Car and Parrinello meet Green and Kubo

simulating atomic heat transport from equilibrium ab-initio molecular dynamics

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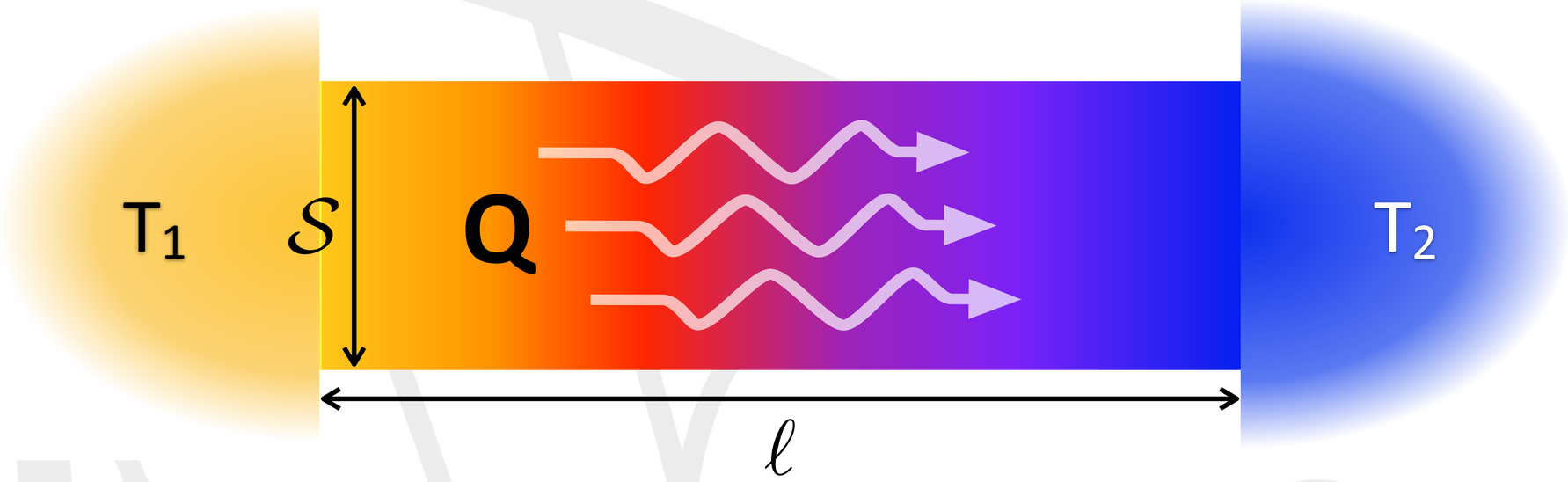
invited talk given at the APS March Meeting 2017, New Orleans, LA, March 15, 2017

the Green-Kubo formalism is not compatible with ab-initio methods based on electronic-structure theory

even if it were, coping with statistical noise would require impractically long MD simulations

what heat transport is all about



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

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

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

Green-Kubo theory

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

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

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

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

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

the classical MD ansatz

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

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

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

hurdles toward an ab initio Green-Kubo theory

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

Thermal Conductivity of Periclase (MgO) from First Principles

Stephen Stackhouse, Lars Stixrude, and Bijaya B. Karki

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

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

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

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

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

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

insights from classical mechanics

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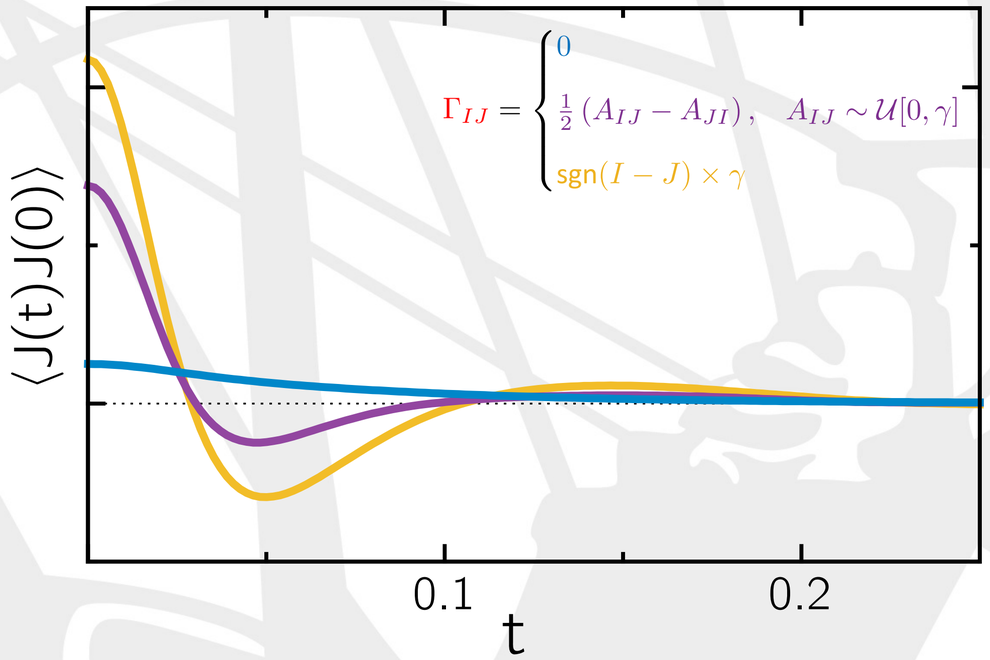

