Onsager's regression hypothesis

Winter School for Theoretical Chemistry and Spectroscopy

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by

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Lars Onsager

Lars Onsager

27/11/1903 – 5/10/1976
Born in Oslo, Norway
Nobel prize for chemistry in 1968

Regression hypothesis

The physics of macroscopic relaxation of a system back to equilibrium is governed by the same physics as the relaxation of spontaneous fluctuations about equilibrium

Linear response to a perturbation

Consider classical* Hamiltonian dynamics from a point in phase space:

generalized momenta and positions at time = 0

$$\big(p(t), q(t)\big) = T_t\big(p(0), q(0)\big)$$

time evolution operator
(Liouvillian)

- (p,q) is short for $(\mathbf{p}^N, \mathbf{q}^N)$
- $N \sim 10^{23}$

In equilibrium, microstates have the canonical distribution:

$$P(p,q) = \frac{1}{Q} e^{-\beta \mathcal{H}(p,q)} \qquad Q = \int dp\, dq\, e^{-\beta \mathcal{H}(p,q)}$$

- *dpdq* is an infinitisemal volume element in phase-space

* for a quantum mechanical treatment of linear response theory see for example the book by Chaikin and Lubensky, “Principles of Condensed Matter Physics”.

Linear response to a perturbation

What happens when we take the system out of equilibrium?

The perturbation should be small enough that the response is linear to the field.

Let's switch of a (small) perturbation field (at t=0), and consider the relaxation to the new equilibrium.

conjugate thermodynamic variables, e.g. pressure and volume; $f = \partial F / \partial A$

$t < 0$ $\quad H' = H + \Delta H$

$t > 0$ $\quad H \quad (\Delta H = 0)$

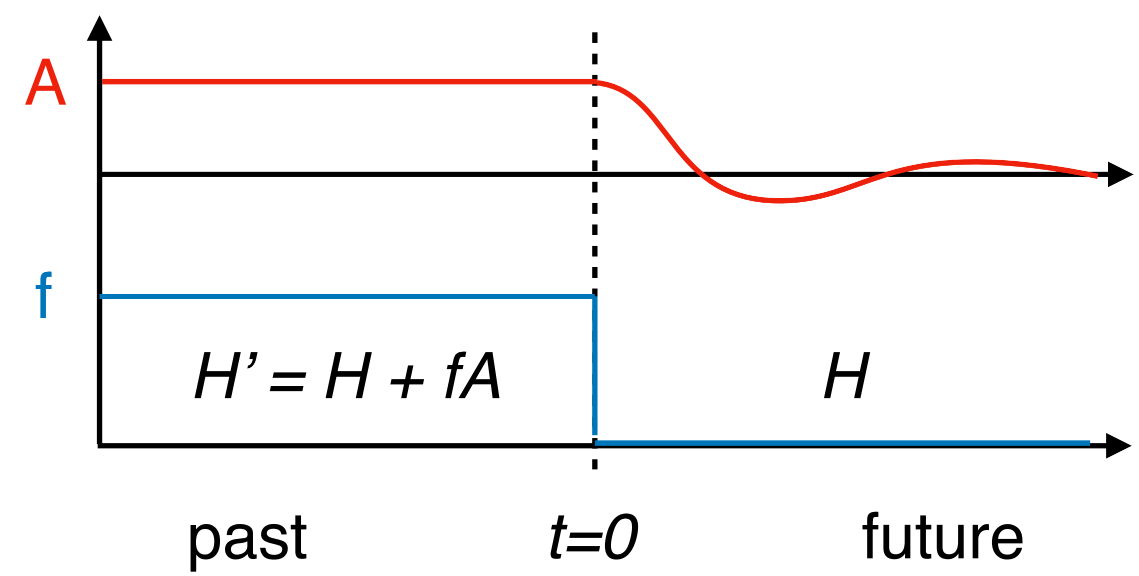
$\Delta H = -f A$

f is an external field

A(p,q) is a macroscopic observable

Initial state:

$$\langle A \rangle = \frac{1}{Q'} \int dp\, dq\, e^{-\beta \mathcal{H}'(p,q)} A(p,q)$$



After field is switched off:

$$\langle A(t) \rangle = \frac{1}{Q'} \int dp\, dq\, e^{-\beta \mathcal{H}'(p,q)} A(T_t(p,q))$$

time operator T_t instead of T_t'

Linear response to a perturbation

After field is switched off:

$$\langle A(t)\rangle = \frac{1}{Q'}\int dp\,dq\,e^{-\beta\mathcal{H}'(p,q)}A(T_t(p,q))$$

$$\langle A(t)\rangle \approx \frac{\int dp\,dq\,e^{-\beta\mathcal{H}(p,q)}(1-\beta\Delta\mathcal{H})\,A(T_t(p,q))}{\int dp\,dq\,e^{-\beta\mathcal{H}(p,q)}(1-\beta\Delta\mathcal{H})}$$

Taylor expansion:
$e^x = 1 + x + \ldots$

$$\frac{1}{1-x} = 1 + x + x^2 + \ldots$$

expanding and keeping only terms of linear order gives:

$$\langle A(t)\rangle \approx \frac{\int dp\,dq\,e^{-\beta\mathcal{H}(p,q)}\,A(T_t(p,q))}{\int dp\,dq\,e^{-\beta\mathcal{H}(p,q)}} + \beta f\frac{\int dp\,dq\,e^{-\beta\mathcal{H}(p,q)}\,A(p,q)A(T_t(p,q))}{\int dp\,dq\,e^{-\beta\mathcal{H}(p,q)}}$$

$$-\beta f\frac{\int dp\,dq\,e^{-\beta\mathcal{H}(p,q)}\,A(p,q)}{\int dp\,dq\,e^{-\beta\mathcal{H}(p,q)}}\frac{\int dp\,dq\,e^{-\beta\mathcal{H}(p,q)}\,A(T_t(p,q))}{\int dp\,dq\,e^{-\beta\mathcal{H}(p,q)}}$$

Thus, to linear order:

$$\langle A(t)\rangle - \langle A(t)\rangle_0 = \beta f\left(\langle A(0)A(t)\rangle_0 - \langle A\rangle_0^2\right)$$

$$\Delta A(t) = \beta f\langle\delta A(0)\delta A(t)\rangle_0$$

- $\delta A(t) = A(t) - \langle A\rangle$
- $\langle\ldots\rangle_0$ ensemble average of the unperturbed system

Fluctuation-Dissipation theorem

Linear response of the system to the force (perturbation)

$$\Delta A(t) = \beta f \langle \delta A(0) \delta A(t) \rangle_0$$

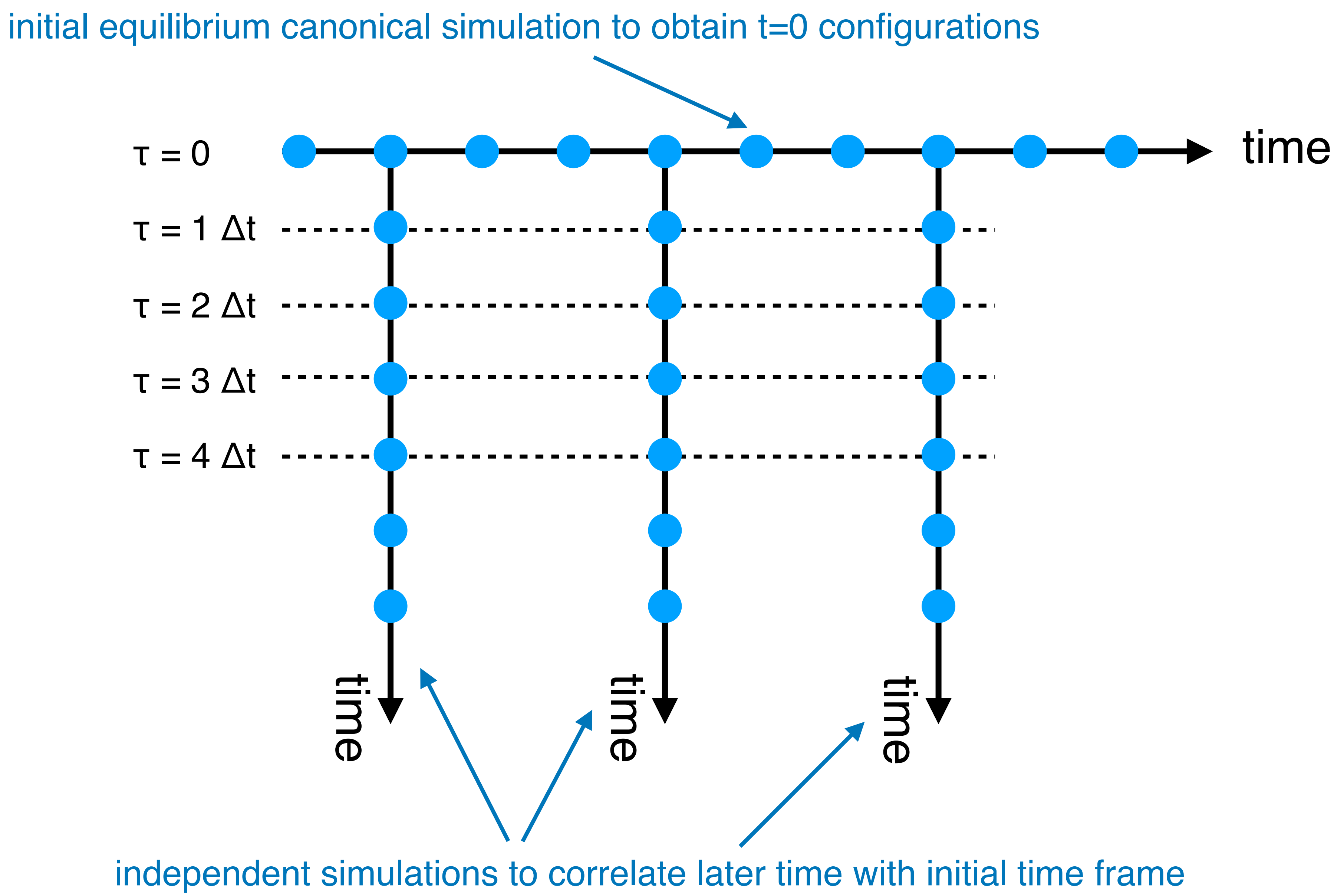
This results is one manifestation of the Fluctuation-Dissipation theorem.

