



材料人

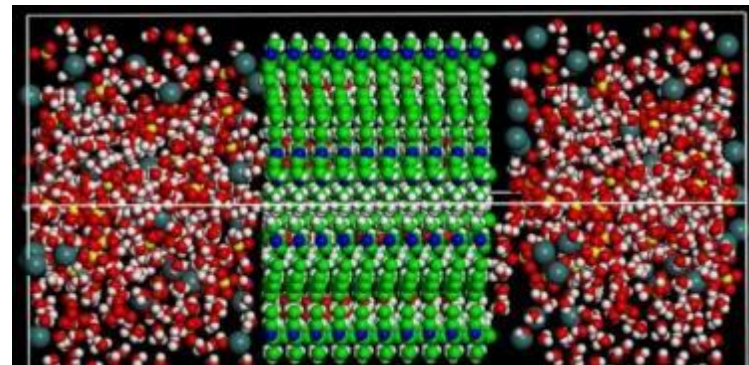
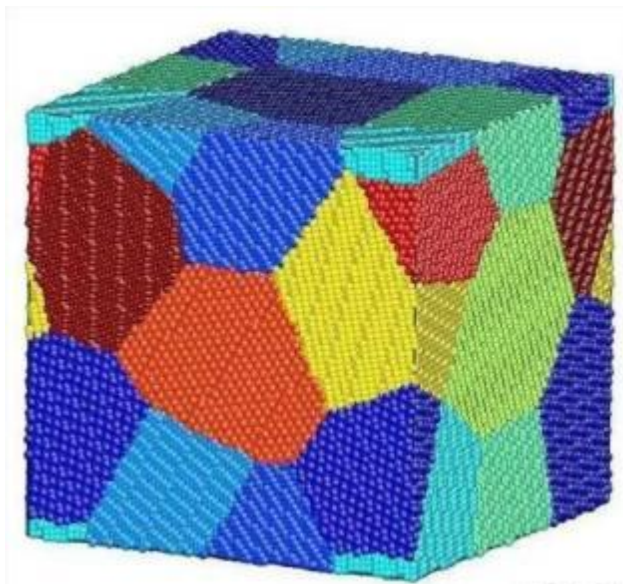
LAMMPS进阶培训

2022.09.22

第一天 上午 (9:00-12:00)

1. 分子动力学简介

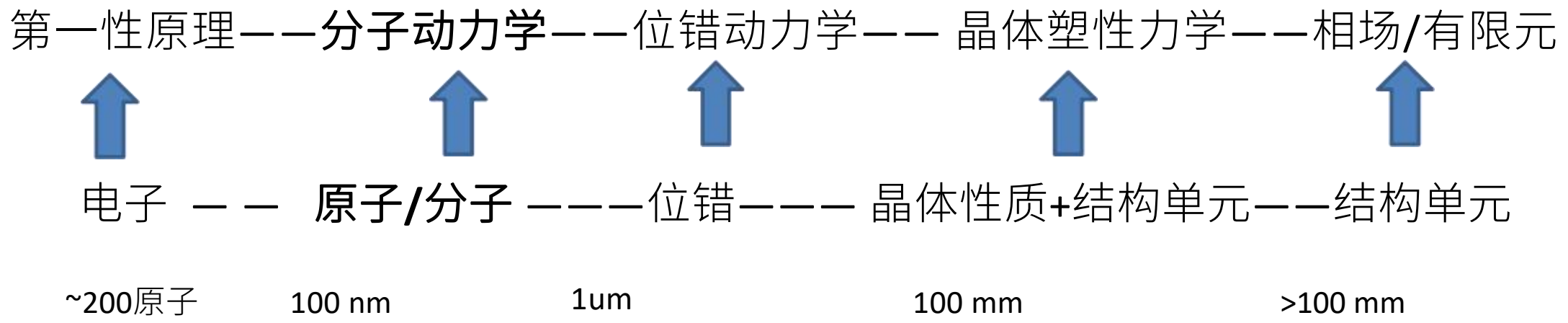
- 1.1 跨尺度视角下的分子动力学模拟
- 1.2 分子动力学模拟的优势和局限
- 1.3 分子动力学模拟的理论基础
- 1.4 分子动力学常用软件介绍



