



**微纳尺度传热计算：
建模及分子动力学模拟基础**

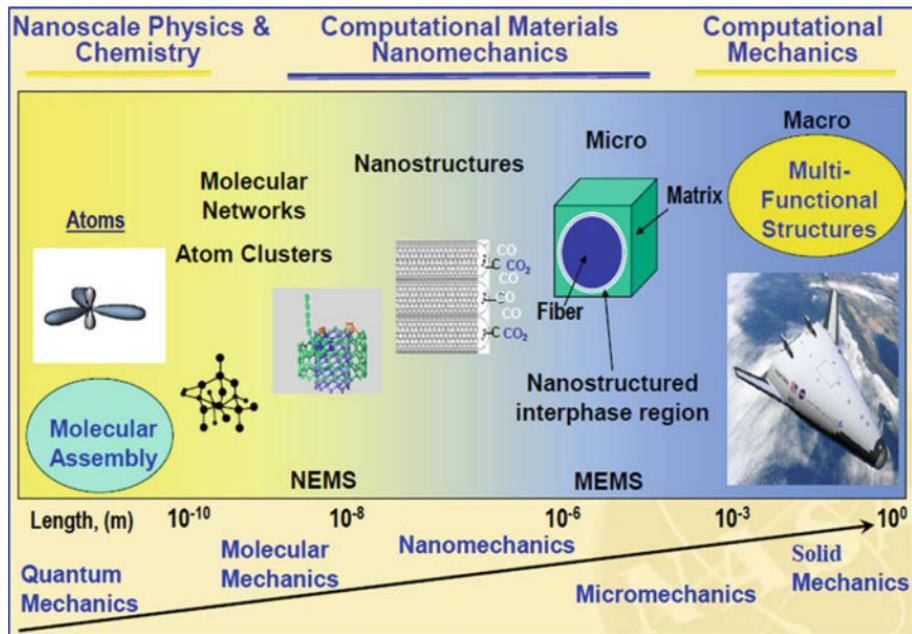


应鹏华

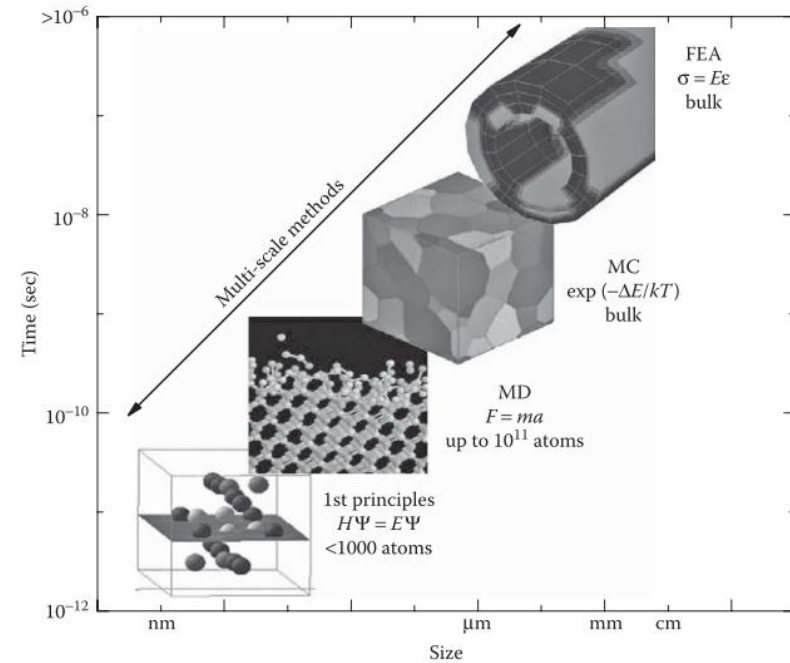
2021.04.10



1 广义力学的计算尺度



广义力学的空间尺度：从量子力学到固体力学¹

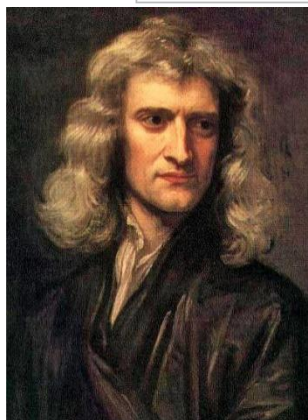


广义力学的时间尺度：从第一性原理到有限元²

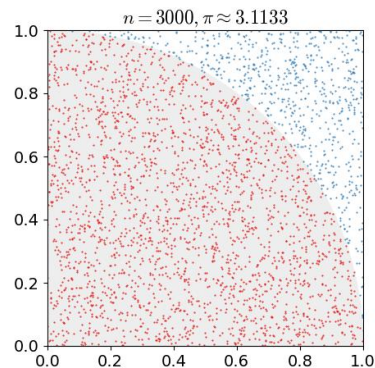
1. Harik, V. (2014). Trends in nanoscale mechanics: Mechanics of carbon Nanotubes, Graphene, Nanocomposites and molecular dynamics, Springer.
2. Lee, J. G. (2016). Computational materials science: an introduction, Crc Press.

2.1

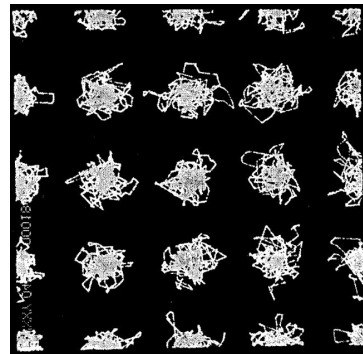
分子动力学发展简史



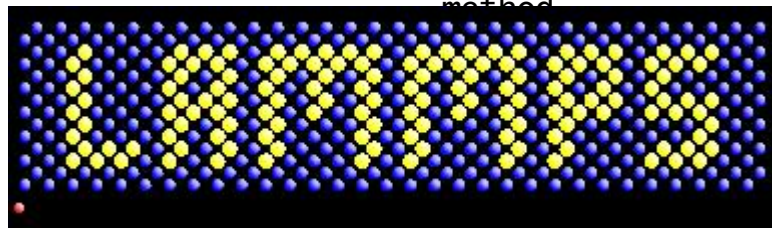
1687: 《自然哲学的数学原理》



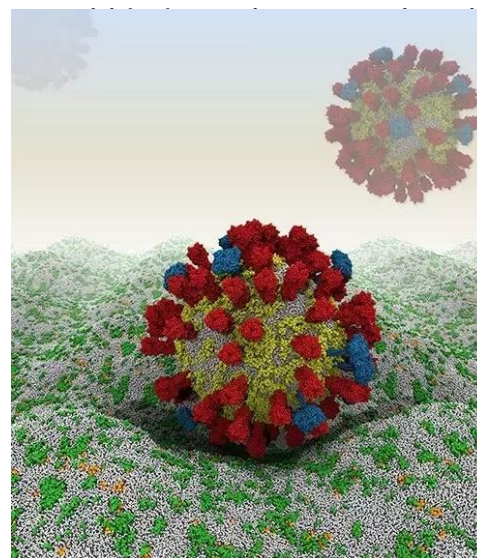
1930: Monte Carlo method



1957: Alder and Wainwright used an IBM 704 computer to simulate perfectly elastic spheres³



1995: a classical free molecular dynamics code release⁴



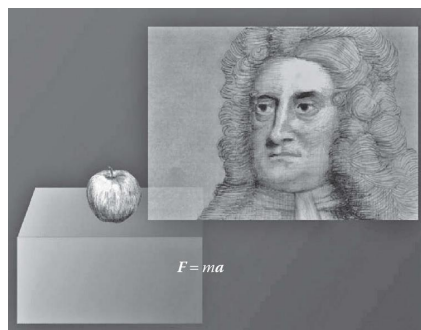
2015: Mark Sansom and his coarse-grain simulations of an influenza virus particle on a mammalian membrane (~120 nm). At > 10 M particles it's pretty huge, and currently stands at an impressive microsecond of simulation time⁵.

3. Alder, B. J.; Wainwright, T. E. (1959). "Studies in Molecular Dynamics. I. General Method". *J. Chem. Phys.* 31 (2): 459.

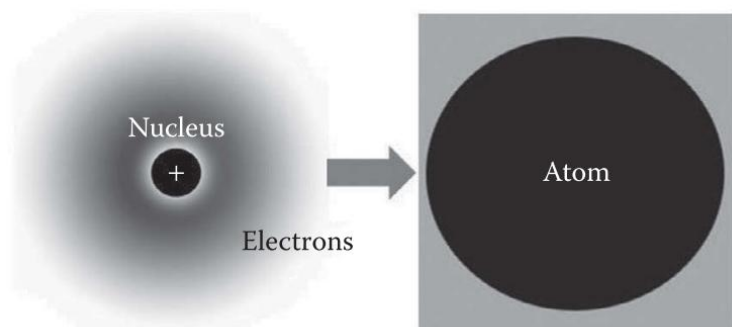
4. LAMMPS, see <http://www.cs.sandia.gov/~sjplimp/lammps.html>

5. Reddy T, Shorthouse D, Parton DL, et al. Nothing to Sneeze At: A Dynamic and Integrative Computational Model of an Influenza A Virion. *Structure*. 2015; 23 (3) : 584-597.

2.2 分子动力学的计算原理

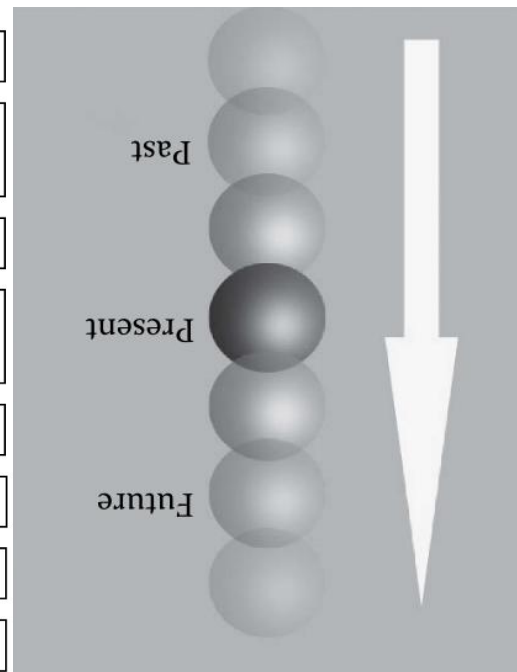
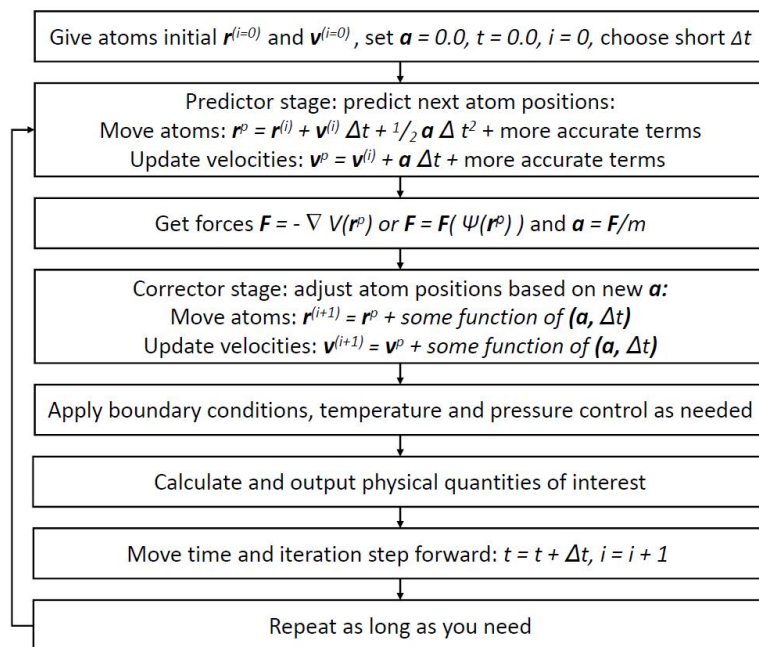