Macroscopic evolution from out-of-equilibrium ⟷ Microscopic fluctuations in equilibrium

Time correlation calculation: the direct method

Most straightforward manner to compute a time-correlation function

$$D = \frac{1}{3}\int_0^\infty d\tau \langle v(0)v(\tau)\rangle$$

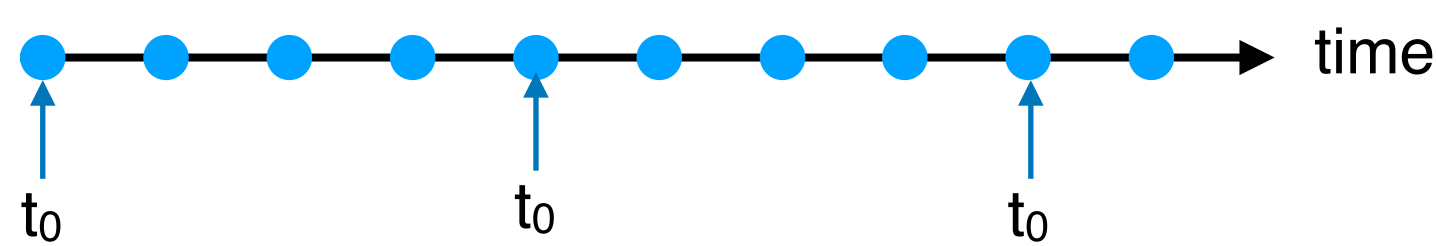


Single trajectory approach

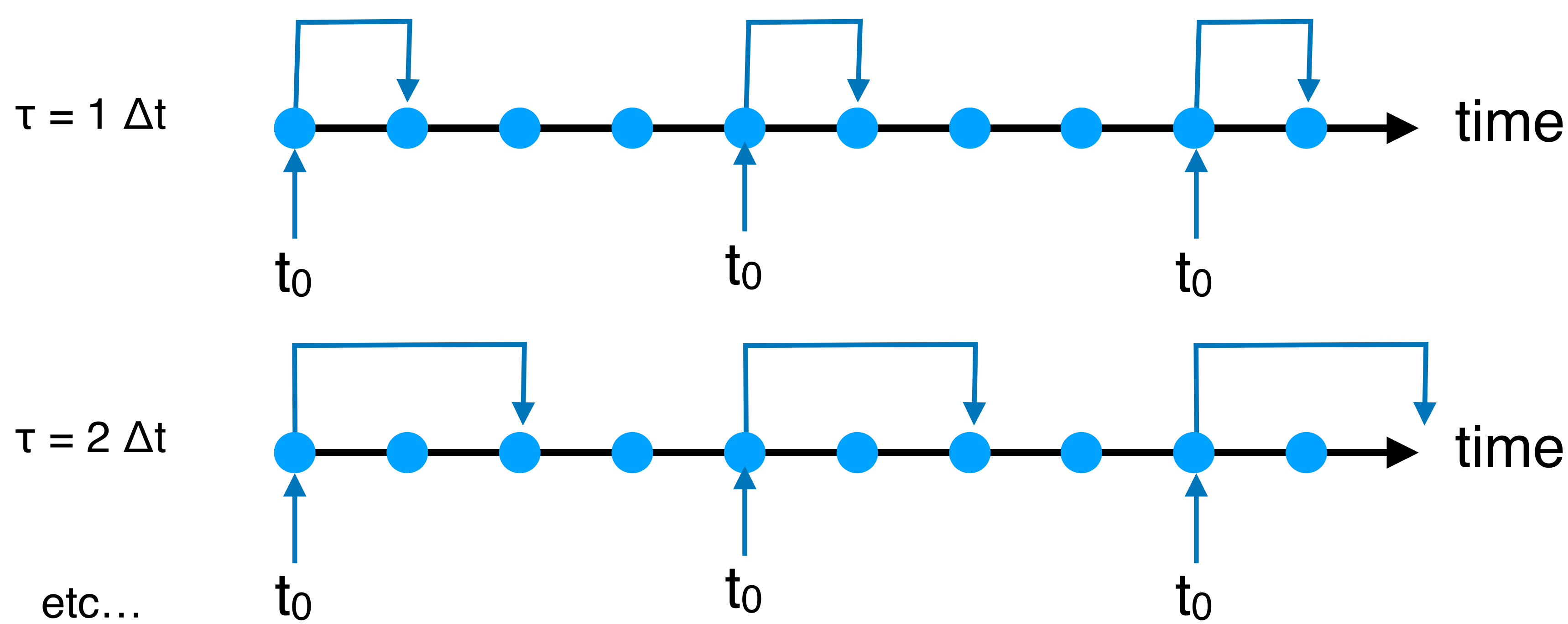
Most used manner to compute a time-correlation function

$$D = \frac{1}{3}\int_0^{\infty} d\tau \langle v(0)v(\tau)\rangle$$

- take t=0 frames at regular (uncorrelated) intervals:



- compute A(0)A(τ) with respect to all t=0 frames



- efficient use of a single trajectory
- many more samples of short time intervals than for long time intervals (1 sample of total trajectory length)
- smart coarse-grain algorithms can avoid excess calculation and storage of short time interval data.

Fast Fourier transform method

Fastest manner to compute a time-correlation function

Direct methods scale approximately as the square of the number of sample points (frames).

$$D = \frac{1}{3}\int_0^\infty d\tau \langle v(0)v(\tau)\rangle$$

$$C_{AB}(\tau) = \lim_{\tau\to\infty}\frac{1}{\tau}\int_{-\tau/2}^{\tau/2} dt\, a(x_t)b(x_{t+\tau})$$

shift time origin

Write a and b in their Fourier transforms:

$$\tilde{a}(\omega) = \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty} dt\, e^{-i\omega t} a(x_t) \qquad \tilde{b}(\omega) = \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty} dt\, e^{-i\omega t} b(x_t)$$

then

$$\tilde{a}(\omega)\tilde{b}^*(\omega) = \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty} d\tau e^{-i\omega\tau}\int_{-\infty}^{\infty} dt\, a(x_t)b(x_{t+\tau})$$

$$\int_{-\infty}^{\infty} d\omega\, e^{i\omega\tau}e^{-i\omega t} = 2\pi\delta(t-\tau)$$

multiply both sides by $e^{i\omega\tau}$ and integrate over τ

$$\int_{-\infty}^{\infty} dt\, a(x_t)b(t_{t+\tau}) = \int_{-\infty}^{\infty} d\omega\, e^{-i\omega\tau}\tilde{a}(x_t)\tilde{b}^*(x_{t+\tau})$$

- In practice, with finite time and discrete time, fast Fourier transforms (FFTs) are used.
- FFTs scale as *N ln N*

