Phonon thermal transport in advanced materials

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Warwick Centre for Predictive Modelling

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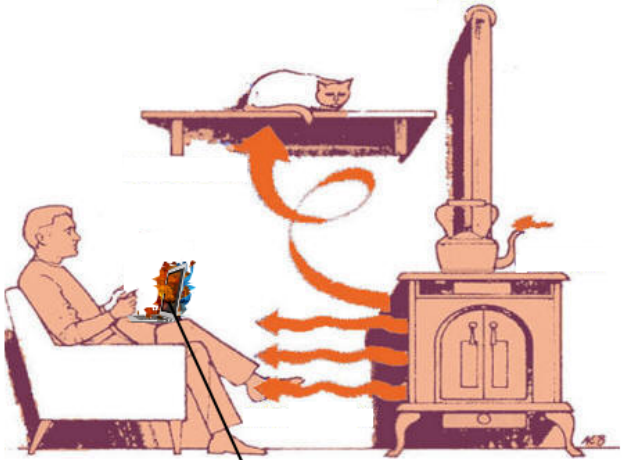
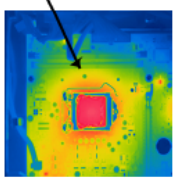
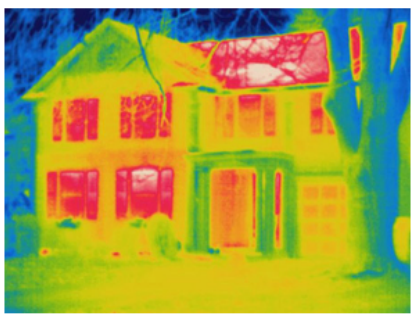
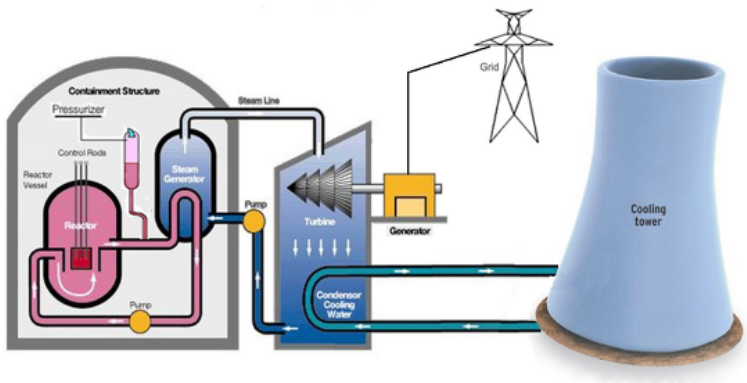
Heat transfer

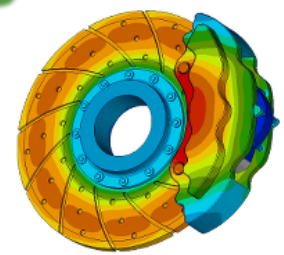
It is everywhere!

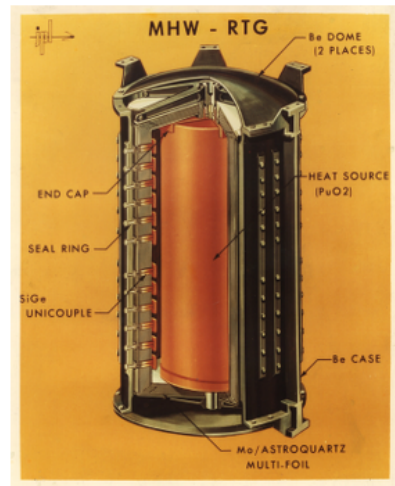










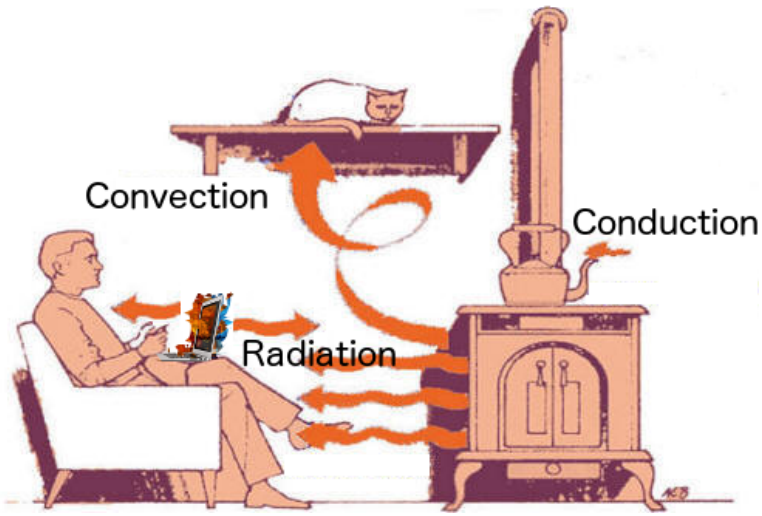


Outline

- ☑ Why thermal transport?
- ☐ Why atomistic-scale simulations?
- ☐ Predicting thermal transport in nuclear materials
- ☐ Switchable thermal conductivity in metal–organic frameworks
- ☐ Uncertainty quantification in the Green–Kubo method

Heat transfer

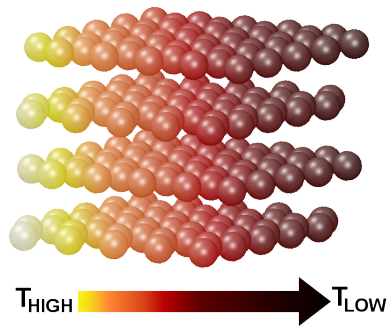
Heat transfer mechanisms



- Conduction

Fourier's law

$$\mathbf{J} = -\mathbf{k}\nabla T$$



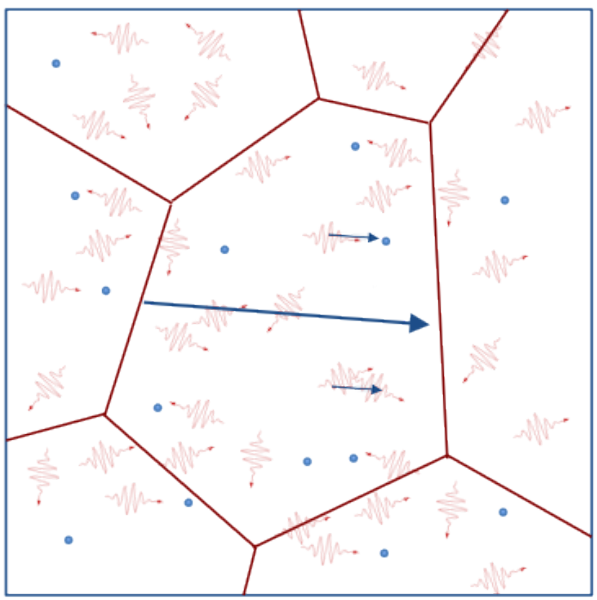
Heat transfer

Conduction at the atomic scale

Carriers:

- Electrons
- Phonons

$$\mathbf{J} = -\mathbf{k}\nabla T$$



Heat transfer

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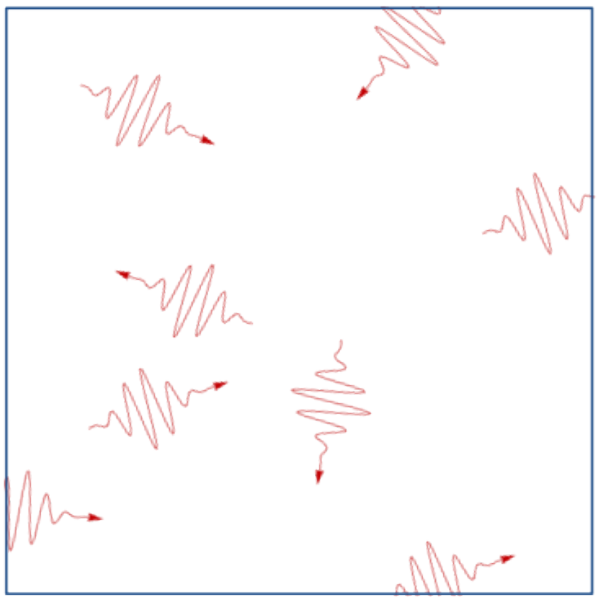

Heat transfer

Conduction at the atomic scale

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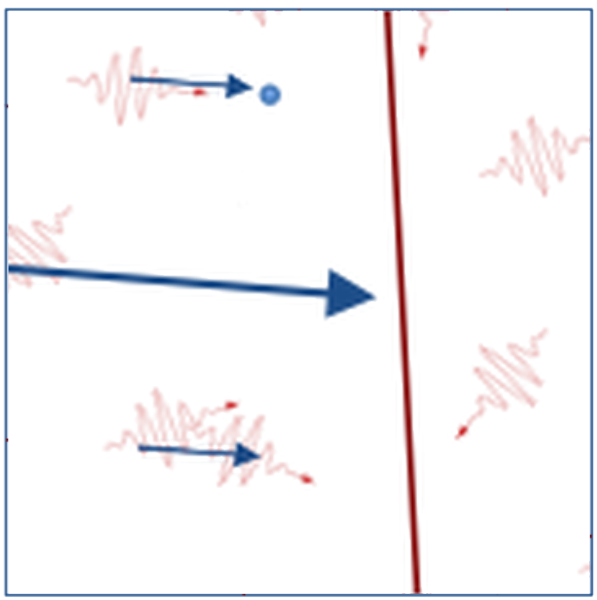


The trouble is:

- Macroscopic transport
- Defined over a continuum
- Assumes diffusive transport
- Ignores the (micro)structure of materials
- Solves a classical problem

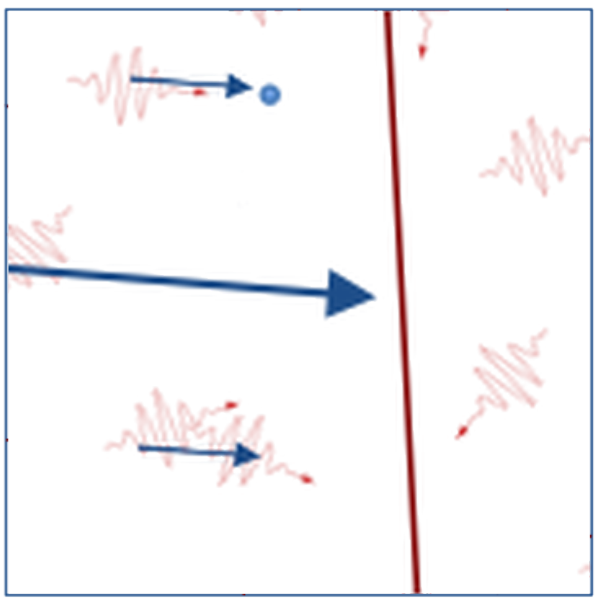
Heat transfer

Conduction at the atomic scale

Carriers:

- Electrons
- Phonons

$$\mathbf{J} = -\mathbf{k}\nabla T$$



- Boltzmann transport equation (BTE)

$$\frac{\partial f_\omega}{\partial t} + \mathbf{v}_\omega \nabla f_\omega = -\frac{f_\omega - f_\omega^0}{\tau_\omega}, f_\omega^0(T,\omega) = \frac{\hbar\omega D(\omega)\langle n\rangle_{BE}(T,\omega)}{4\pi}$$

- *Ab initio* calculations e.g. density functional theory (DFT)

$$\kappa = \int_0^{\omega_{max}} \hbar\omega D(\omega)\frac{\partial\langle n\rangle_{BE}}{\partial T}\mathbf{v}_g^2\tau d\omega$$

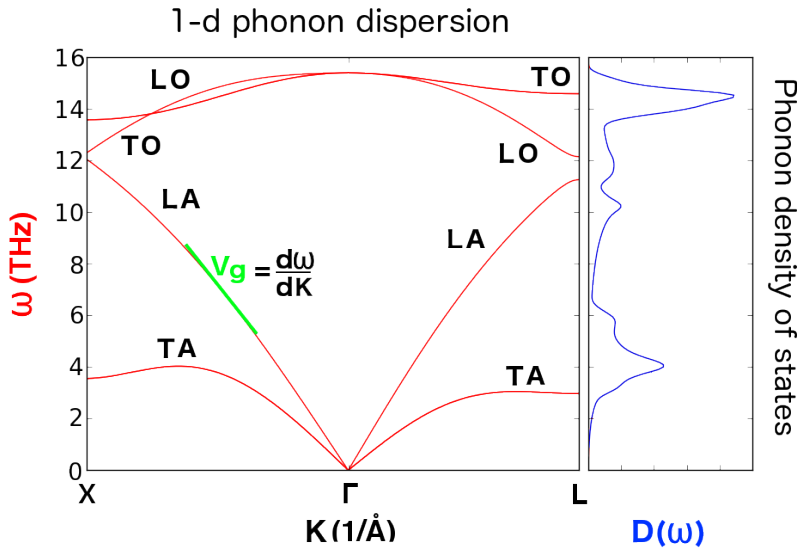
- Matthiessen's rule

$$\frac{1}{\tau} = \frac{1}{\tau_{\text{impurities}}} + \frac{1}{\tau_{\text{lattice}}} + \frac{1}{\tau_{\text{defects}}} + \cdots$$

Calculating intrinsic materials properties

Ab initio (but also classical MD)

- E.g. silicon

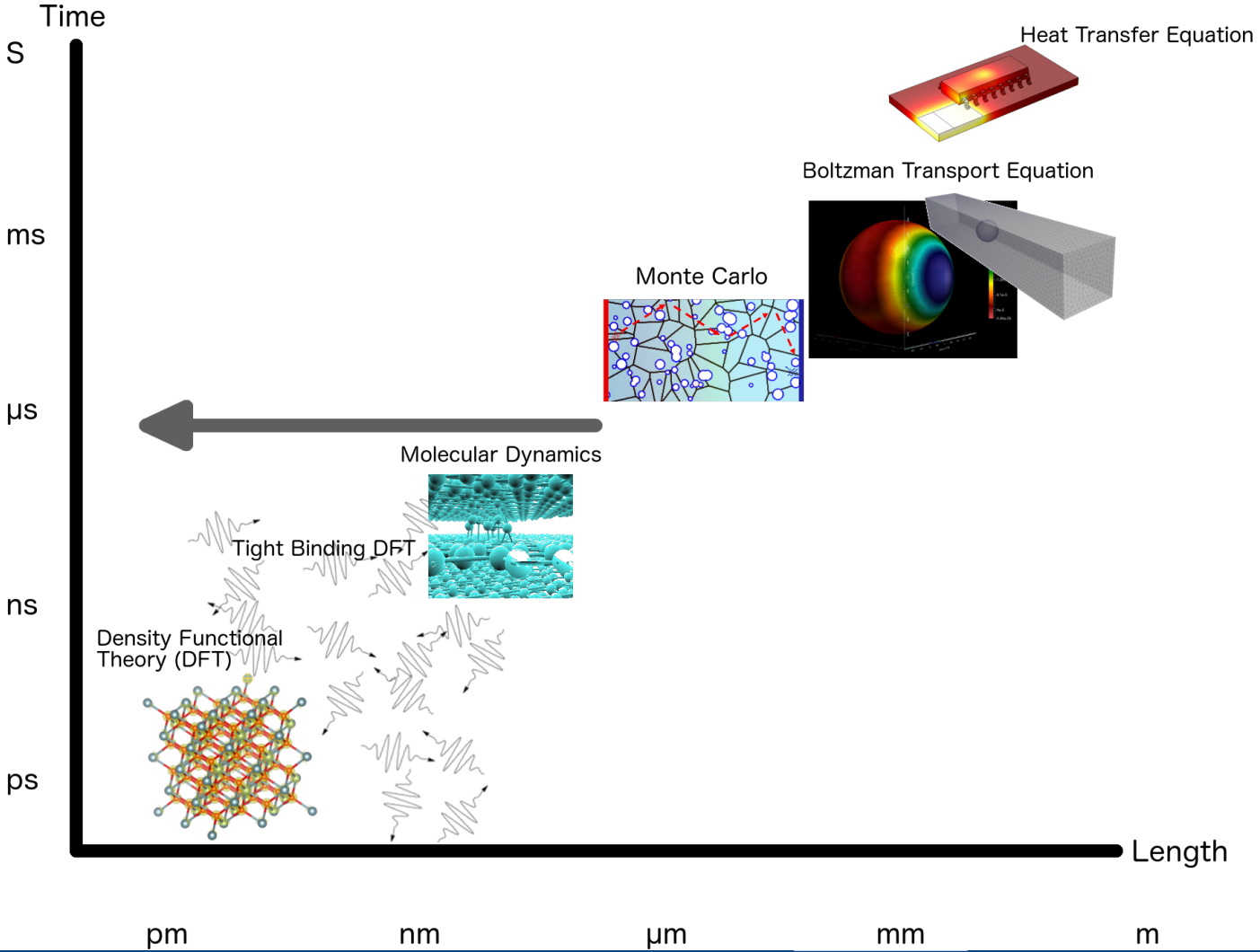


LA — longitudinal acoustic mode
TA — transverse acoustic mode
LO — longitudinal optical mode
TO — transverse optical mode

$$\kappa = \int_0^{\omega_{max}} \hbar\omega D(\omega) \frac{\partial \langle n \rangle_{BE}}{\partial T} \mathbf{v}_g^2 \tau d\omega$$

In the scale of heat transfer simulations

$$\frac{1}{\tau} = \frac{1}{\tau_{\text{impurities}}} + \frac{1}{\tau_{\text{lattice}}} + \frac{1}{\tau_{\text{defects}}} + \cdots$$



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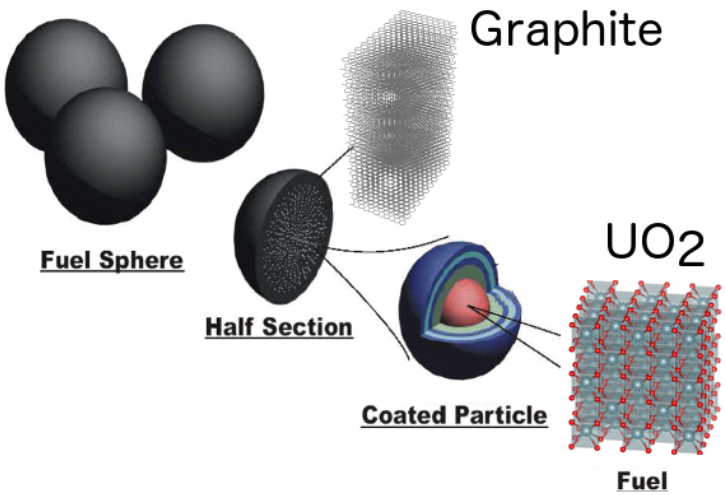
Predicting thermal properties in nuclear materials

- Evolution of defects in nuclear graphite while in service as a direct result of radiation
- In materials which undergo fission (e.g. UO2), isotopic byproducts affect heat transfer at a microscopic level