2. LAMMPS软件简介

1. LAMMPS运行的几个重要文件
(.in文件, .eam势函数文件, .data结构文件)
 1. 一个简单的金属拉伸运行实例演示
 2. in文件 (核心运行文件) 及其结构讲解
 3. 常用命令详解 (fix, compute, boundary等)
 4. 势函数文件设置及其选择原则
 5. 势函数文件设置的注意事项
 6. 势函数文件的测试方法

跨尺度视角下的分子动力学模拟

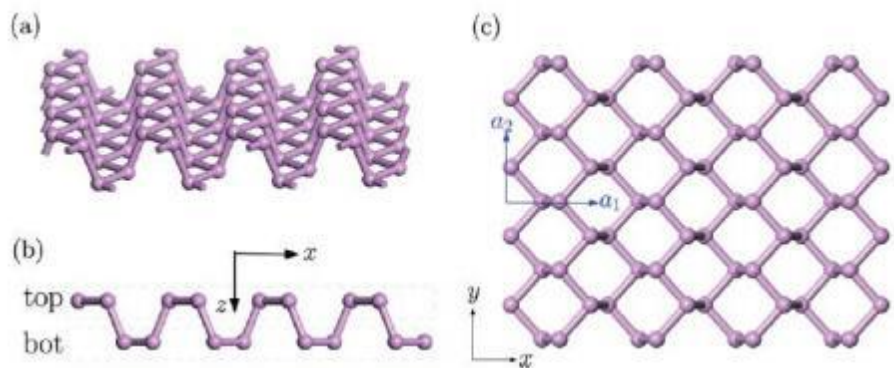


可以单独建模，也可以参数传递

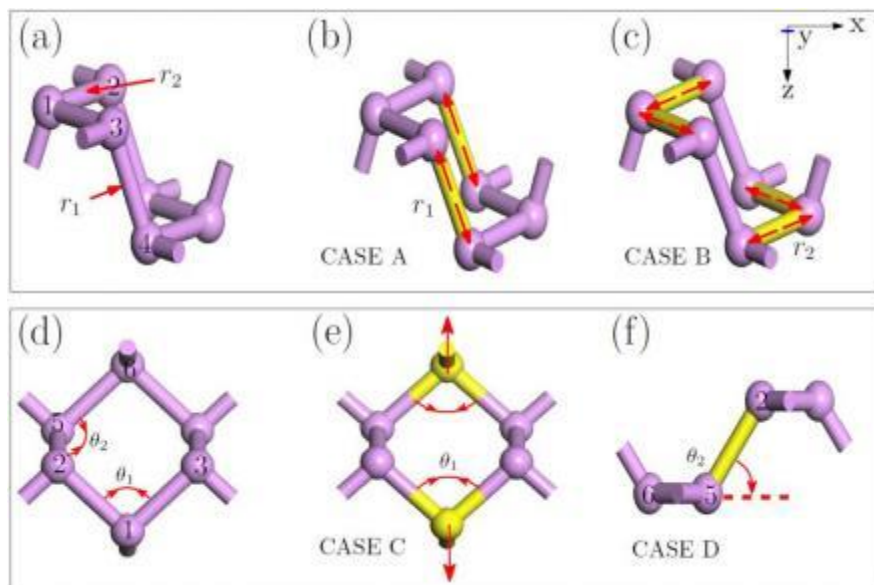


物理本质的区别，算力的限制

磷烯势函数构建与分子动力学跨尺度应用



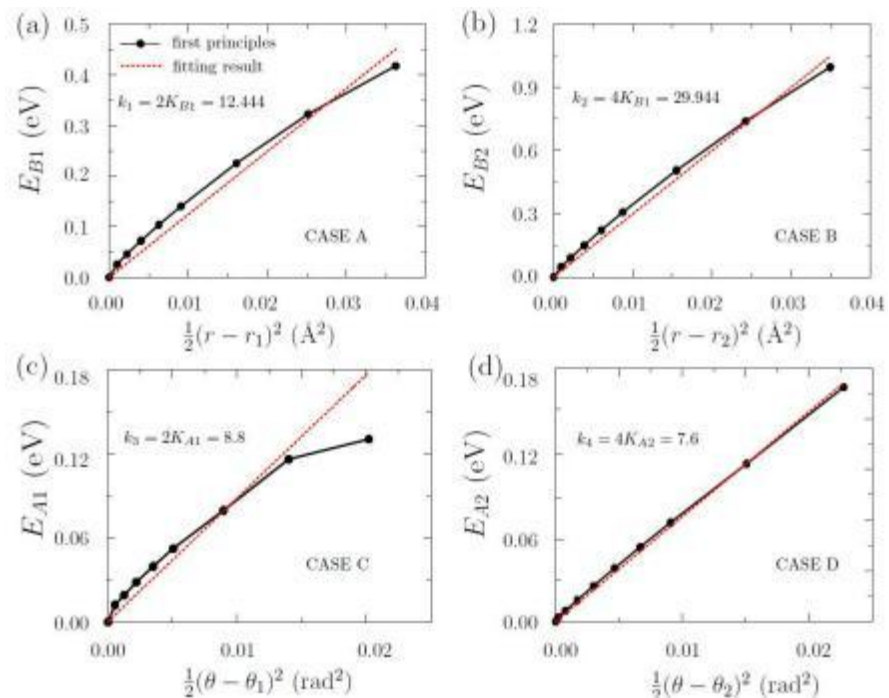
不同角度单层黑磷的结构



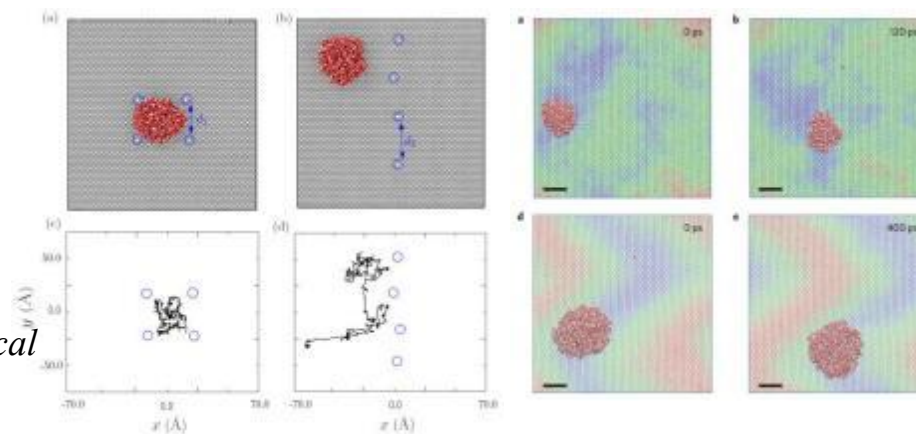
基于第一性原理的单层黑磷单胞数据计算

Lijun Deng, Nian Zhou, et al. *Physical Chemistry Chemical Physics*. 2019, 21, 16804-16817.

Lijun Deng, Nian Zhou, et al. *Computational Materials Science*, 2020, 178, 109623.



能量与键的拉伸或角的旋转之间的关系曲线



水滴在石墨烯上的扩散