牛顿和他的苹果



与第一性原理不同，分子动力学模拟认为原子就是最小的计算元素，不可再分。

Simplified schematic of the molecular dynamics algorithm



分子动力学模拟计算流程：
未来所发生的由时间尺度上的过程所决定

分子动力学是基于牛顿力学在热力学系统下研究原子与分子的物理运动的计算模拟方法。

时间尺度：fs, ps, ns

空间尺度：nm, 1000~10000000原子的系统

计算的核心要素：初始结构、时间步、系综、力场、边界条件

2.3 初始结构、系综

600He@(40,40)SWCNT
 $\alpha_1=5.95\%$



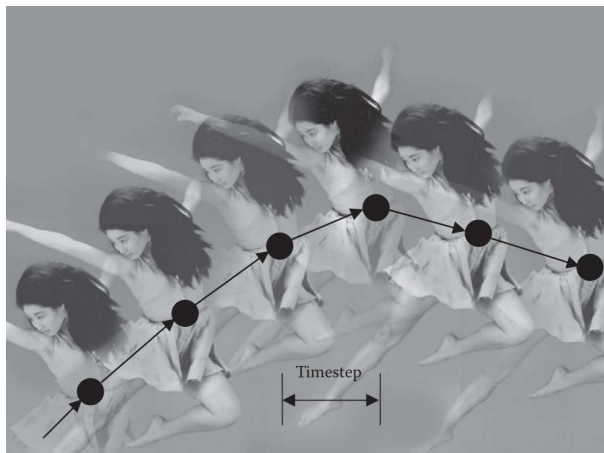
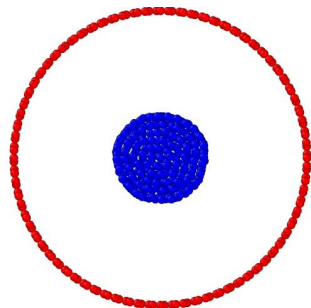
1640He@(40,40)SWCNT
 $\alpha_2=16.27\%$



2340He@(40,40)SWCNT
 $\alpha_3=23.21\%$



初始结构

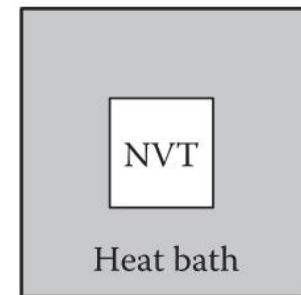


为什么分子动力学只能计算时间尺度很小的系统???

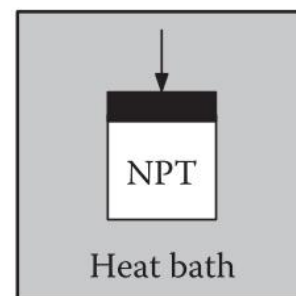
时间步



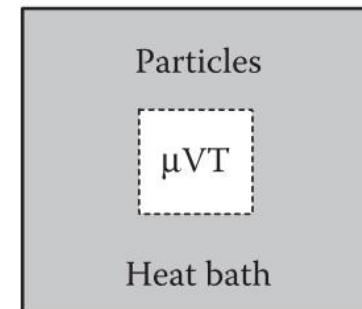
Microcanonical



Canonical



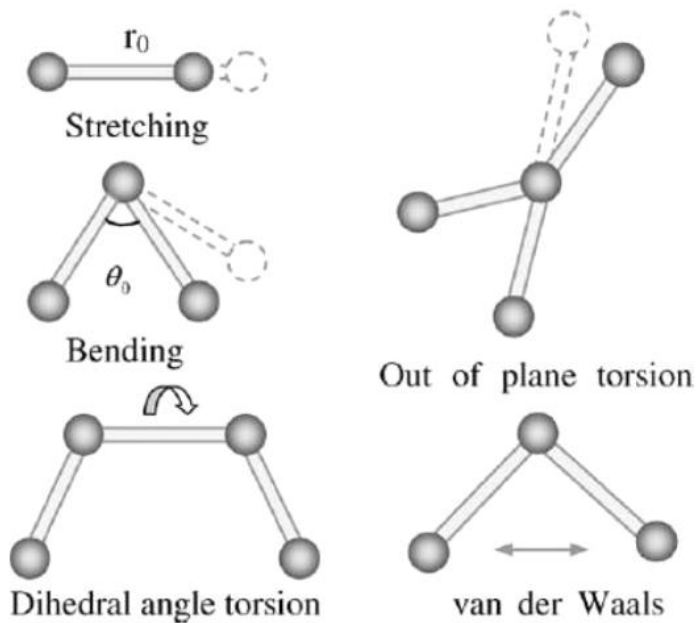
Isothermal-isobaric



Grand canonical

系综

2.4 力场



力场势函数的组成部分⁷

(a)

VFF: $V_r = \frac{1}{2}K_r(\Delta r)^2$

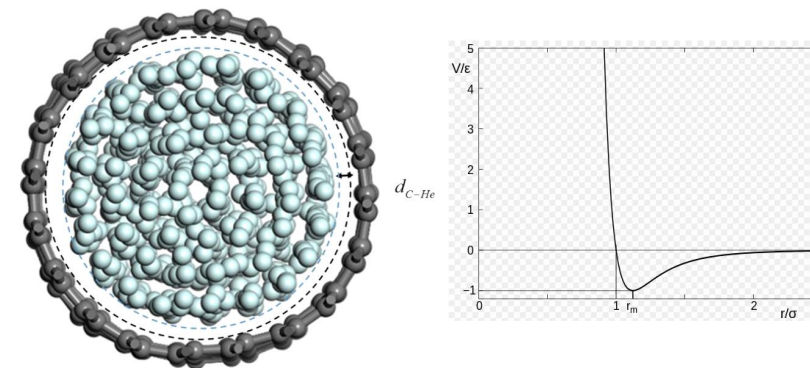
SW: $V_2 = Ae^{\rho/(r-r_{max})} (B/r^4 - 1)$

(b)

VFF: $V_\theta = \frac{1}{2}K_\theta d_1 d_2 (\Delta\theta)^2$

SW: $V_3 = Ke^{\rho_1/(r_{12}-r_{max12})+\rho_2/(r_{13}-r_{max13})} (\cos\theta - \cos\theta_0)^2$

共价材料的力场⁶



储氮碳纳米管碳原子与氮原子之间的力场：LJ势⁸

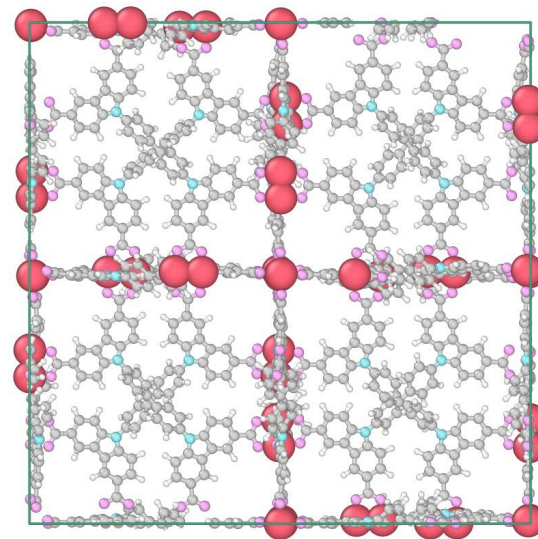
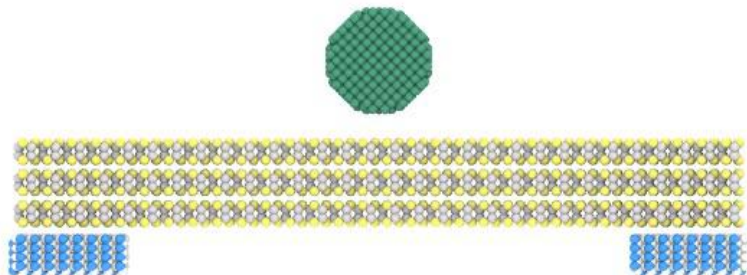
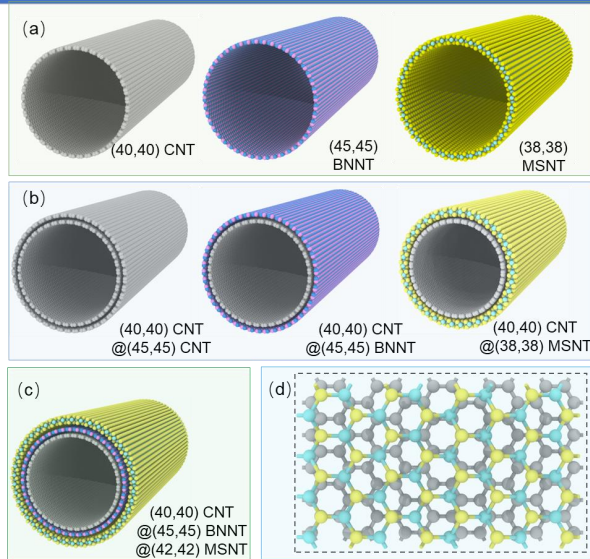
6. Jiang, J. W. (2015). "Parametrization of Stillinger-Weber potential based on valence force field model: application to single-layer MoS2 and black phosphorus." *Nanotechnology* 26(31): 315706.

7. Li C, Chou T W. A structural mechanics approach for the analysis of carbon nanotubes[J]. *International Journal of Solids & Structures*, 2003, 40(10):2487-2499.

8. 应鹏华. 储氮单壁碳纳米管坍塌行为控制研究[D]. 2018.

3.1 原子结构建模

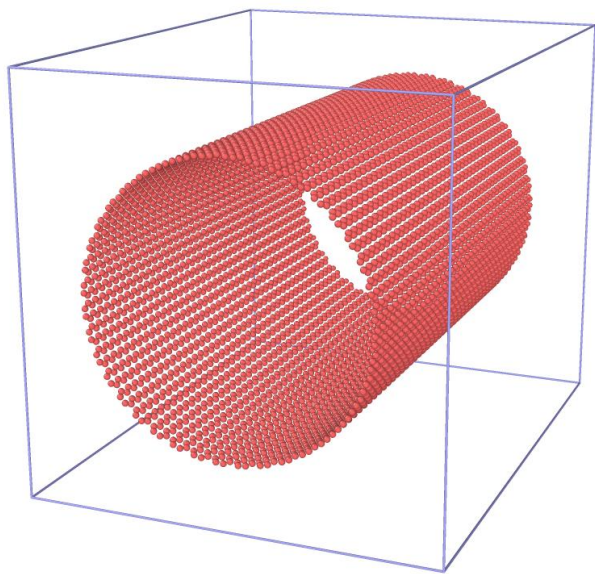
- 1. 1D: 碳纳米管、二硫化钼纳米管
- 2. 2D: 石墨烯、二硫化钼
- 3. 3D: 金属有机框架材料