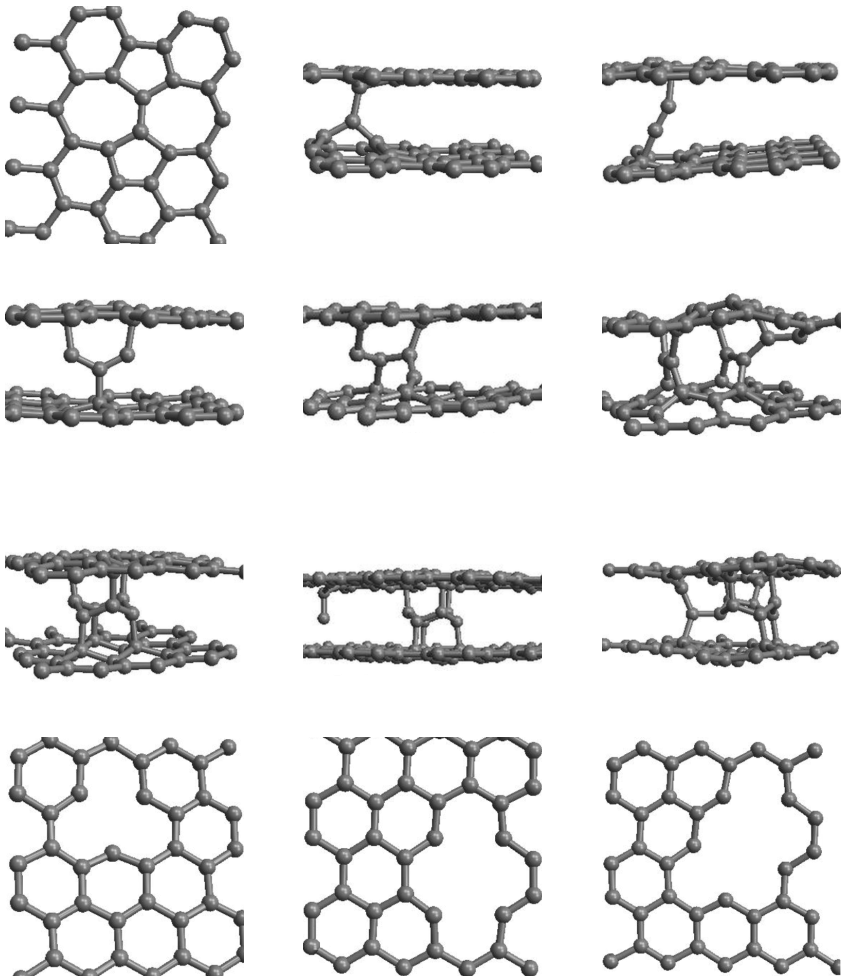
(Fuel sphere design for pebble bed reactor)

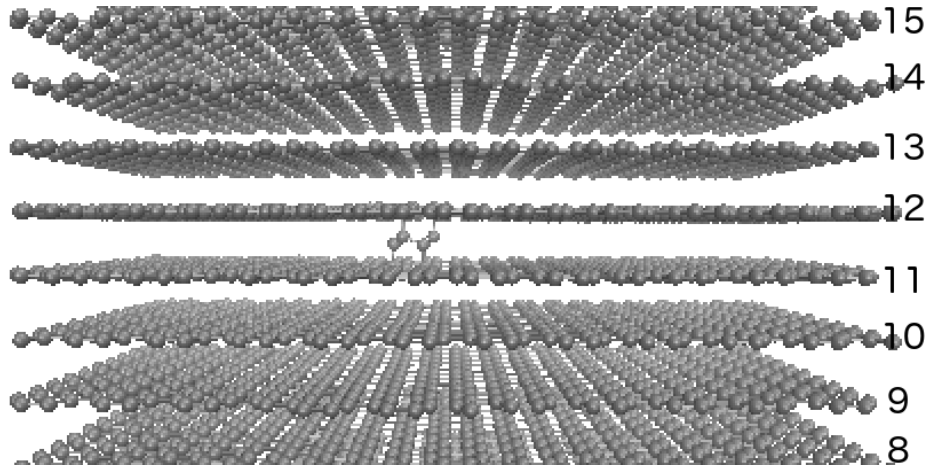
(TREAT — Transient REActor Test facility)

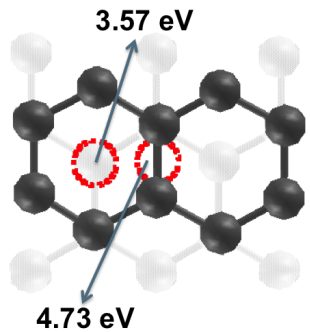
- The insight we gain can be incorporated into approaches for quantitatively predicting the lattice thermal conductivity based on solving the Boltzmann transport equation

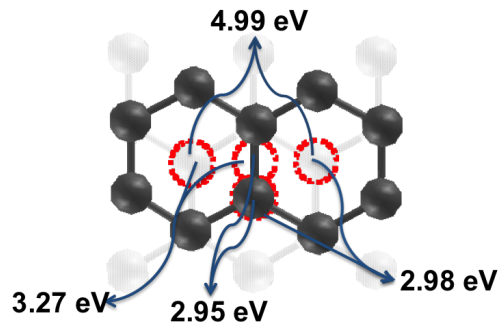
Predicting thermal properties in nuclear materials

Molecular dynamics simulations







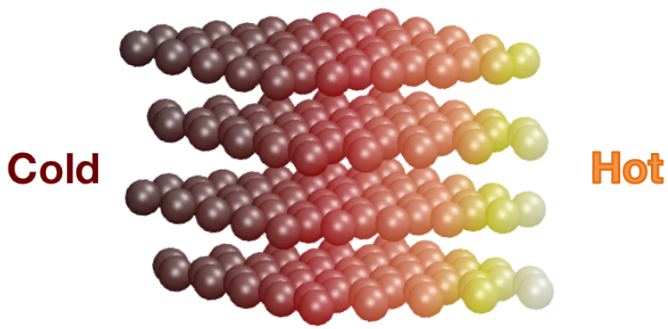


The rate of heat transfer

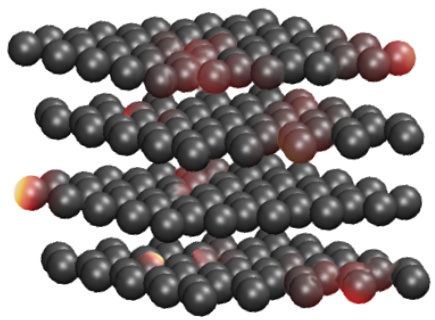
Molecular dynamics — The Green–Kubo method

$$\frac{1}{\tau} = \frac{1}{\tau_{\text{impurities}}} + \frac{1}{\tau_{\text{lattice}}} + \frac{1}{\tau_{\text{defects}}} + \cdots$$

Thermal conductivity



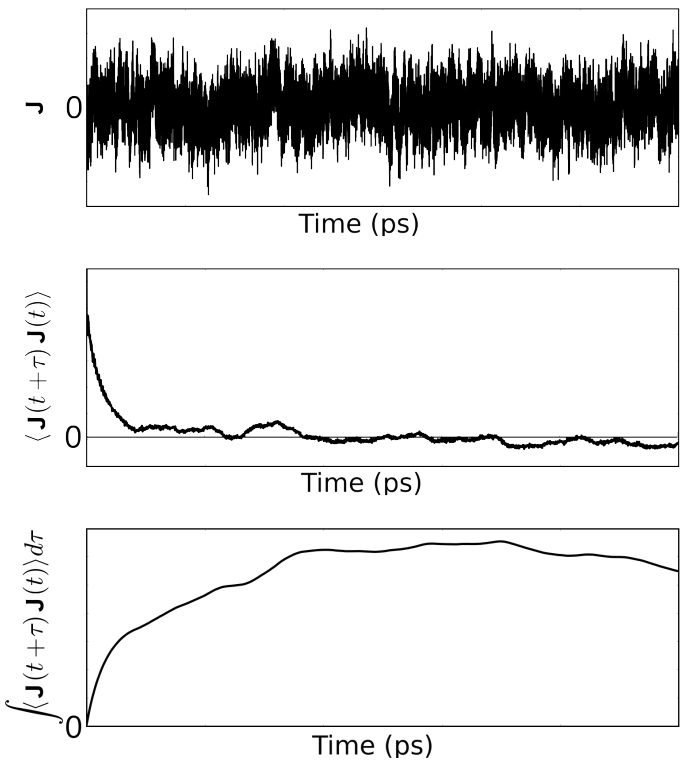
Imposed temperature gradient
or heat flux



Natural heat fluctuations
around equilibrium

The rate of heat transfer

Molecular dynamics — The Green–Kubo method



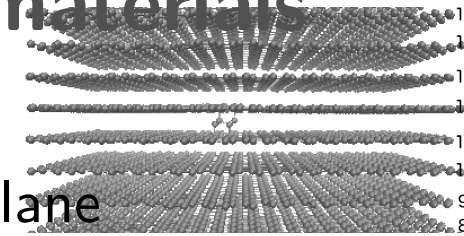
$$HCACF_{\mathbf{J}}(\tau) = \langle \mathbf{J}(t)\mathbf{J}(t+\tau)\rangle$$

$$\kappa = \frac{V}{k_B T^2}\int_0^{\infty} HCACF_{\mathbf{J}}(\tau)d\tau$$

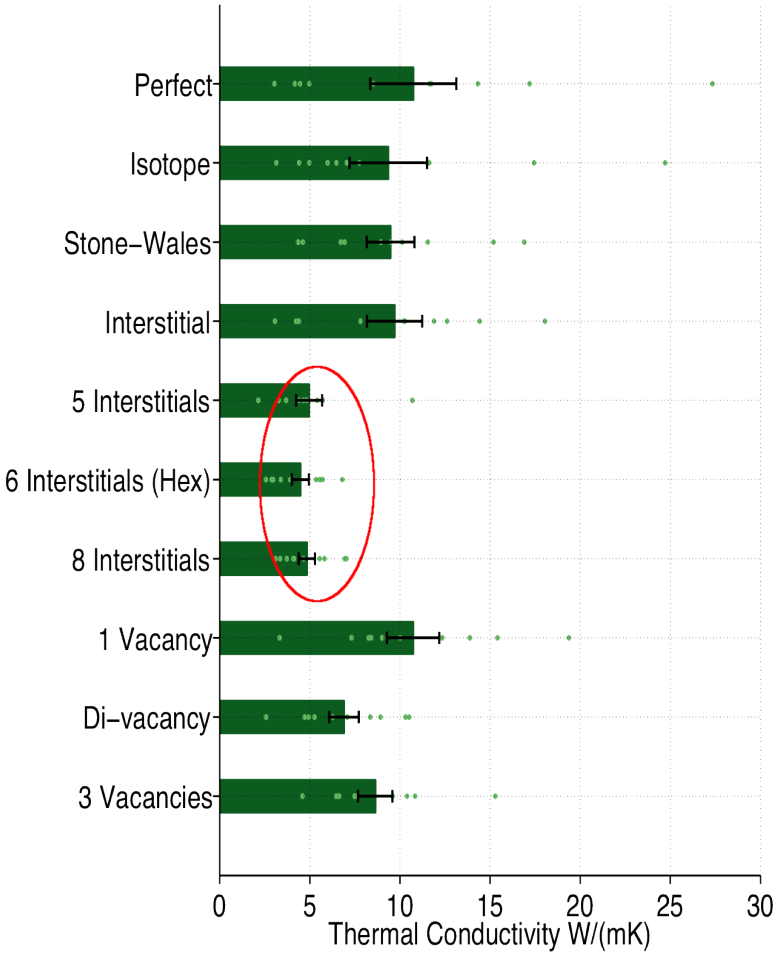
$$HCACF_{\mathbf{J}}(\tau) \approx HCACF_{\mathbf{J}_m} \equiv \sum_{n=0}^{N-m}\frac{\mathbf{J}_n\mathbf{J}_{m+n}}{N-m}$$

Predicting thermal properties in nuclear materials

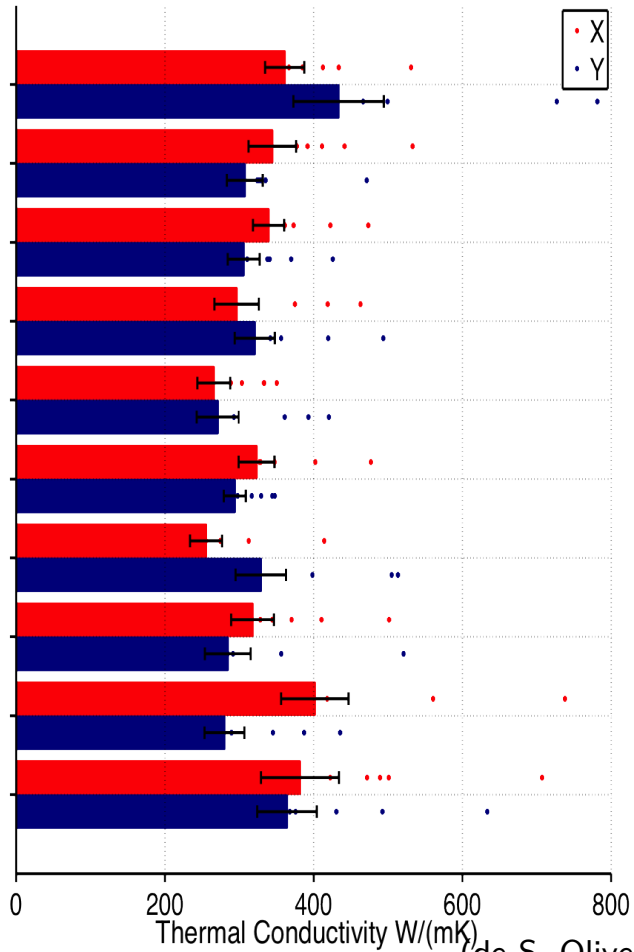
Results



Along the *c*-axis



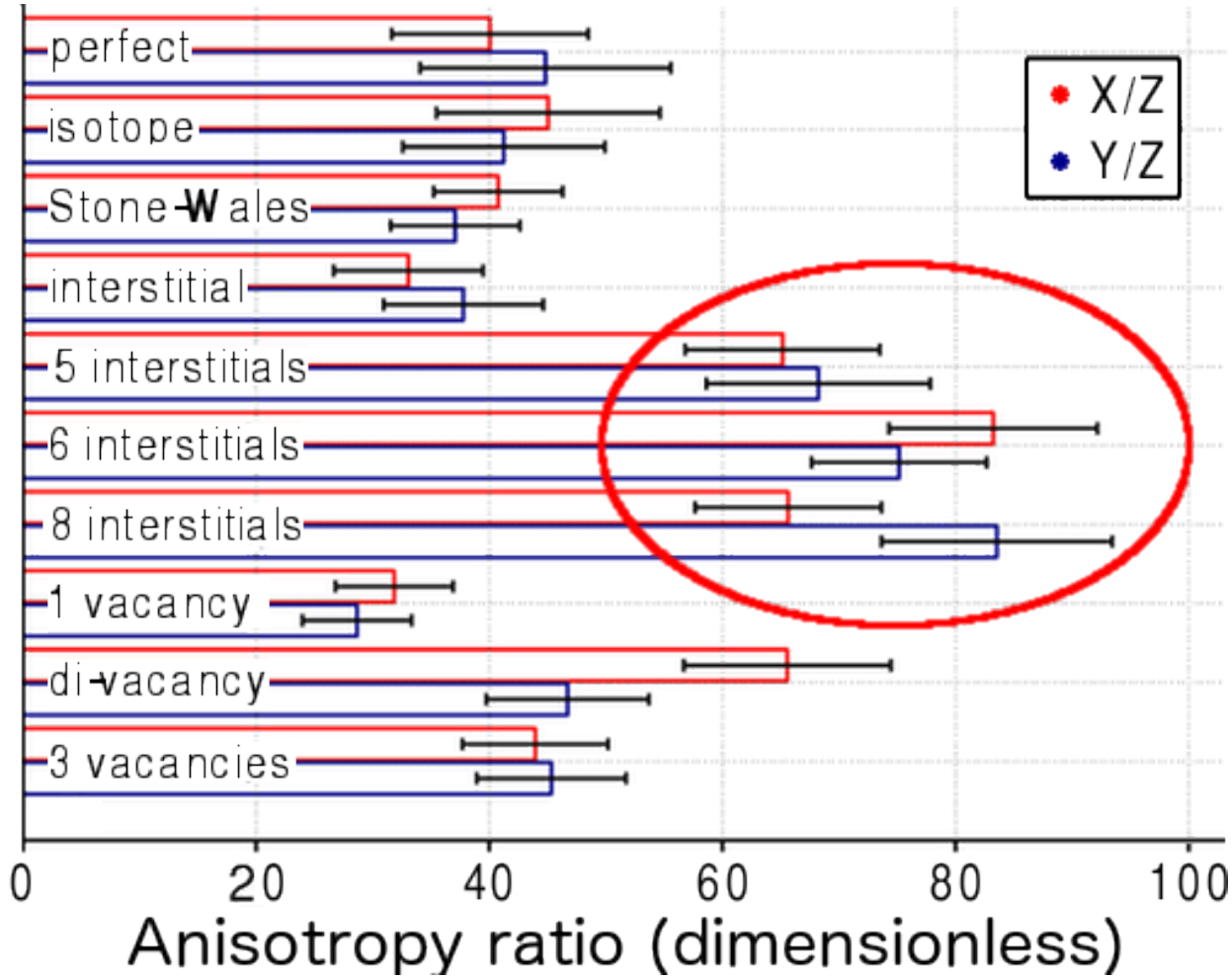
Along the basal plane



(de S. Oliveira, *et al.*, 2015)

Predicting thermal properties in nuclear materials

Results



(de S. Oliveira, *et al.*, 2015)

Predicting thermal properties in nuclear materials

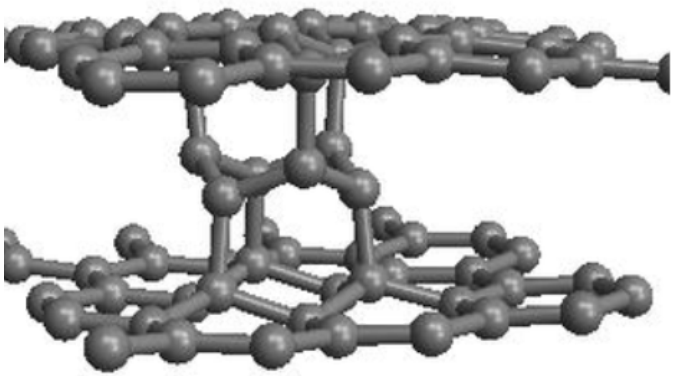
Thermal resistance along the C-axis

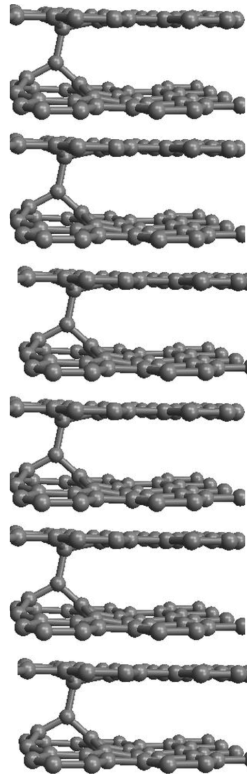
$$\frac{1}{\tau} = \frac{1}{\tau_{\text{impurities}}} + \frac{1}{\tau_{\text{lattice}}} + \frac{1}{\tau_{\text{defects}}} + \cdots$$

$$r_{\text{defective}} = r_{\text{perfect}} + r_{\text{defects}}$$

Predicting thermal properties in nuclear materials

Thermal resistance along the C-axis



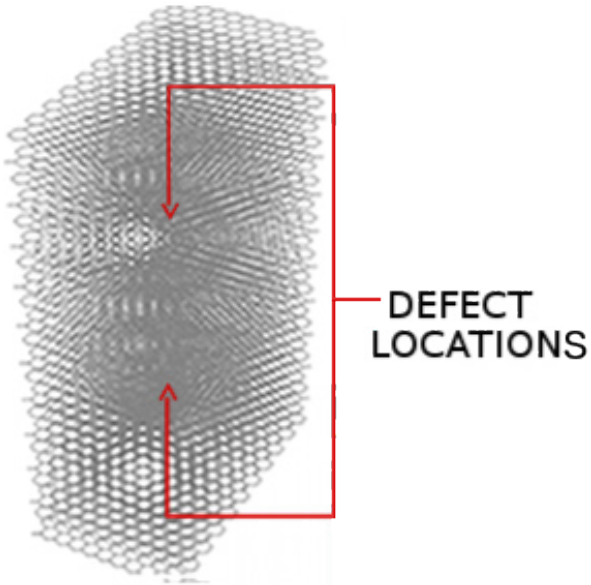


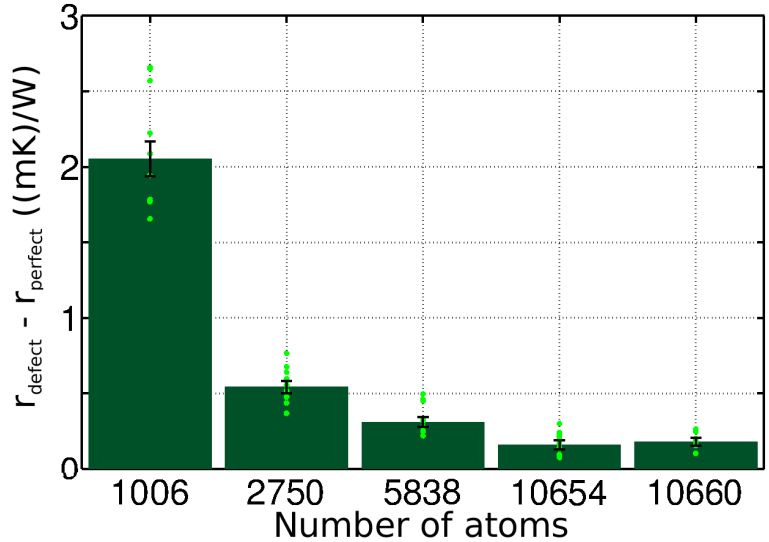
$r_{6\text{ interstitials}} = 0.16 \pm 0.03 (mK/W)$