Applications

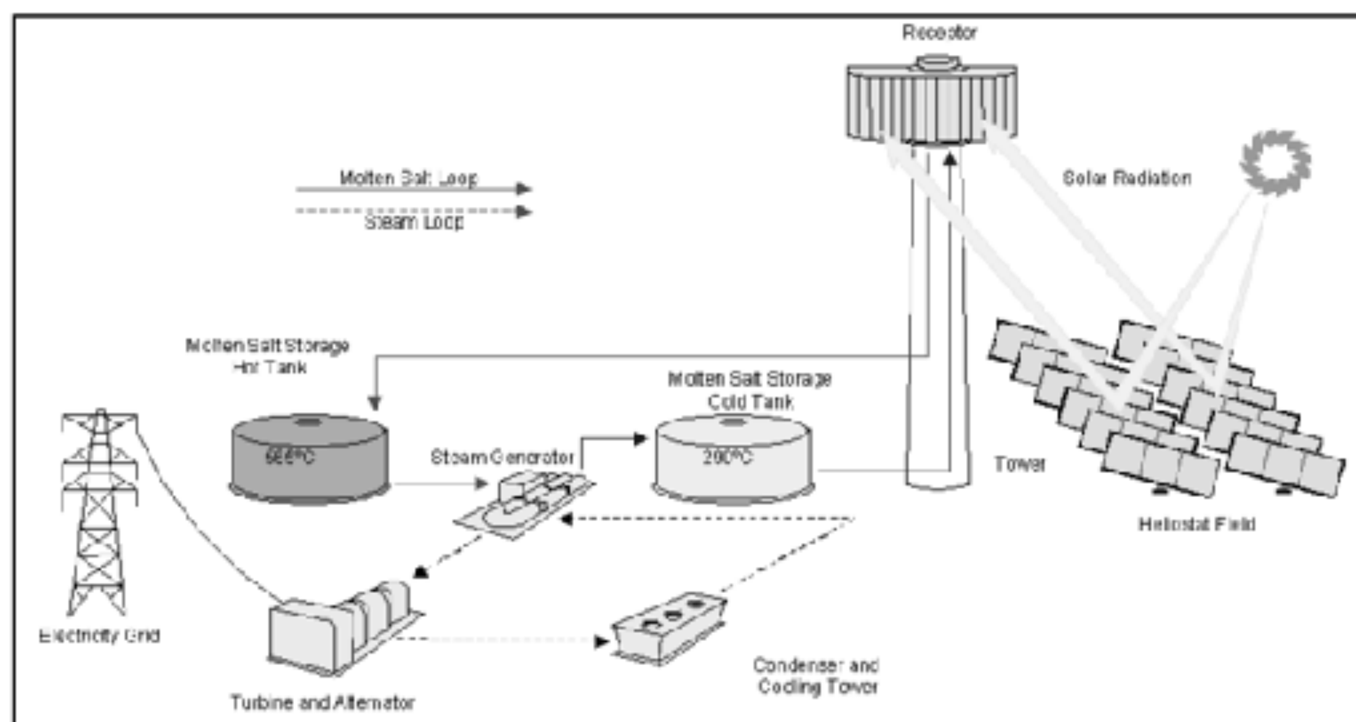
- Anisotropy decay in aqueous solutions
- thermal conductivity in nano fluids
- reaction rate theory

ABENGOA

Innovative technology solutions for sustainability

Molten salts:

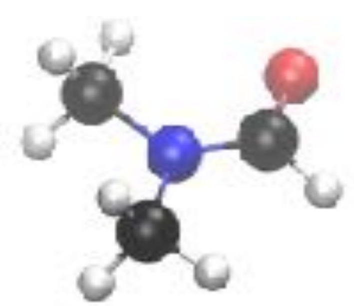
- Heat storage and transport medium
- Allow electric energy generation in the absence of sunlight (with heat stored during daylight)
- Carbonates (M_2CO_3), Chlorides (MCl, MCl_2); Nitrates (MNO_3), and mixtures
- Melting: ~200ºC
- Operation: ~500ºC
- High heat capacity



Heat Transfer Fluids

- Room temperature applications - Cooling and thermal management
- Graphene nanofluids – very large effect on thermal properties
- Large literature on Graphene nanofluids
- Experimental work at ICN2 (preparation and thermal properties)

DMF: Dimethylformamide



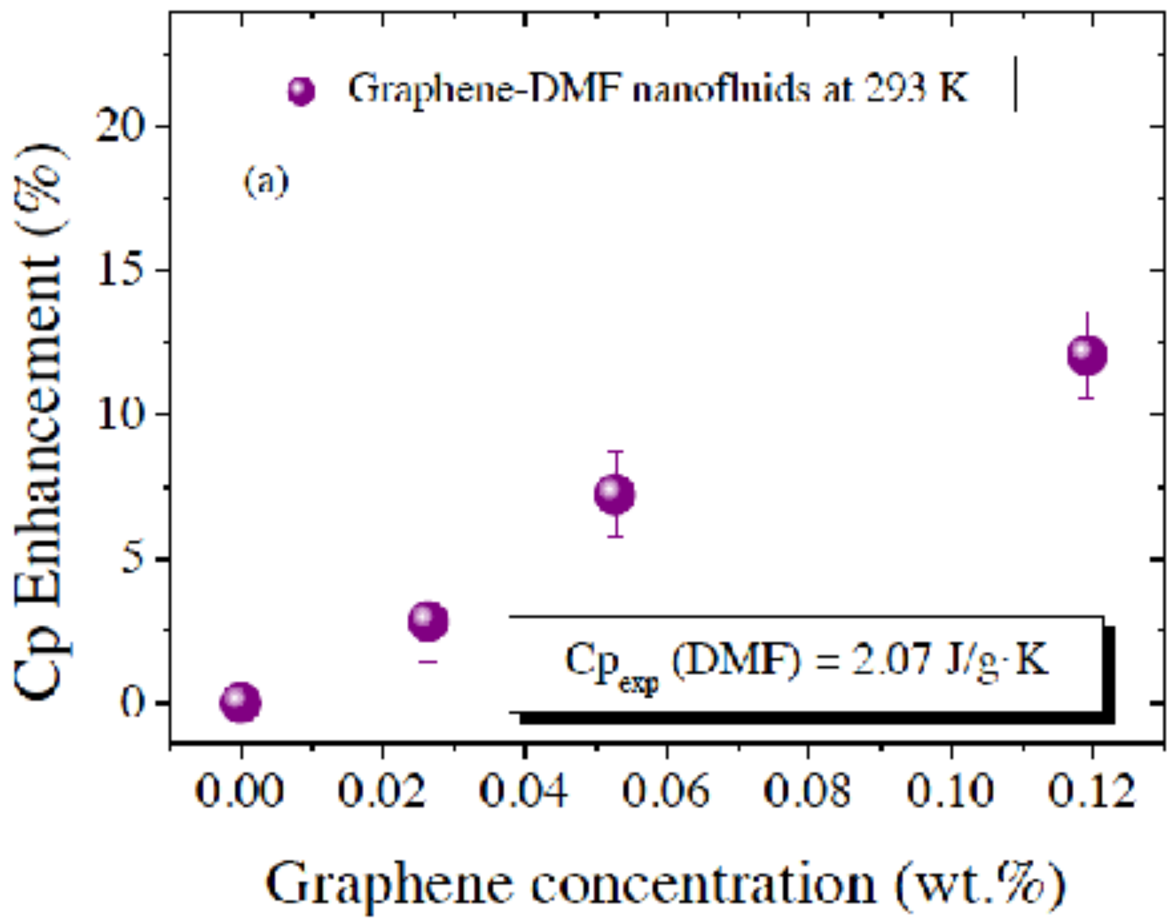
Organic solvent for Graphite Nanoflakes
currently used by P. Gómez (ICN2)

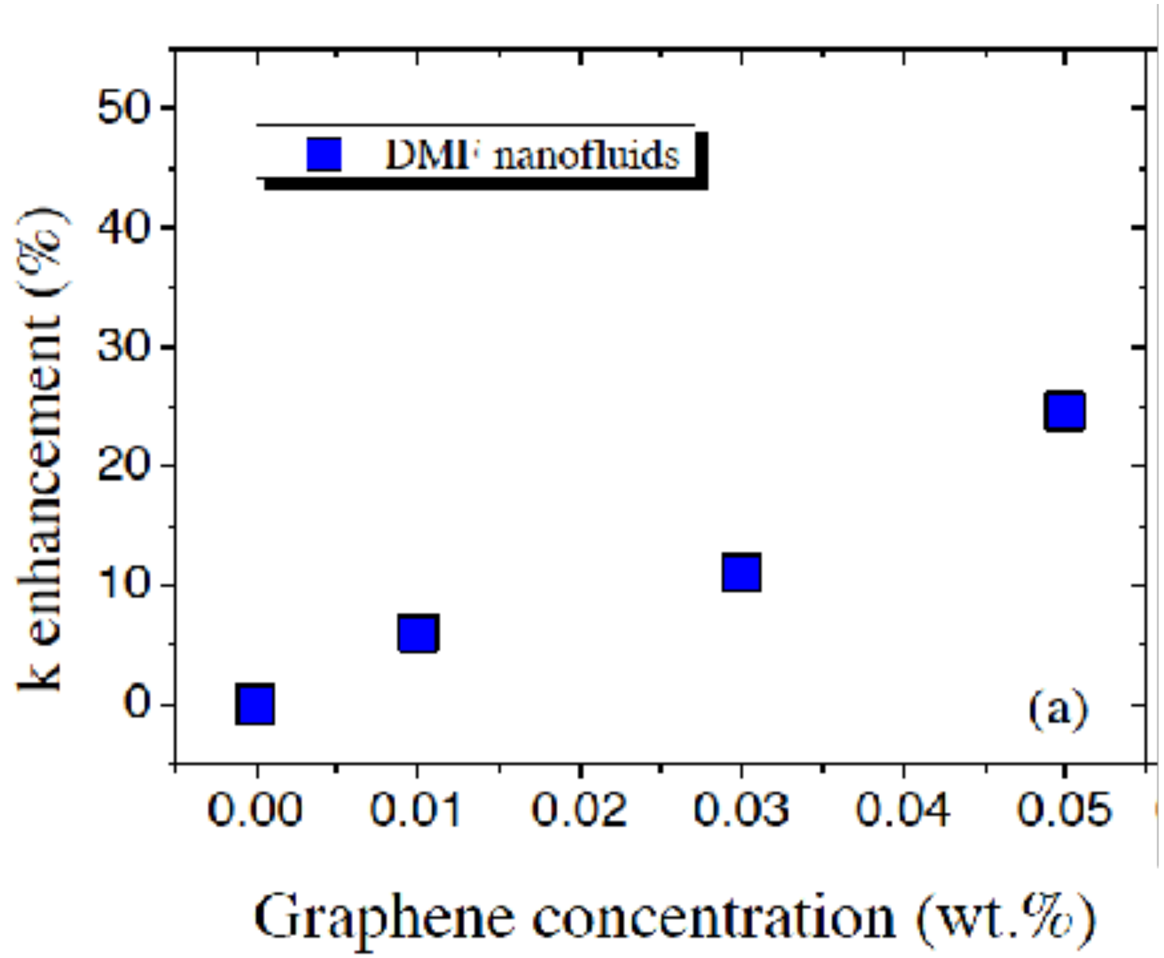
Very stable dispersions - low concentration of NFs: 0 - 0.05 wt %

