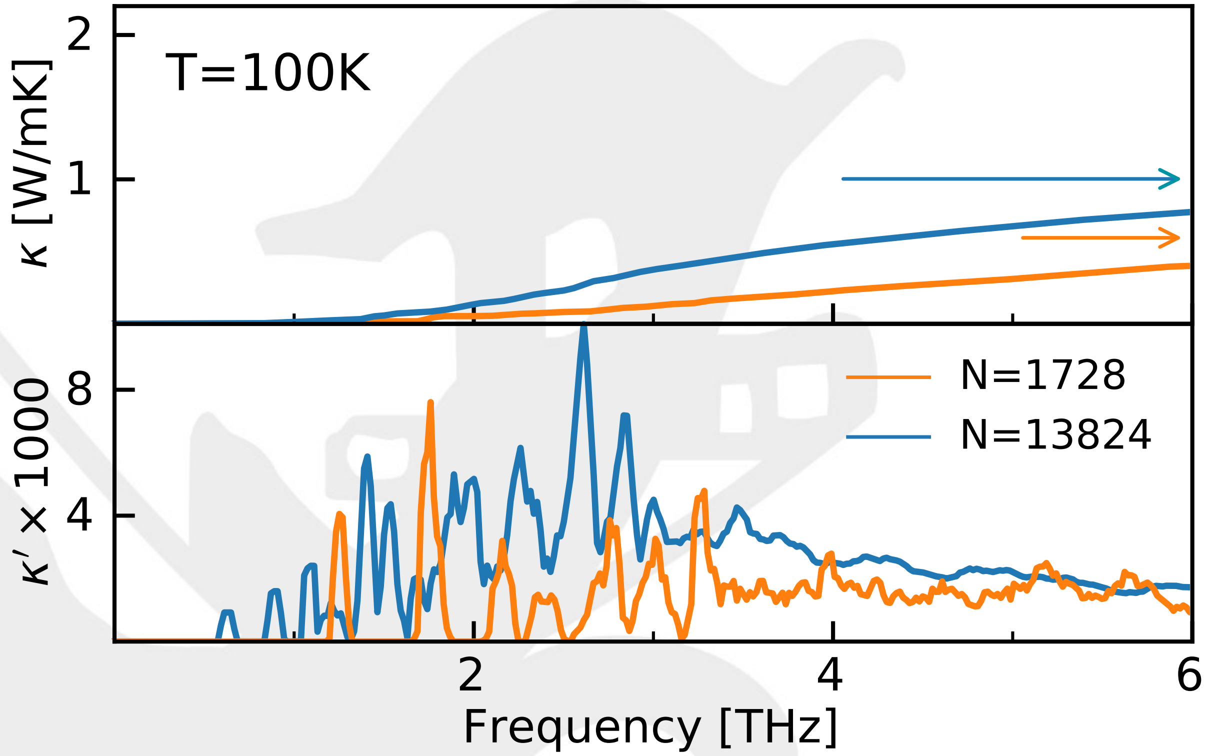
L. Isaeva, G. Barbalinardo, D. Donadio, and S. Baroni, Nature Commun. in press (2019), https://arxiv.org/abs/1904.02255

# heat transport from lattice dynamics

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

$$\boxed{\kappa = \frac{1}{V}\sum_{nm} c_{nm}\left(v_{nm}\right)^2 \tau^\circ_{nm}}$$



