计算物质科学
教育部重点实验室(复旦大学)
Key Laboratory of Computational Physical Sciences
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Thermal Conductivity Calculation of Argon by Molecular Dynamics

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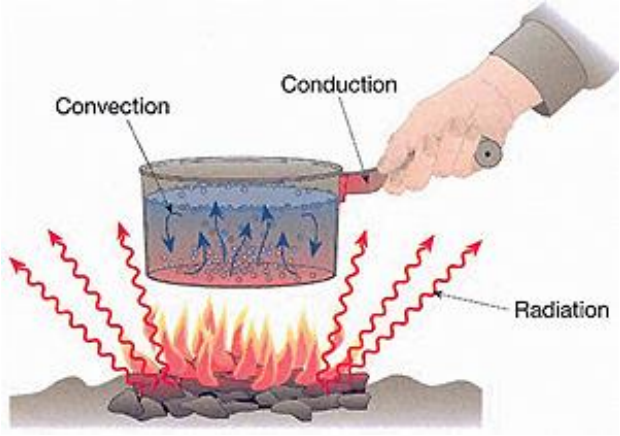
Lecture 3 Calculate Thermal conductivity with LAMMPS

Heat Transfer

Heat transfer： The phenomenon that heat energy transfer spontaneously from high temperature region to low temperature region when ΔT is presented.



Heat transfer

- Heat conduction： physical contact
- Convection： fluid motion
- Radiation： electromagnetic wave.

Fourier's Law

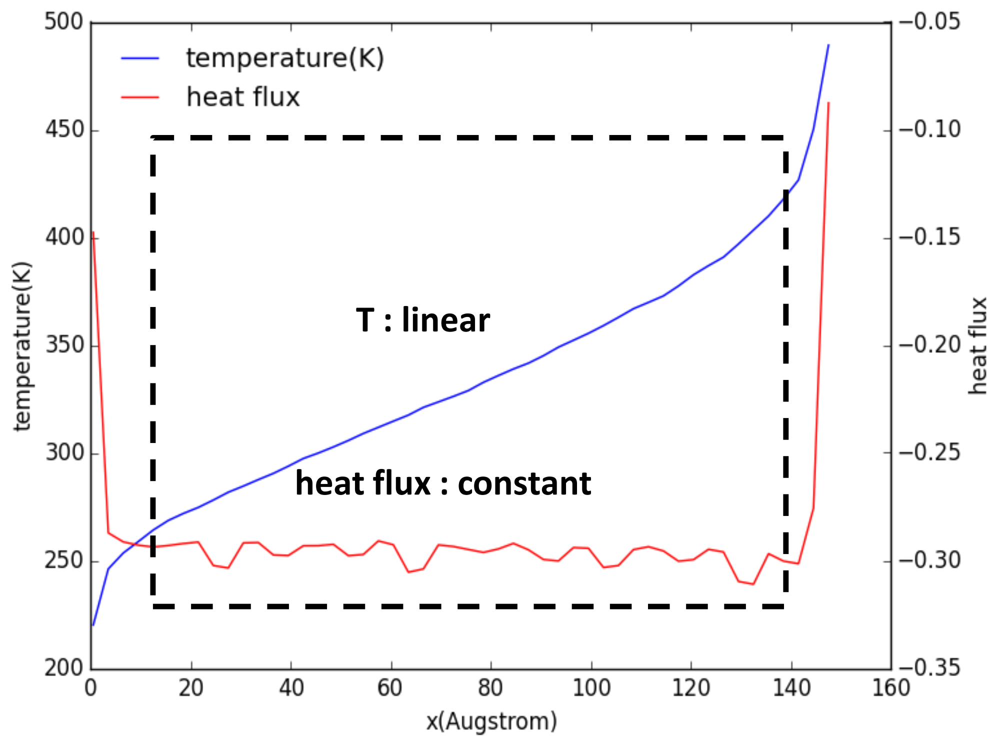
Thermal conductivity : capability of heat conduction

∇T : gradient of temperature

$\vec{j}$: heat flow density

κ : thermal conductivity

Fourier's Law : $\vec{j} = -\kappa \nabla T$



Diffusion Equation

$$\left.\begin{aligned} J_u &= -\kappa_{uv} \nabla^v T \\ \frac{\partial e}{\partial t} + \nabla^u \cdot J_u &= 0 \\ e &= c_V T \end{aligned}\right\} \quad \begin{aligned} &\frac{\partial T}{\partial t} = \frac{\kappa_{uv}}{c_V} \nabla^u \nabla^v T \\ &c_V \, the\ specific\ heat \end{aligned}$$