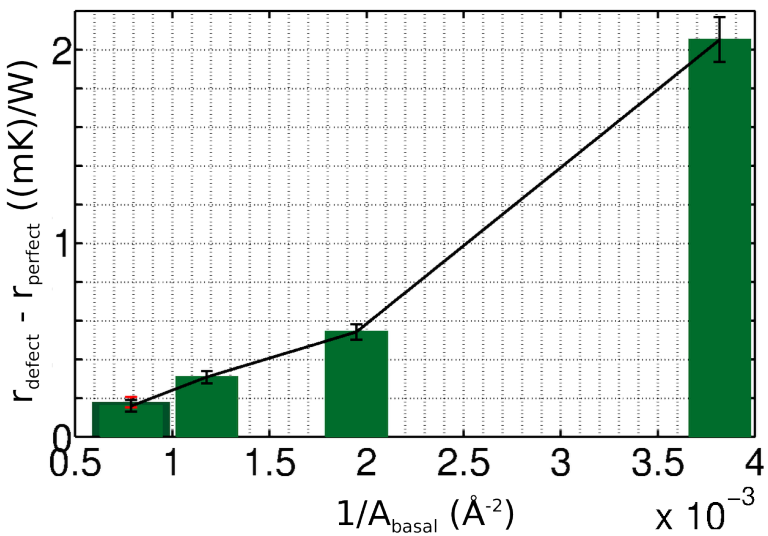
$6 \cdot r_{1\text{ interstitial}} = 0.04 \pm 0.17\ (mK/W)$

Predicting thermal properties in nuclear materials

Thermal resistance along the C-axis







Expected:

$r_{\mathrm{defective-2}} = r_{\mathrm{perfect}} + 2 \cdot r_{\mathrm{defect}}$

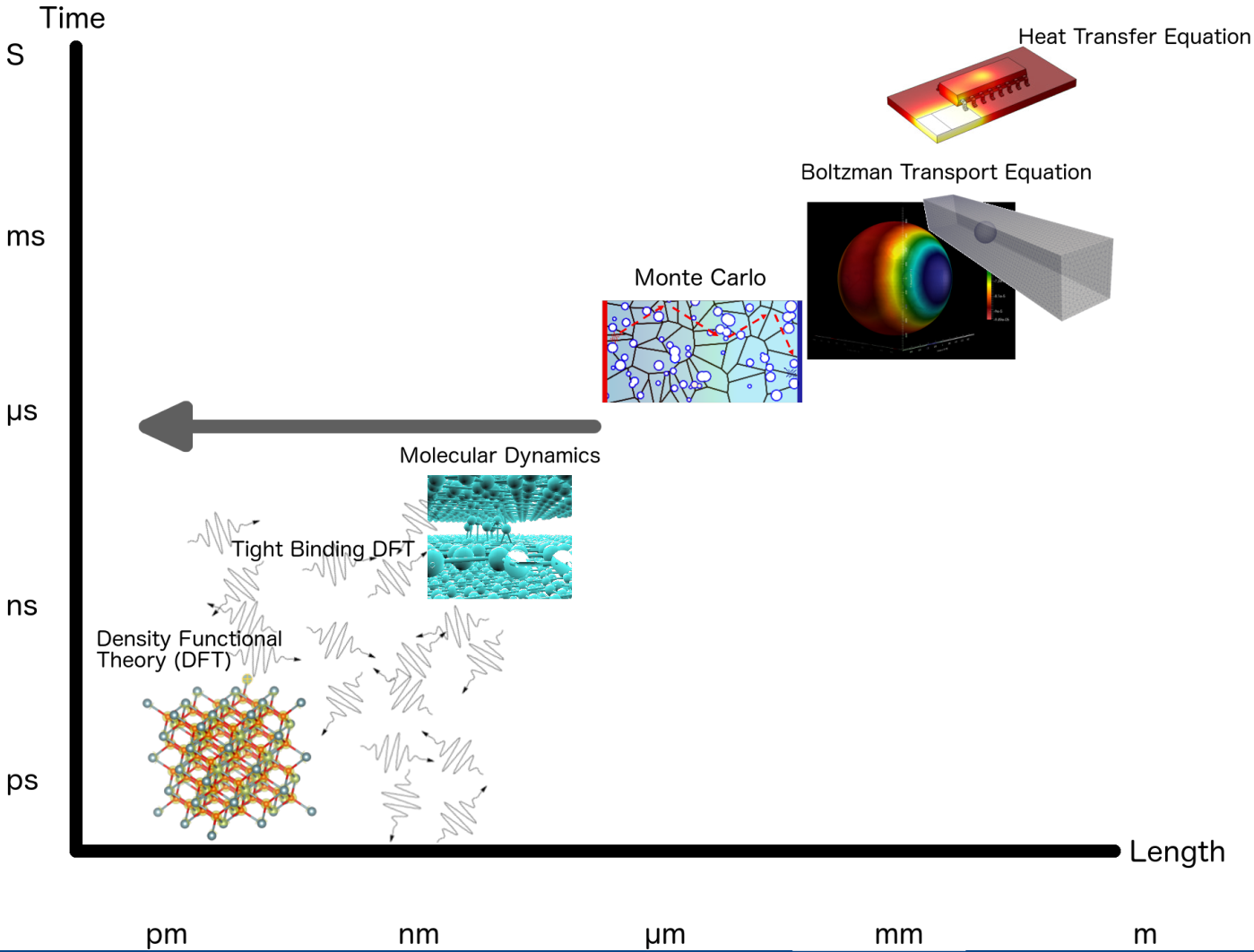
$r_{\mathrm{defective-2}} = 0.43 \pm 0.06$ (mK)/W

Actual:

0.29 ± 0.06 (mK)/W

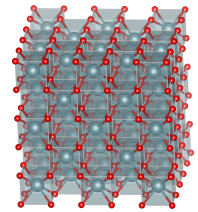
(de S. Oliveira, *et al.*, 2015)

Predicting thermal properties in nuclear materials



Predicting thermal properties in nuclear materials

Gray approximation



- Neutron transport code (Rattlesnake) modified for phonon transport

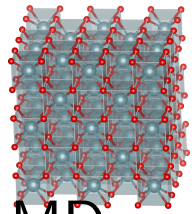
$$\Lambda\hat{\mathbf{\Omega}} \cdot \nabla \left[I(\mathbf{r}, \hat{\mathbf{\Omega}}) \right] = I^0(\mathbf{r}) - I(\mathbf{r}, \hat{\mathbf{\Omega}})$$

$$\frac{1}{4\pi} \int_{4\pi} I(\mathbf{r}, \hat{\mathbf{\Omega}}) = I^0(\mathbf{r})$$

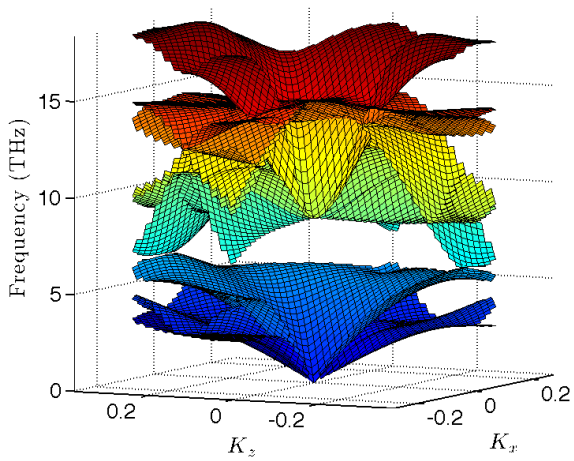
$$I^0(T, \mathbf{r}) = \frac{1}{4\pi} \sum_p \int_0^{\omega_{max}} v_g \hbar \langle n \rangle_{BE}(\omega, T) \omega D(\omega) d\omega$$

Predicting thermal properties in nuclear materials

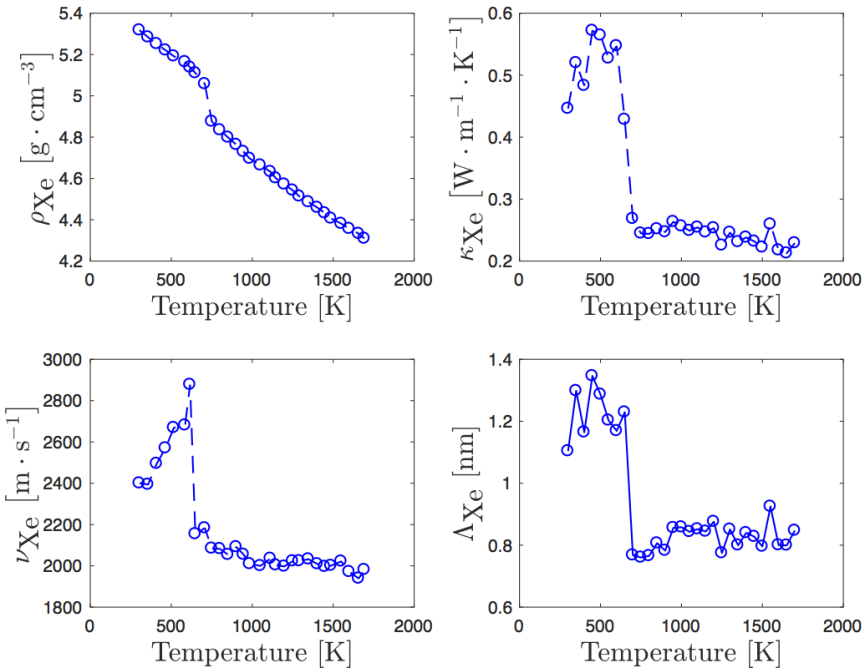
Informing the Boltzmann Transport equation



UO_2 2-D phonon dispersion



Xenon properties from MD

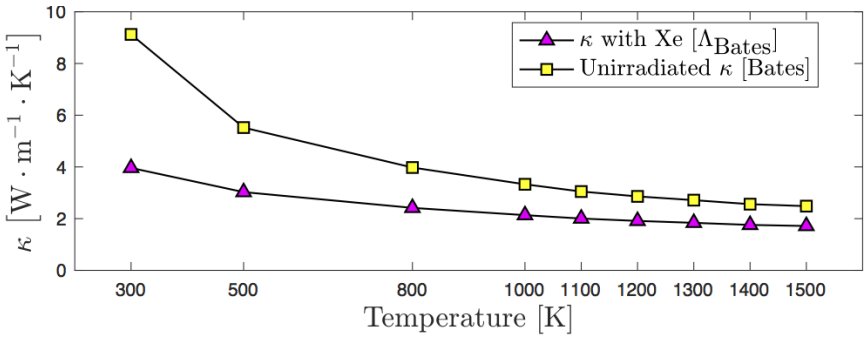


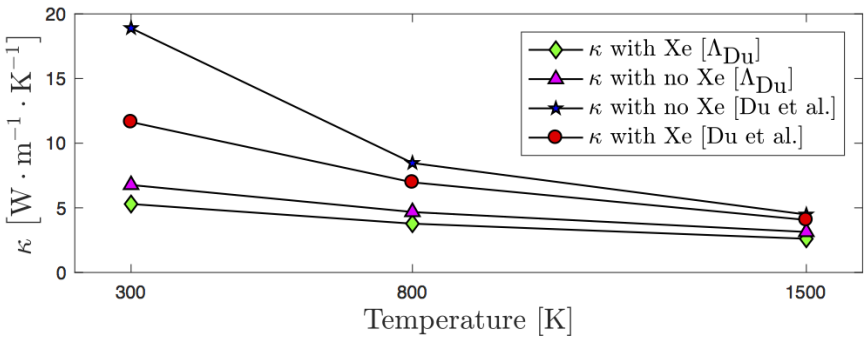
(Harter, *et al.*, 2015)

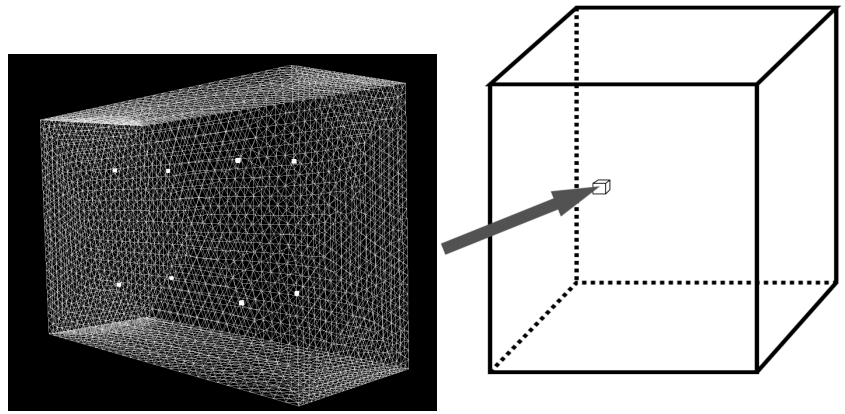
$$I^0(T, \mathbf{r}) = \frac{1}{4\pi} \sum_p \int_0^{\omega_{max}} v_g \hbar \langle n \rangle_{BE}(\omega, T) \omega D(\omega) d\omega$$

Predicting thermal properties in nuclear materials

Informing the Boltzmann Transport equation







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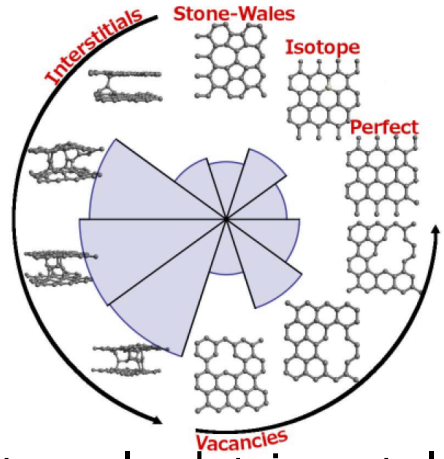
(Harter, *et al.*, 2015)

Predicting thermal properties in nuclear materials

Conclusions



- Tease apart κ from defects
- Not all defects are created equal:
  - Clustered interstitial defects are stable and strongly detrimental to thermal transport along the *c*-axis
  - Thermal resistance of platelets is approximately 4 times larger than their constituent number of interstitials long the *c*-axis
- Xenon lowers thermal conductivity at a constant ratio with temperature change
- Developed an efficient and versatile method for predicting phonon transport that can be informed by atomistic simulations

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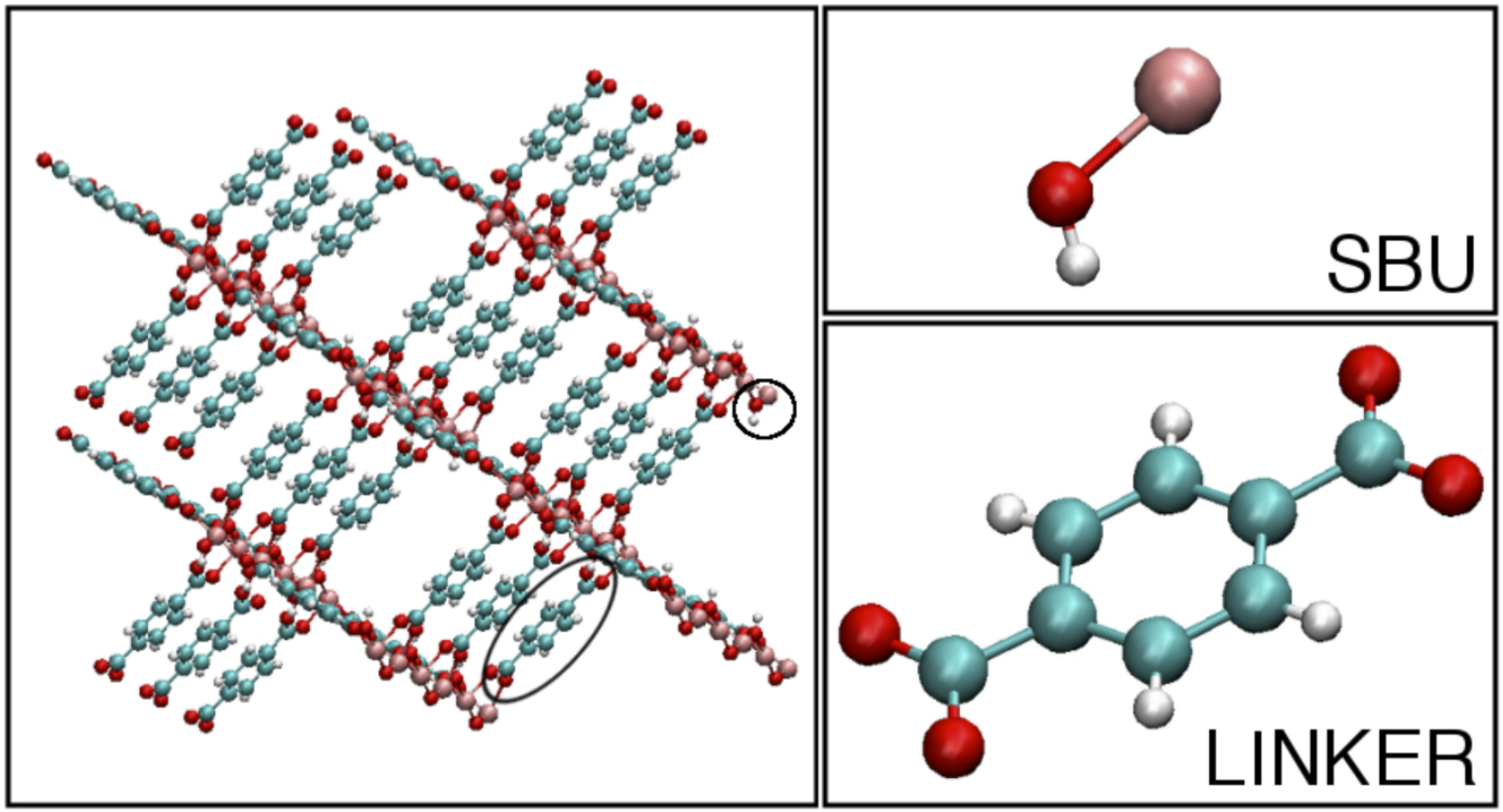
Switchable thermal conductivity in the breathing metal-organic framework MIL-53