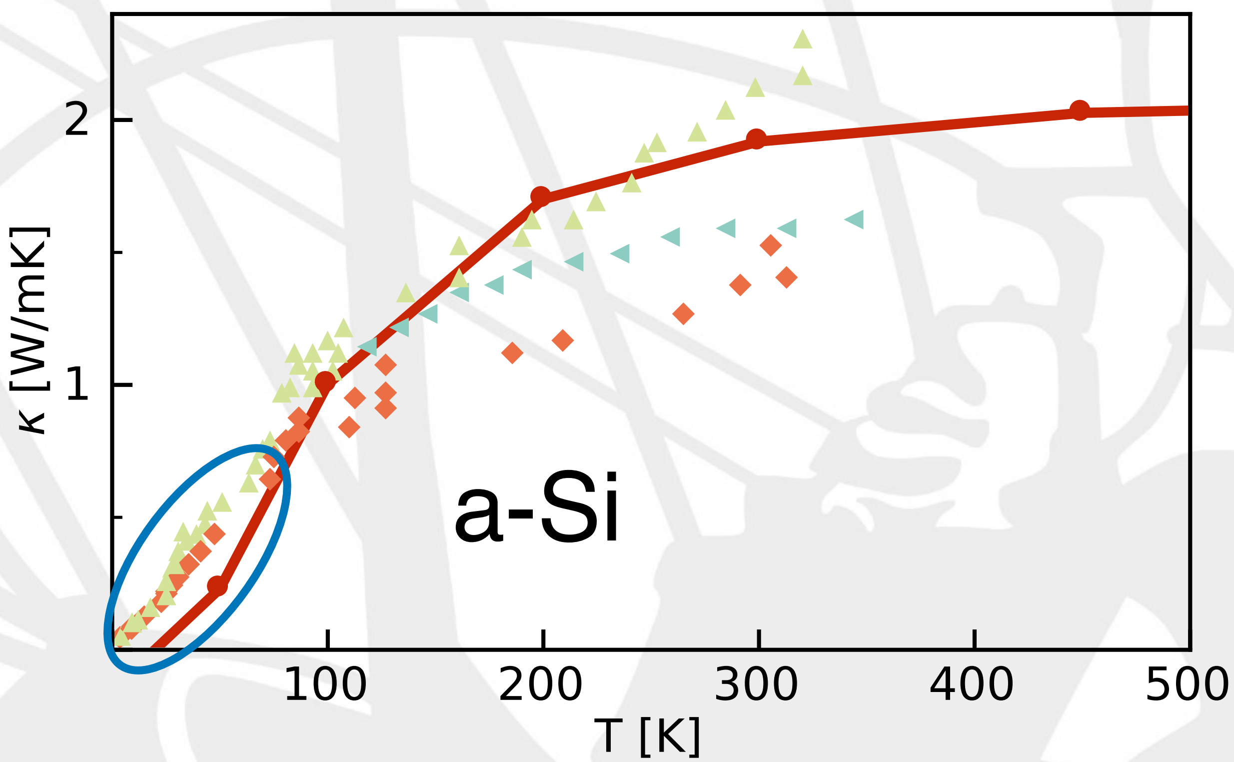



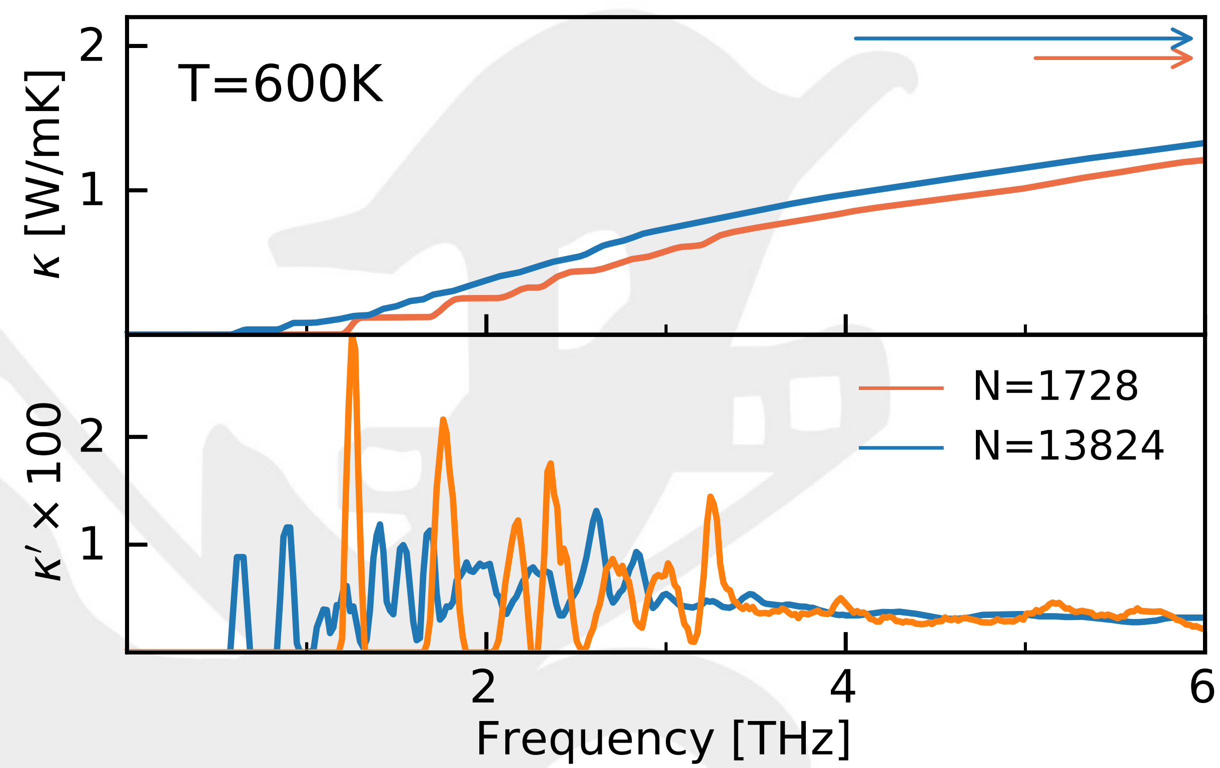

L. Isaeva, G. Barbalinardo, D. Donadio, and S. Baroni, Nature Commun. in press (2019), https://arxiv.org/abs/1904.02255

# heat transport from lattice dynamics

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

$$\boxed{\kappa = \frac{1}{V}\sum_{nm} c_{nm}\left(v_{nm}\right)^2 \tau^\circ_{nm}}$$