NFs: 100 – 400 nm diameter;   1-10 layers

Experimental Results

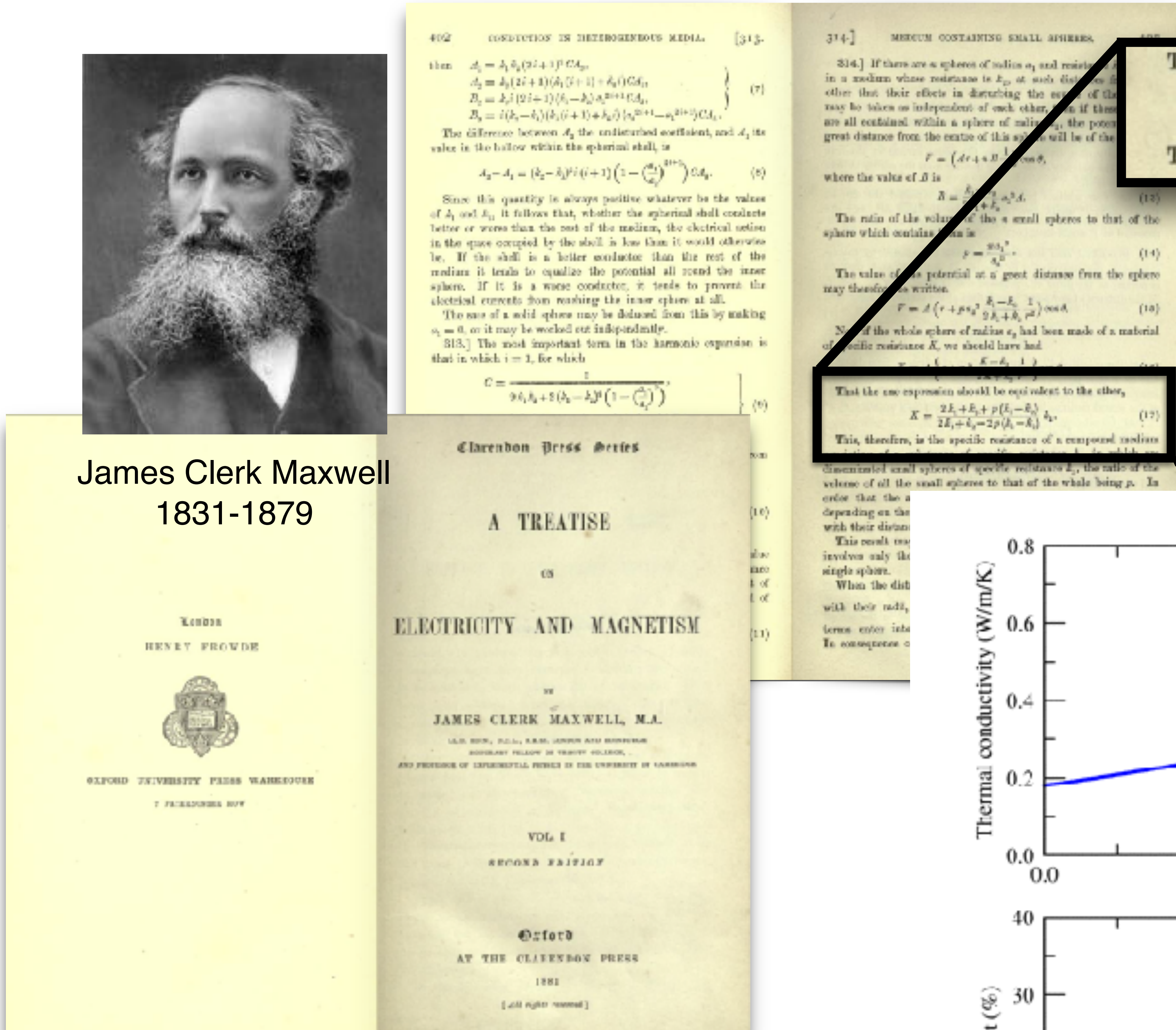
Thermal properties: Specific Heat and Thermal Conductivity



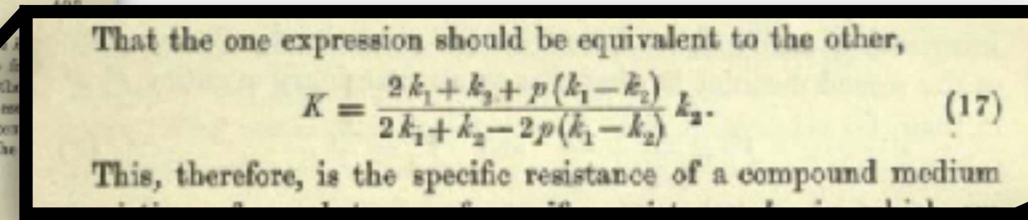


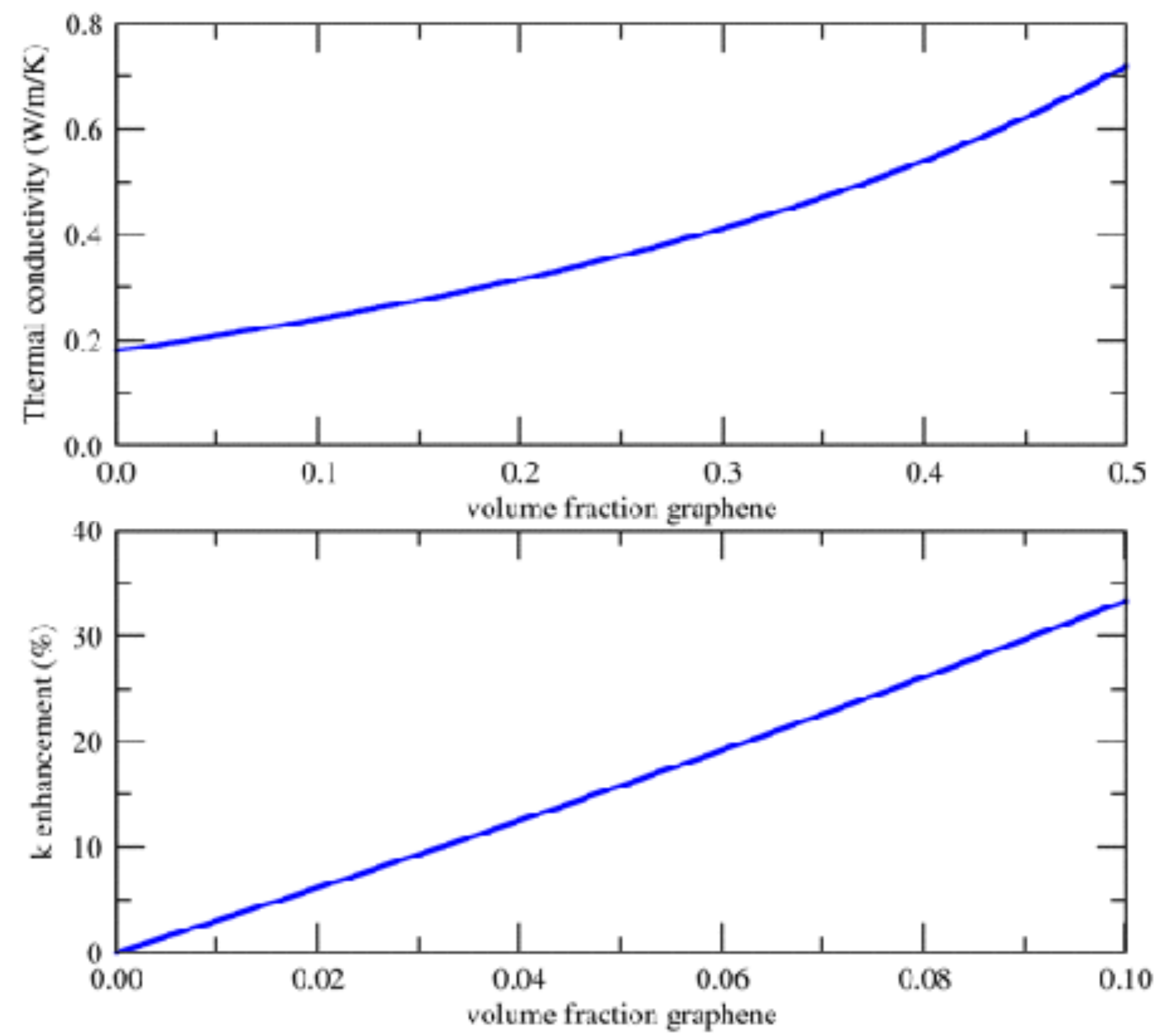
Experiments: R. Rodriguez, E. Chavez, P. Gomez, C. Sotomayor – ICN2