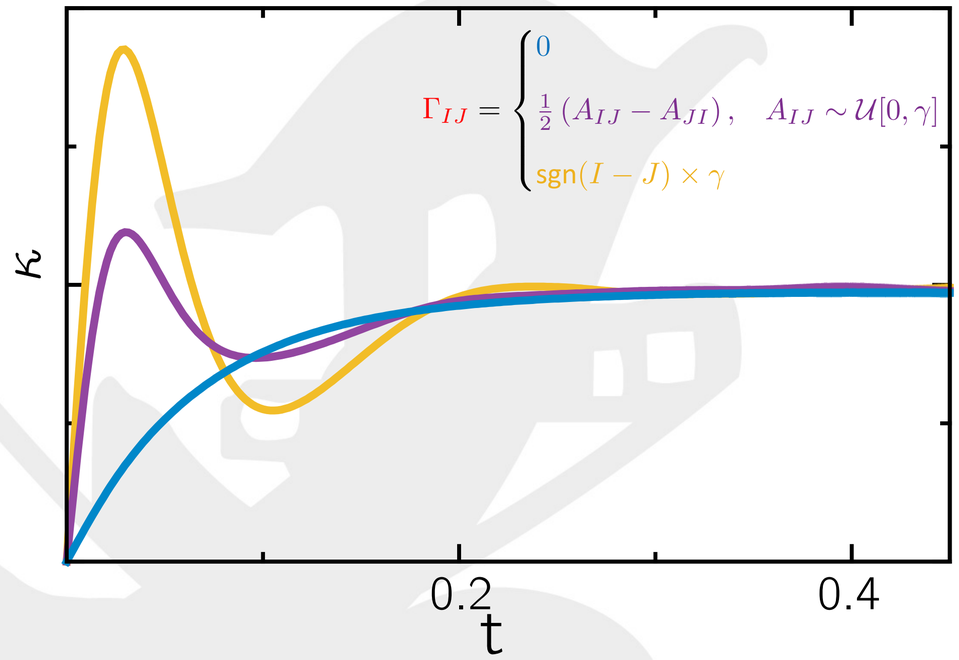

insights from classical mechanics

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

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

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

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

insights from classical mechanics

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

$$\kappa' = \kappa$$

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

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

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

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

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

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

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

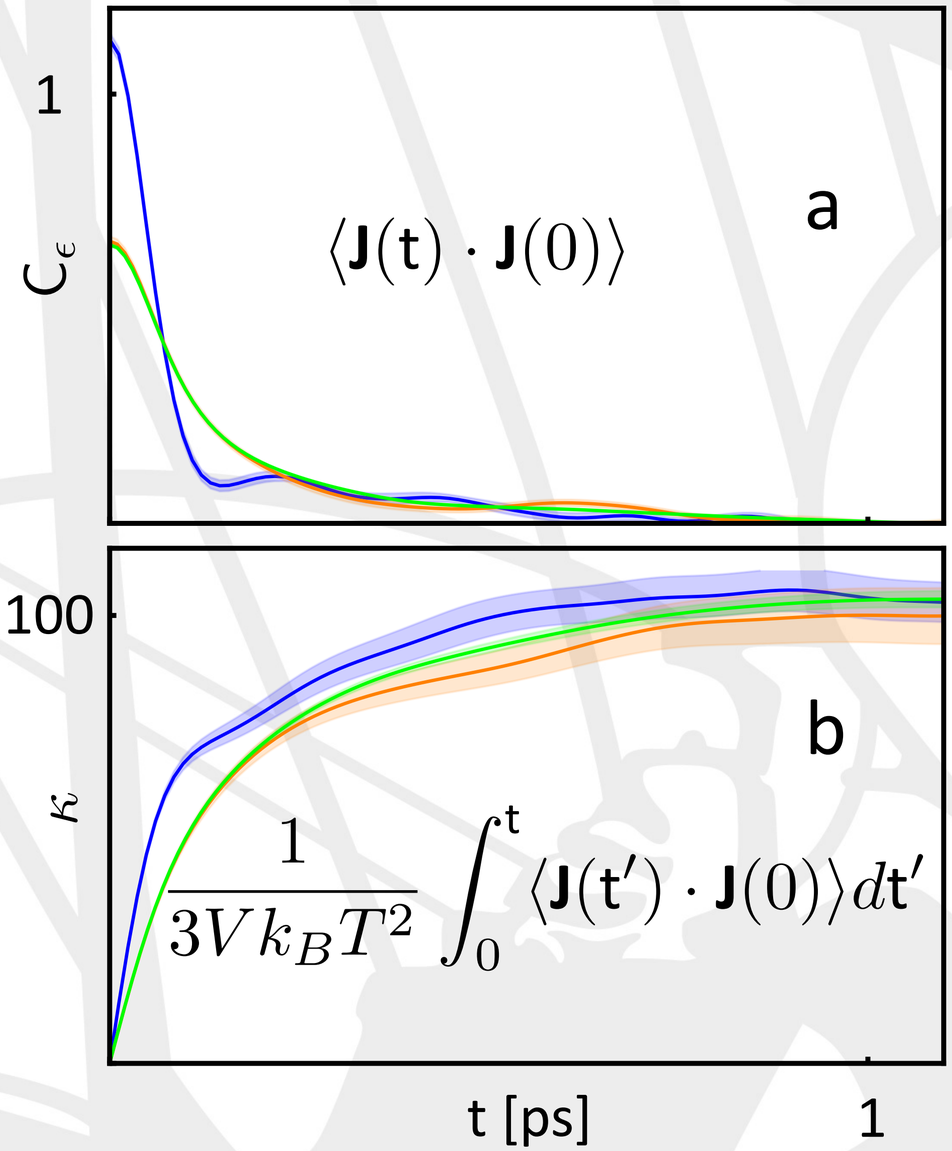
$$\mathbf{J}_{DFT} = \int \mathbf{r}\dot{e}_{DFT}(\mathbf{r},t)d\mathbf{r}$$