3.2 lammps原子结构的data格式

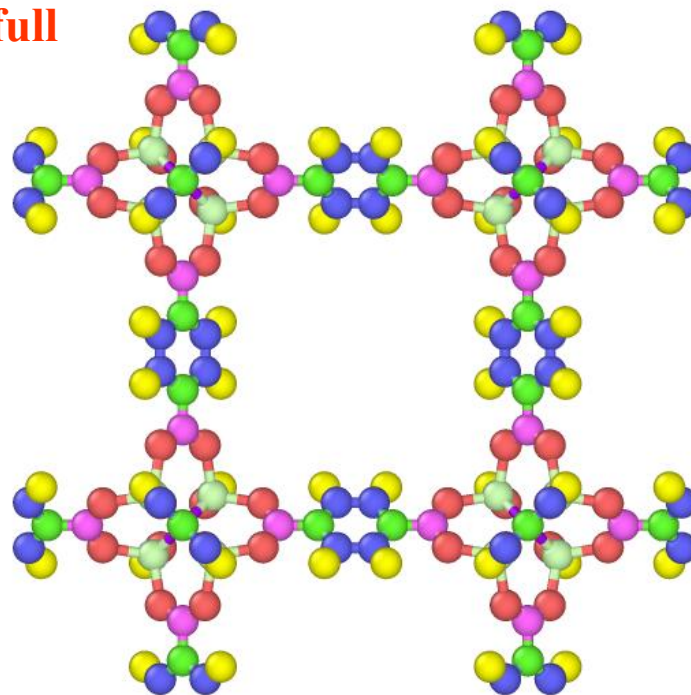
详细介绍见: https://lammps.sandia.gov/doc/read_data.html

atomic



不包含拓扑关系
依赖力场根据原子坐标建立拓扑关系

full



直接包含拓扑关系

■ 展示两种不同格式data的区别

3.3 原子结构建模的开源工具

1. **VMD**：碳纳米管、碳化硼纳米管、石墨烯建模 <http://www.ks.uiuc.edu/Research/vmd/>
2. **OVITO**：可视化及扩胞、旋转、结构后处理 <https://www.ovito.org/>（Basic版本学术免费）
3. **VESTA**：读取CIF结构文件进行可视化和后处理 <http://www.jp-minerals.org/vesta/en/download.html>
4. **自行编程建模**：怎么建立一个MoS₂纳米管结构

■ 展示如何建立石墨烯、碳纳米管模型

1. 建立一个石墨烯结构
2. 建立一个（10,10）碳纳米管

■ 展示如何利用OVITO进行扩胞等后处理操作

3. 建立一个中间含圆形孔洞的石墨烯
4. 建立一个碳纳米管和二硫化钼纳米管的复合结构

■ 展示如何通过CCDC搜索MOF结构并通过lammmps-interface生成支持lammmps “full” 格式的data文件

5. 建立一个可以2*2*10的MOF-5的supercell

lammmps-inferface: https://github.com/peteboyd/lammmps_interface

CCDC主页: <https://www.ccdc.cam.ac.uk/structures/?ccdc-check=4242fc559bad366308d7001e15131efa>

4.1 lammps 计算脚本的结构

```
### Basic setup ###
variable      simname index 4040CNT_10nm
variable      temperature equal 300
log           log.${simname}.txt
units         metal
boundary      s s p
timestep      0.001 #1fs
atom_style    atomic
neighbor      2.0 bin

### Structure ###
read_data     ${simname}.data

### Potentials ###
mass          1 12.01
pair_style    tersoff
pair_coeff     * * BNC.tersoff C

### Output Setting ###
variable      length equal lz
variable      energy equal etotal
thermo        1000
thermo_style  custom step temp lz pzz etotal
dump          1 all atom 1000 ${simname}.lammprj

### Energy Minimization ###
fix           1 all box/relax z 0.0
min_style     cg
minimize      1e-25 1e-25 50000 100000
unfix         1

### Relaxation ###
velocity      all create ${temperature} 12345 mom yes rot no
fix           NPT1 all npt temp ${temperature} ${temperature} 0.1 z 0 0 1.0
run           100000
unfix         NPT1
```

基本设置



结构



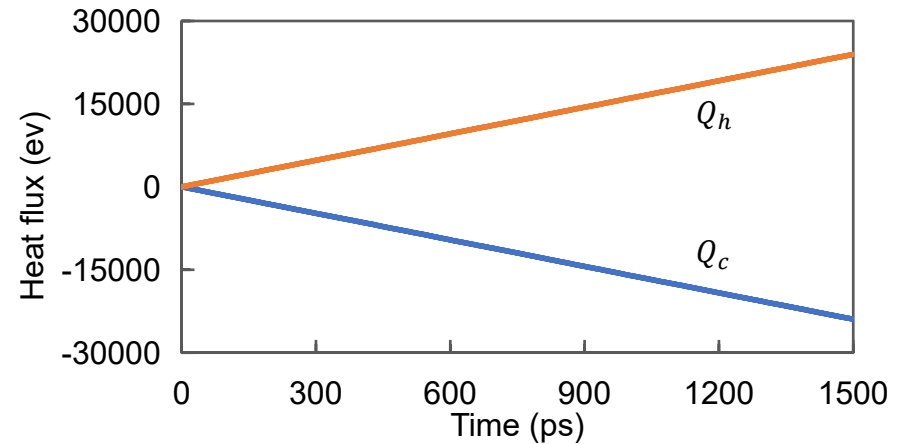
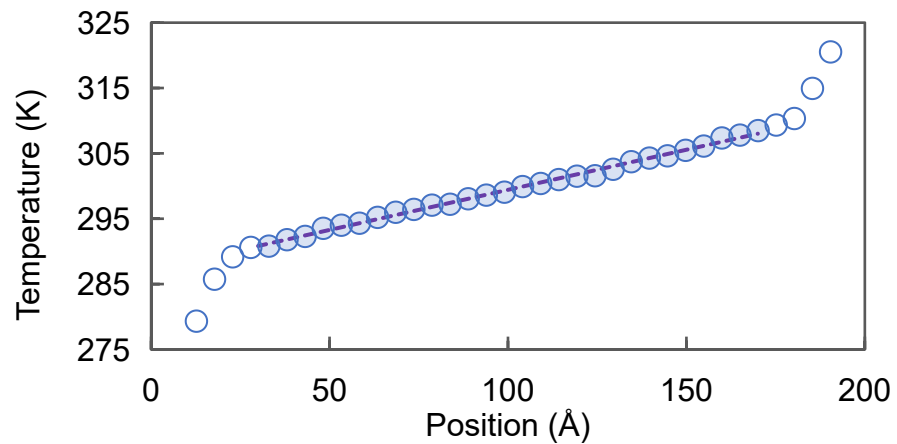
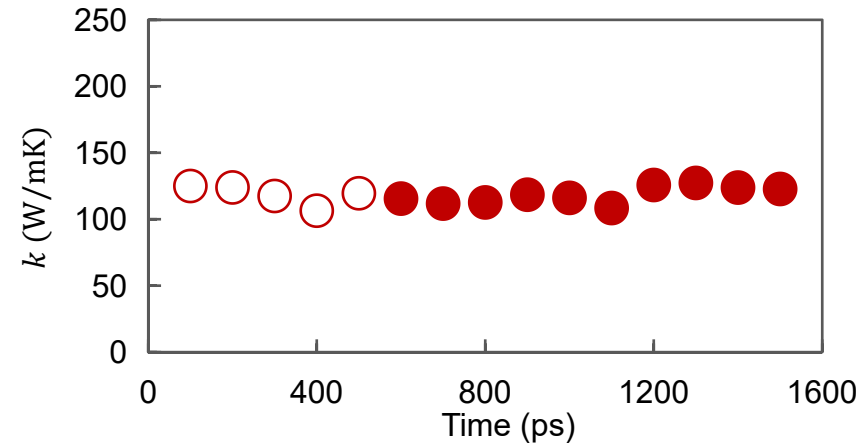
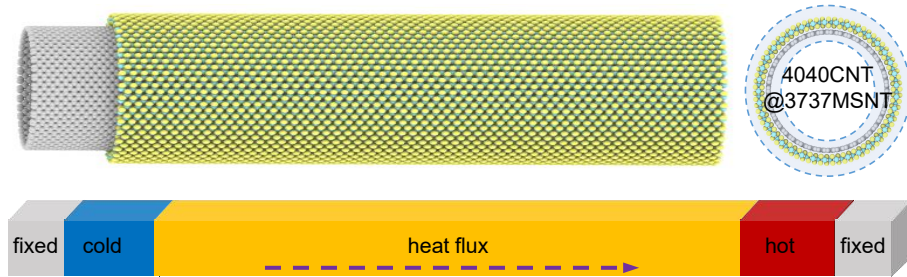
输出设置



能量最小化&弛豫&产出

- 展示一个碳纳米管计算的结果
作业：计算碳纳米管在300K下的热膨胀系数和比热容（可以分别计算250K、300K和350K结果拟合）

4.2 How to calculate thermal conductivity



读lammps manual的how to calculate thermal conductivity 及相关的examples
作业：完成并明白一个计算热导率例子的脚本



THANK YOU
Q&A

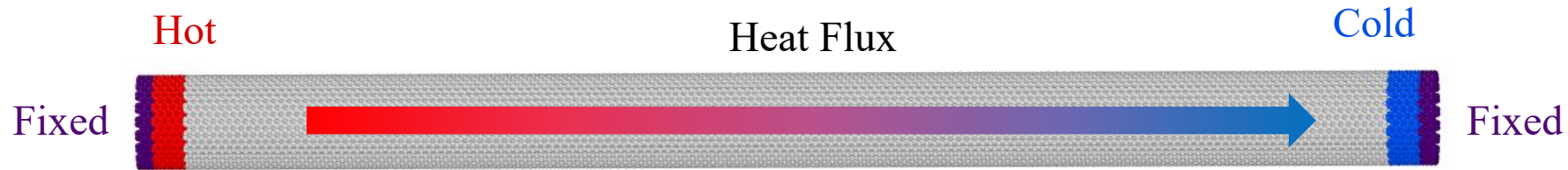


微纳尺度传热计算：
非平衡态、平衡态、界面热传导

应鹏华

2021.04.17

1.1 傅里叶热传导定律：非平衡态下的热运输

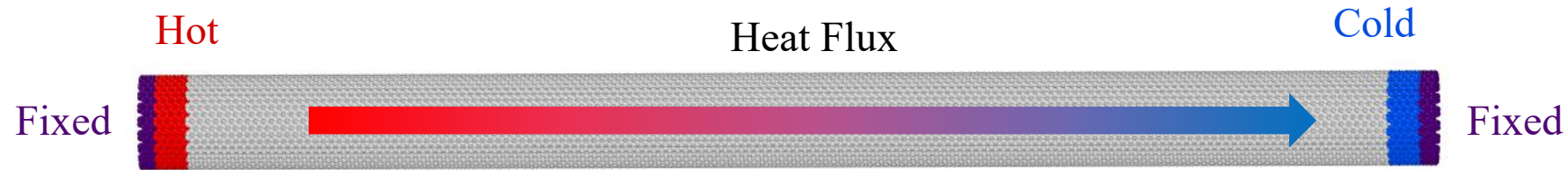


运输过程 (transport process)：热力学性质的不均匀性导致的热力学过程

- **能量运输**：热传导中的傅里叶定律
- **动量运输**：粘滞现象中的牛顿定律
- **质量运输**：扩散中的菲克定律

非平衡态：将一个系统置于两个温度不同的热源之间，最终会在系统内建立一个稳定的温度分布，系统处于**稳态**，但不处于一个**平衡态**。平衡态时可以认为温度是相同的，因此是非平衡态。