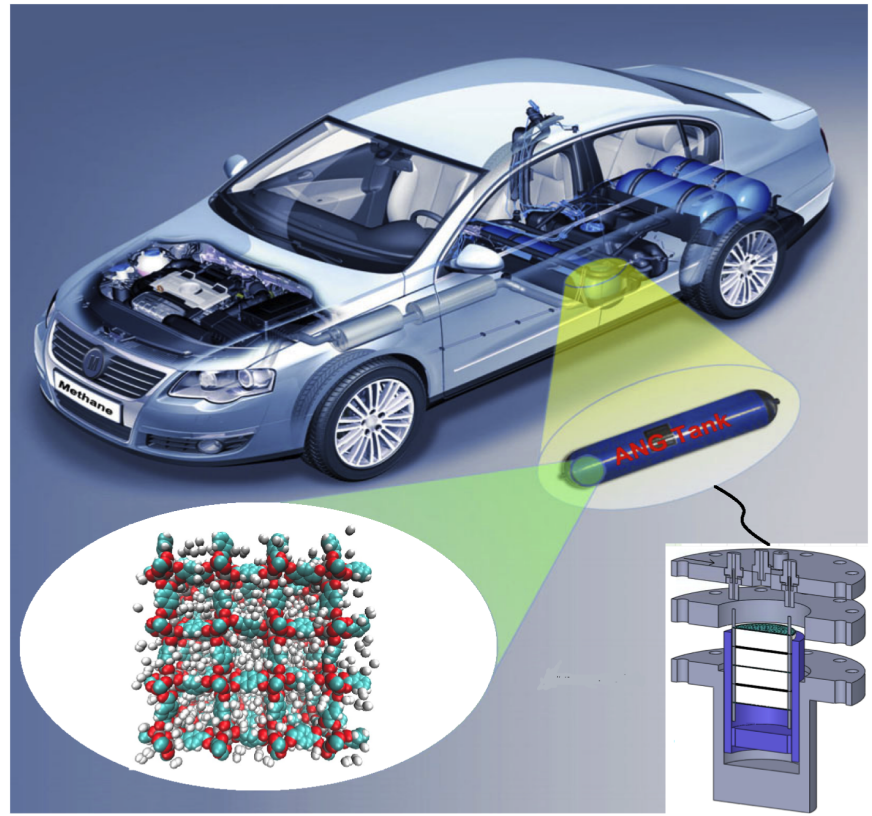
Metal–organic frameworks



Switchable thermal conductivity in the breathing metal-organic framework MIL-53

Heat transfer in metal–organic frameworks

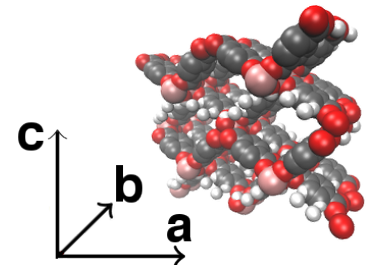
- Large surface area convenient for gas sorption applications
- Poor thermal conductivity
- Heat dissipation for sorption applications

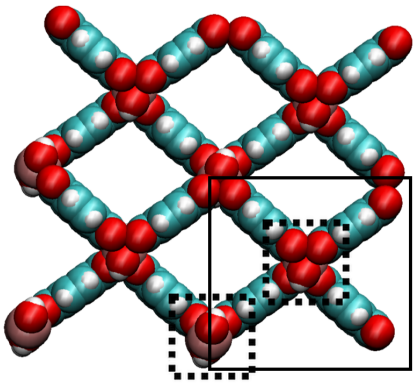


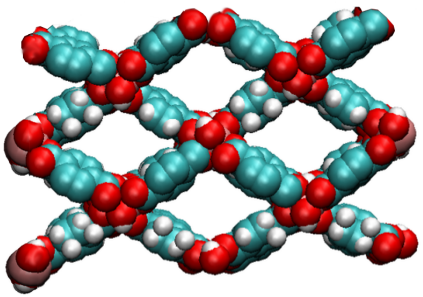
A MOF-5 based H_2 adsorption tank developed at Oregon State University

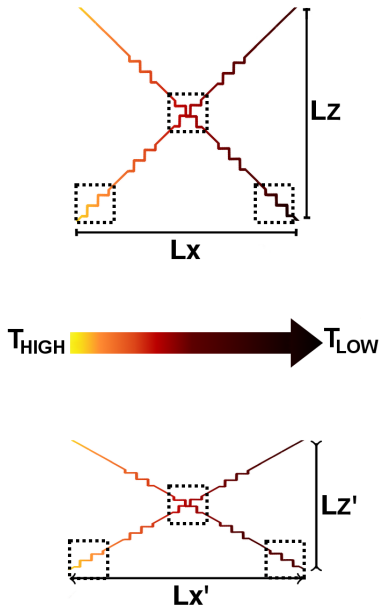
Switchable thermal conductivity in the breathing metal-organic framework MIL-53

Simple κ model









$$J_{xx} = -\frac{2C_{\text{linker}}\Delta T}{L_y L_z}$$
$$= -2C_{linker}\frac{L_x}{L_y L_z}\frac{\partial T}{\partial x}$$
$$= -\kappa_{xx}\frac{\partial T}{\partial x}$$

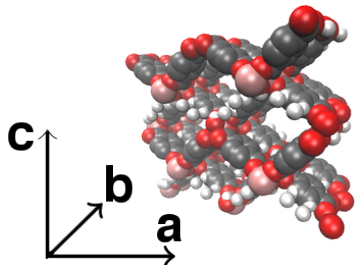
Then:

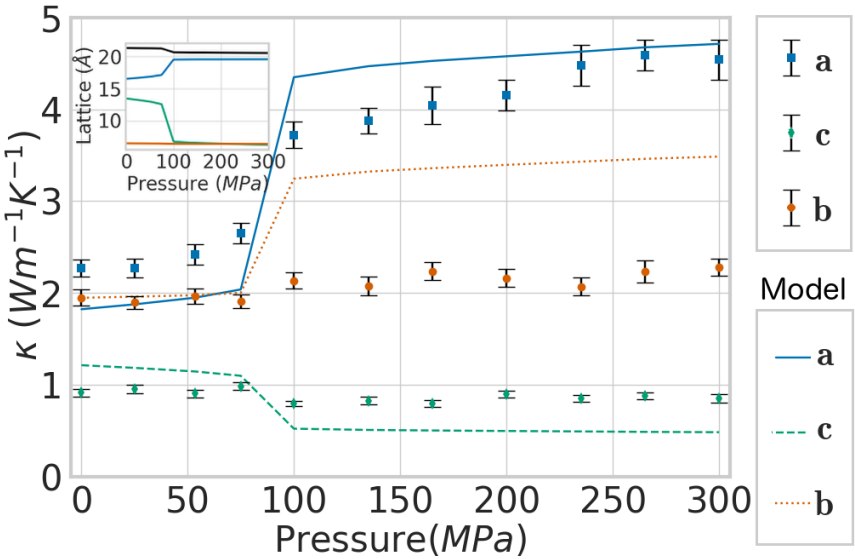
$$\dot{Q} = -2C_{\text{linker}}\Delta T,\ C_{\text{linker}} = \frac{1}{2(R_N + R_L)}$$

$$\kappa = 2C_{\text{linker}}\begin{pmatrix} \frac{L_x}{L_y L_z} & 0 & 0 \\ 0 & \frac{C_{\text{chain}}}{C_{\text{linker}}}\frac{L_y}{L_x L_z} & 0 \\ 0 & 0 & \frac{L_z}{L_x L_y} \end{pmatrix}$$

MIL-53

Simple κ model — MD calculations





(Data: Luping Han)

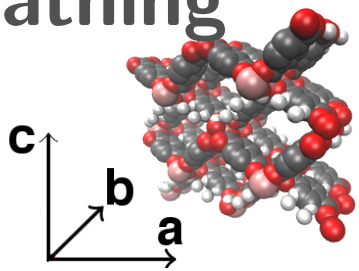
$$\kappa = 2C_{\text{linker}} \begin{pmatrix} \frac{L_x}{L_y L_z} & 0 & 0 \\ 0 & \frac{C_{\text{chain}}}{C_{\text{linker}}} \frac{L_y}{L_x L_z} & 0 \\ 0 & 0 & \frac{L_z}{L_x L_y} \end{pmatrix}$$

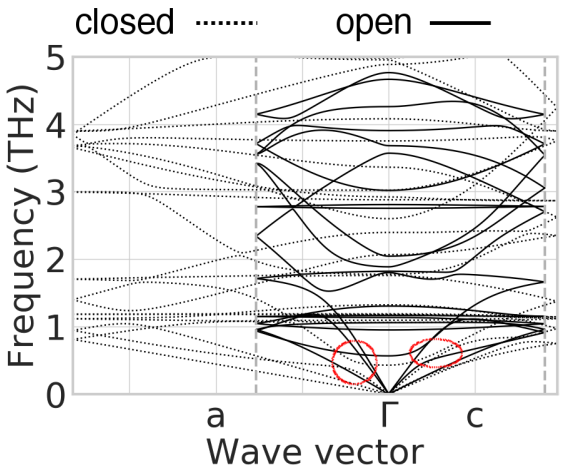
$R_n + R_l = 0.083$ K/W (along a)
and 0.138 K/W (along c)

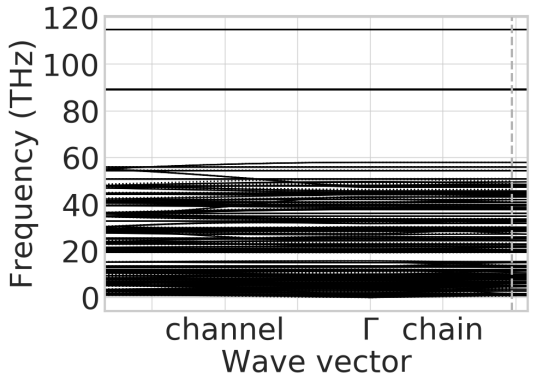
$R_N = 0.015\ K/W$

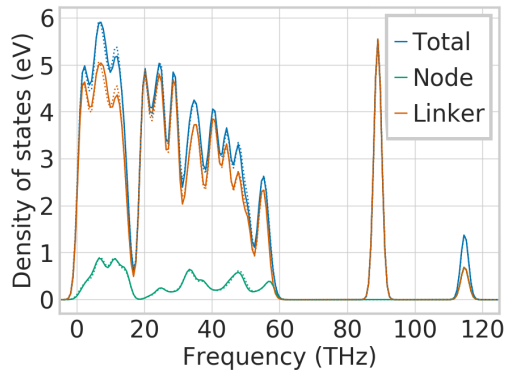
Switchable thermal conductivity in the breathing metal-organic framework MIL-53

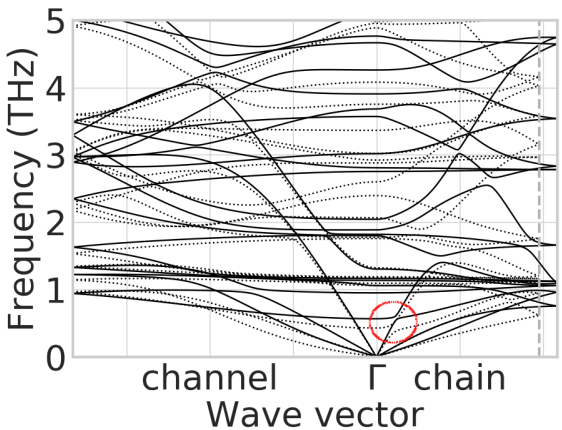
Ab initio calculations — dispersion relations



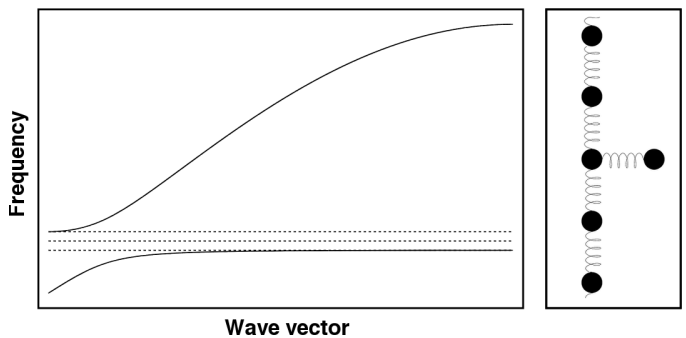








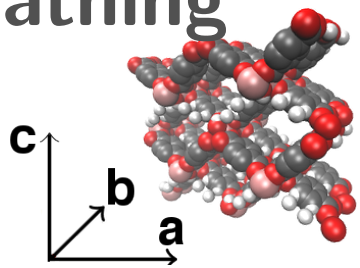
Rattler Model

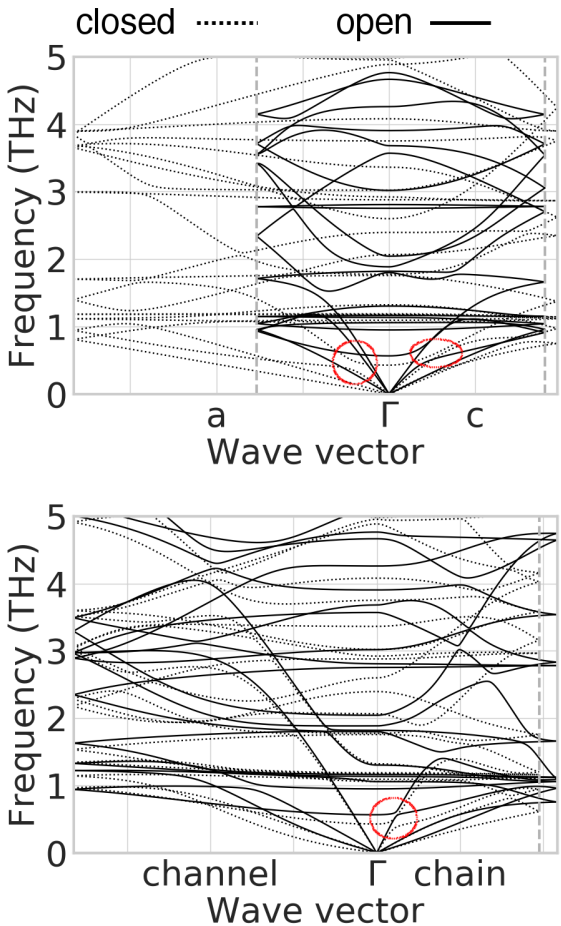


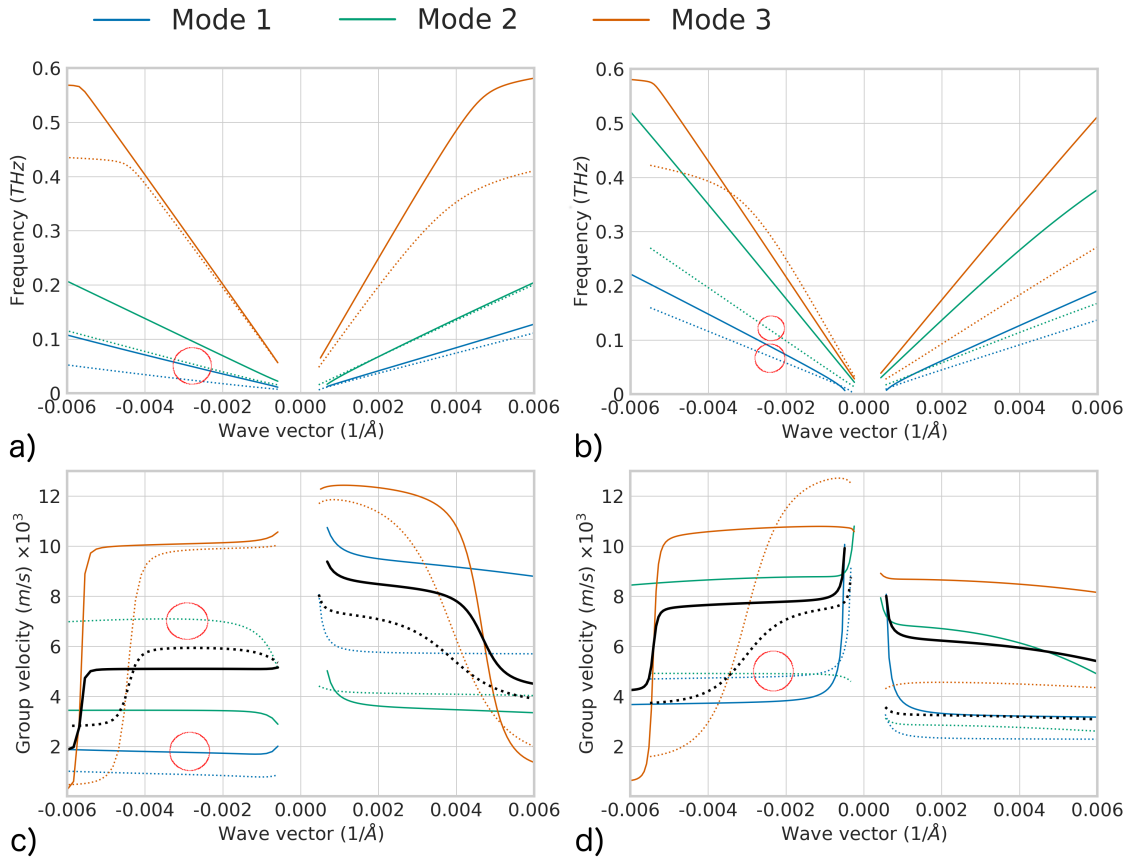
(Credit: Agnieszka Truszkowska)

Switchable thermal conductivity in the breathing metal-organic framework MIL-53

Ab initio calculations — dispersion relations

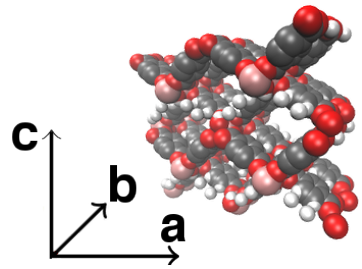






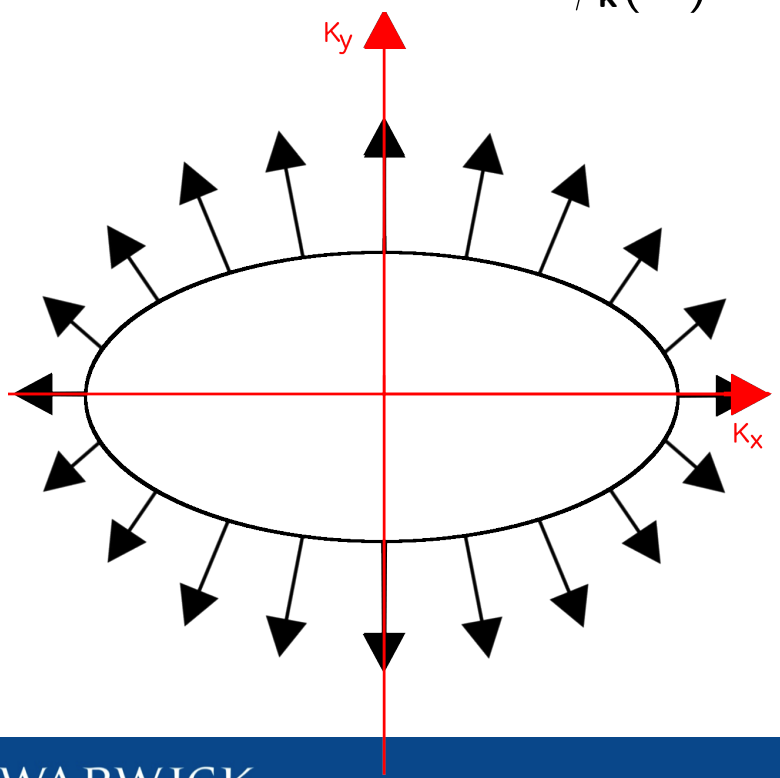
Switchable thermal conductivity in the breathing metal-organic framework MIL-53