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

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

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

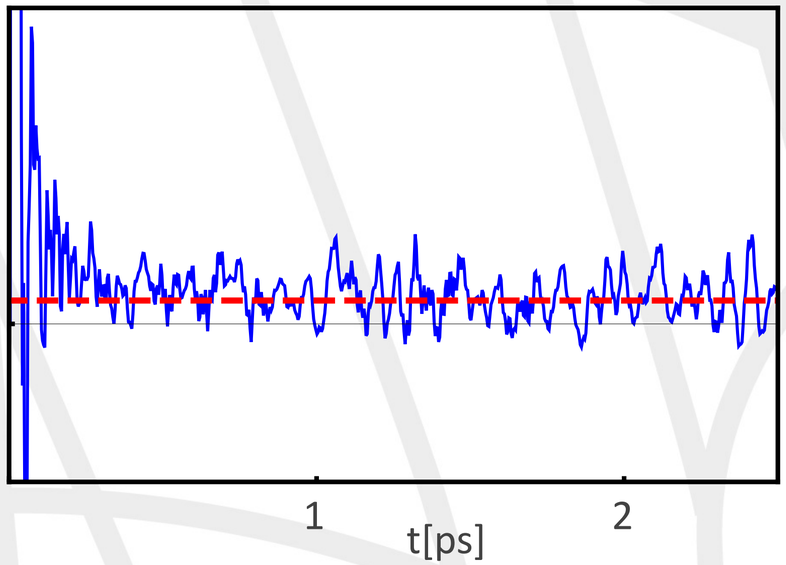


108 “LDA Ar” atoms
@bp density, T= 250 K

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

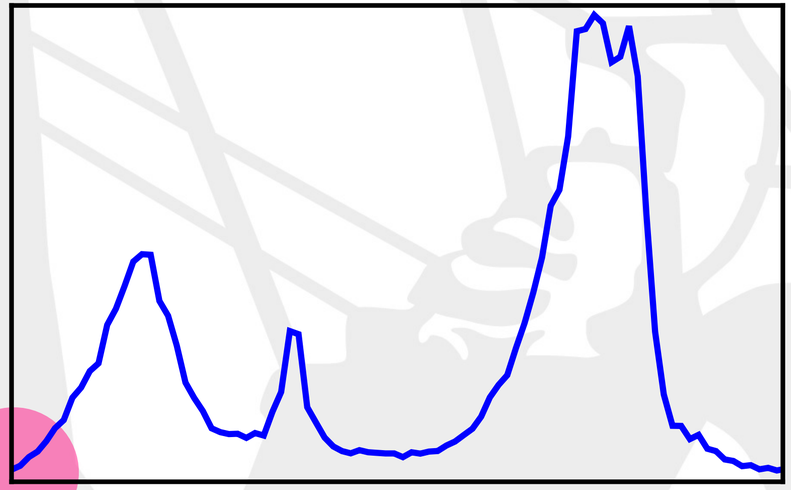
same behavior at T=400 K

liquid (heavy) water



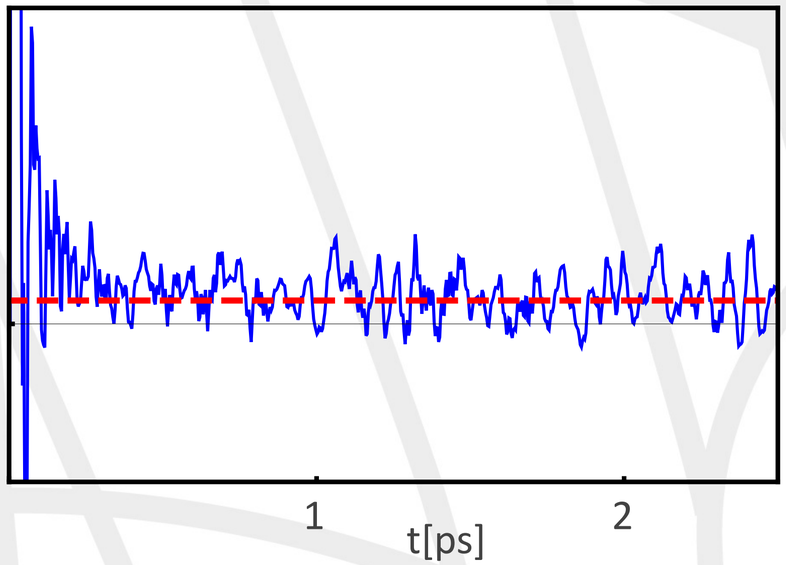
64 molecules, T=385 K
expt density @ac

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



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

liquid (heavy) water



64 molecules, T=385 K
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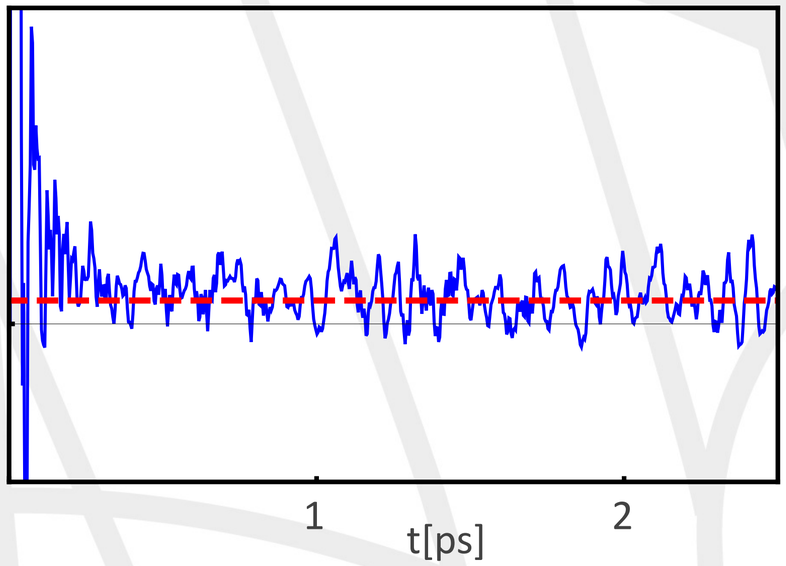
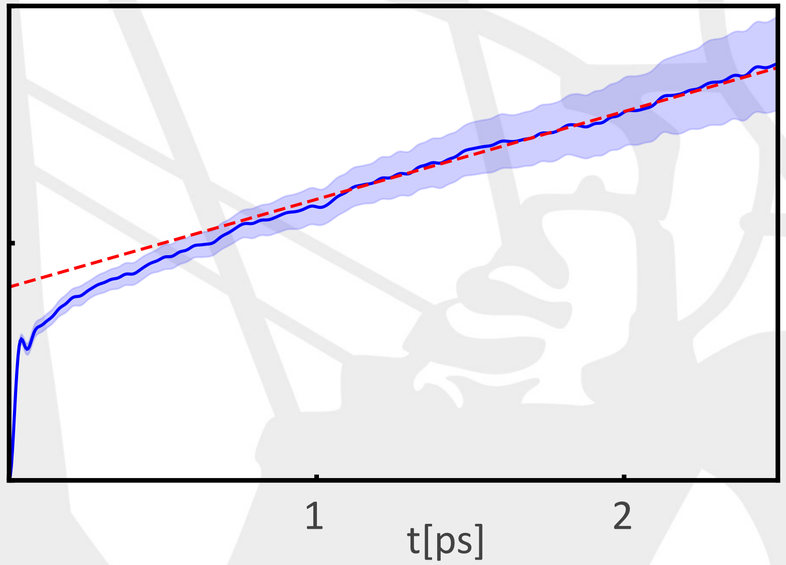
$$\frac{1}{3Vk_BT^2}\int_0^t \langle \mathbf{J}(t') \cdot \mathbf{J}(0)\rangle dt'$$