Electrical Resistance of spheres in medium



James Clerk Maxwell
1831-1879





Thermal conductivity of <u>spheres</u> in medium

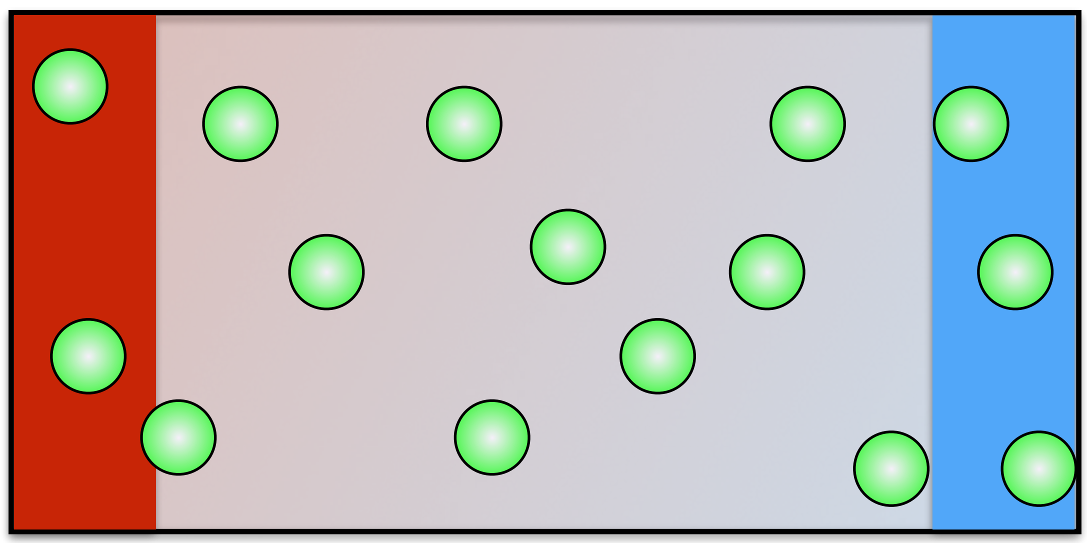
$$k_e = \frac{2k_f + k_s + 2\phi_s \cdot (k_s - k_f)}{2k_f + k_s - \phi_s \cdot (k_s - k_f)} \cdot k_f$$

Experiments see the same enhancement at ~200 smaller concentration!

Heat conduction

- Conduction, convection, radiation
- Electronic, photonic, phononic
- Not a good theory developed for liquids

a) Non-equilibrium simulation



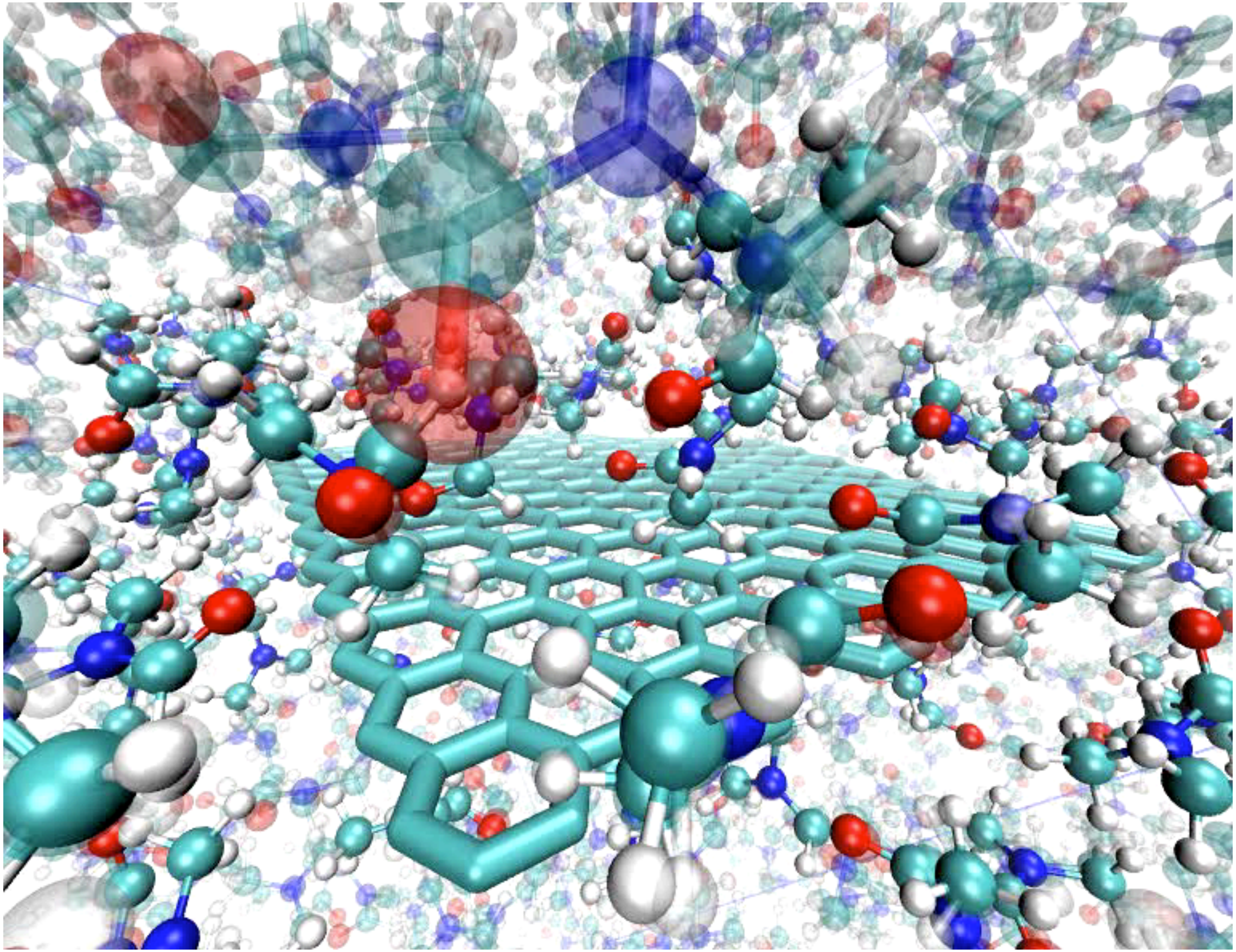
hot cold

b) Equilibrium simulation

- Green-Kubo equation

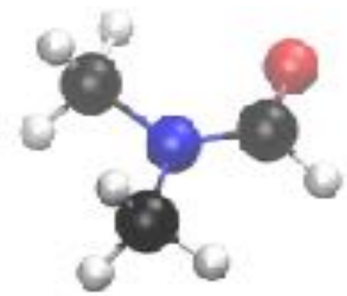
conductivity from auto-correlation of the heat flux, *J*