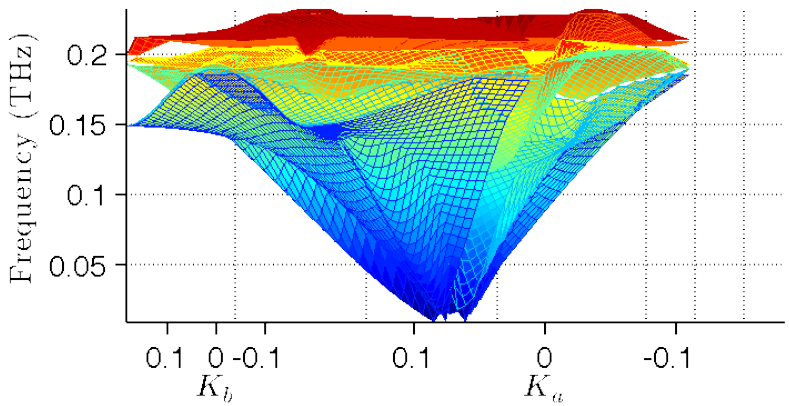
"Radiant flux"



$$\phi(\mathbf{k},\omega,T) \propto |\mathbf{v}_g(\mathbf{k},\omega)|\hbar\omega(\mathbf{k})D(\mathbf{k},\omega)\langle n\rangle_{BE}(\omega,T)$$

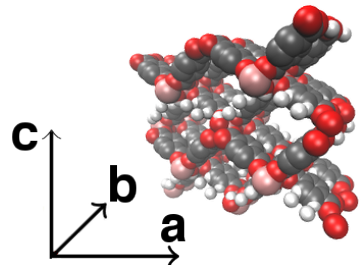
$$\phi_{\mathbf{k}}(T) = \sum_{m=\nu}^{3N} \phi_m(\mathbf{k},T)$$





Switchable thermal conductivity in the breathing metal-organic framework MIL-53

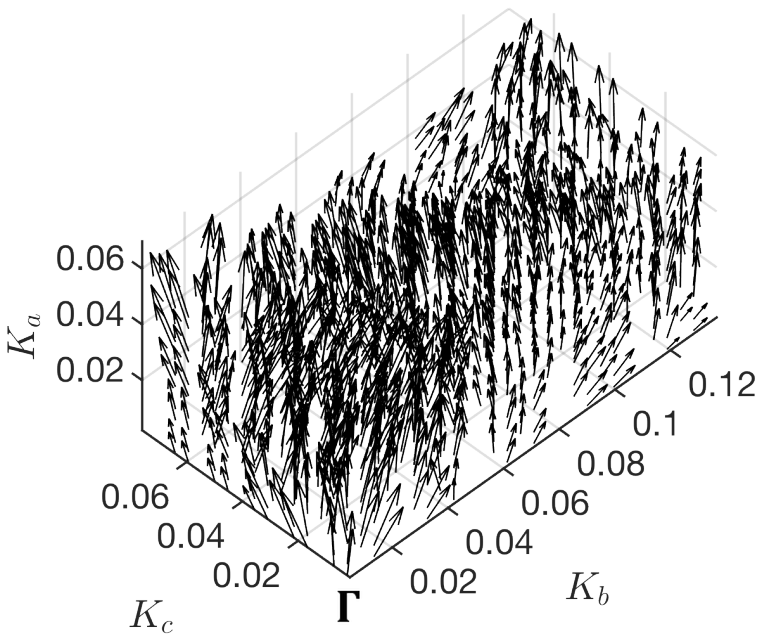
"Radiant flux"



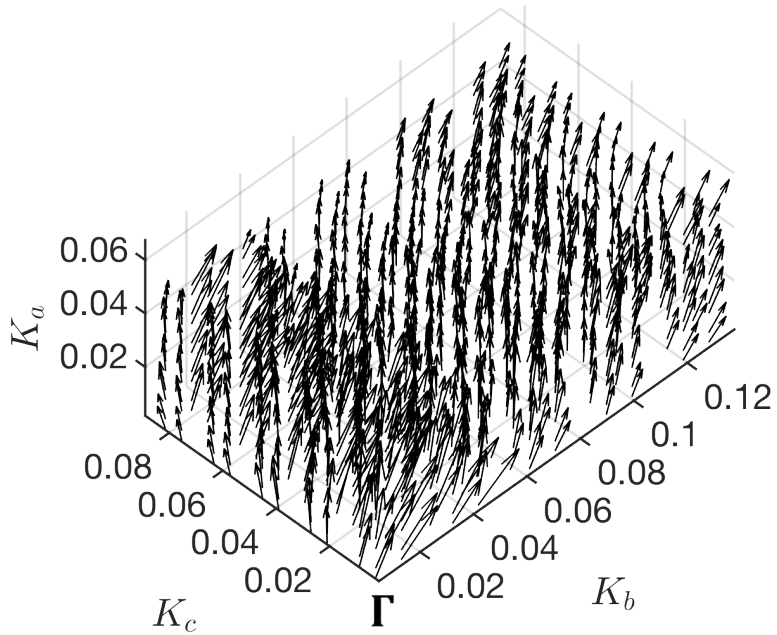
$$\phi(\mathbf{k},\omega,T) \propto |\mathbf{v}_g(\mathbf{k},\omega)|\hbar\omega(\mathbf{k})D(\mathbf{k},\omega)\langle n\rangle_{BE}(\omega,T)$$

$$\phi_{\mathbf{k}}(T) = \sum_{m=\nu}^{3N} \phi_m(\mathbf{k},T)$$

open-pore

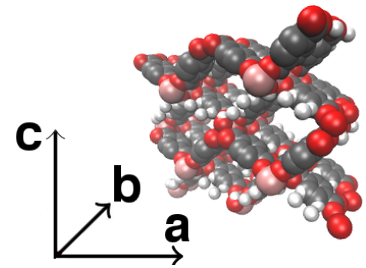


closed-pore



Switchable thermal conductivity in the breathing metal-organic framework MIL-53

Conclusions



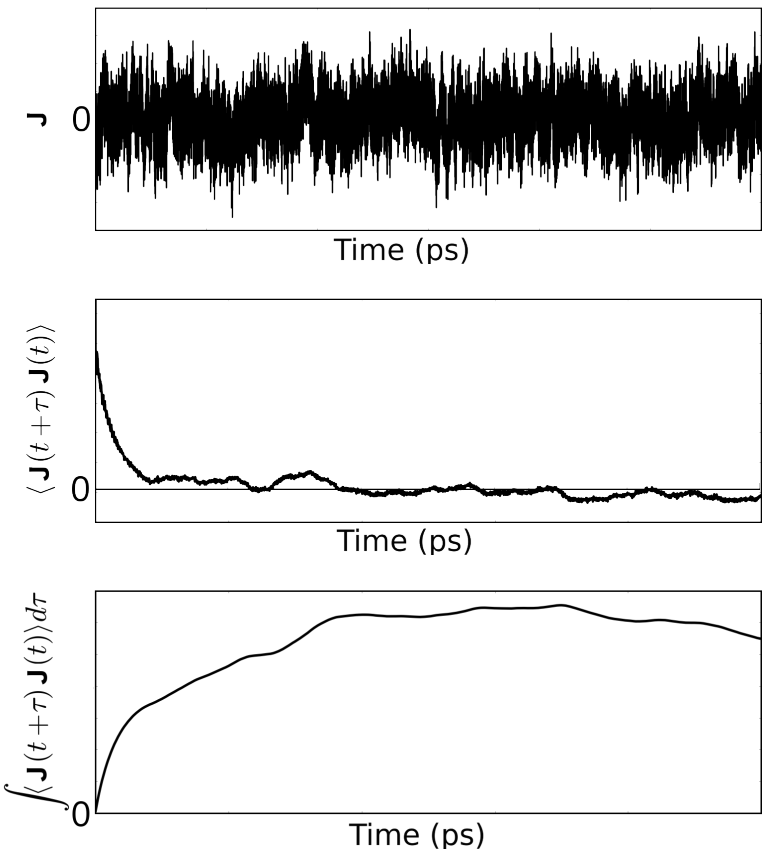
- A first look at κ in MIL-53
- Switchable κ conductivity
- Observed rattler modes
- Phonon focusing effects

Outline

- ☑ Why thermal transport?
- ☑ Why atomistic-scale simulations?
- ☑ Predicting thermal transport in nuclear materials
- ☑ Switchable thermal conductivity in metal–organic frameworks
- ☐ Uncertainty quantification in the Green–Kubo method

Green–Kubo method

The equilibrium molecular dynamics approach



$$HCACF_{\mathbf{J}}(\tau) = \langle \mathbf{J}(t)\mathbf{J}(t+\tau)\rangle$$

$$\kappa = \frac{V}{k_B T^2}\int_0^{\infty} HCACF_{\mathbf{J}}(\tau)d\tau$$

$$HCACF_{\mathbf{J}}(\tau) \approx HCACF_{\mathbf{J}_m} \equiv \sum_{n=0}^{N-m}\frac{\mathbf{J}_n\mathbf{J}_{m+n}}{N-m}$$

Green–Kubo method

Applications of the Green–Kubo

- Thermal conductivity

$$\kappa_{xx} = \frac{V}{k_B T^2} \int_0^\infty \langle \mathbf{J}_{xx}(t)\mathbf{J}_{xx}(t+\tau)\rangle \; d\tau$$

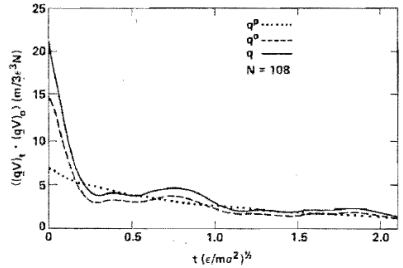


FIG. 1. Heat flux autocorrelation functions of q, q^o, and q^p for $N = 108$ and $T = 0.546\epsilon/k_B$. Only the initial portions of the correlation functions are shown.

(Ladd, Moran & Hoover, 1986)

- Diffusivity

$$D_{xx} = \int_0^\infty \langle \mathbf{v}_{xx}(t)\mathbf{v}_{xx}(t+\tau)\rangle \, d\tau$$

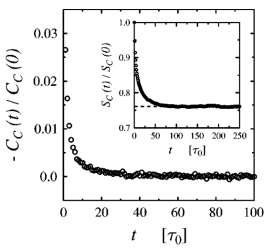


FIG. 1. The correlation function $C_C(t)$ in a lattice-gas model of the O/W(110) system at $\theta = 0.45$ and $T = 0.833T_c$. The time interval $\tau_0 = 1$ MCS. The vertical scale has been expanded to show the decay. The convergence of $D_{\text{c.m.}}$ via $S_C(t) = C_C(0) + 2\sum_{k=1}^{k_{\max}} C_C(k\tau_0)$ with $t = k_{\max}\tau_0$ is shown in the inset. The asymptotic value of $S_C(t)$, as determined by the Kubo-Green method at long times [Eq. (2)], is denoted by a dashed line.

(Ying *et al.*, 1998)

- Viscosity

$$\eta_{xy} = \frac{V}{k_B T} \int_0^\infty \langle \mathbf{P}_{xy}(t)\mathbf{P}_{xy}(t+\tau)\rangle \, d\tau$$

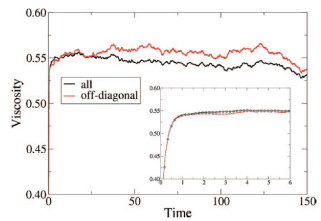


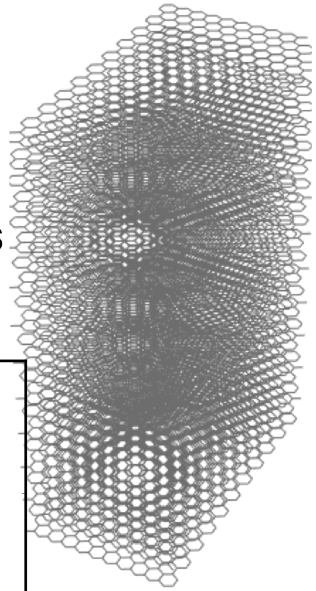
FIG. 1. The viscosity as a function of maximum time taken in the integration of Eq. (1) for the LJ fluid. The viscosity reaches a plateau for an integration time longer than the correlation length. At longer times, the statistical error in the correlation functions causes the deviation from the plateau value. The inset shows the short-time behavior where lines and symbols are results based on the GK formula and the Einstein relation, respectively.

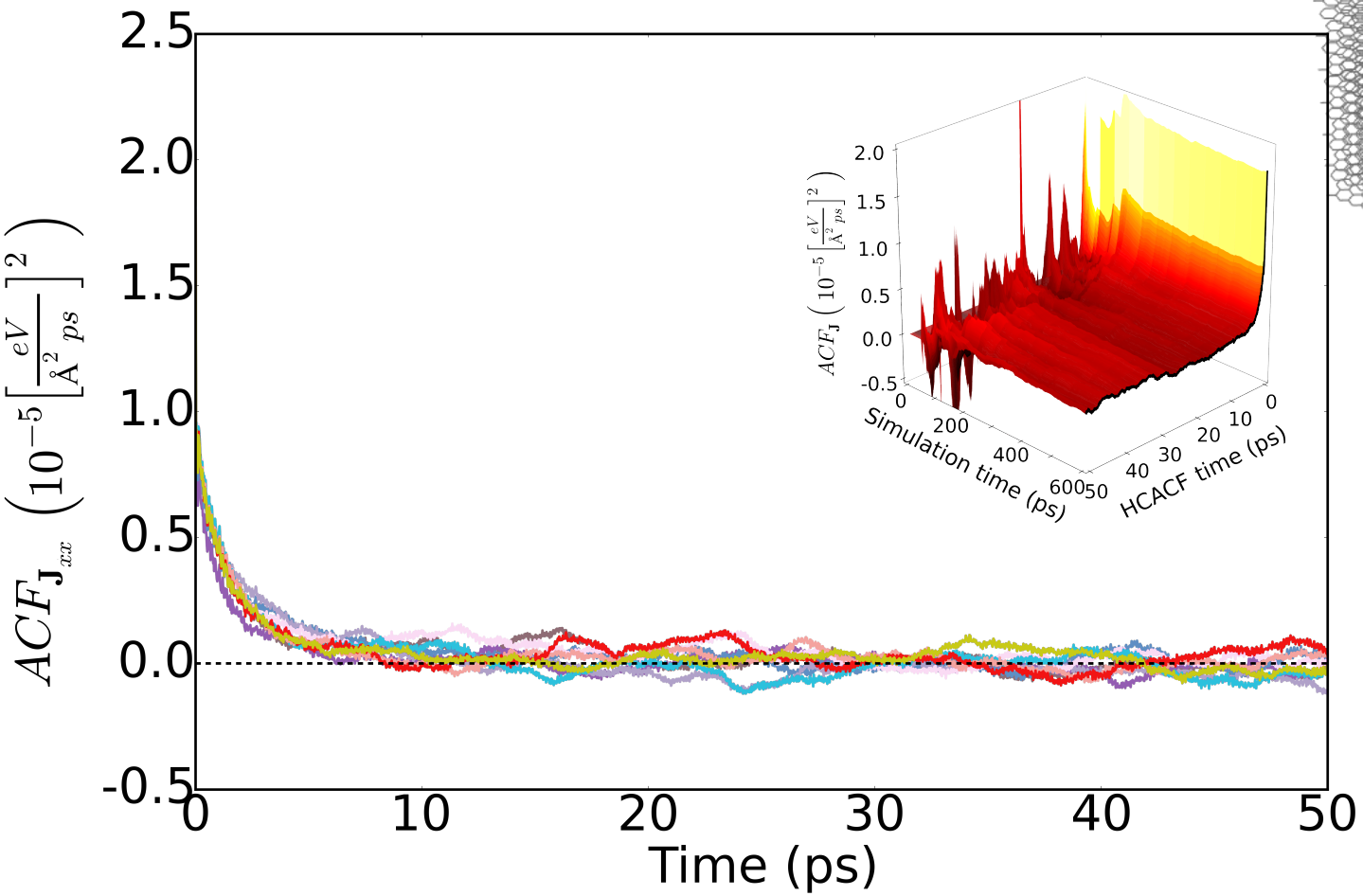
(Chen, Smit & Bell, 2009)

Green–Kubo method

The heat current autocorrelation function

10648 atom system
600 ps simulation, dt = 0.2 fs





(d. S. Oliveira & Greaney, 2015)

Green–Kubo method

The heat current autocorrelation function

10648 atom system
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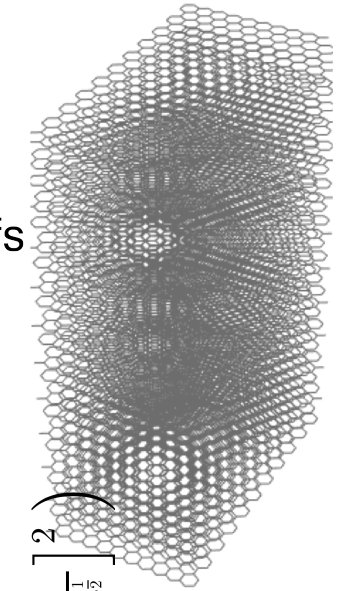
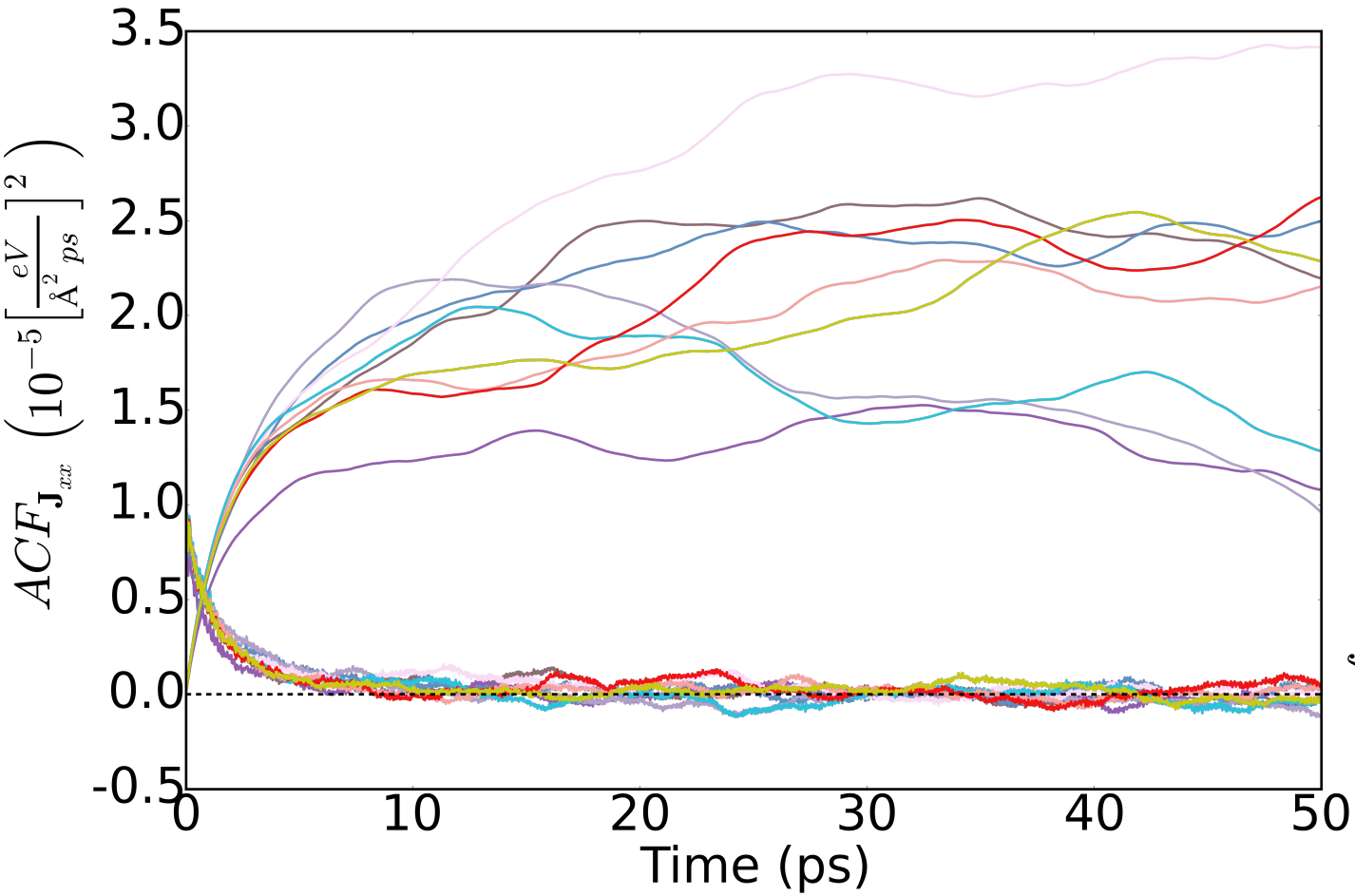