Einstein's relation

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

liquid (heavy) water





64 molecules, T=385 K
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$$\frac{1}{3Vk_BT^2}\int_0^{t}\langle \mathbf{J}(t')\cdot\mathbf{J}(0)\rangle dt'$$

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

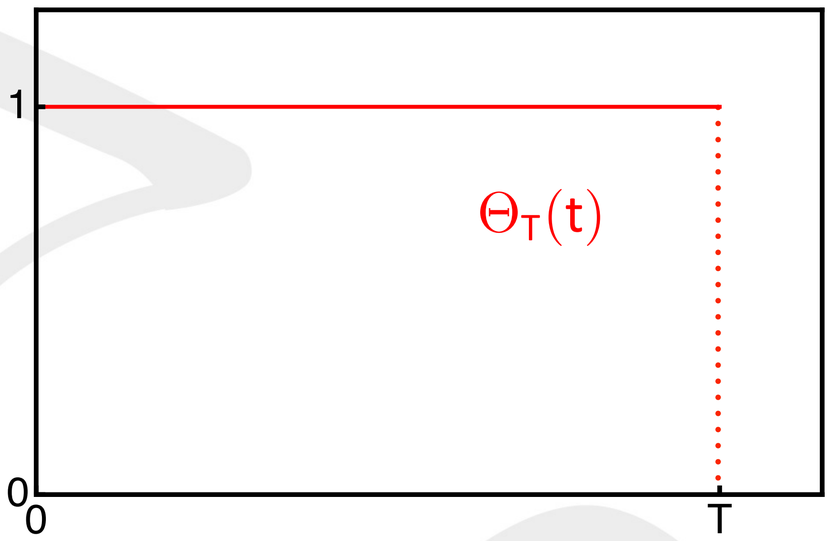
$$\kappa_{\text{expt}} = 0.60$$

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

Einstein *vs.* Green-Kubo

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

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



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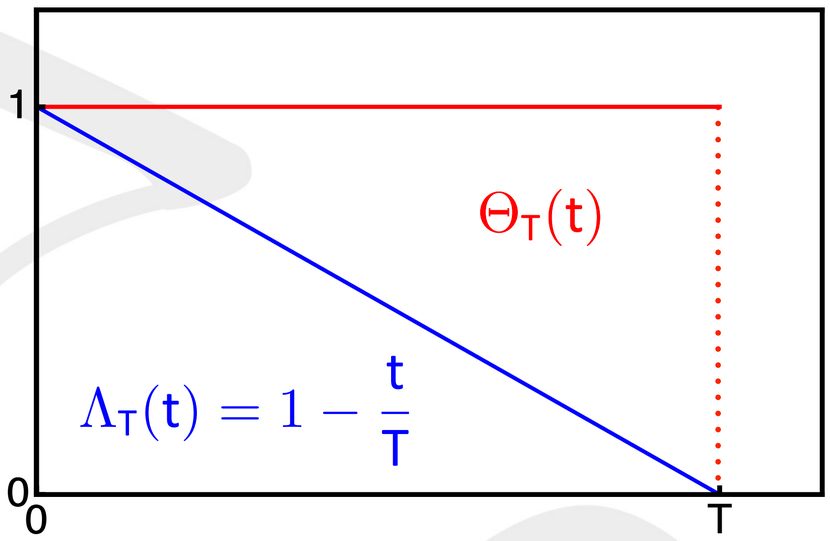
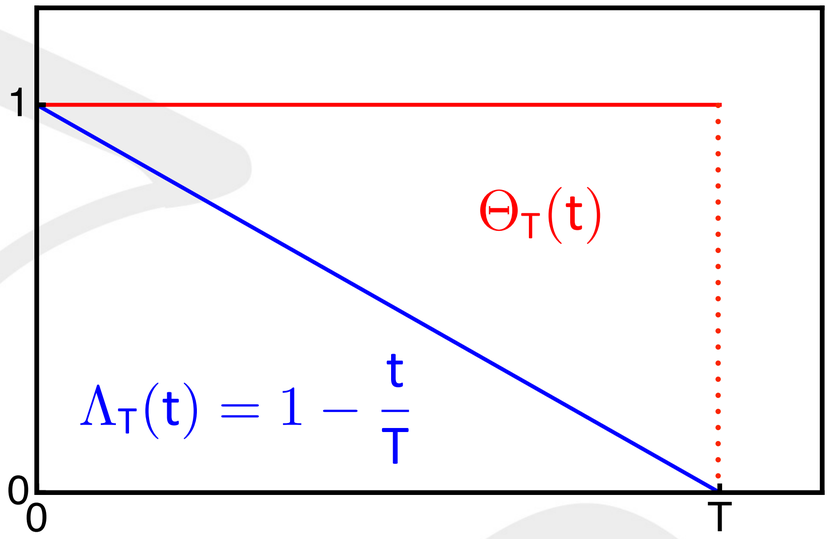


$$\kappa_E(T) = \frac{1}{2T}\left\langle \left| \int_0^T v(t)dt \right|^2 \right\rangle$$
$$= \int_0^\infty \langle v(t)v(0)\rangle \Lambda_T(t) dt$$