1.1 傅里叶热传导定律：非平衡态下的热输运

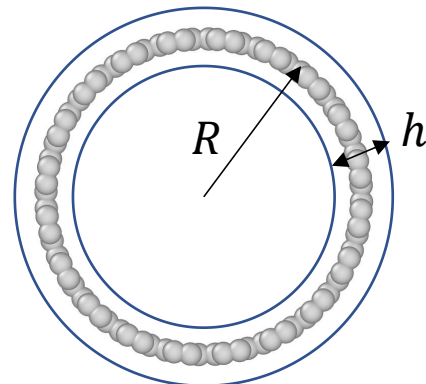
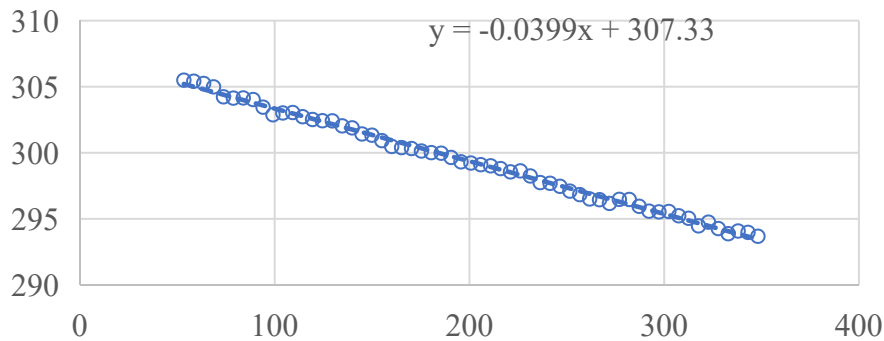
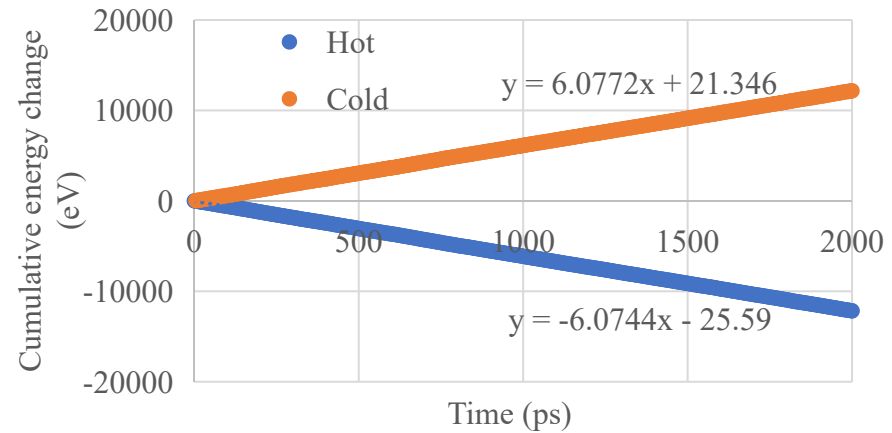
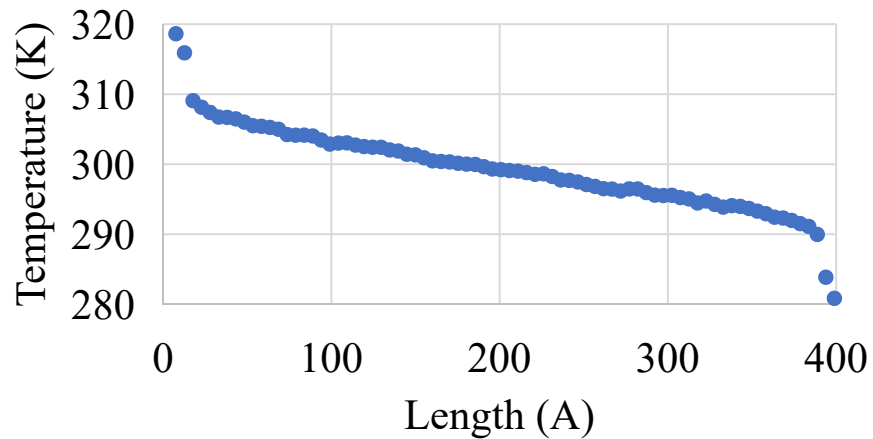
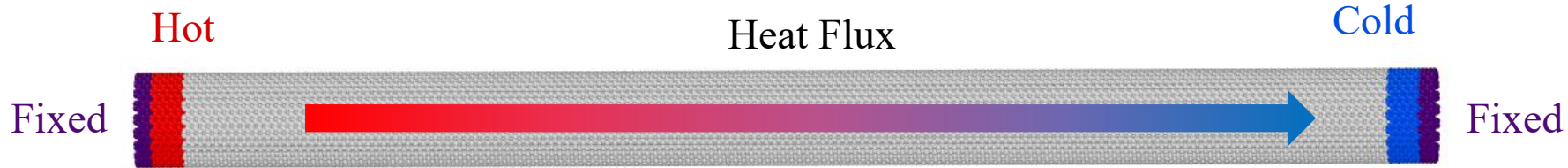


假设输运方向沿着一个特定方向（假设是 x 方向）的情形。热传导现象的宏观规律由傅里叶定律描述。傅里叶定律是说热流密度(heat flux, 或者heat current) J , 即单位时间穿过单位面积的热量, 在数量上正比于温度梯度 $\frac{dT}{dx}$:

$$J = -k \frac{dT}{dx}.$$

这里的 κ 就反映了热量输运的难易程度： k 越大代表热量越容易被输运。这样的物理量被称为输运系数(transport coefficient)。具体到热传导, 输运系数 κ 叫做**热导率(thermal conductivity)**。注意等式右边有个负号, 它表示热量的传导方向与温度梯度的方向相反, 指向温度降低的方向(一个物理量的梯度的方向指向它增加的方向)。在国际单位制中, 温度梯度的单位为K/m, 热流密度的单位是W/m², 故热导率的单位是Wm⁻¹K⁻¹。

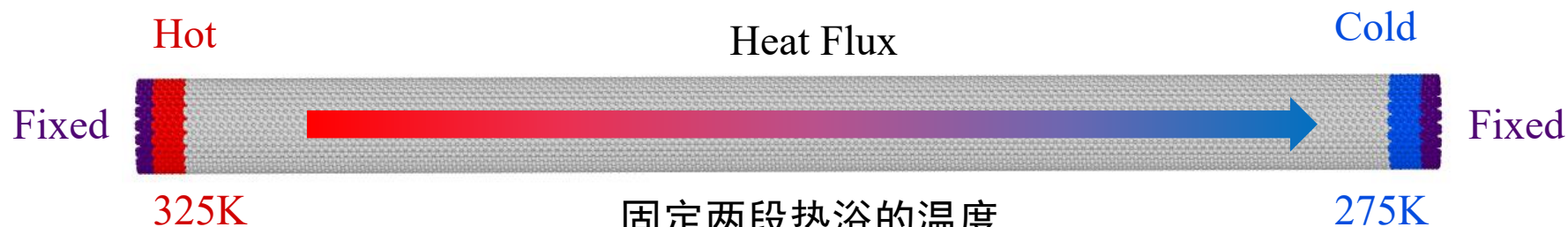
1.3 傅里叶热传导定律：热导率的表达式



$$A = 2\pi R h$$

■ 展示如何基于已有结果计算热导率

2.1 非平衡态热导率计算：局部热浴法/固定温差法



固定两段热浴的温度
统计：

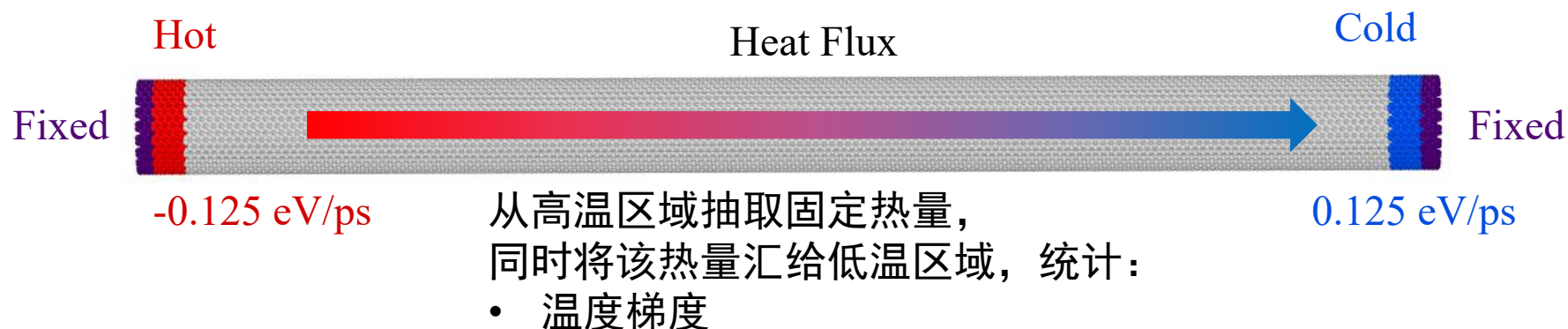
- 温度梯度
- 热流

核心in 文件

```
fix NVE3 innt nve
fix hot1 gthigh langevin ${thigh} ${thigh} ${Tdamp} 59804 tally yes
fix cold1 gtlow langevin ${tlow} ${tlow} ${Tdamp} 287859 tally yes
run 500000

reset_timestep 0
compute KE all ke/atom
variable KB equal 8.625e-5
variable TEMP atom c_KE/1.5/${KB}
compute BLOCKS1 all chunk/atom bin/1d z lower 0.0125 units reduced
fix T_PROFILE1 all ave/chunk 10 100000 1000000 BLOCKS1 v_TEMP file temp.${simname}.txt
thermo_style custom step c_innernt_temp c_hot_temp c_cold_temp f_hot1 f_cold1 etotal
run 2000000
```

2.2 非平衡态热导率计算：热量交换法



核心in 文件

```
fix NVE innt nve
fix hot all heat 1 0.0028825 region thigh #给热处输入0.125ev/ps,换算系数:0.0230605
fix cold all heat 1 -0.0028825 region tlow #给冷处抽出0.125ev/ps能量。
thermo_style custom step c_innernt_temp lz pzz etotal c_hot_temp c_cold_temp
compute KE all ke/atom
variable KB equal 1.989e-3 # 玻尔兹曼常数, Kcal/(mole*K)
variable TEMP atom c_KE/1.5/{KB}
compute BLOCKS1 all chunk/atom bin/1d z lower 0.025 units reduced
fix T_PROFILE1 all ave/chunk 10 10000 100000 BLOCKS1 v_TEMP file temp.${simname}.txt
run 500000
```

- 展示如何采用lammmps-interface获得HKUST-1的结构和Dreiding力场
- 展示如何基于热量交换法计算HKUST-1热导率

2.3 非平衡态热导率计算：界面热导

$$J = -k \frac{dT}{dx}$$

傅里叶热传导

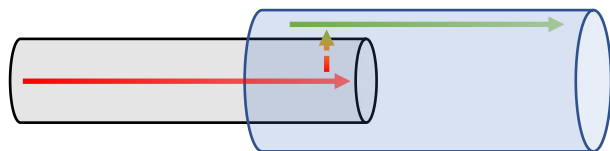
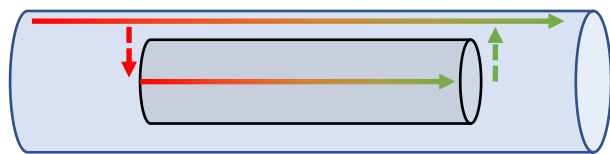
$$k = -\frac{Jdx}{dT}$$