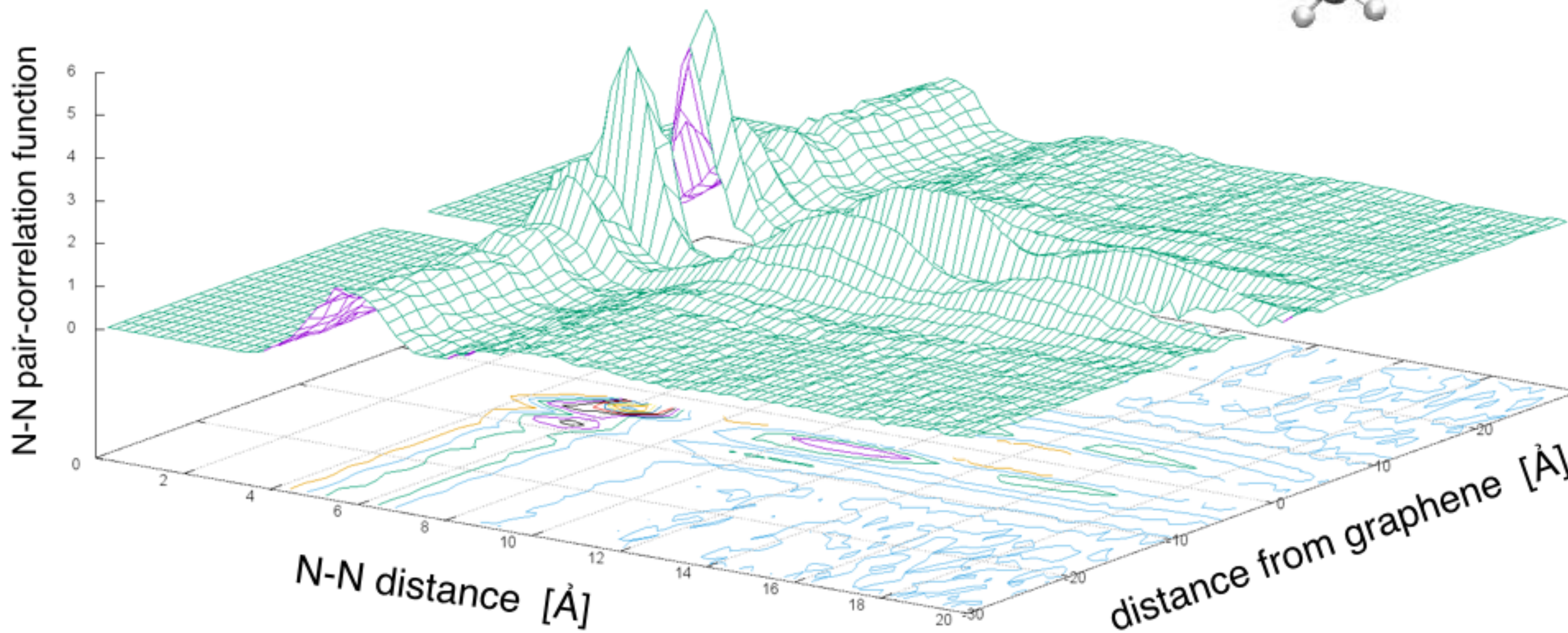
$$\kappa = \frac{1}{3Vk_BT^2} \lim_{\tau \to \infty} \int_0^{\tau} \langle \mathbf{J}(t)\mathbf{J}(0) dt$$



6 ps movie
(out of a 1 ns simulation)

Layering of DMF on graphene flake





Thermal conductivity (TC) by Green Kubo equation

Thermal conductivity calculated from Green-Kubo equation from a long classical MD simulation

$$\kappa = \frac{V}{k_B T^2} \int_0^\infty \langle J_x(0) J_x(t) \rangle \, dt = \frac{V}{3 k_B T^2} \int_0^\infty \langle \mathbf{J}(0) \cdot \mathbf{J}(t) \rangle \, dt$$

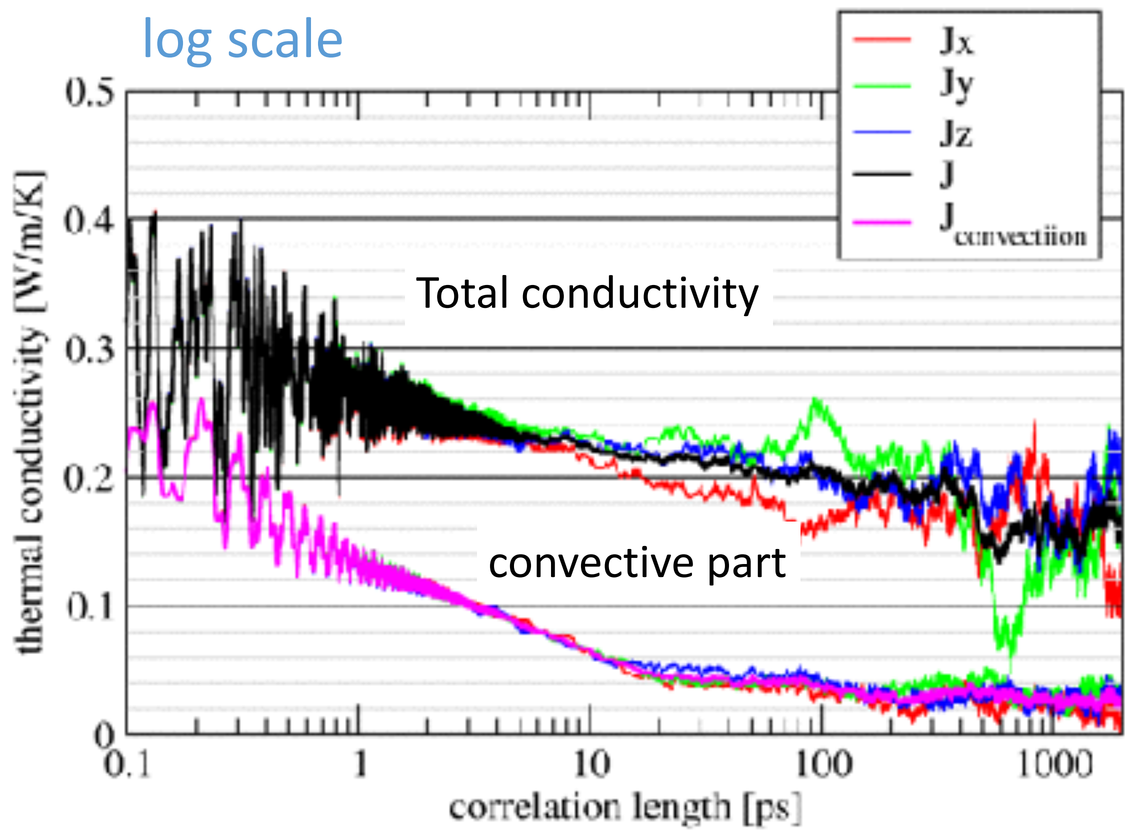
heat flux

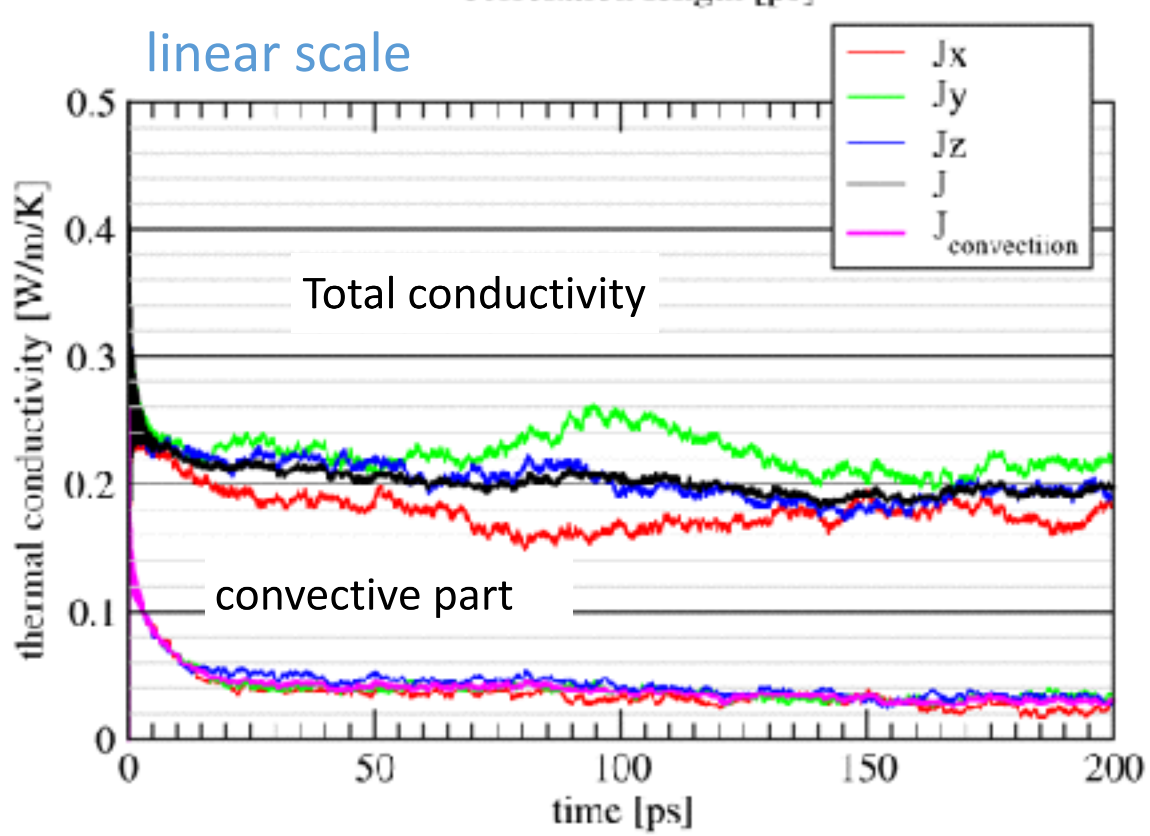
$$\begin{aligned}
\mathbf{J} &= \frac{1}{V}\left[\sum_i e_i \mathbf{v}_i - \sum_i \mathbf{S}_i \mathbf{v}_i\right] \\
&= \frac{1}{V}\left[\sum_i e_i \mathbf{v}_i + \sum_{i<j} (\mathbf{f}_{ij} \cdot \mathbf{v}_j)\, \mathbf{x}_{ij}\right] \\
&= \frac{1}{V}\left[\sum_i e_i \mathbf{v}_i + \frac{1}{2}\sum_{i<j} (\mathbf{f}_{ij} \cdot (\mathbf{v}_i + \mathbf{v}_j))\, \mathbf{x}_{ij}\right]
\end{aligned}$$