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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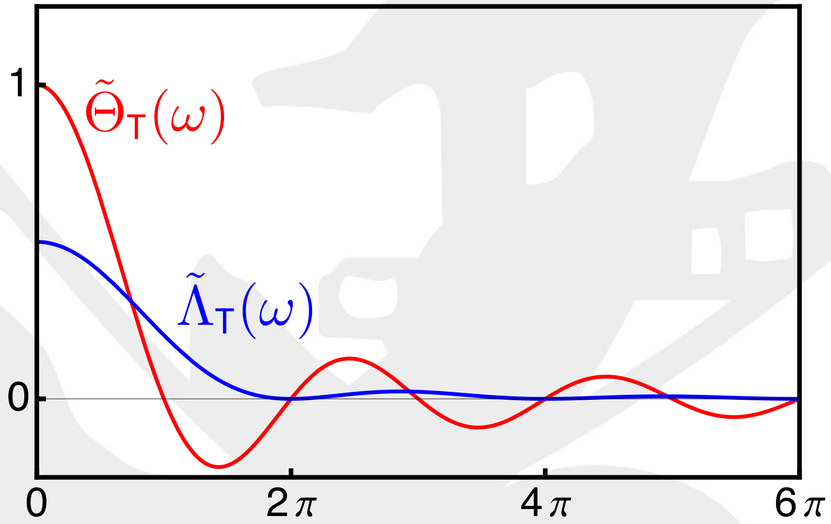

Einstein, Green-Kubo, and block analysis

$$\langle a \rangle \sim \frac{1}{N} \sum_i a_i \pm \sqrt{\frac{\tau}{N}} \Delta a$$

$$A_I = \frac{1}{n} \sum_{i=0}^{n-1} a_{I+i}$$

$$\Delta A^2 \sim \frac{\tau}{n} \Delta a^2 \qquad\qquad \tau \sim n \frac{\Delta A^2}{\Delta a^2}$$

$$\left\langle \left(\sum_i \left(a_i - \langle a \rangle \right) \right)^2 \right\rangle \sim n \tau \Delta a^2$$

hurdles toward an ab initio Green-Kubo theory

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arXiv:1608.06917v3 [cond-mat.mtrl-sci] 6 Feb 2017

***Ab initio* Green-Kubo Approach for the Thermal Conductivity of Solids**

Christian Carbogno, Rampi Ramprasad, and Matthias Scheffler

lations: Due to the limited time scales accessible in aiMD runs, thermodynamic fluctuations dominate the HF-ACF, which in turn prevents a reliable and numerically stable assessment of the thermal conductivity via Eq. (2). Furthermore, achieving convergence with re-

squeezing more juice fro a time series

$$\kappa \propto 2\int_0^\infty C(t)dt$$
$$= S(\omega = 0)$$

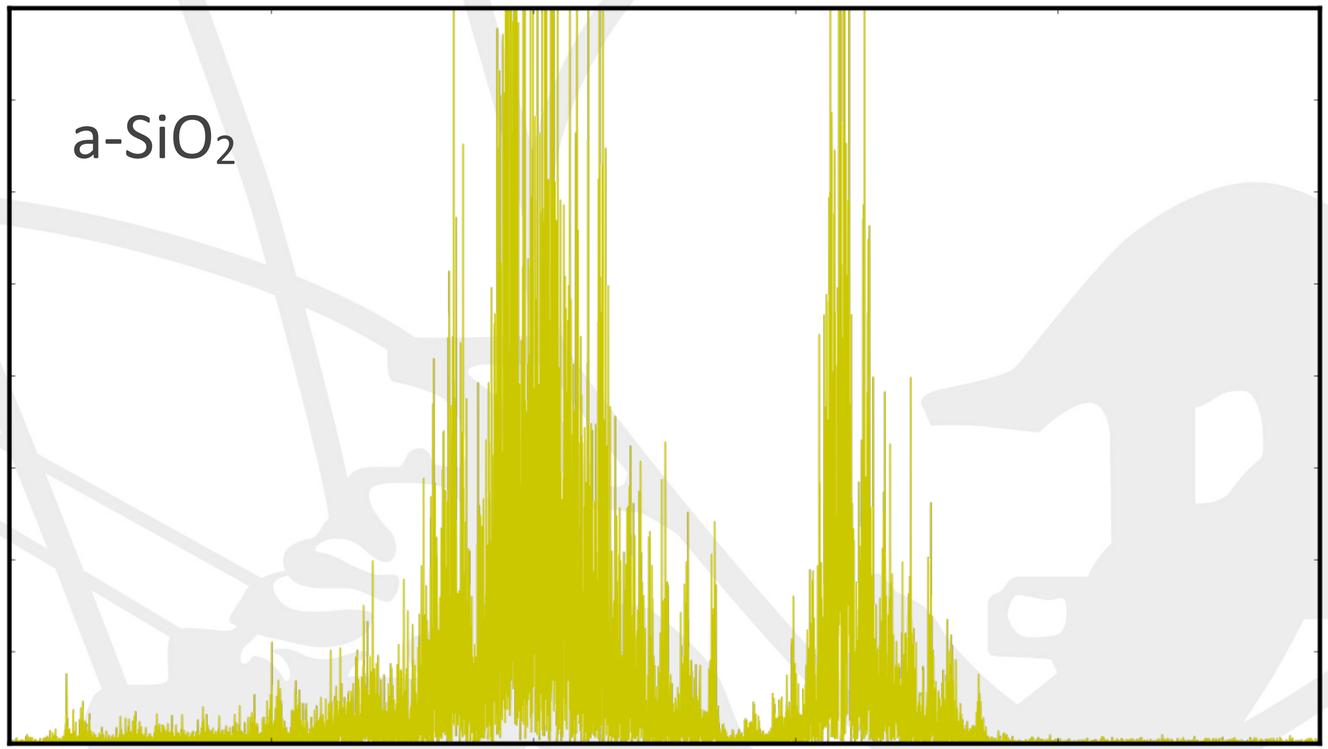
$$C(t) = \langle J(t)J(0)\rangle$$
$$S(\omega) = \int_{-\infty}^{\infty} C(t)\mathrm{e}^{-i\omega t}dt$$

$$C(n\epsilon) \sim \hat{C}(n)$$
$$\hat{C}(n) = \frac{1}{N}\sum_{m=0}^{N-n-1} J(n+m)J(m)$$