热导G

$$G = \frac{k}{l} = -\frac{J}{l(\frac{dT}{dx})} = \frac{J}{dT}$$

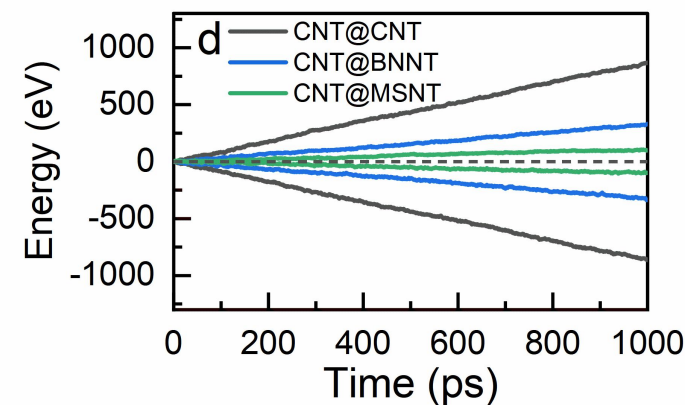
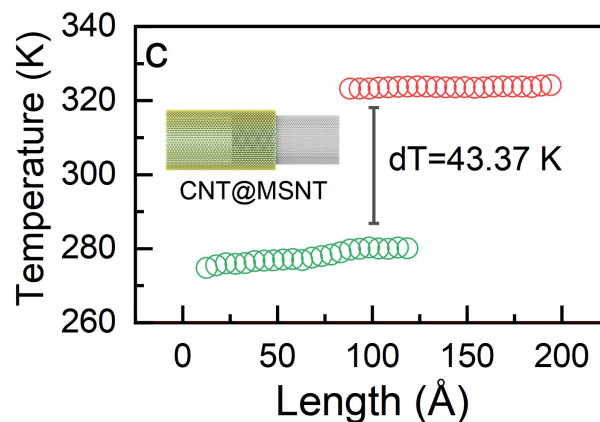
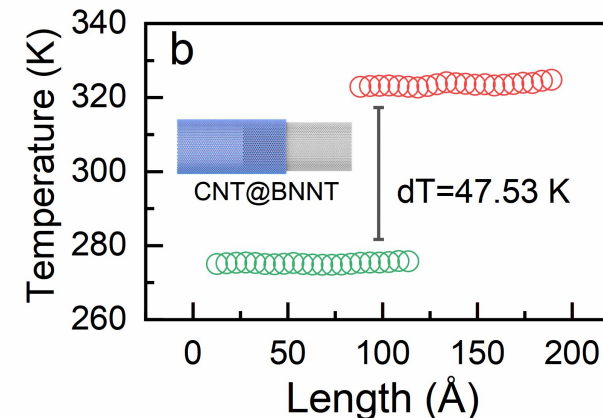
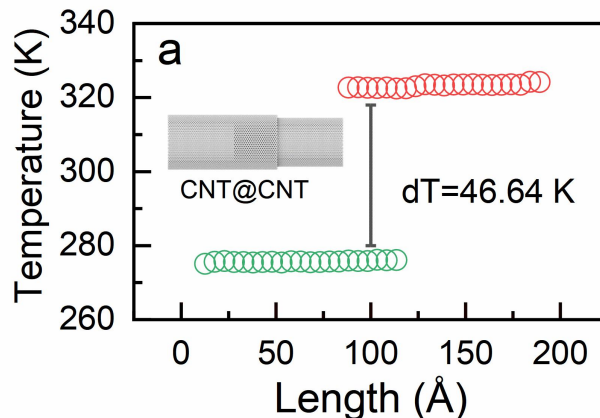
界面热阻H

$$H = \frac{dT}{J}$$



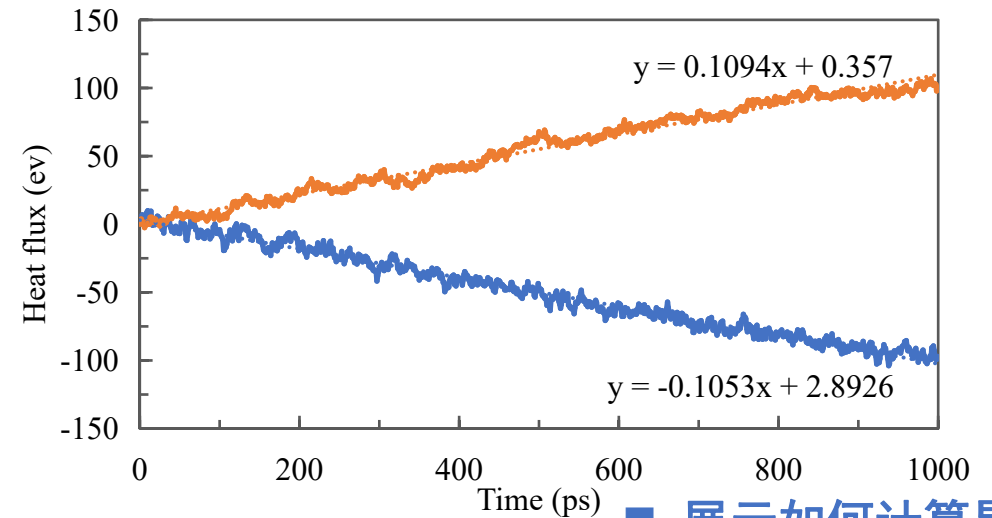
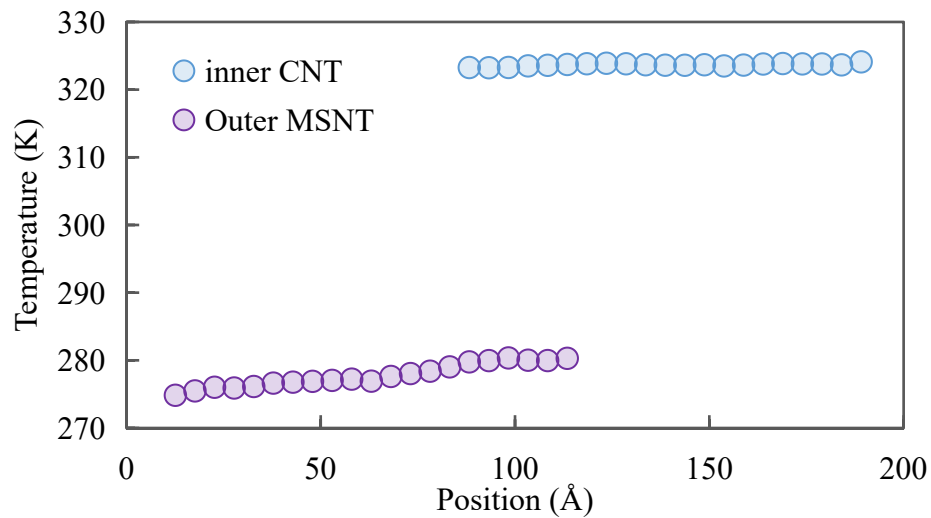
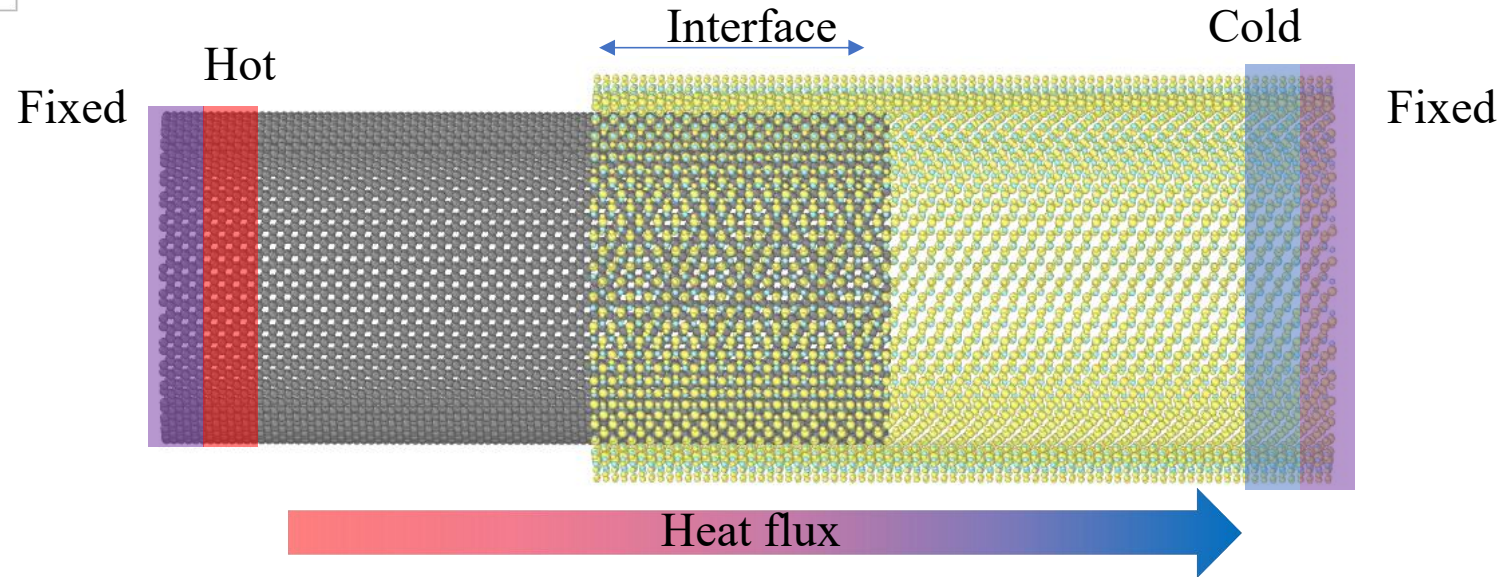
CNT base

Nanotube coating



Ying, P., et al. (2021). "Effects of coating layers on the thermal transport in carbon nanotubes-based van der Waals heterostructures." *Carbon* **176**: 446-457.

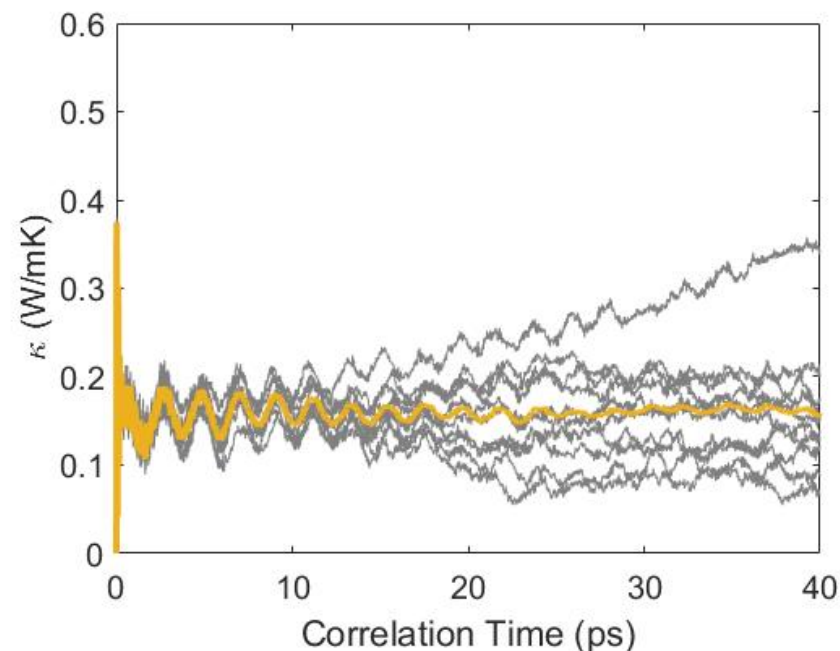
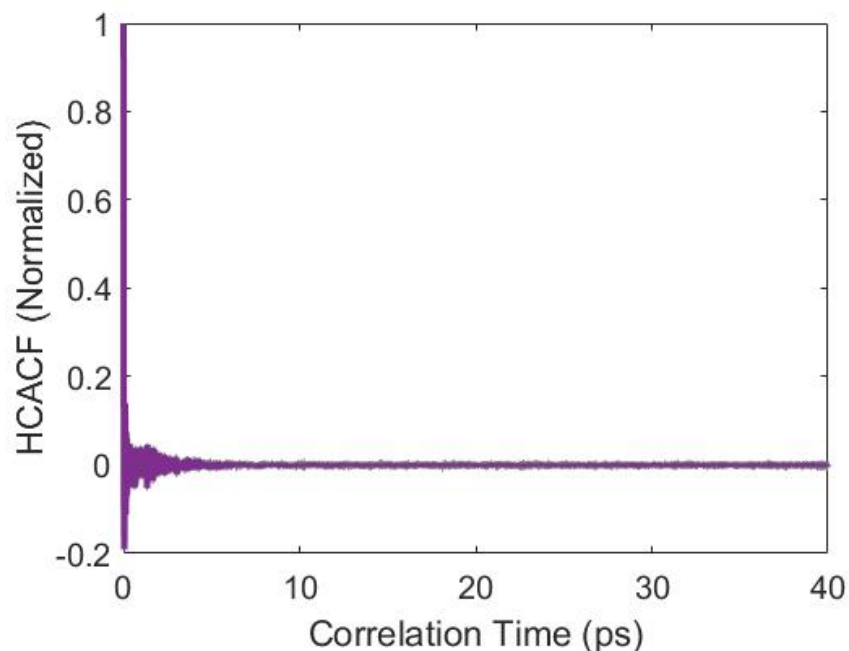
2.3 非平衡态热导率计算：界面热导