分子动力学

分子动力学 (MD) 是原子和分子物理运动的计算模拟。原子的运动轨迹通过求解牛顿运动方程来预测。允许原子和分子互相作用一段时间以观察原子的运动过程。

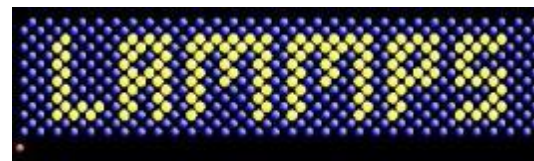
$$m_i r_i = f_i$$

原子间力和势能是通过分子力学中的势函数定义。

r_i 原子初始位置很重要

$$f_i = - \frac{\partial U}{\partial r_i}$$

原子相互作用很重要



<https://www.lammps.org/>

开源

下载, 安装, window, linux

LAMMPS

计算尺度: 1-100 nm

优点: 得到原子/分子/缺陷形成和演变过程, 探索构造纳米尺度组织

缺点: 但计算准确性依赖势函数

The first molecular dynamics (MD) simulations

THE JOURNAL OF CHEMICAL PHYSICS

VOLUME 31, NUMBER 2

AUGUST, 1959

Studies in Molecular Dynamics. I. General Method*

B. J. ALDER AND T. E. WAINWRIGHT

Lawrence Radiation Laboratory, University of California, Livermore, California

(Received February 19, 1959)

