Thermal Transport – Software and Validation

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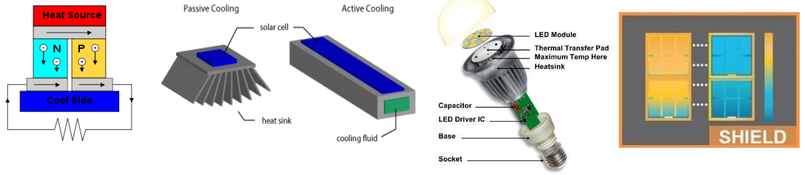
Motivation

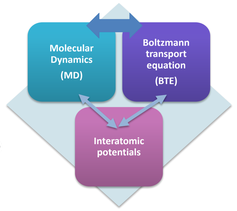


The prediction of thermal properties of solids and liquids is central to numerous problems in condensed matter physics and material science, including:

- Thermal management of optoelectronic and energy conversion devices, e.g. solar and photoelectrical cells
- Efficient thermoelectric materials

1. We present and validate methods to compute the thermal conductivity of solids and we compare the effect of approximations present in molecular dynamics (MD) and Boltzmann Transport Equation (BTE) based approaches.

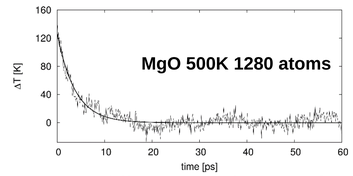
   We first validated the approximations of the theoretical approaches using empirical potentials.



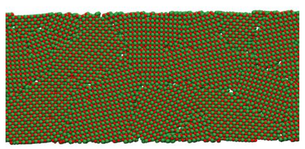
2. We developed MD-based techniques to compute the thermal conductivity of solids and liquids from first principles.

Solids: Sinusoidal Approach to Equilibrium

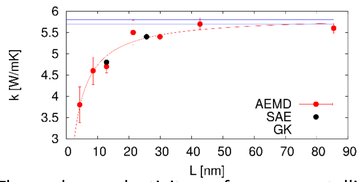
- Impose a temperature profile
- Let the system approach equilibrium in an NVE simulation
- Compute the thermal conductivity from the time evolution of the temperature



Temperature difference as a function of time; averages over multiple replicas



Section of a sample of nanocrystalline MgO



Thermal conductivity of nanocrystalline MgO at 1000K, simulated with an empirical potential

Main findings:

- Green-Kubo and NEMD requires longer simulation time than SAEMD
- *FPMD simulations are feasible with SAEMD using the Qbox software*

Method	GK	NEMD	SAEMD
Min # atoms	4096	11520	3840
Min volume of sim. cell (nm^3)	40	109	39
Min sim. time per max size (ns)	24	24	3.6
κ (W/mK)	32	31-40	31-40

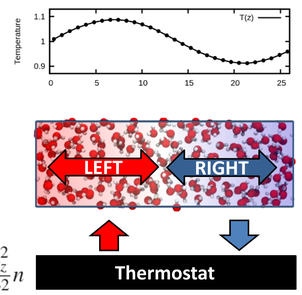
See M. Puligheddu, F. Gygi, G. Galli PRM **1**, 060802 (2017)

Fluids: Non Homogeneous Steady State

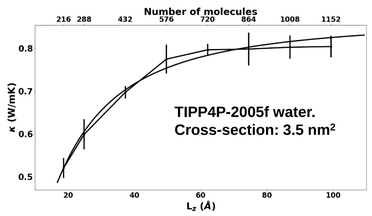
Impose and maintain a nonhomogeneous temperature profile

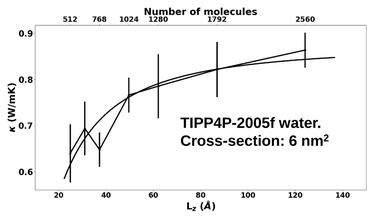
Energy naturally propagates from the hot to the cold part of the system

To maintain the temperature profile the thermostat transfers energy to and from the system



The thermal conductivity is given by $\kappa = \frac{\dot{q}}{\Delta T}\frac{L_z^2}{\pi^2}n$ where $\dot{q}$ is the energy transferred and ΔT is the temperature difference between the two sides





	NHSS 3.5 nm^2	NHSS 6 nm^2	Green-Kubo
Max # of molecules	1152	2560	4096
Simulation time	3 ns	2 ns	7 ns
κ	0.87	0.88	0.94
δκ	0.01	0.03	0.02

We studied TIP4P-2005f water at 300K 1 atm, tested 2 different cross-sections and compared Non Homogeneous Steady State (NHSS) results against GK results