2.4 平衡态方法计算热导率：Green-Kubo方法

Green-Kubo方法基于涨落-耗散理论来计算晶体的热导率，主要是建立了热导率与热流自关联函数之间的关系。计算公式如下：

$$k_{uv} = \frac{V}{k_B T^2} \int \langle J_u(t_0) J_v(t_0 + \Delta t) dt \rangle$$





微纳尺度传热计算： 声子计算简介



应鹏华

2021.04.25

1.1 通过VACF计算PDOS： 单次计算

速度自关联函数 (velocity autocorrelation function, VACF) :

$$r(t) = \frac{\sum_i v_i(0) \cdot v_i(t)}{\sum_i v_i(0) \cdot v_i(0)}$$

声子态密度 (phonon density of states, PDOS) :

$$VDOS(\omega) = \sum_i \gamma(t) \exp(-2i\pi\omega t) dt$$

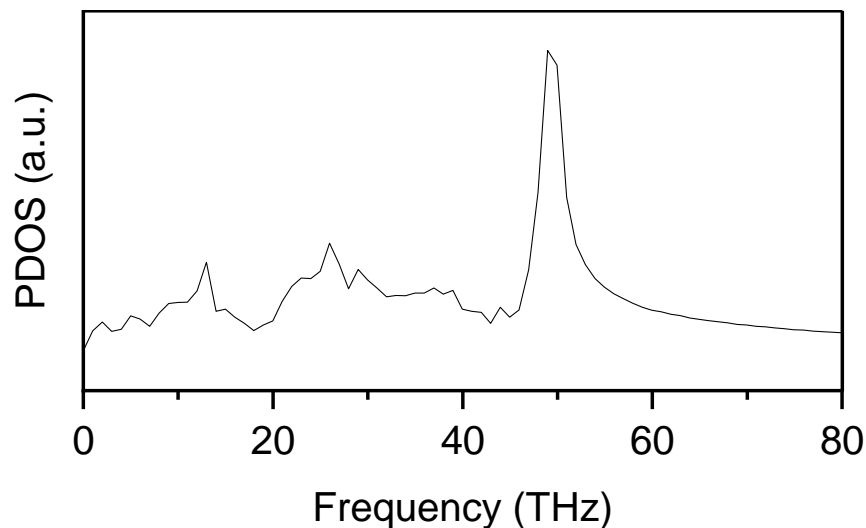
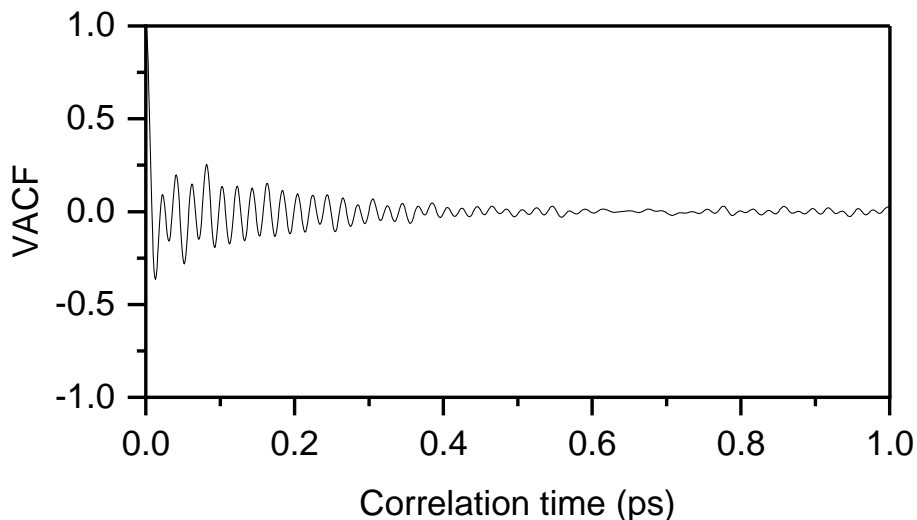
```

### Equilibration run###
fix          1 all box/relax z 0.0
min_style    cg
minimize     1e-25 1e-25 50000 100000
unfix       1

fix          NPT1 all npt temp 300 300 0.1 z 0 0 1.0
run          1000000

### VACF production ###
compute     myvacf all vacf
fix         3 all ave/time 1 1 1 c_myvacf[1] c_myvacf[2] c_myvacf[3]
c_myvacf[4] file ${simname}_VACF.txt format %20.10f
run         100000
    
```

一次VACF结果:

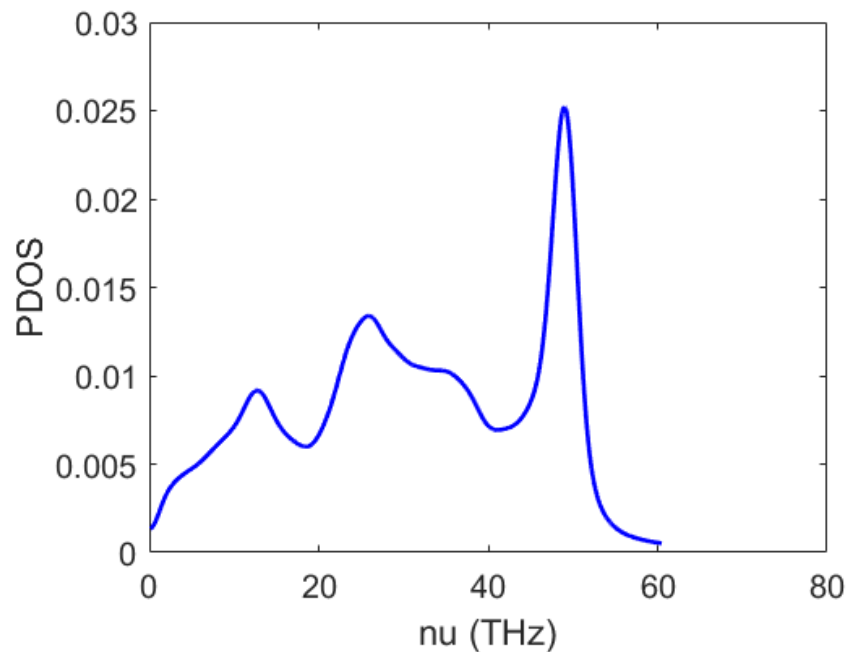
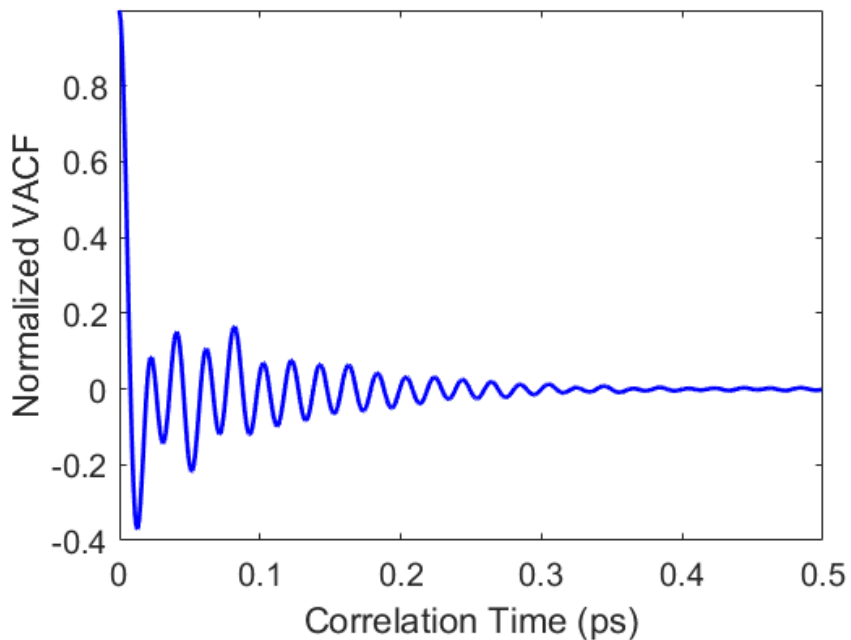


展示计算VACF的in文件及后处理

1.2 通过VACF计算PDOS：多次平均

提取速度轨迹文件进行多次平均：

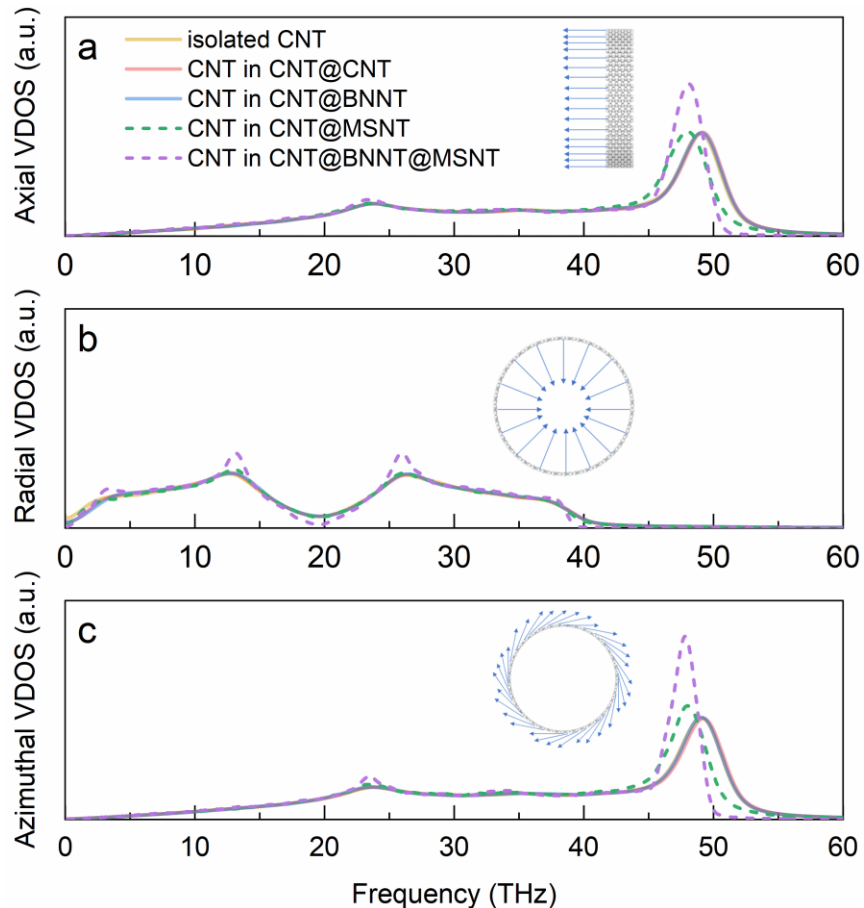
```
dump          2 gvDOS custom 1 ${simname}_voutput_all.lammpstrj id type
vx vy vz
run          5000
```