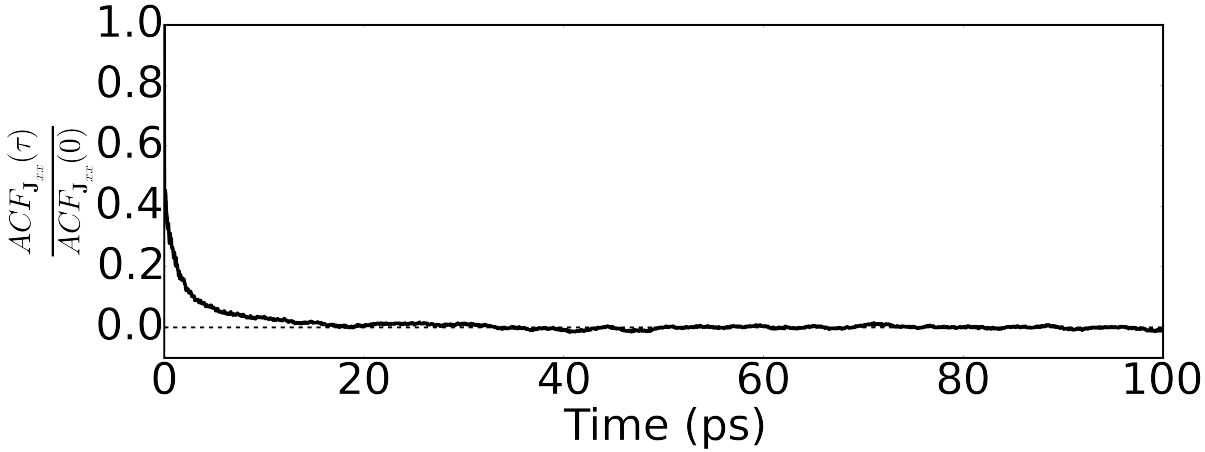
(d. S. Oliveira & Greaney, 2015)

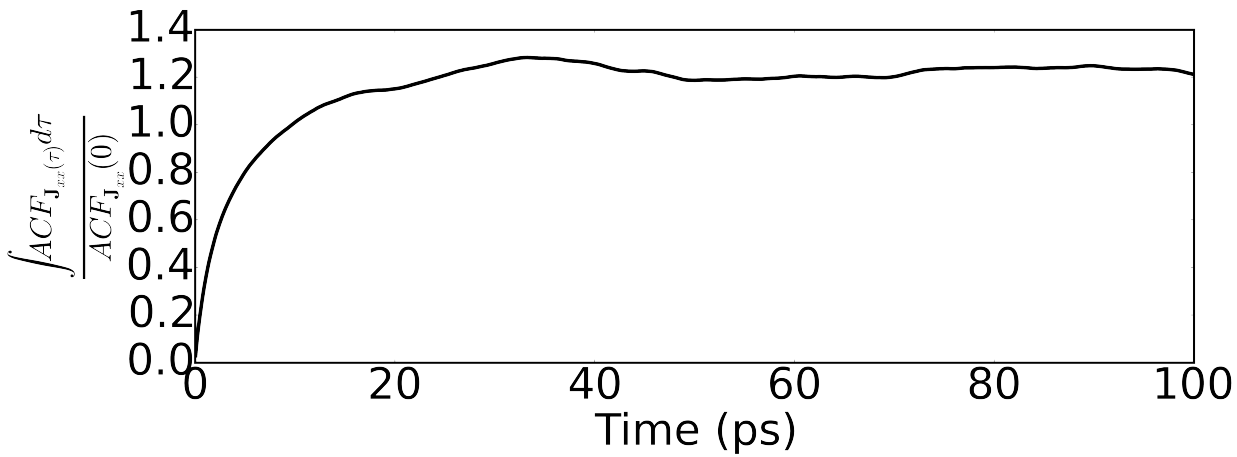
Green–Kubo method

Approaches commonly used

10648 *atom system*
8 *ns simulation*, $dt = 0.4$ *fs*

Numerical integration of data

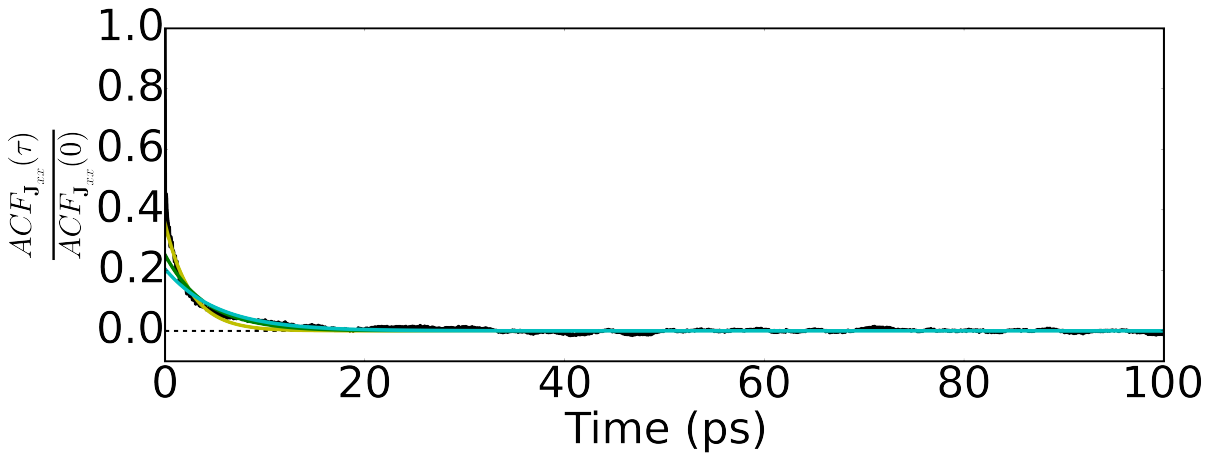


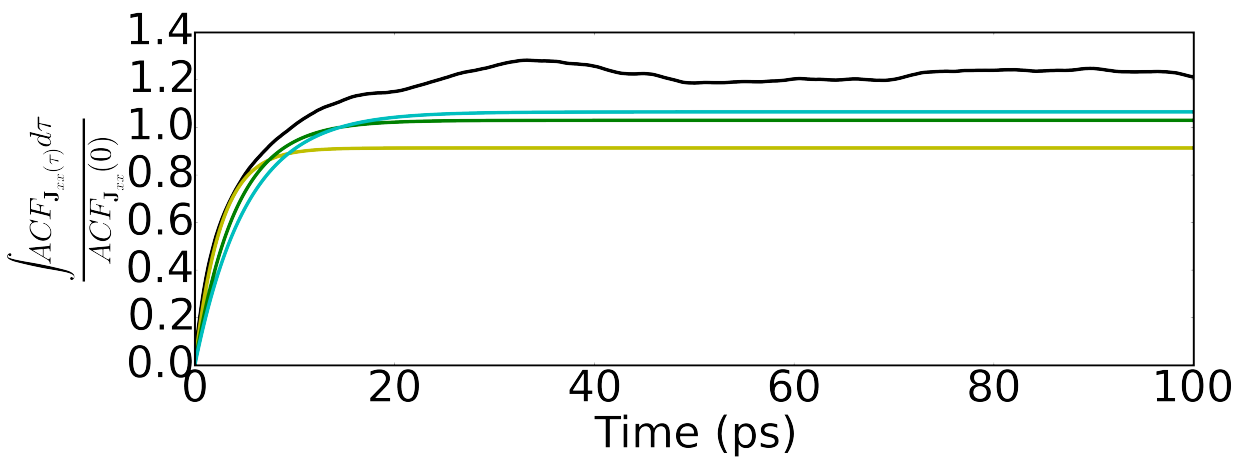


Green–Kubo method

Approaches commonly used

10648 *atom system*
8 *ns simulation*, $dt = 0.4$ *fs*

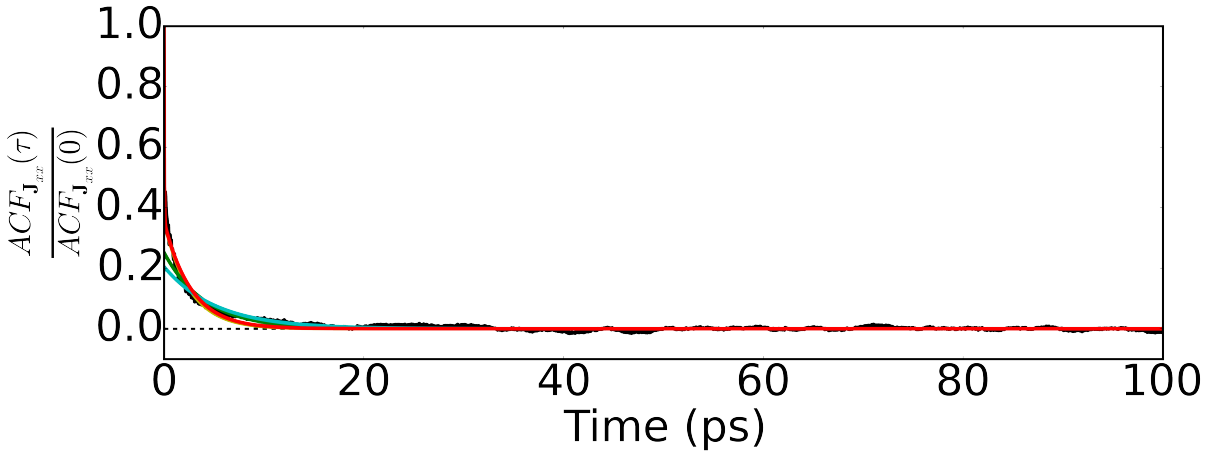


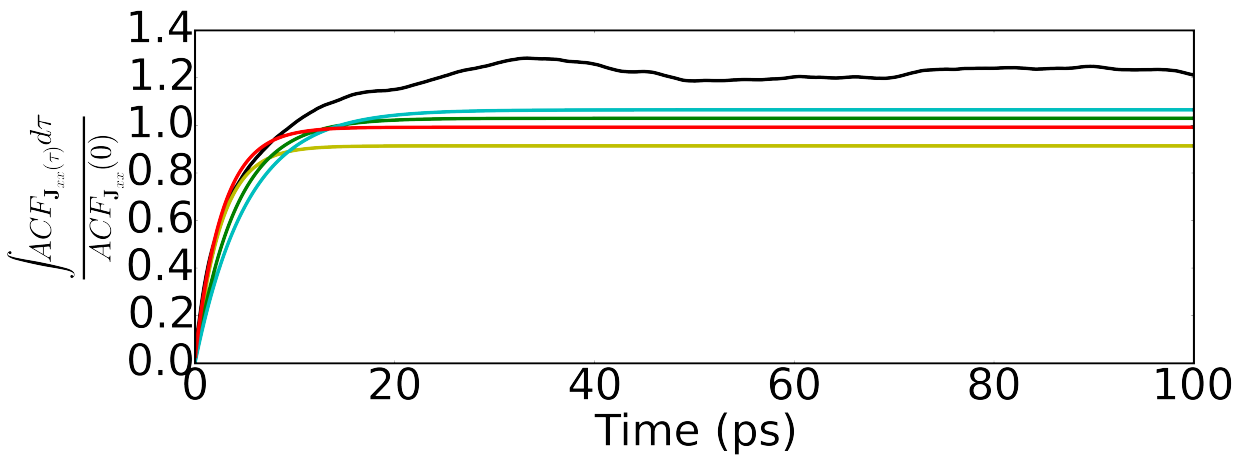


- *Numerical integration of data*
- *Fit* $a_1 e^{-\frac{\tau}{t_1}}$ *to* 5 *ps*
- *Fit* $a_1 e^{-\frac{\tau}{t_1}}$ *to* 10 *ps*
- *Fit* $a_1 e^{-\frac{\tau}{t_1}}$ *to* 15 *ps*

Green–Kubo method

Approaches commonly used



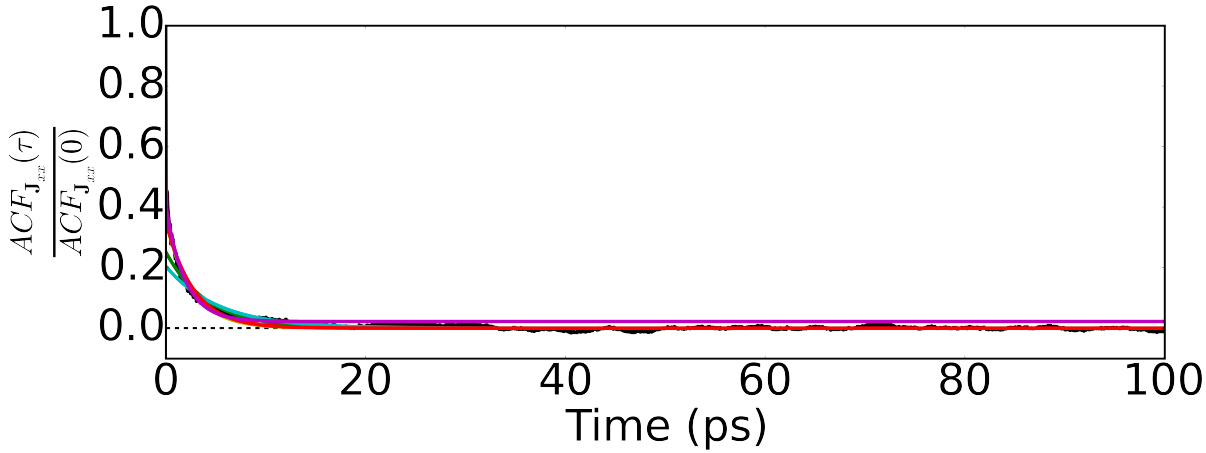


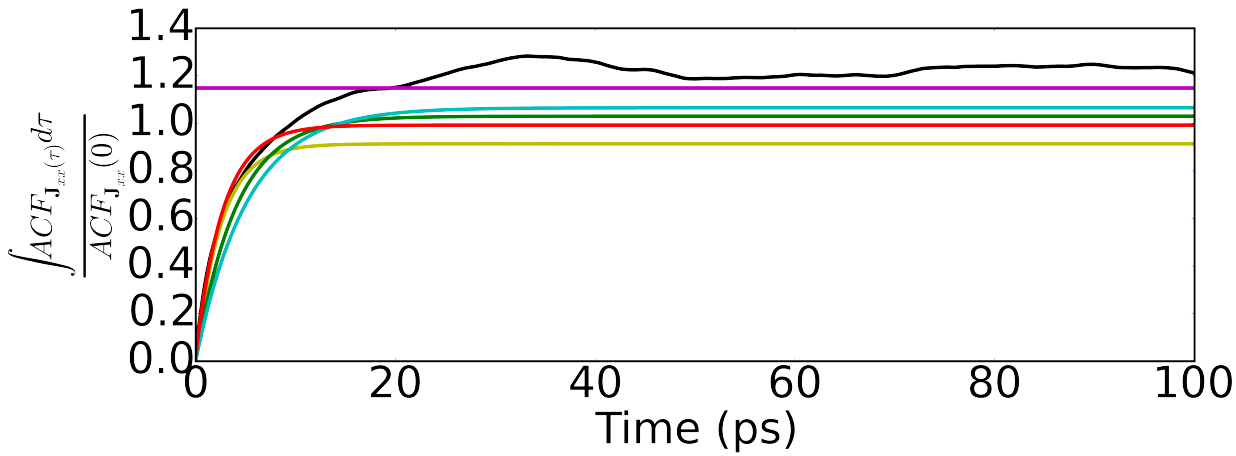
10648 *atom system*
8 *ns simulation*, $dt = 0.4$ *fs*

- *Numerical integration of data*
- *Fit* $a_1 e^{-\frac{\tau}{t_1}}$ *to* 5 *ps*
- *Fit* $a_1 e^{-\frac{\tau}{t_1}}$ *to* 10 *ps*
- *Fit* $a_1 e^{-\frac{\tau}{t_1}}$ *to* 15 *ps*
- *Fit* $a_1 e^{-\frac{\tau}{t_1}} + a_2 e^{-\frac{\tau}{t_2}}$

Green–Kubo method

Approaches commonly used





10648 *atom system*
8 *ns simulation*, $dt = 0.4$ *fs*

— *Numerical integration of data*

— *Fit* $a_1 e^{-\frac{\tau}{t_1}}$ *to* 5 *ps*

— *Fit* $a_1 e^{-\frac{\tau}{t_1}}$ *to* 10 *ps*

— *Fit* $a_1 e^{-\frac{\tau}{t_1}}$ *to* 15 *ps*

— *Fit* $a_1 e^{-\frac{\tau}{t_1}} + a_2 e^{-\frac{\tau}{t_2}}$

— *Fit* $a_1 e^{-\frac{\tau}{t_1}} + a_2 e^{-\frac{\tau}{t_2}} + a_3$

$$F(t) = \left| \frac{\sigma(ACF_{\mathbf{J}})}{E(ACF_{\mathbf{J}})} \right| \leq 1, \quad (t, t + \delta t)$$

$$\kappa_{xx} = \frac{VACF_{\mathbf{J}xx}(0)}{k_B T^2}(A_1 t_1 + A_2 t_2 + Y_0 t_c)$$

(Chen, Zhang & Li , 2010)

Green-Kubo method

Approach examples

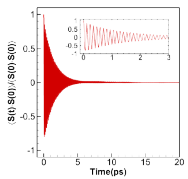


Figure 1. Green-Kubo autocorrelation function for an $8a$ x $8a$ x $8a$ slab at 500 K with a vacancy concentration of 0.0%, where a is the unit cell length.

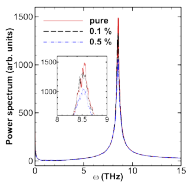


Figure 3. Fourier transform of the Green-Kubo autocorrelation functions for $8a$ x $8a$ x $8a$ slabs at 500 K with vacancy concentrations of 0.0%, 0.1%, and 0.5 % (b). The inset shows the absolute maxima at around 8.5 THz.

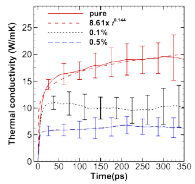


Figure 4. Thermal conductivities calculated using the Green-Kubo methodology as a function of the system size at 500 K. The errors bars are plotted every 50 ps to show the standard deviations.

(Saiz & Amon, 2015)

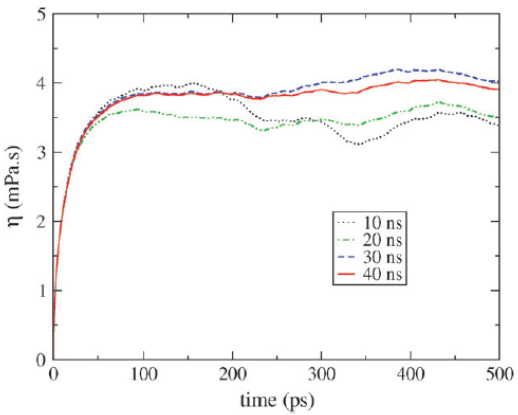


Fig. 1 Influence of the simulation durations on the determination of the GK viscosity for four different values.