§ Green-Kubo Formula $\kappa_{uv} = \frac{1}{V k_B T^2} \int_0^\infty \langle J_u(t) J_v(0) \rangle dt$ at equilibrium of T

prof. Kaviany, Massoud, Heat Transfer Physics

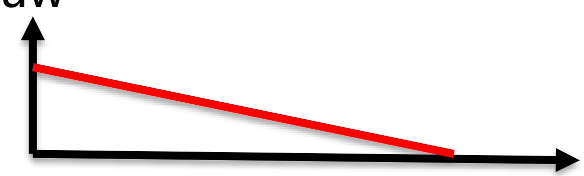
Temperature Profile

- Ballistic Phonon

when MFP is larger than the system then the temperature profile is like this , and phonon translate without scattering like this is called ballistic phonon.

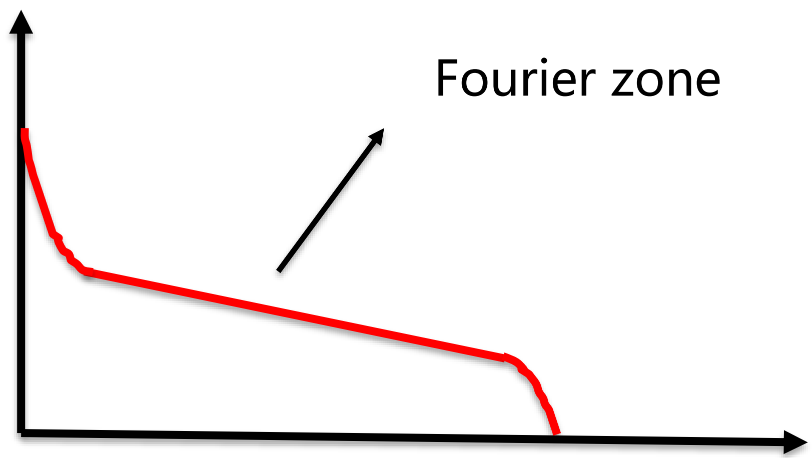
$$T_3^4 = T_1^4 + T_2^4$$

sufficient scattering could build local equilibrium and we get Fourier law



this can be understand using black body radiation and Stefan-Boltzmann law

MFP~L



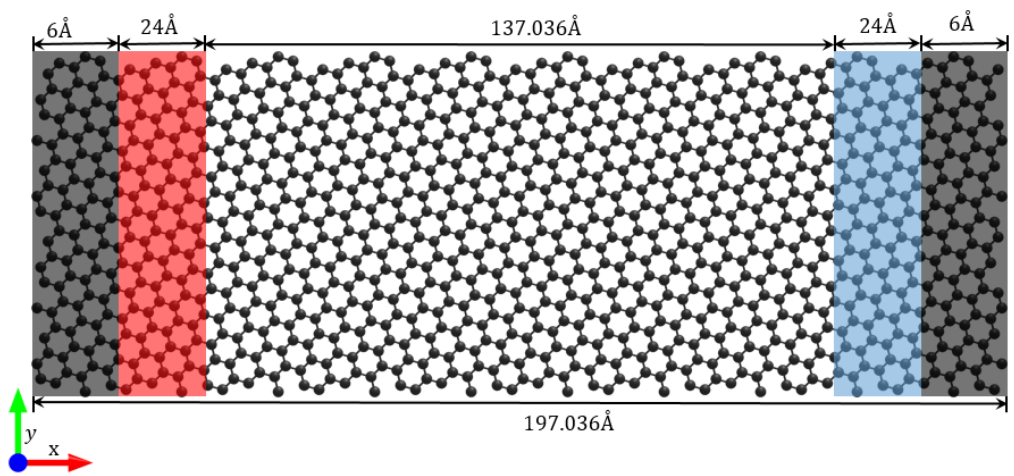
Direct method

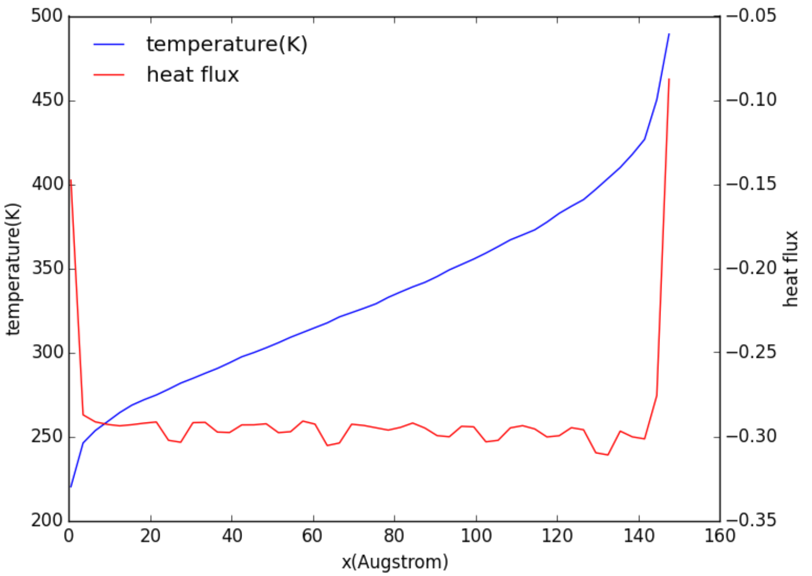
Direct method：

1) Fix the two ends
2) Heat baths of high and low temperature is applied
3) Get into steady state, heat flow and temperature gradient is measured.
4) Calculate with $\kappa = \frac{\langle J_x \rangle}{S \langle \nabla T \rangle}$

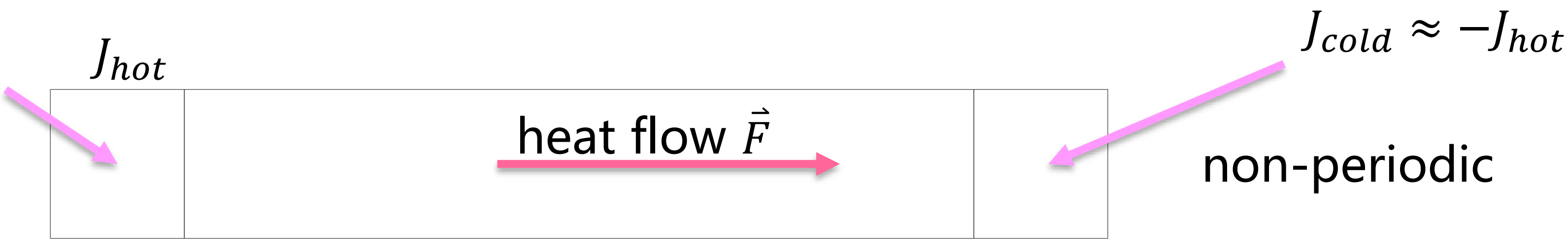
Disadvantage:

1) Only solids could be explored
2) Finite length effect
3) One direction a time





NEMD



two ways to calculate heat flux

from source $\left|\overrightarrow{F_1}\right| = \dfrac{J_{hot}}{S}$

from definition $\overrightarrow{F_2} = \dfrac{1}{V}\dfrac{d}{dt}\sum_i e_i \overrightarrow{r_i} = \dfrac{1}{V}\left[\sum_i e_i \overrightarrow{v_i} - \sum_i S_i\, \overrightarrow{v_i}\right]$

particle flow

through potential

continuation equation: $\left|\overrightarrow{F_1}\right| = \left|\overrightarrow{F_2}\right|$

fit the temperature profile to get ∇T

so we get $\kappa = \dfrac{\left|\overrightarrow{F_1}\right|}{\nabla T}$

NEMD

$$e_i(v_i, \{r_j\})$$

$$\overrightarrow{F_2} = \frac{1}{V}\frac{d}{dt}\sum_i e_i\overrightarrow{r_i} = \frac{1}{V}\left[\sum_i e_i\frac{d\overrightarrow{r_i}}{dt} - \sum_i \frac{de_i}{dt}\overrightarrow{r_i}\right] = \frac{1}{V}\left[\sum_i e_i\overrightarrow{v_i} - \sum_i\left(\nabla_{v_i}e_i\frac{d\overrightarrow{v_i}}{dt} + \sum_j \nabla_{r_j}e_i\cdot\frac{d\overrightarrow{r_j}}{dt}\right)\overrightarrow{r_i}\right]$$