convective contribution

vibrational/phononic contribution

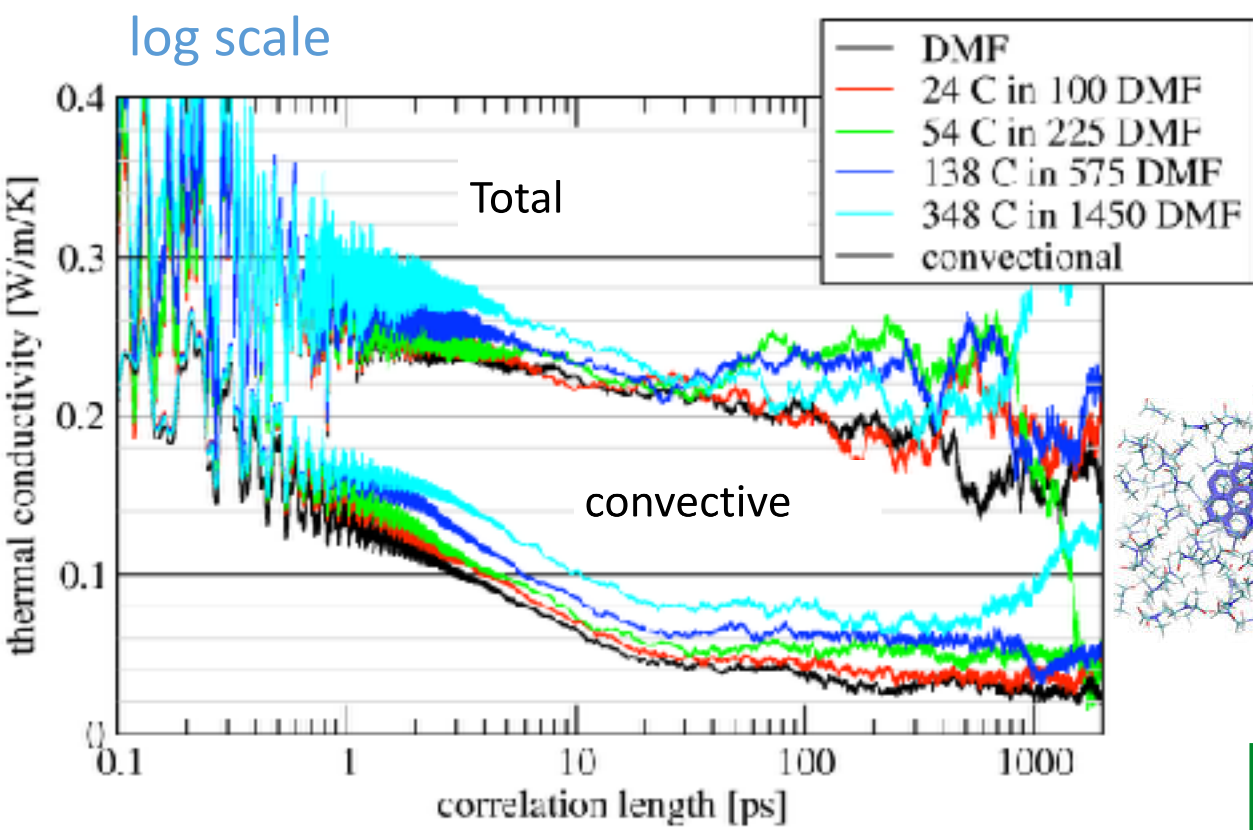
TC for DMF with 20 ns of NVT simulations

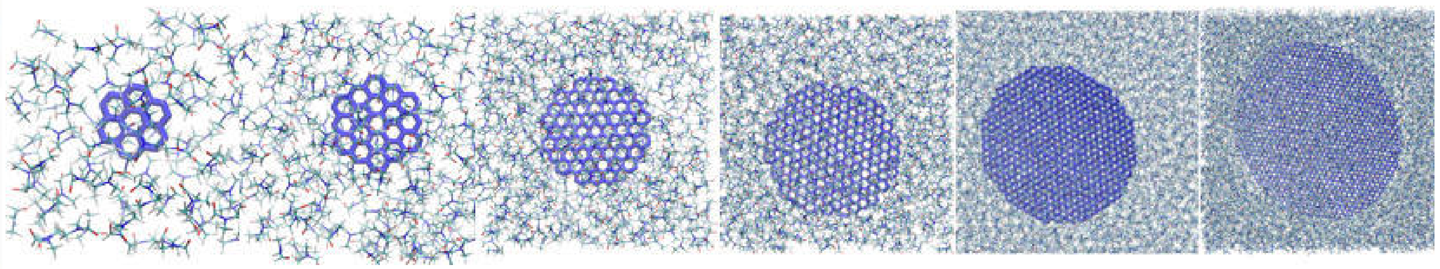




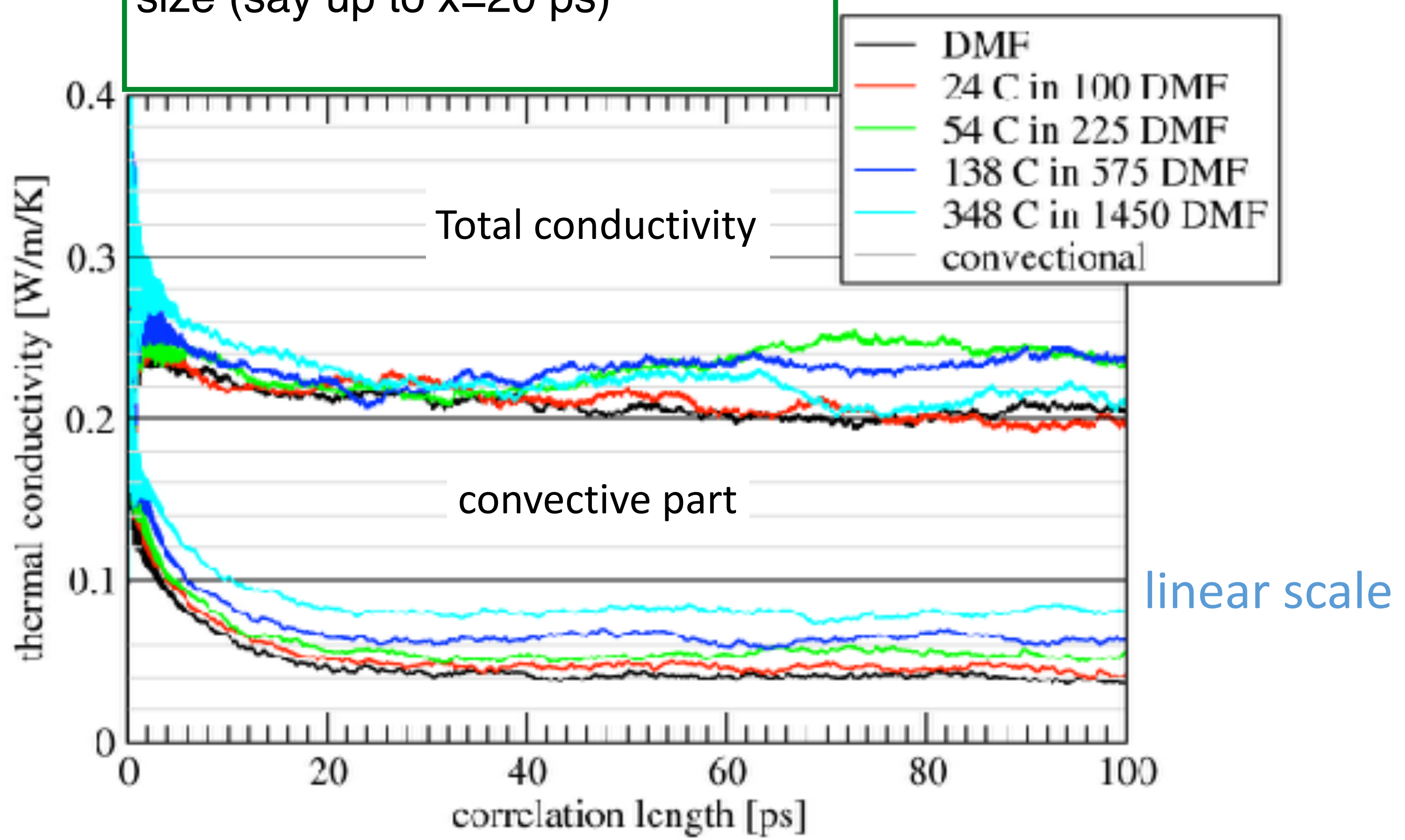
- After 10 ps, the x,y,z components start to deviate, which is a measure for the statistical error.
- The convection part reached a plateau between 10-100 ps, of **0.04 ± 0.01** W/mK.
- The plateau in the total TC is less clear; **0.20 ± 0.02** W/mK.
- The exp. number is **0.18** W/mK.