$$S\left(k\frac{2\pi}{N\epsilon}\right) \sim \hat{S}(k)$$
$$\hat{S}(k) = \frac{\epsilon}{N}\left|\tilde{J}(k)\right|^2$$

squeezing more juice fro a time series

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



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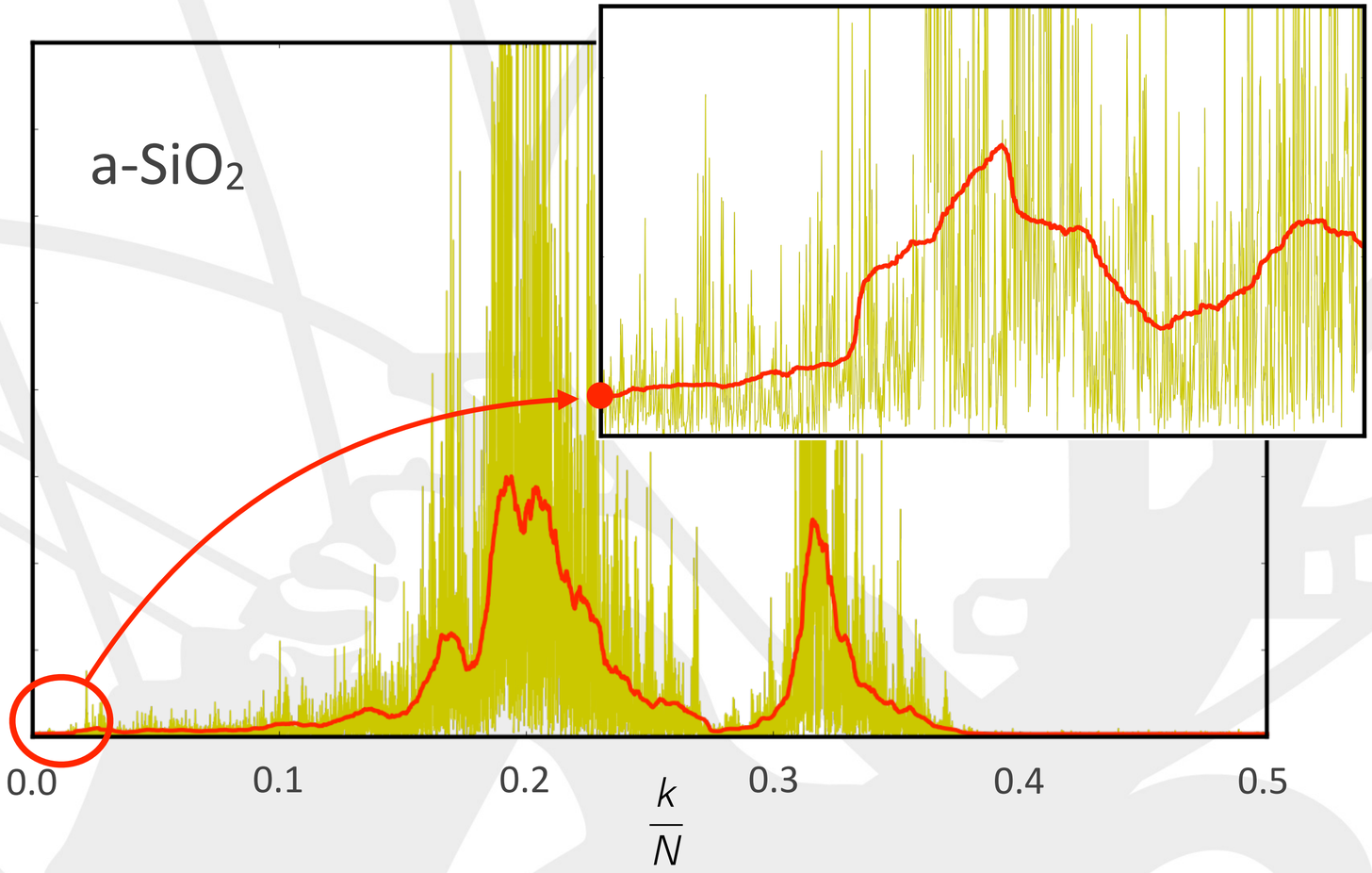
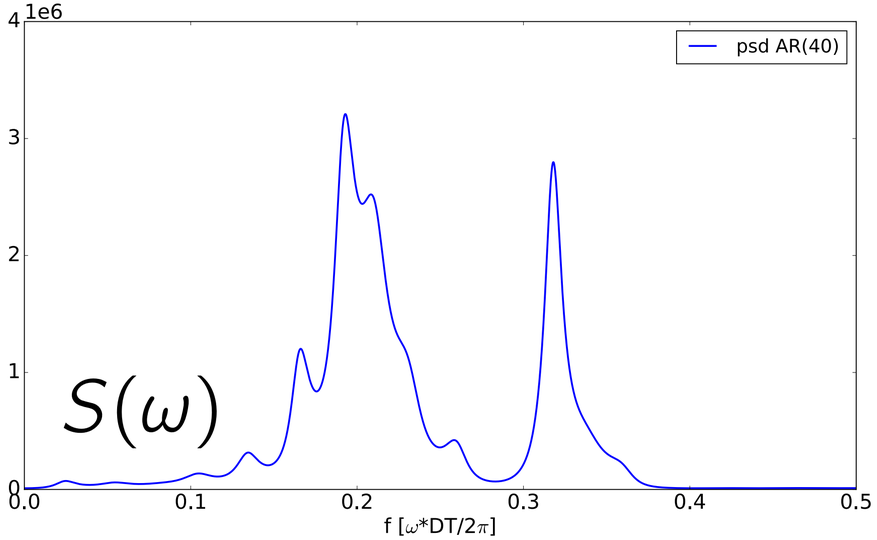
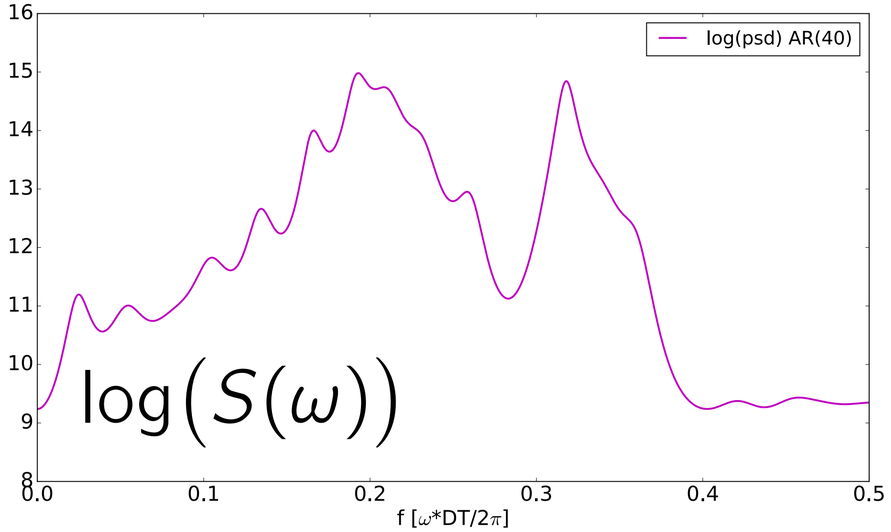