展示dump速度的轨迹文件
及后处理

1.3 通过VACF计算PDOS：模式分解

速度的极坐标分解：



```

for k = 1:length(data)

    % transformation matrix
    c = cos(theta(k));
    s = sin(theta(k));

    v_x = data(k,6);
    v_y = data(k,7);
    v_r = v_y*s+v_x*c;
    v_theta = v_x*s-v_y*c;

    data_pol(k,3) = v_r;
    data_pol(k,4) = v_theta;
    data_pol(k,5) = data(k,8);

end
    
```

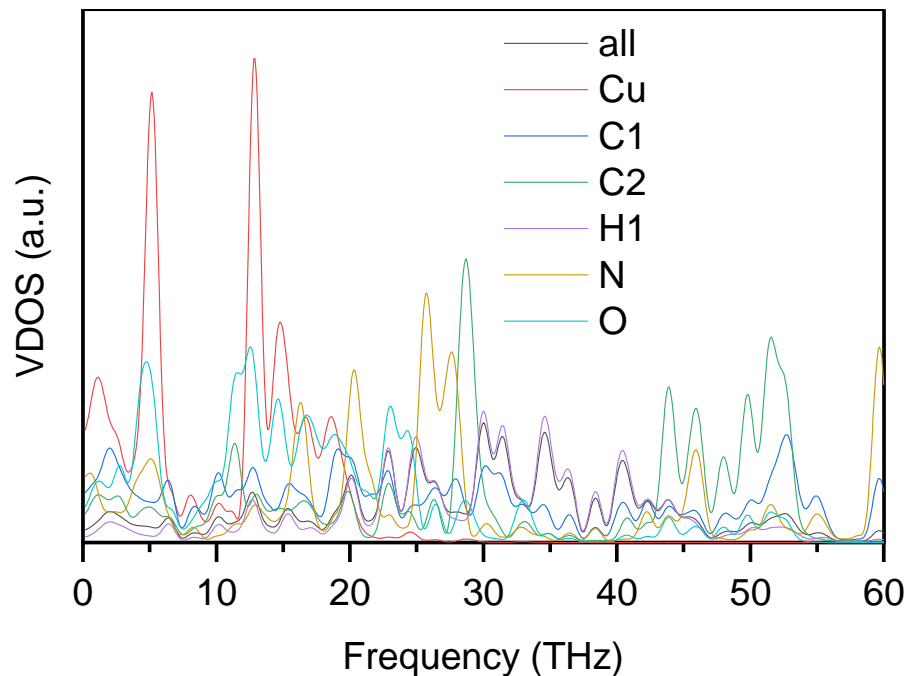
Ying, P., et al. (2021). "Effects of coating layers on the thermal transport in carbon nanotubes-based van der Waals heterostructures." Carbon 176: 446-457.

1.4 通过VACF计算PDOS：安装原子类型或group进行分解

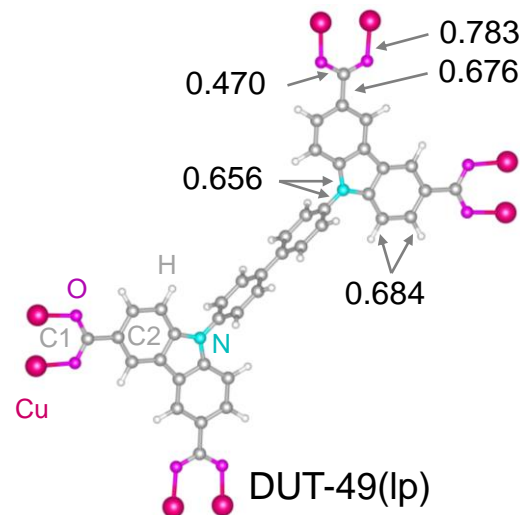
按照原子类型进行分解：

```

dump      2 all  custom 1 ${simname}_voutput_all.lampstrj id type vx vy vz
dump      3 Cu  custom 1 ${simname}_voutput_Cu.lampstrj id type vx vy vz
dump      4 H1  custom 1 ${simname}_voutput_H1.lampstrj id type vx vy vz
dump      5 C1  custom 1 ${simname}_voutput_C1.lampstrj id type vx vy vz
dump      6 C2  custom 1 ${simname}_voutput_C2.lampstrj id type vx vy vz
dump      7 N   custom 1 ${simname}_voutput_N.lampstrj id type vx vy vz
dump      8 O   custom 1 ${simname}_voutput_O.lampstrj id type vx vy vz
run
undump    2
undump    3
undump    4
undump    5
undump    6
undump    7
undump    8
    
```



$$\gamma = \frac{\int f(T)g(T)dT}{\sqrt{\int f^2(T)dT \int g^2(T)dT}}$$

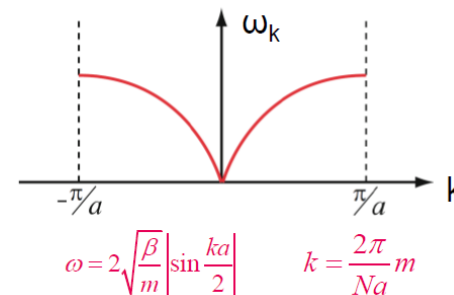
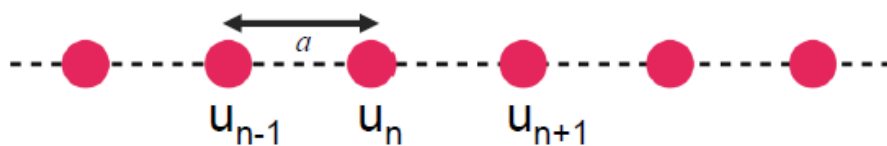


Ying, Penghua; Zhang, Jin; Zhong, Zheng (2021): Abnormal Effect of Phase Transition on Thermal Transport in Soft Porous Crystals. ChemRxiv. Preprint. <https://doi.org/10.26434/chemrxiv.14229134.v2>

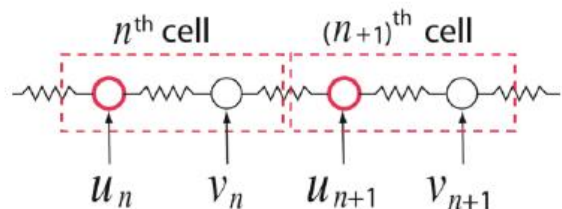
展示按照原子类型
或group进行分解

2.1 声子色散关系理论简介

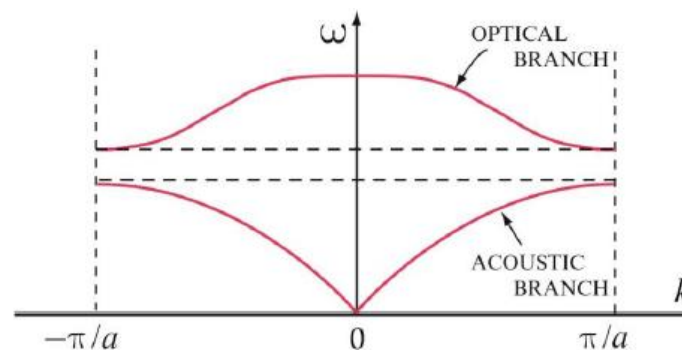
一维单原子链:



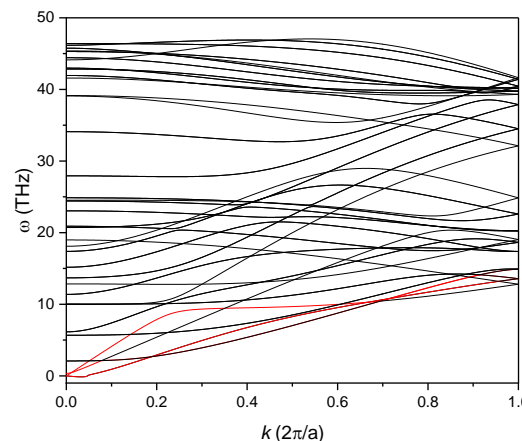
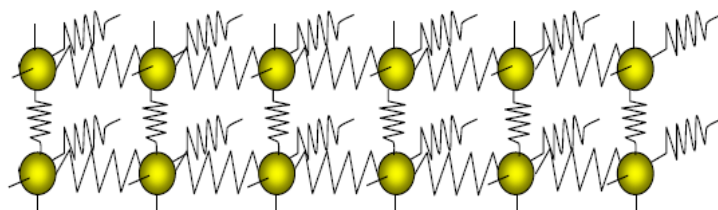
一维双原子链:



$$\omega_{\pm}^2 = \frac{\beta}{Mm} [(M+m) \pm \sqrt{M^2 + m^2 + 2Mm \cos(ak)}]$$



三维晶体:

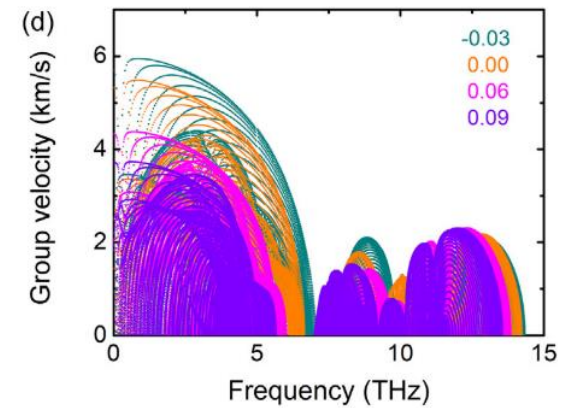
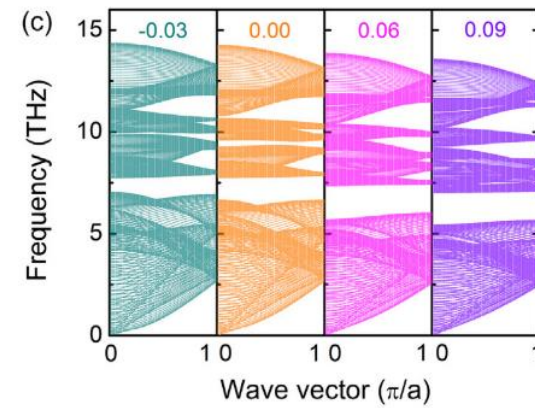
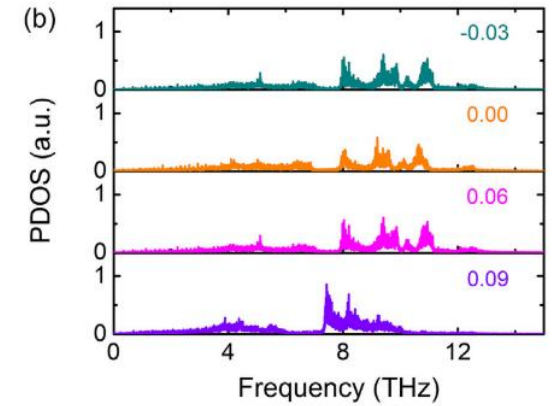
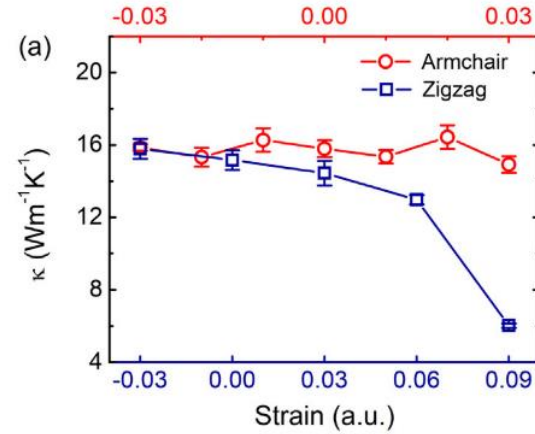
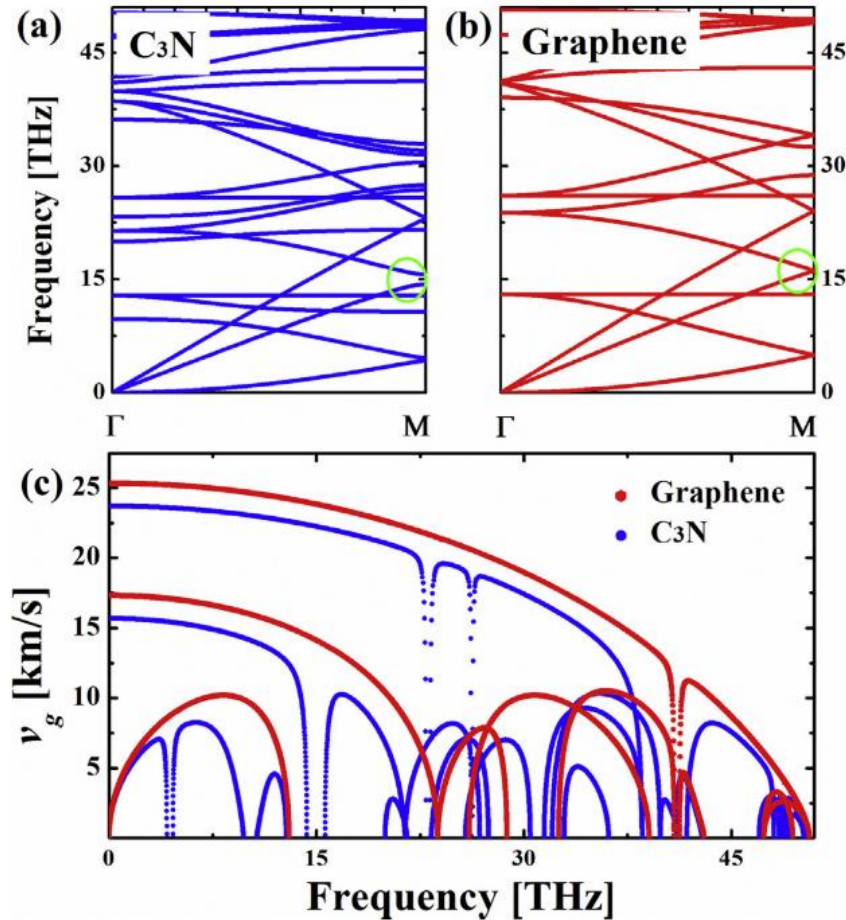


(5, 5) CNT

2.2 声子色散关系理论简介

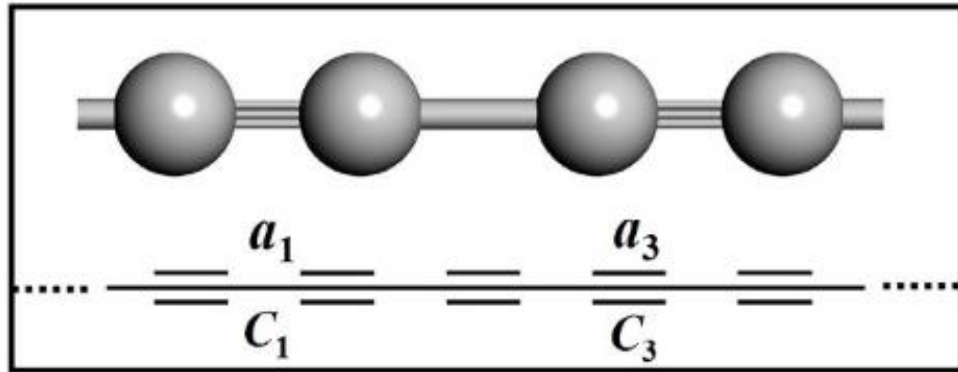
	原胞数	晶格振动波矢数	原胞内原子数	总自由度数	独立格波数	分支数	分支情况
一维单原子链	N	N	1	N	N	1	1支声学波
一维双原子链	N	N	2	$2N$	$2N$	2	1支声学波 1支光学波
一维P原子链	N	N	P	PN	PN	P	1支声学波 P-1支光学波
三维单原子链 (三维单原子晶体)	N	N	1	$3N$	$3N$	3	3支声学波 (1纵2横)
三维P原子链 (三维晶体)	N	N	P	$3PN$	$3PN$	3P	3支声学波 (1纵2横) 3P-3支光学波

2.2 声子色散关系理论简介

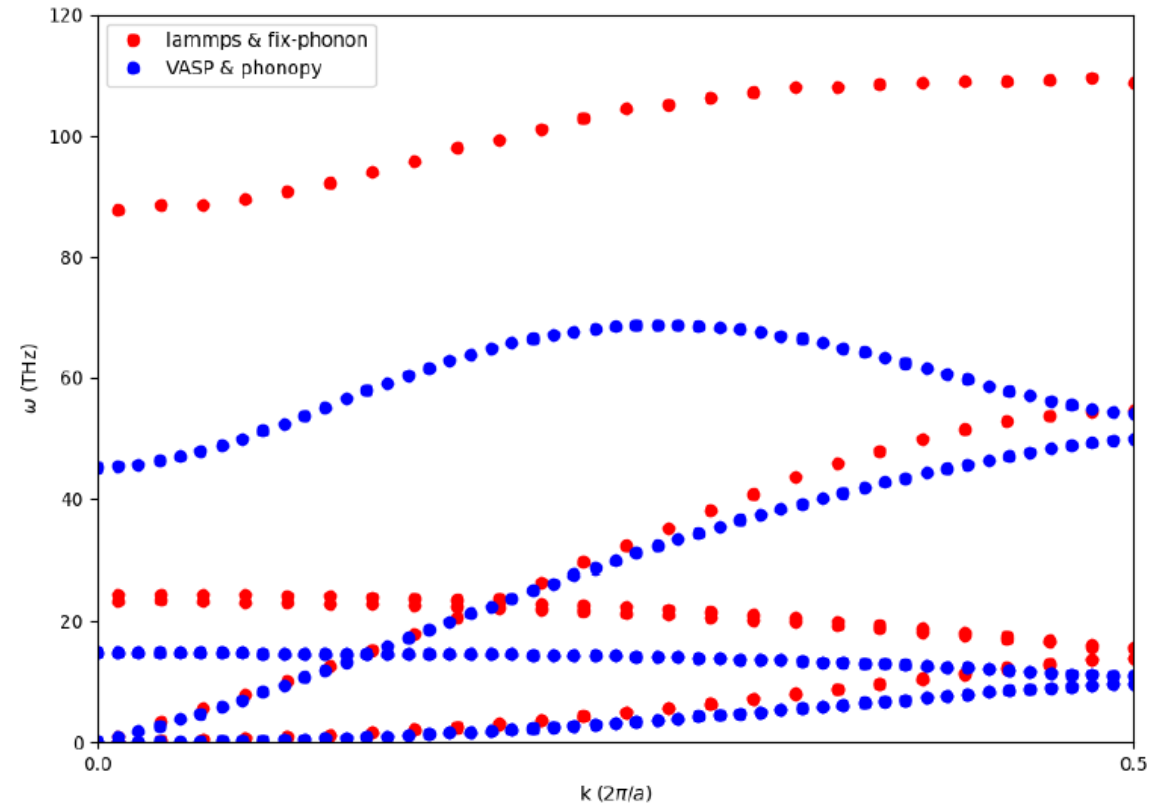


2.3 有限温度声子色散关系计算: fix phonon

Kong, L. T. (2011). "Phonon dispersion measured directly from molecular dynamics simulations." *Computer Physics Communications* 182(10): 2201-2207.



展示如何通过fix phonon 计算一维Carbyne室温下的的声子色散



2.4 0K下的声子色散关系计算：phonopy

与第一性计算软件做接口：

- 直接法，或称frozen-phonon方法，是通过在优化后的平衡结构中引入原子位移，计算作用在原子上的Hellmann-Feynman力，进而由动力学矩阵算出声子色散曲线。直接法的缺陷在于它要求声子波矢与原胞边界supersize正交，或者原胞足够大使得Hellmann-Feynman力在原胞外可以忽略不计。
- DFPT方法。DFPT通过计算系统能量对外场微扰的响应来求出晶格动力学性质。该方法最大的优势在于它不限定微扰的波矢与原胞边界正交，不需要超原胞也可以对任意波矢求解。直接计算出原子的移动而导致的势场变化，再进一步构造出动力学矩阵。进而计算出声子谱。

<http://phonopy.github.io/phonopy/>

<https://yh-phys.github.io/2019/10/11/vasp-phonon/>

与LAMMPS做接口：

0K

<https://phonolammps.readthedocs.io/en/master/>

有限温度

<http://abelcarreras.github.io/DynaPhoPy>

<https://zhuanlan.zhihu.com/p/344803376>

2.5 GPUMD简介



由阿尔芬托大学樊哲勇博士 (brucenju@gmail.com) 开发, 使用GPU硬件在Cuda语言编写而成。

<https://gpumd.zheyongfan.org>

<https://github.com/brucefan1983/GPUMD>

优势:

- 计算效率非常高, 相对于LAMMPS是数量级的提升
- 计算输入脚本简单, 拥有热流分解, 更加快捷的计算声子谱和平衡态热导率输出
- 可以进行HNEMD方法计算热导率

不足:

- 目前支持的势函数比较少, 只包括SW势函数、Tersoff势等
- 相对于LAMMPS可实现的功能较少, 主要集中在一些经典二维碳材料、Si材料等

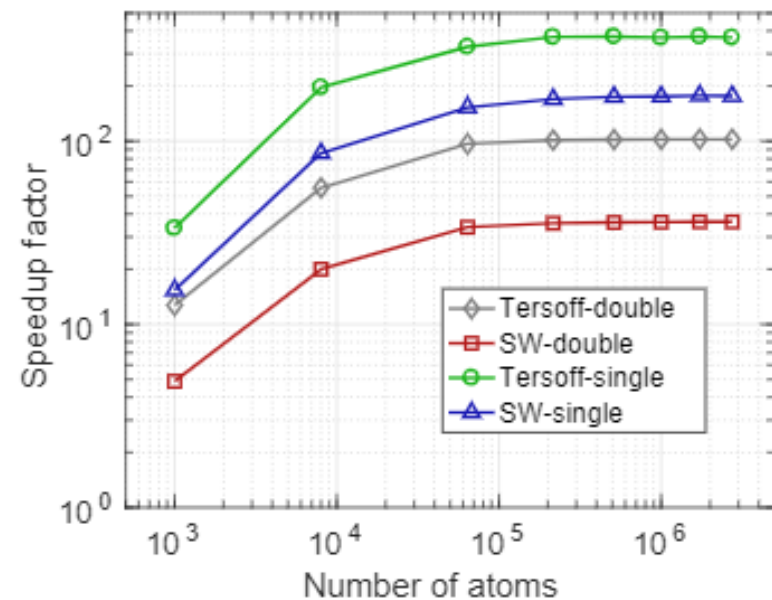


Figure 2: (color online) Speedup factor of GPUMD (running on a Tesla K40 GPU) as a function of the number of atoms with respect to the serial version of LAMMPS running on Intel Xeon CPU X5670 @ 2.93 GHz. The test system is silicon crystal at 300 K and zero pressure.