(Van-Oanh, Hourier & Rousseau, 2009)

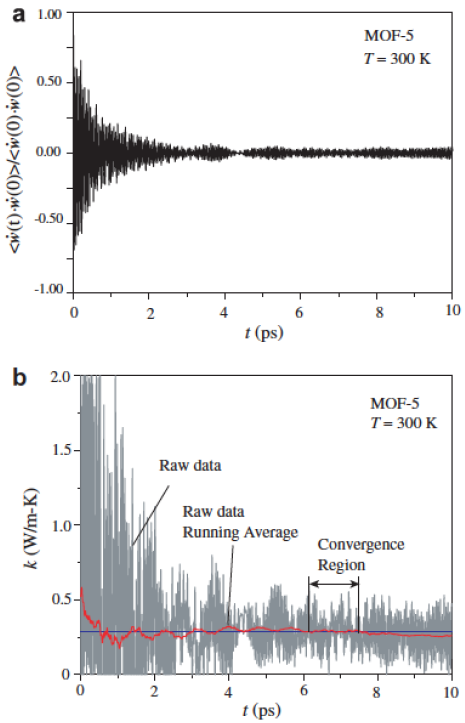
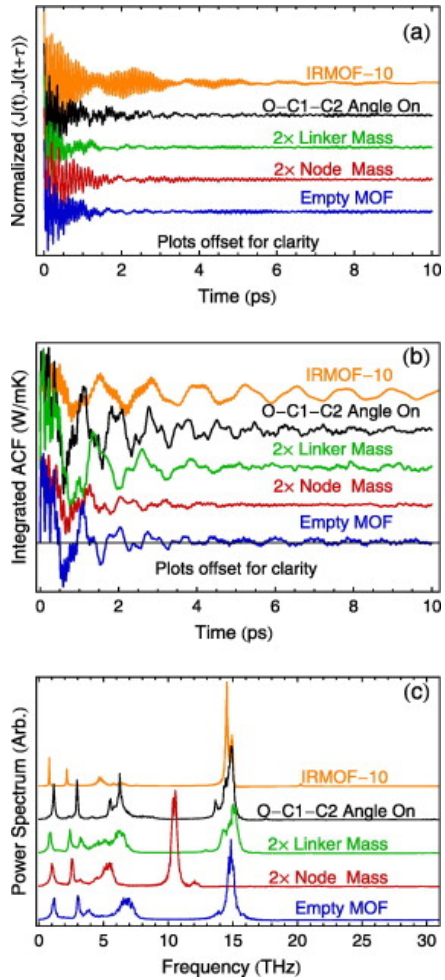


Fig. 4. (a) Decay of the normalized HCACF for MOF-5 and (b) its integral (the thermal conductivity) at a temperature of 300 K.

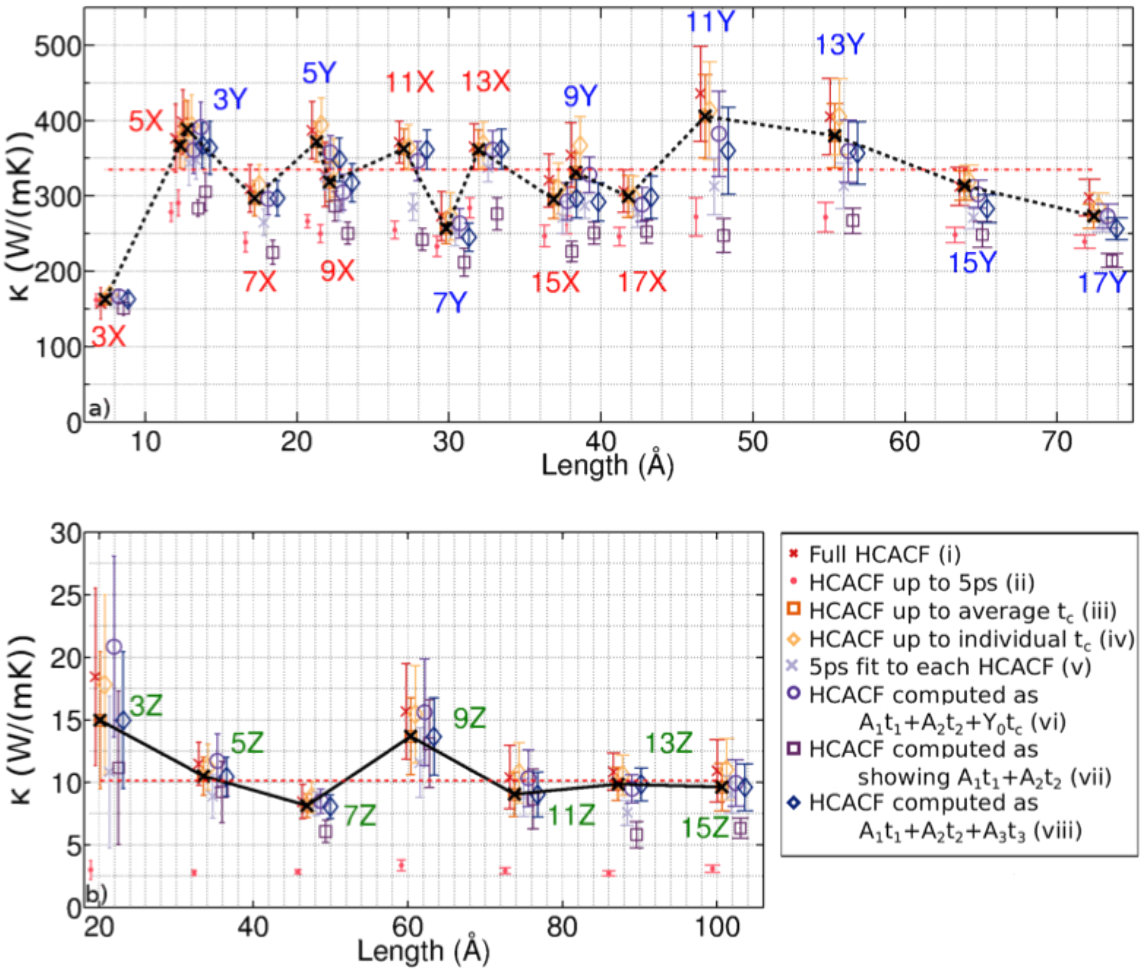
(Huang, McGaughey & Kaviany, 2006)



(Han & Greaney, 2014)

Green–Kubo method

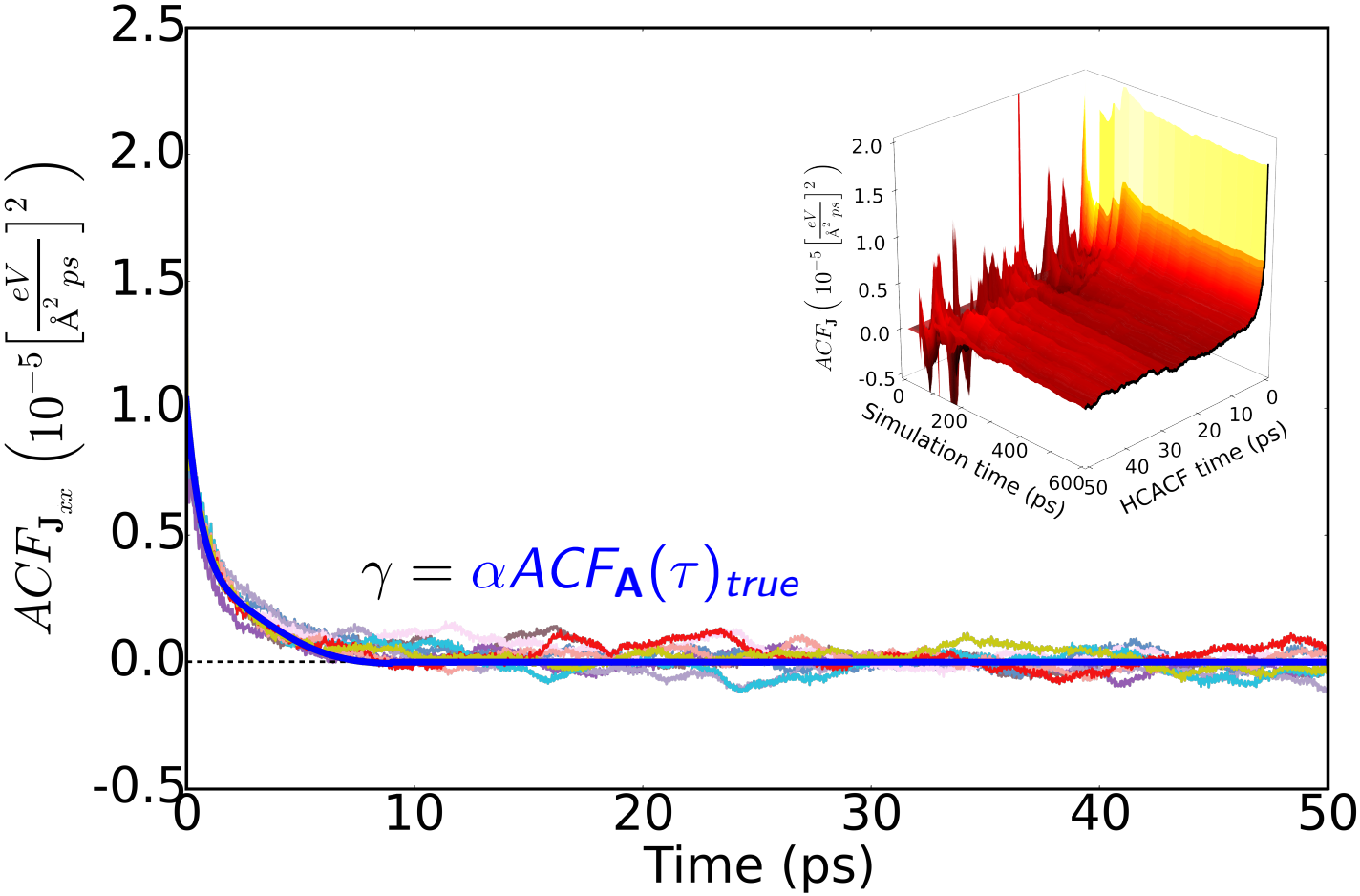
Approaches commonly used



(d. S. Oliveira & Greaney, 2015)

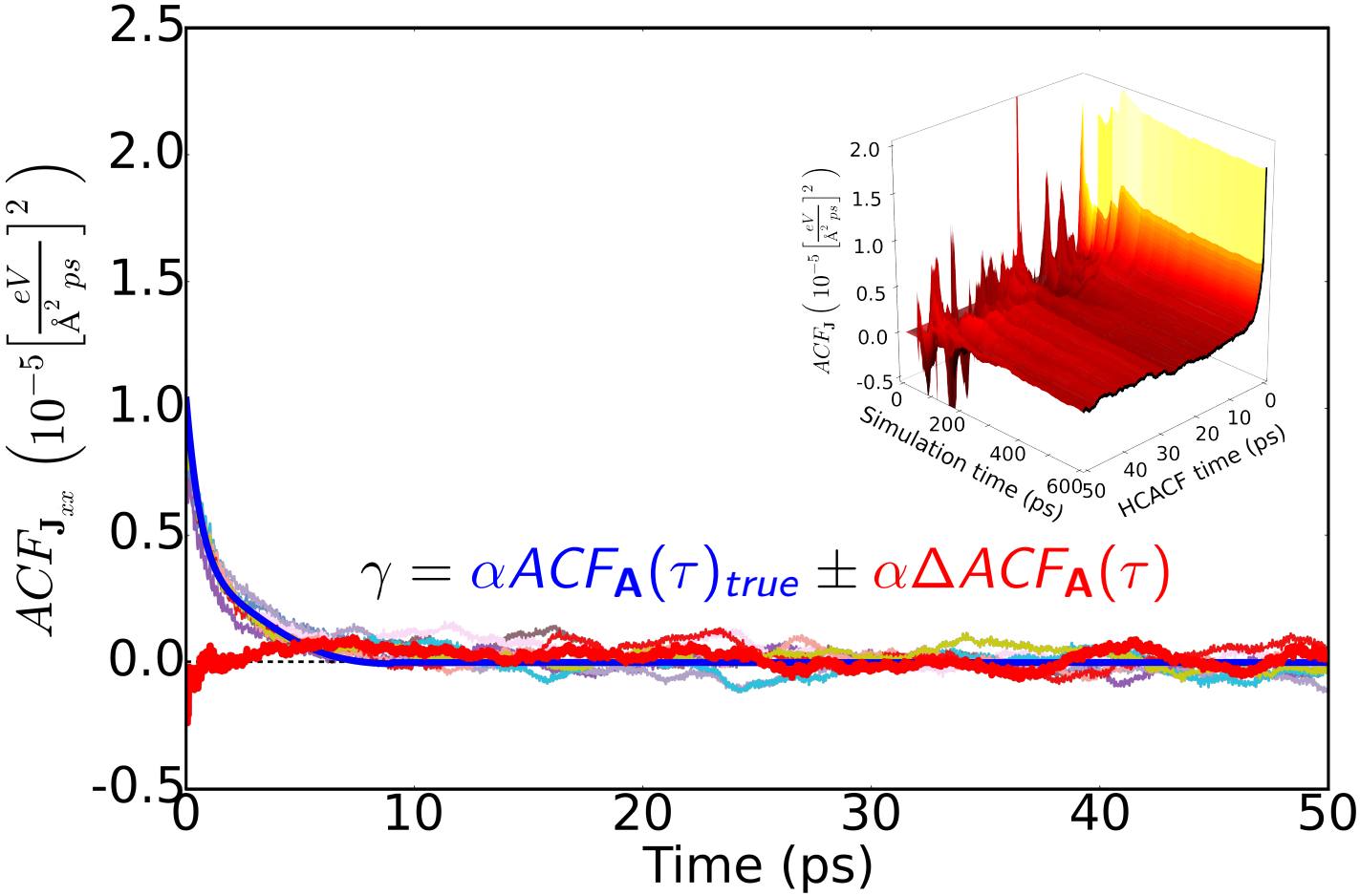
Green–Kubo method

The heat current autocorrelation function



Green–Kubo method

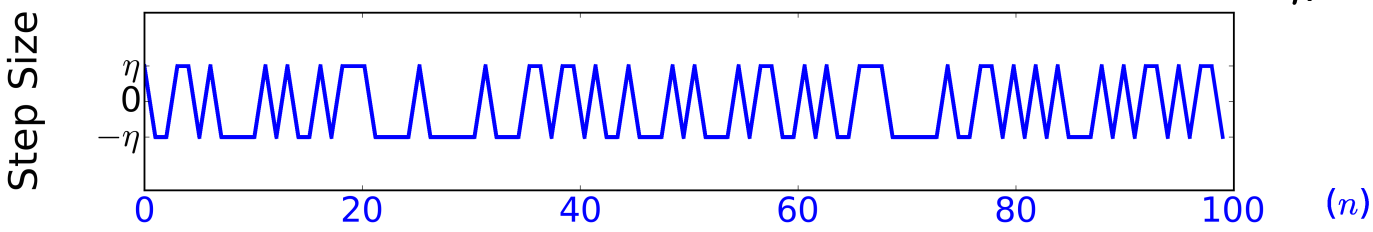
The heat current autocorrelation function