We developed a new method to compute the thermal conductivity of both fluids and solids

- Generalizable in a straightforward way to FPMD
- No need to calculate, or define, the heat flux J
- Shorter simulation times than Green-Kubo simulations
- No need to exclude regions with unphysical energy exchange, as in NEMD

Fluids: 3D Steady State

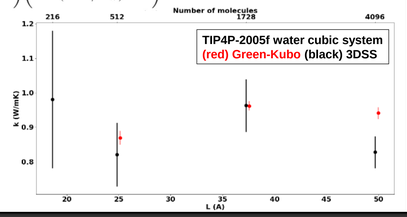
All non-equilibrium methods (NEMD, AEMD, SAEMD and NHSS) share two characteristics: one preferred direction for heat transport and sizeable finite size effects. GK simulations do not require to define a preferred direction of transport and exhibit smaller finite size effects. However GK requires the calculation of energy densities.

To reduce finite size effects in NHSS simulations, we defined a isotropic temperature profile, compatible with PBC:

$$T(x,y,z) = T_0 + \frac{\Delta T}{2}\Big(\cos(2\pi x/L_x) - 1\Big)\Big(\cos(2\pi y/L_y) - 1\Big)\Big(\cos(2\pi z/L_z) - 1\Big)$$

We applied the method to the calculations of the thermal conductivity of TIP4P-2005f water

- preliminary results

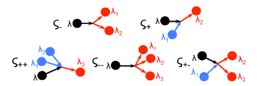


Boltzmann Transport Equation

- Taylor expansion of total energy using interacting clusters

$$E_a = E_0 + \Phi_a u_a + \frac{1}{2}\Phi_{ab}u_a u_b + \frac{1}{3!}\Phi_{abc}u_a u_b u_c + \cdots$$

Energy from DFT or potential — Use compressed sensing to fit force constants → lifetimes



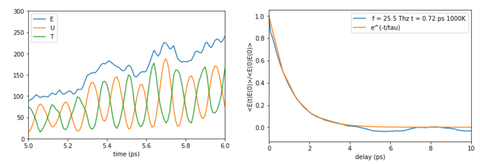
- Anharmonic terms→ lifetimes

Most accurate results: 3rd + 4th order scattering and PRN

Lifetimes From MD

Same wavevectors and eigenvectors from PRN used in BTE

We computed the phonon mode energy as a function of time for trajectories obtained from equilibrium MD.
From autocorrelation functions of phonon mode energies, we computed phonon lifetimes

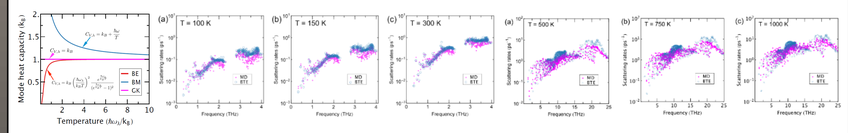


Comparison of BTE and MD results

Despite using different approximations MD and BTE yield similar values of the thermal conductivity.
➢ Is this due to error cancellation?

	MD	BTE
Phonon-phonon interactions	all orders included	3rd and 4th orders only
Statistics	Classical (equipartition)	Bose-Einstein
Contribution to k	Integrated	Single-mode approximation

We computed the mode-resolved heat capacity and lifetimes using both MD and BTE for MgO and PbTe



- Using MD lifetimes reduces thermal conductivity due to inclusion of scattering to all orders
- Using classical statistics changes occupation of phonon modes and hence κ
- Difference between GK and $(\tau_{MD} + C_{MD})$ lifetimes is due to single-mode approximation used the BTE approach

Sample	GK	$\tau_{MD} + C_{MD}$	$\tau_{BE} + C_{BE}$	$\tau_{MD} + C_{BE}$	$\tau_{BE} + C_{MD}$
PbTe 100K	10.4	11.2	12.4	10.7	13.0
PbTe 150K	6.5	7.0	7.7	6.8	7.9
PbTe 300K	3.0	3.1	3.4	3.1	3.4
MgO 500 K	32.6	29.4	32.8	27.0	35.3
MgO 750 K	19.6	16.3	20.2	15.6	20.9
MgO 1000 K	14.1	10.4	14.4	10.2	14.7

Thermal conductivity from Green-Kubo (GK) and BTE calculations using different statistics. τ_{MD} indicates lifetimes computed from MD. C_{MD} calculations use MD heat capacity. τ_{BE} indicates lifetimes computed with the Bose-Einstein statistic. C_{BE} calculations use the heat capacity calculated using the BE statistics

Acknowledgements

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