what is to be done?

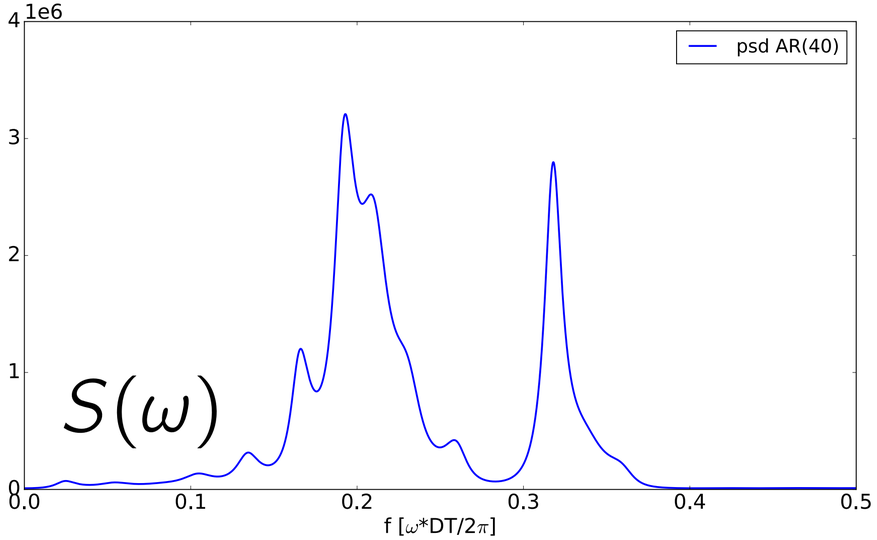


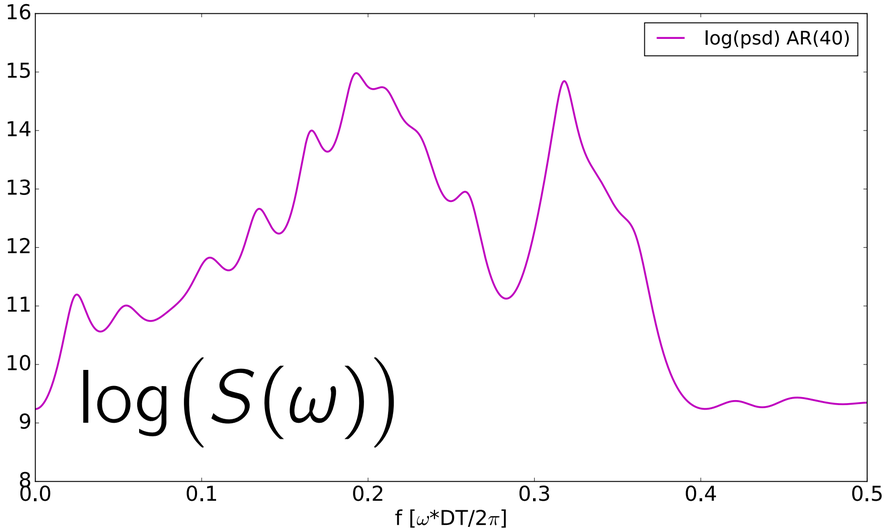


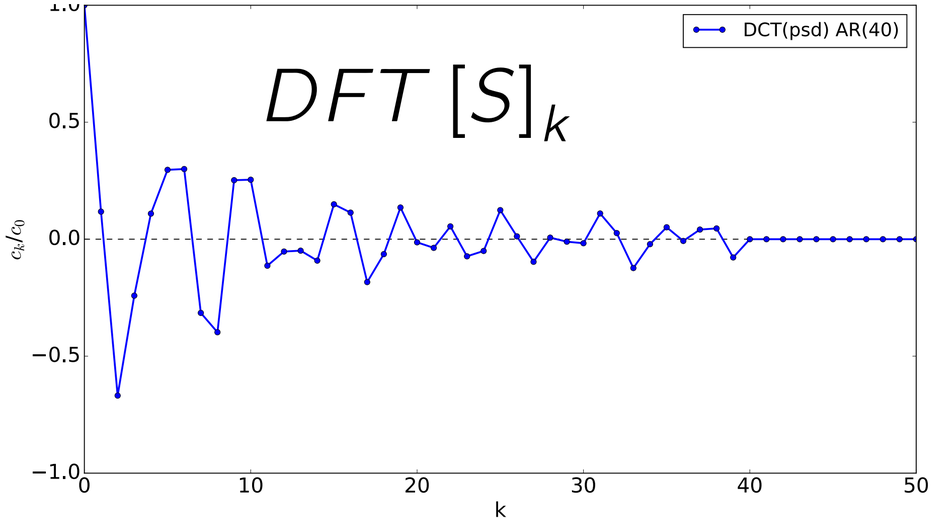
$$\hat{S}(k) = S(\omega_k)\hat{\xi}_k$$

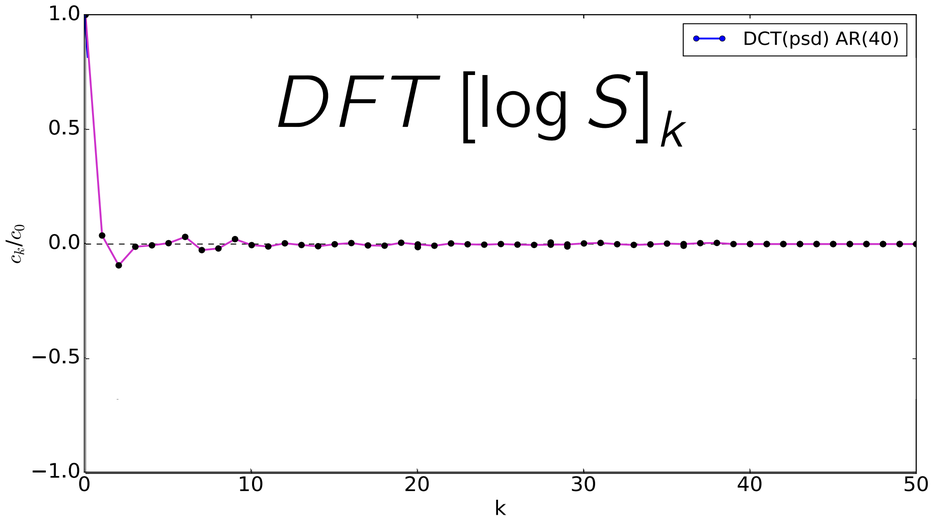
$$\log\left(\hat{S}(k)\right) = \log\left(S(\omega_k)\right) + \log\left(\hat{\xi}_k\right)$$

what is to be done?





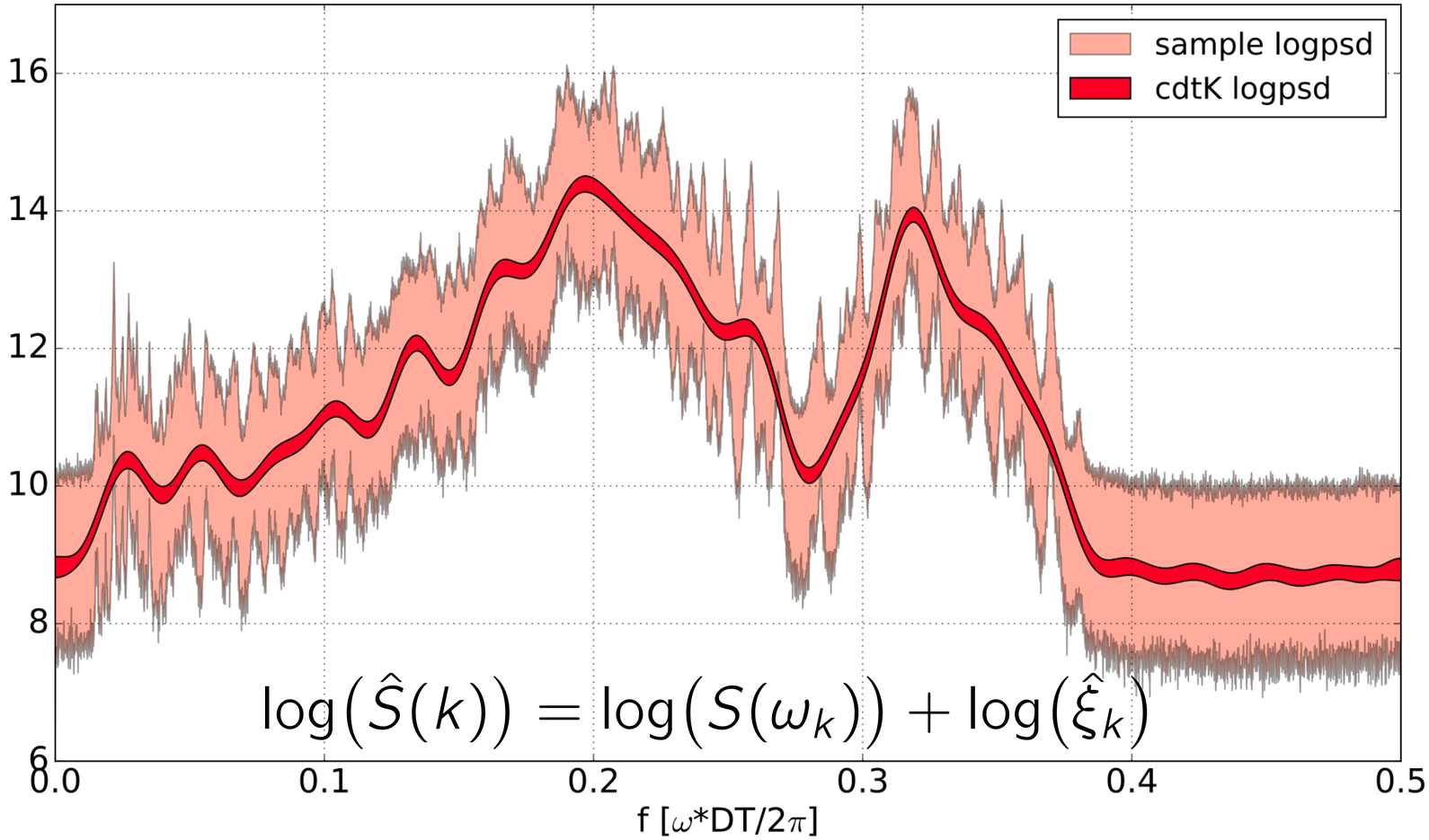




$$\log\left(\hat{S}(k)\right) = \log\left(S(\omega_k)\right) + \log\left(\hat{\xi}_k\right)$$

what is to be done?

use a low-pass linear filter
on the logarithm of the spectrum



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).

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SISSA, now @EPFL

Paolo Umari,
University of Padua

thanks to:

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an EU Centre of Excellence
for HPC & HTC applications

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

nature physics

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Microscopic theory and quantum simulation of atomic heat transport

Aris Marcolongo[1], Paolo Umari[2] and Stefano Baroni[1]*

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DOI 10.1007/s10909-016-1617-6

CrossMark

Gauge Invariance of Thermal Transport Coefficients

Loris Ercole[1] · Aris Marcolongo[2] · Paolo Umari[3] · Stefano Baroni[1]

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