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

# heat transport from lattice dynamics

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

$$\boxed{\kappa = \frac{1}{V}\sum_{nm} c_{nm}\left(v_{nm}\right)^2 \tau^\circ_{nm}}$$

In a periodic system

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

$$\boxed{\kappa = \frac{1}{V}\sum_{\mathrm{q}\nu} c_\nu(\mathbf{q}) v_\nu(\mathbf{q})^2 \tau_\nu(\mathbf{q})}$$

BTE

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

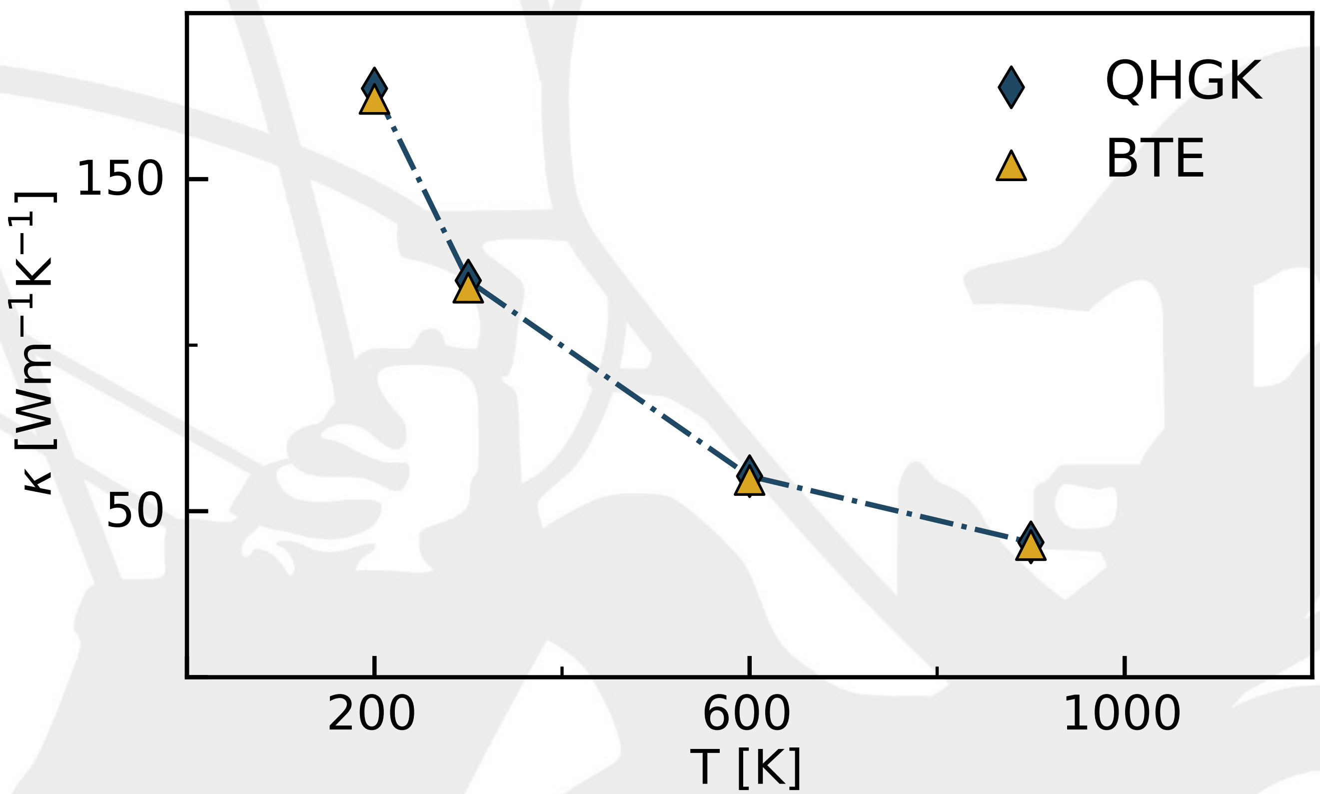
# heat transport from lattice dynamics

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

In a periodic system

$$\boxed{\kappa = \frac{1}{V}\sum_{\mathrm{q}\nu} c_\nu(\mathbf{q}) v_\nu(\mathbf{q})^2 \tau_\nu(\mathbf{q})}$$

BTE




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

QUANTUM ESPRESSO

QUANTUM ESPRESSO FOUNDATION

MAX

# thanks to:


Aris Marcolongo


Loris Ercole


Riccardo Bertossa


Leyla Isaeva


Giuseppe Barbalinardo


Davide Donadio


Federico Grasselli


Paolo Pegolo


Davide Tisi


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