$$= \frac{1}{V}\left[\sum_i e_i\overrightarrow{v_i} - \sum_i(-\overrightarrow{v_i}\cdot\overrightarrow{F_i})\,\overrightarrow{r_i} - \sum_{ij}\left(\nabla_{r_j}e_i\cdot\frac{d\overrightarrow{r_j}}{dt}\right)\overrightarrow{r_i}\right] = \frac{1}{V}\left[\sum_i e_i\overrightarrow{v_i} - \sum_i(-\overrightarrow{v_i}\cdot\overrightarrow{F_i})\,\overrightarrow{r_i} - \sum_{ij}\left(\nabla_{r_i}e_j\cdot\frac{d\overrightarrow{r_i}}{dt}\right)\overrightarrow{r_j}\right]$$

$$= \frac{1}{V}\left[\sum_i e_i\overrightarrow{v_i} - \sum_i(-\overrightarrow{v_i}\cdot\overrightarrow{F_i})\,\overrightarrow{r_i} - \sum_{ij}(\overrightarrow{v_i}\cdot\nabla_{r_i}e_j)\overrightarrow{r_j}\right] = \frac{1}{V}\left[\sum_i e_i\overrightarrow{v_i} - \sum_{i\neq j}(\overrightarrow{v_i}\cdot\nabla_{r_i}e_j)\overrightarrow{r_j}\right]$$

$$= \frac{1}{V}\left[\sum_i e_i\overrightarrow{v_i} - \sum_i S_i\overrightarrow{v_i}\right]$$

$S_i = \sum_{j\neq i}\overrightarrow{r_j}\nabla_{r_i}e_j$ is called stress tensor

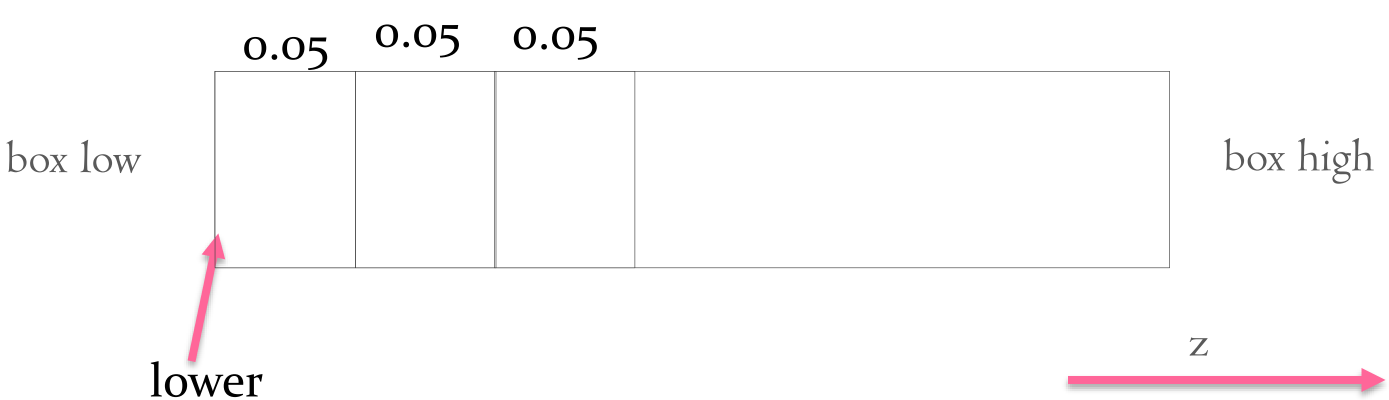
```
compute     myKE all ke/atom
compute     myPE all pe/atom
compute     myStress all stress/atom NULL virial
compute     flux all heat/flux myKE myPE myStress
variable    Jx equal c_flux[1]/vol
variable    Jy equal c_flux[2]/vol
variable    Jz equal c_flux[3]/vol
```

NEMD

same with ave/time

fix 2 all ave/spatial 10 100 1000 z lower 0.05 v_temp
file profile.langevin units box

real length unit



Muller-Plathe Method

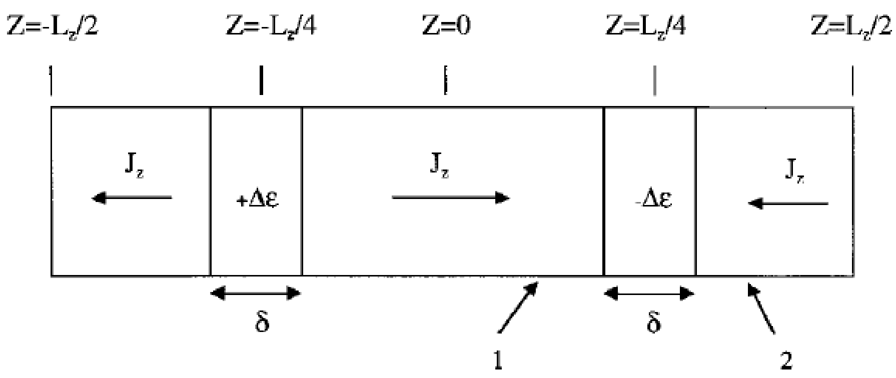
1) Constantly exchane the energy of the hottest atom within the cold region and the coldest atom within the hot region.
2) Calculation using $\kappa = \frac{\langle J_x \rangle}{2S\langle \nabla T \rangle}$ Besides solids