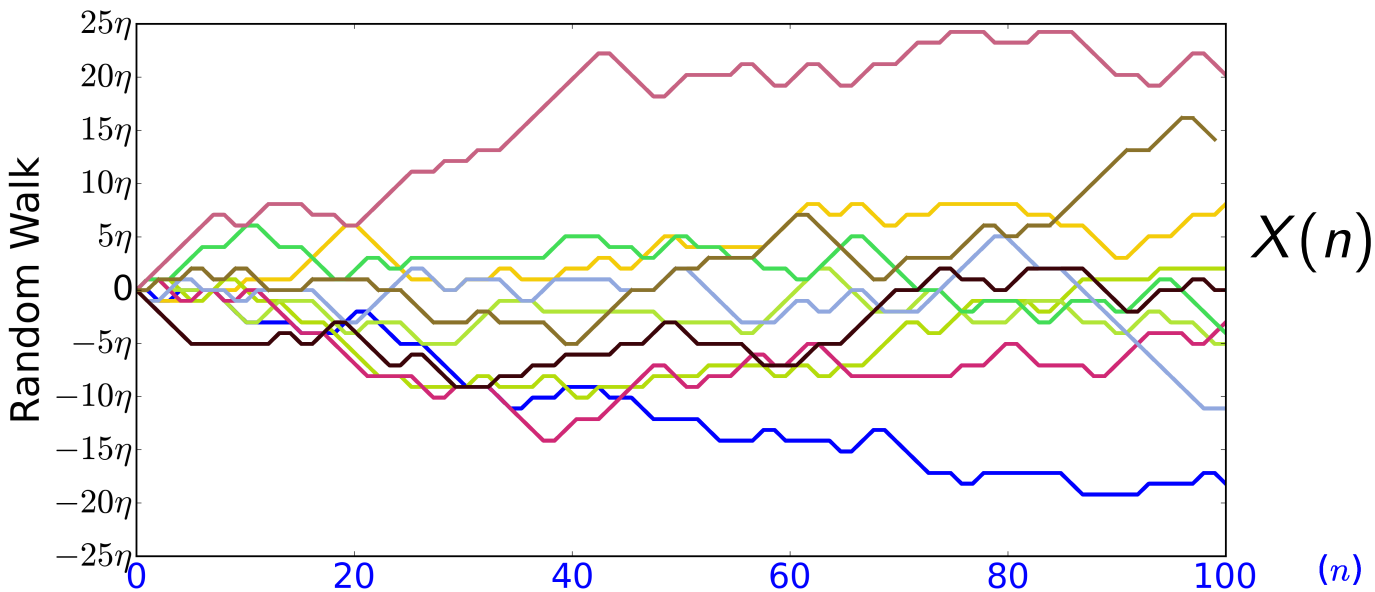


Method to manage integration error in the Green–Kubo method

Random walk

$\eta_i = -\eta$ *or* η



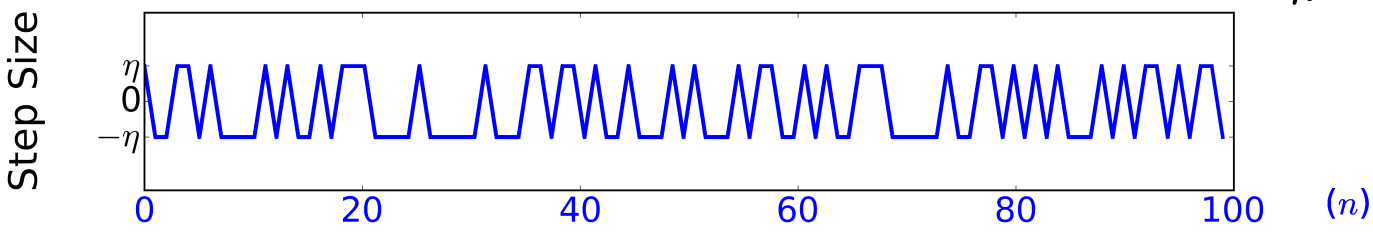


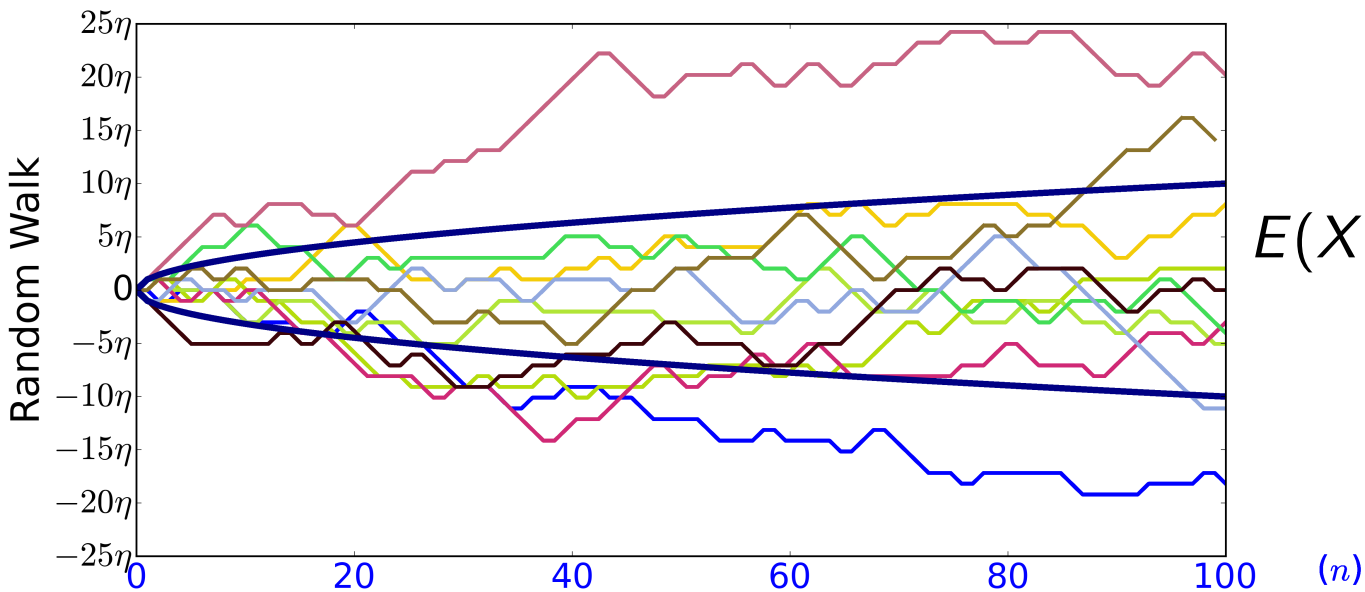
$X(n) = \sum_{i=1}^{n} \eta_i$

Method to manage integration error in the Green–Kubo method

Random walk

$\eta_i = -\eta$ *or* η

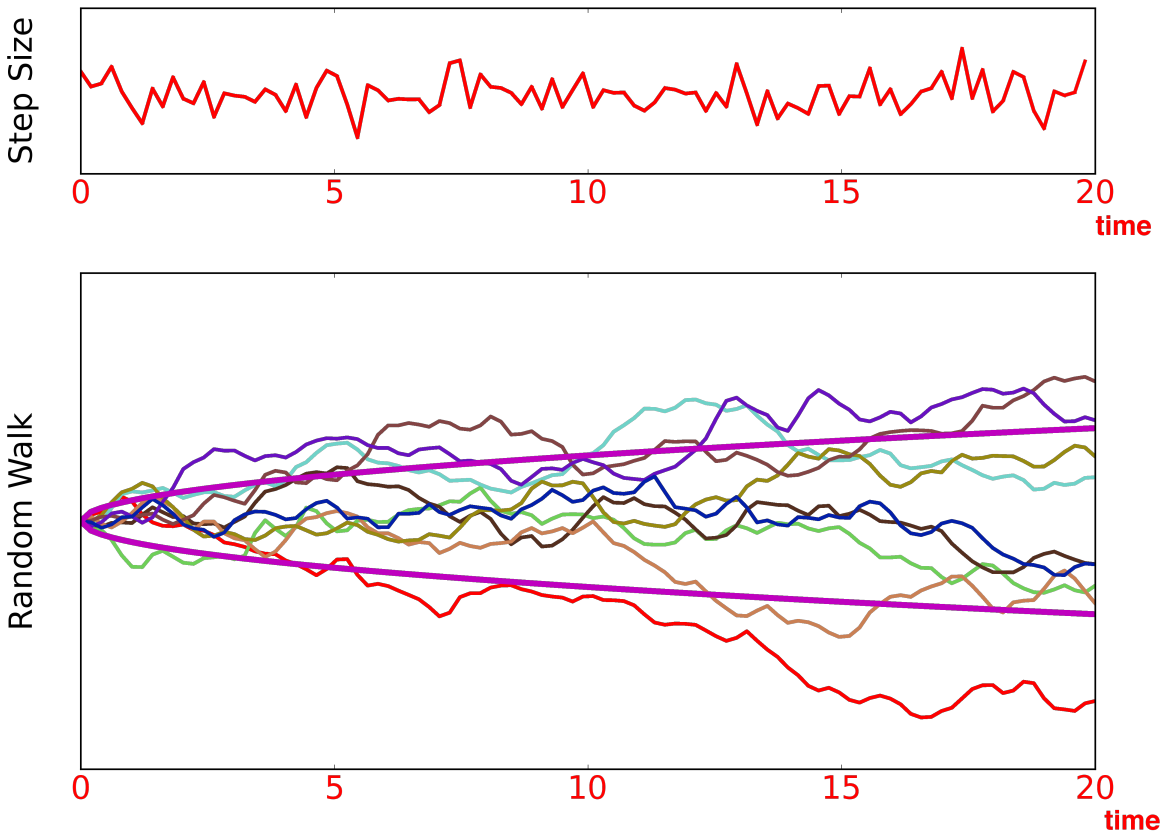


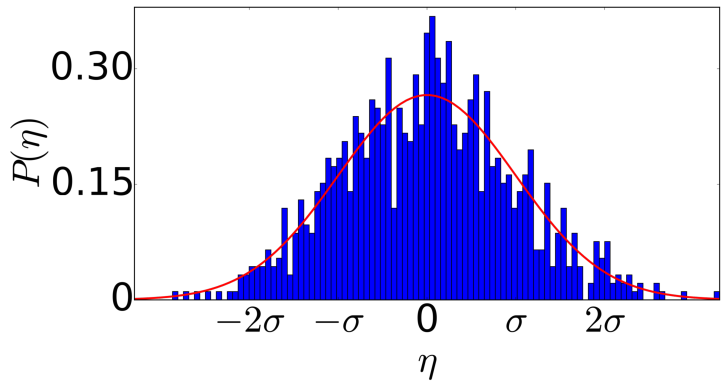


$E(X(n)) = \eta\sqrt{n}$

Method to manage integration error in the Green–Kubo method

Random walk

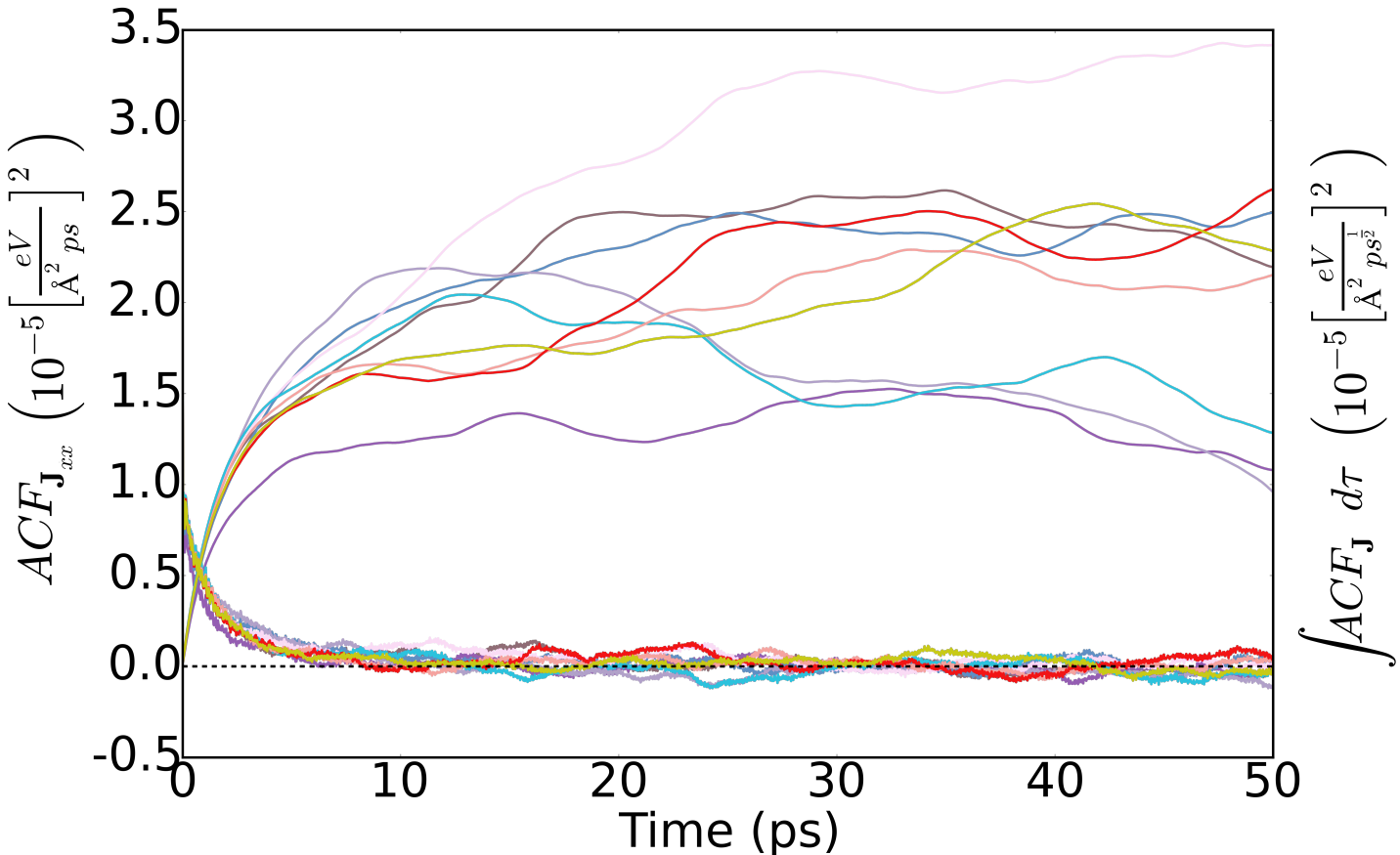




$$E(X(t)) = dt\sigma_\eta\sqrt{\frac{t}{dt}}$$
$$= \sigma_\eta\sqrt{t\ dt}$$

Method to manage integration error in the Green–Kubo method

Random walk in the integrated autocorrelation function

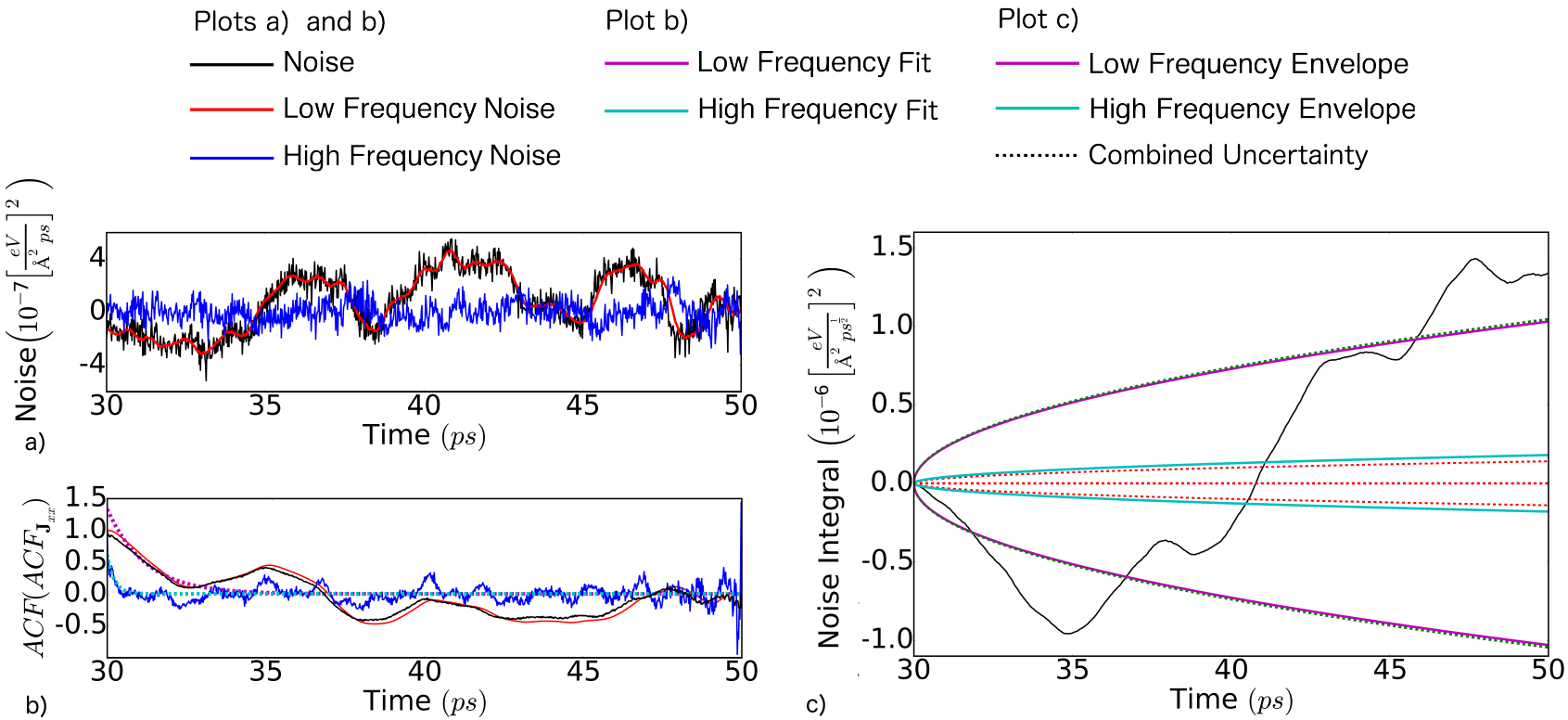


(d. S. Oliveira & Greaney, 2015)

Method to manage integration error in the Green–Kubo method

Random walk in the integrated autocorrelation function

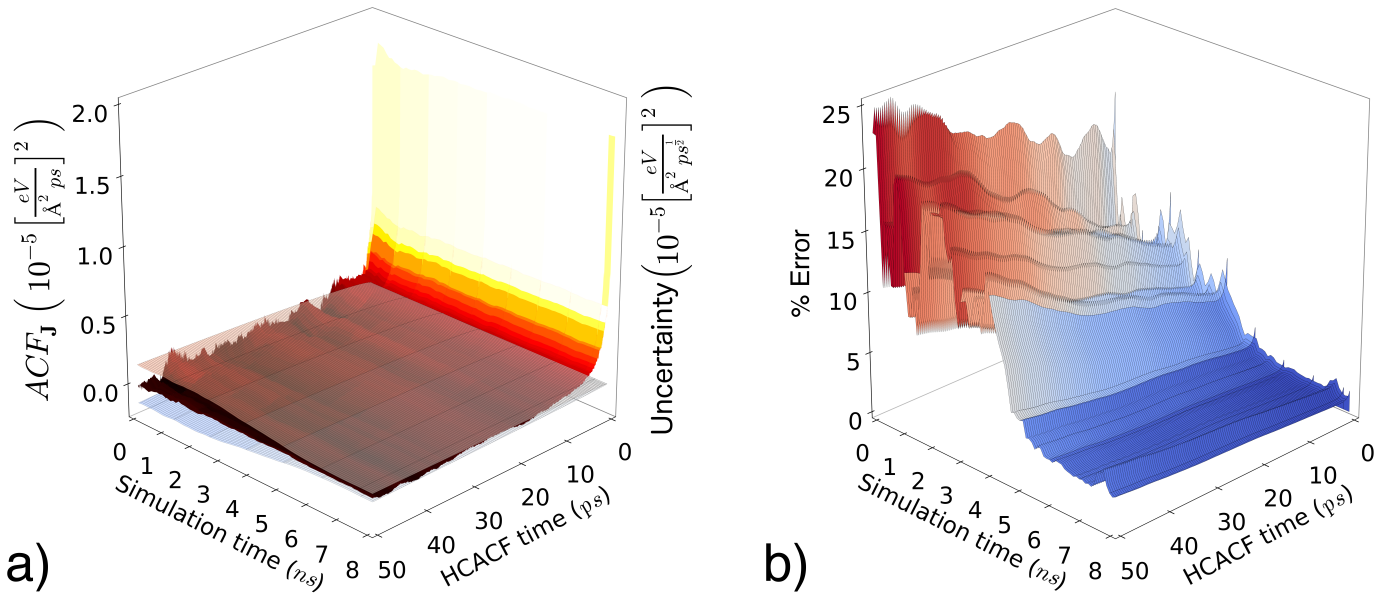
$$\sigma_\eta \sqrt{t\ dt}$$



(d. S. Oliveira & Greaney, 2017)

Method to manage integration error in the Green–Kubo method

Random walk in the integrated autocorrelation function

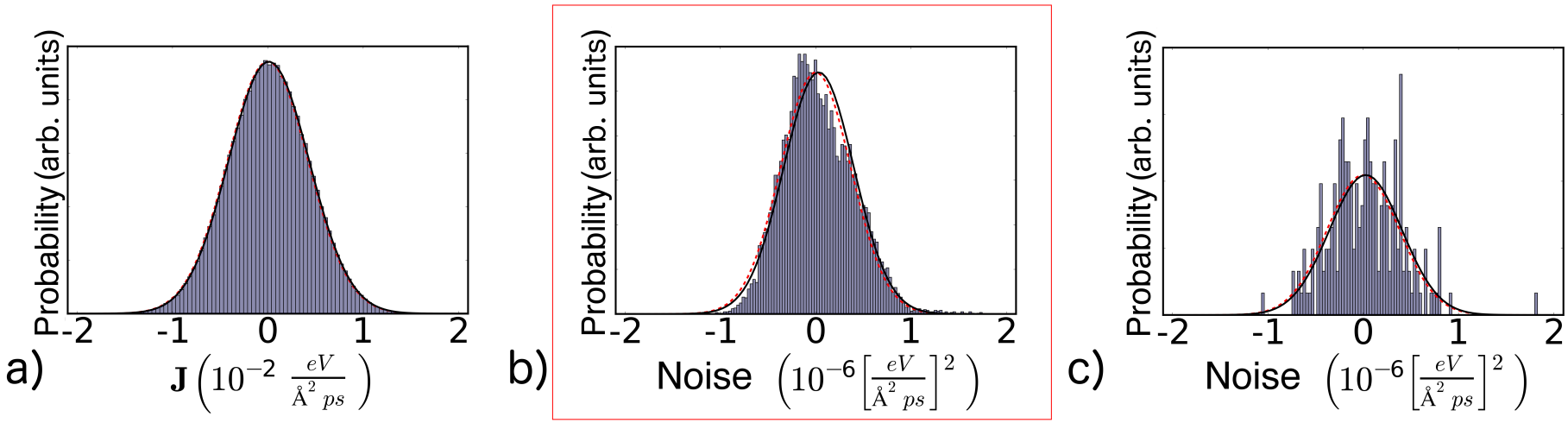


(d. S. Oliveira & Greaney, 2017)

Method to manage integration error in the Green–Kubo method

Random walk in the integrated autocorrelation function

- Fit error distribution to determine if slow decay processes are present in the ACF



(d. S. Oliveira & Greaney, 2017)

- Noise coupled with overall trend of heat flux

Method to manage integration error in the Green–Kubo method

Conclusions

- The noise of the flux autocorrelation grows as a random walk
- Noise coupled with overall trend of heat flux
- One simulation suffices to quantify the error
- Determine optimal simulation time on-the-fly
- Trade smaller sampling step for longer simulation
- Fit error distribution to determine if slow decay processes are present in the ACF

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