TC for NF/DMF at 3.9% in wt



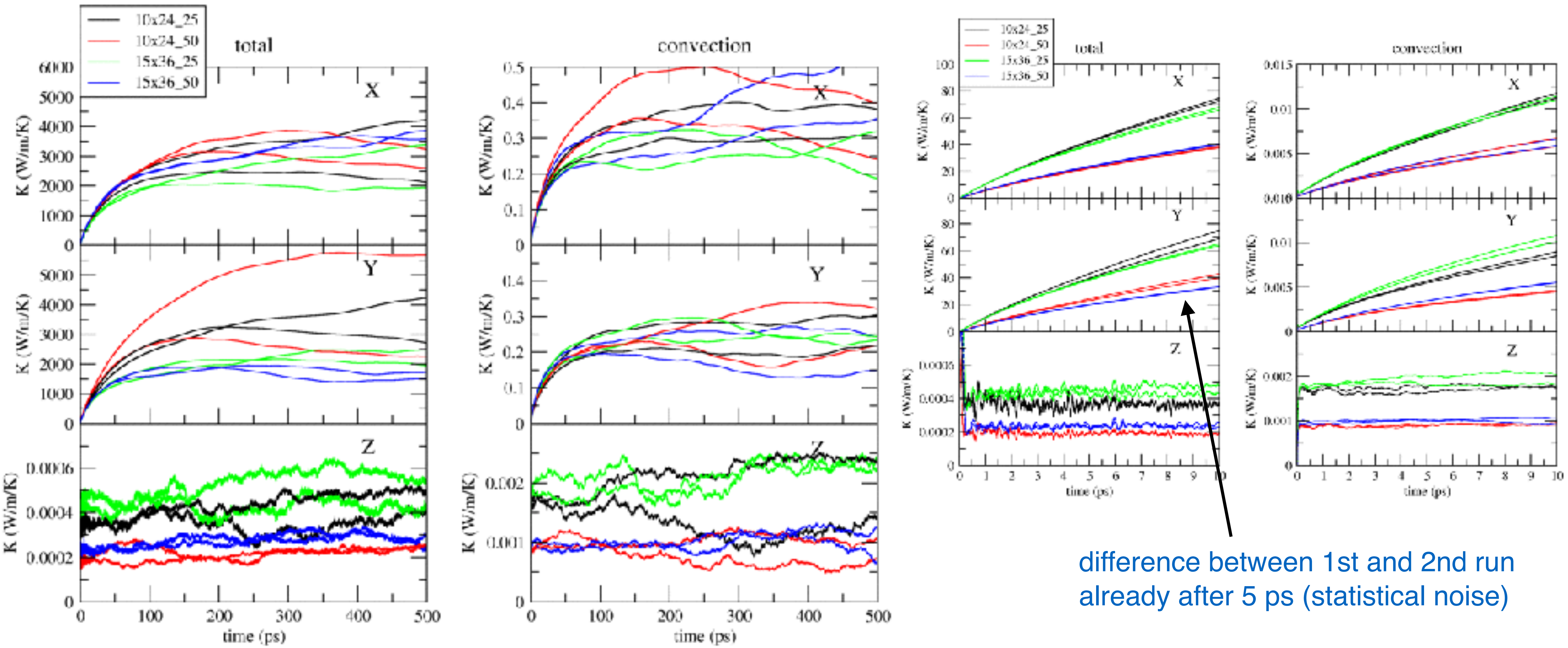


TC especially the convective part shows an increase with system size (say up to x=20 ps)



TC for periodic flake in gas phase

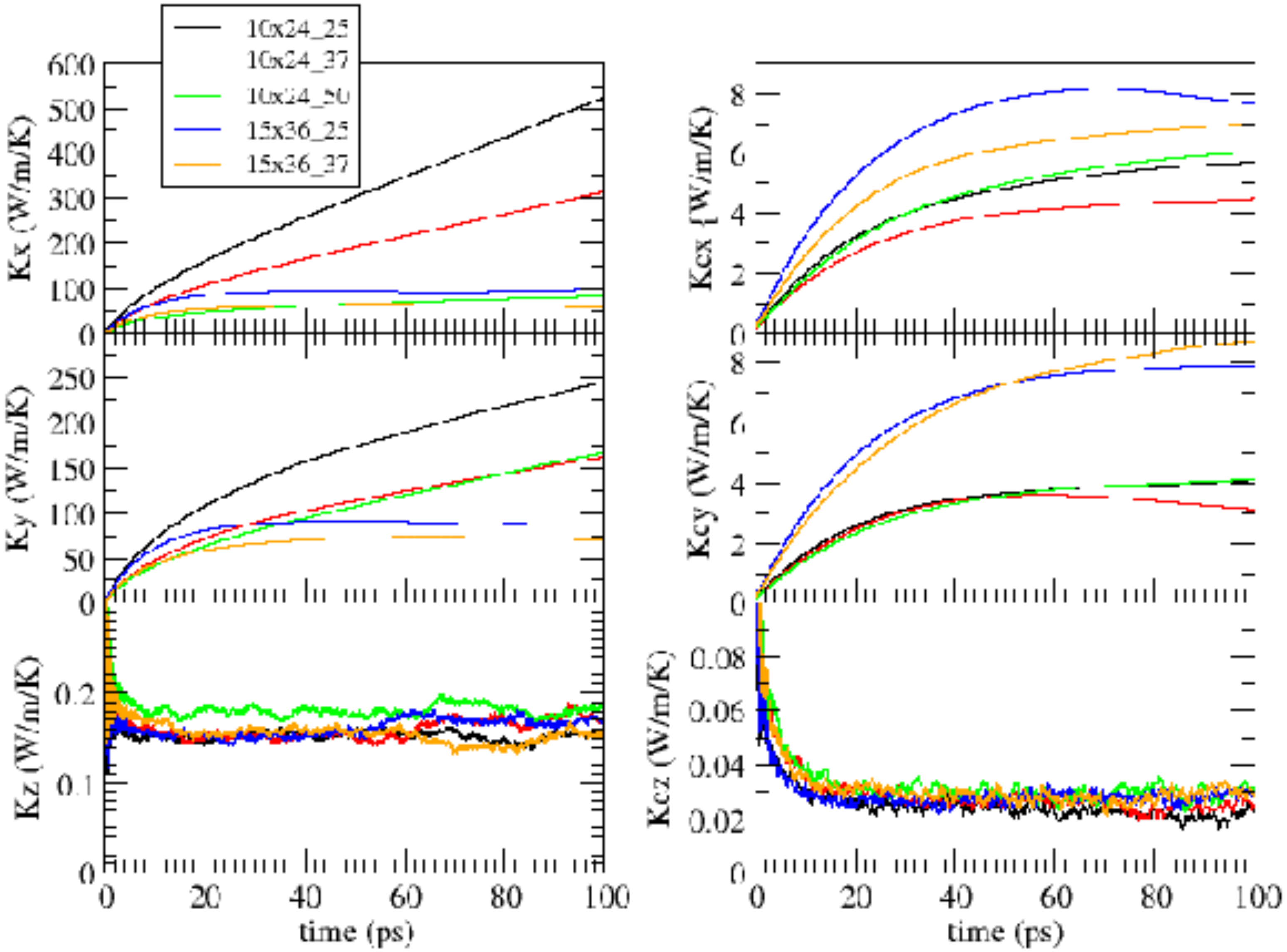
- two periodic flake sizes: 10x24=240 C atoms and 15x36=540 C atoms
- two independent simulations per system to check convergence



- Mode coupling theory predicts that the thermal conductivity does not converge in 2D systems (flexural modes are neglected!)
- We see convergence in ca. 500 ps towards the experimental number (2500 - 3000 W/m/K)
- Large error bars due to statistical noise. We need many (10-100) more runs… (see also Donadio et al.)

TC for periodic flake in DMF

- Hypothesis: interaction of flake flexural modes with DMF solvent enhances phonon scattering and thus thermal conductivity



- Similar slow convergence in DMF as in the gas phase
- We need many (10-100) more runs… Work in progress.

Summary

- Onsager's regression hypothesis: microscopic fluctuations at equilibrium follow same laws as macroscopic relaxation to equilibrium.
- Linear response theory gives us the relation between a perturbation source and the response of the system using a time correlation function.
- Green-Kubo relations allow for calculation of transport properties by integration over a time (auto-) correlation function.
- Thermal conductivity can be computed from an equilibrium simulation using a Green-Kubo equation.