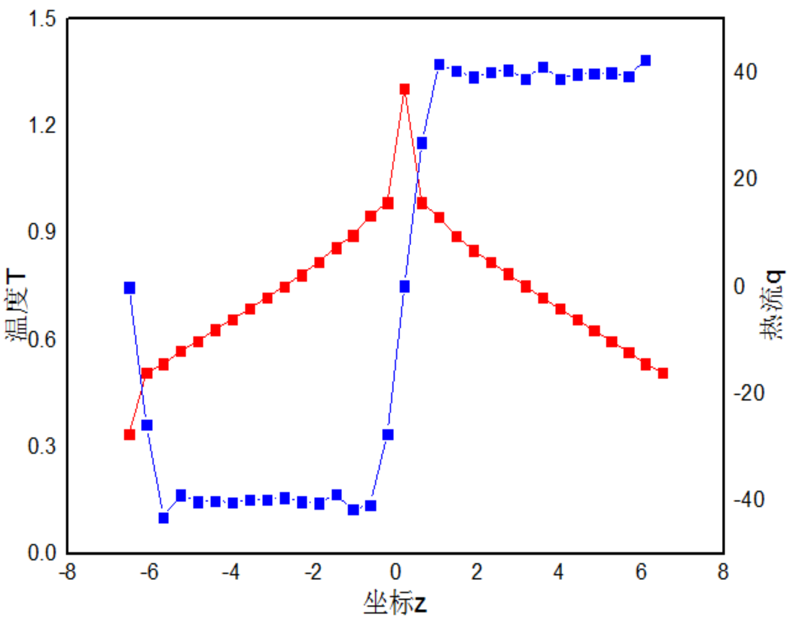
Advantages

1) Liquids and gas could be simulated
2) Heat flow could be controlled accurately.

Disadvantages

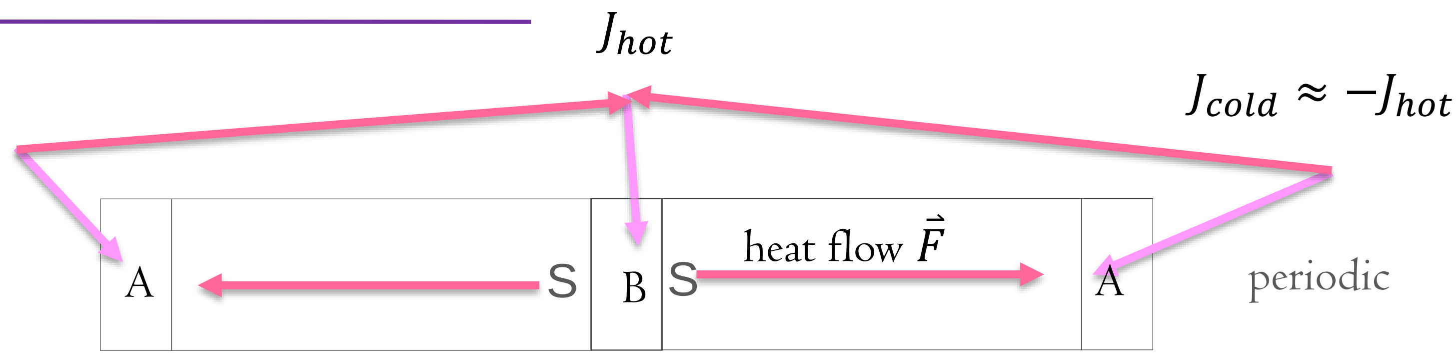
1) Double atoms must be use.





Muller-Plathe Method

Florian Muller-Plathe. J. Chem. Phys. 1997, 106(14)

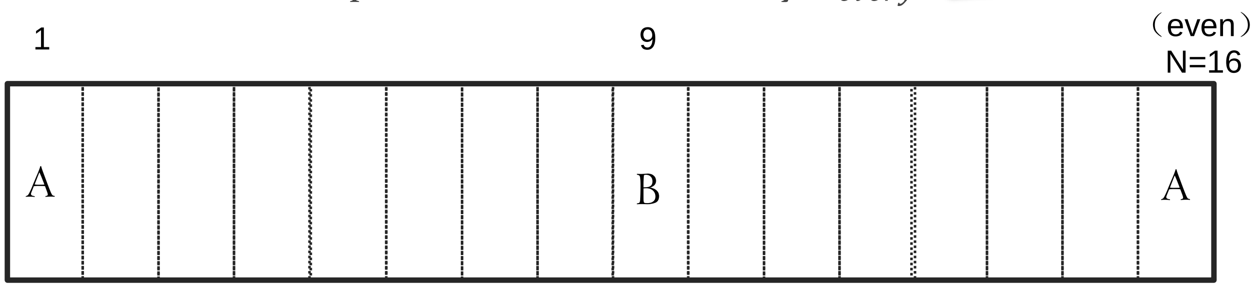


1. the two regions A are one region in fact because of periodicity
2. exchange the energy of the atom of min energy in A (e1) and the atom of max energy in B (e2). So energy in B increases by $\Delta e = e_1$-$e_2 > 0$
3. if exchange is carried out by every N_e steps so the power is E=$\frac{\Delta e}{n_{every} dt}$
4. the total surface area of region B is 2B so heat flux $J = \frac{E}{2S} = \frac{\Delta e}{2S n_{every} dt}$
5. fit the temperature profile between AB so we get$\kappa = \frac{J}{\nabla T}$

Muller-Plathe Method

direction

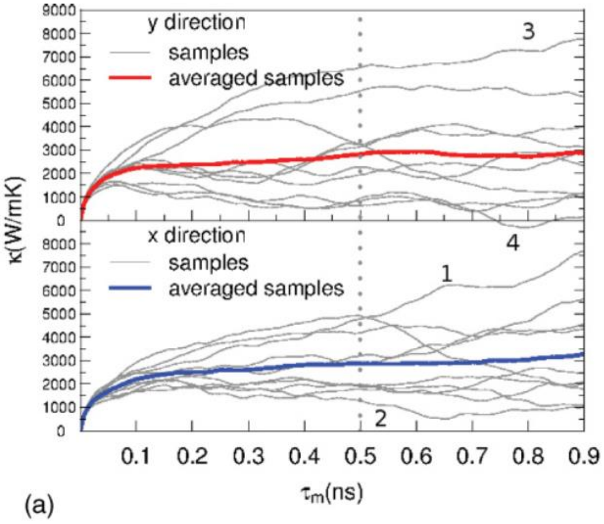
fix heat_swap all thermal/conductivity n_{every} z N



Green-Kubo Method

Calculated by integrate the heat flux autocorrelation function , which is based on a formula from Fluctuation dissipation theorem.

Advantages:
1) The size of the system is not needed to be too large
2) The whole thermal conductivity tensor could be obtained within one simulation
3) The temperature is uniform under equilibrium.



Zhang, H. et.al. *Phys. Rev. B* **2011**, *84* (11), 115460.

$$\kappa_{\mu\nu}(\tau_m) = \frac{1}{\Omega k_B T^2} \int_0^{\tau_m} \langle J_\mu(\tau) J_\nu(0) \rangle d\tau,$$

Disadvantages:
The average heat flux autocorrelation function converges really slow =>much computational affordance.

Compare

At $\mathrm{T} = 0.71$, $\rho = 0.844$, thermal conductivity of Argon calculated with three methods:

	direct	Muller-Plathe	Green-Kubo
Condition	20x10x10	20x10x10	10x10x10 , 12 seeds
Tc (W/mK)	0.126	0.127	0.124

Project

1、影响热导率的因素：

- 测量不同长度Lz，不同宽度Lx时的热导率，并拟合得出无穷大体系的热导率。
- 研究热导率与温度的关系
- 研究热导率与晶格常数的关系(加压)

2、分析讨论:

- 分析热导率计算误差的主要来源。
- 如何更准确统计温度分布?
- 交换间隔Δt的不同对结果有何影响？对温度分布有何影响？热源宽度δ对结果有何影响。
- 体会计算机‘实验’与真实物理实验的异同。

3、撰写实验报告

Homework

- 仔细阅读本节课涉及的lammps命令，弄清热导率计算的详细过程。
- 开始课程大作业

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THANK FOR YOUR ATTENTION!

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