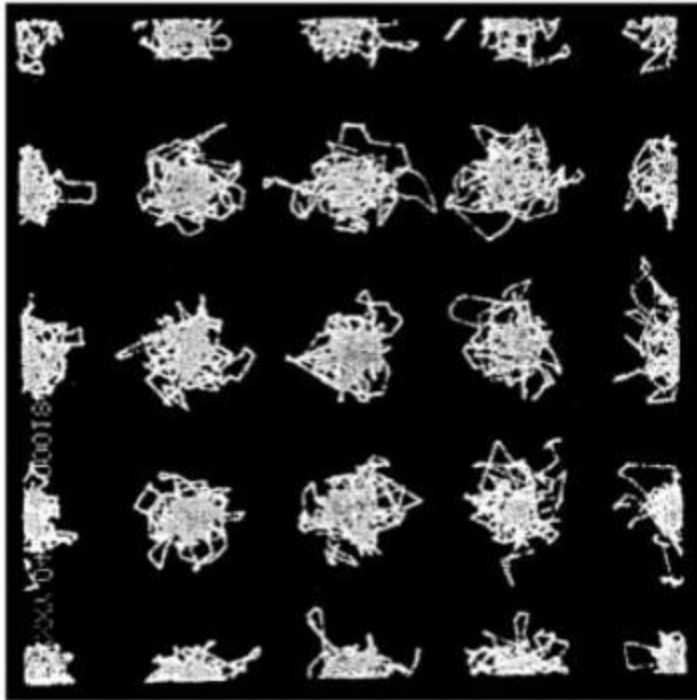
A method is outlined by which it is possible to calculate exactly the behavior of several hundred interacting classical particles. The study of this many-body problem is carried out by an electronic computer which solves numerically the simultaneous equations of motion. The limitations of this numerical scheme are enumerated and the important steps in making the program efficient on the computers are indicated. The applicability of this method to the solution of many problems in both equilibrium and nonequilibrium statistical mechanics is discussed.

Study of micro-dynamics of liquids and solids (32 atoms)
using the hard-sphere potential.

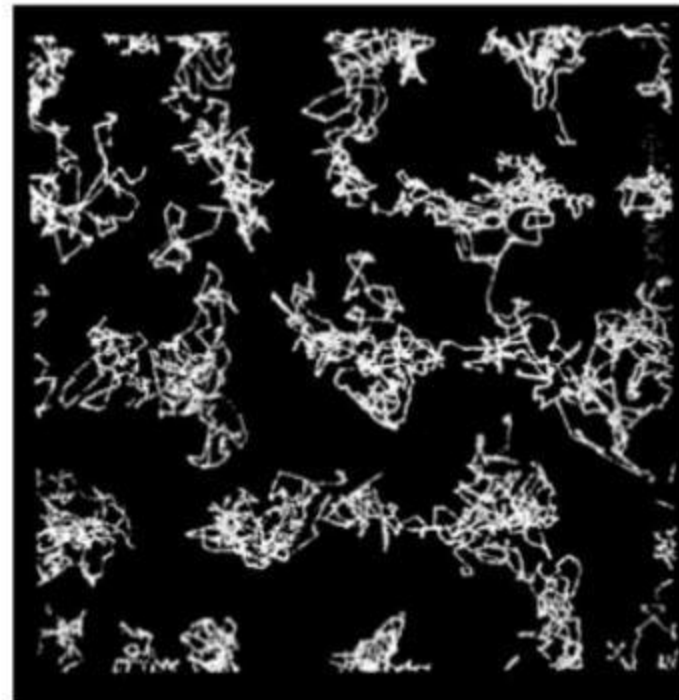
The first molecular dynamics (MD) simulations

Simulation approach:

1. Identify next pair of spheres to collide and calculate when the collision will occur.
2. Calculate the positions of all the spheres at the collision time.
3. Determine the new velocities of the two colliding spheres after the collision.
4. Repeat from (1) until finished.



Solid phase (3000 collisions).



Fluid phase (3000 collisions).

时间积分算法

程序不能直接采用解析形式快速的求解大量运动方程 (轨迹)。

如何快速的用数值的形式算运动方程？

GOAL: To obtain the trajectories $\mathbf{r}_i(t)$ of all of the N particles as a function of time t , in a specific time interval. And naturally we will obtain their velocities.

These trajectories are solutions to classical equations of motion

$$\frac{d^2\mathbf{r}_i(t)}{dt^2} = \frac{\mathbf{f}_i(t)}{m_i}$$

Analytic solutions are not possible in general, so we turn to numerical solutions.

In MD, beginning with the initial condition $(\mathbf{r}_i(0), \mathbf{v}_i(0))$, one recursively generates the positions and velocities at successive times.

$$\{\mathbf{r}_i(t), \mathbf{v}_i(t)\} \rightarrow \{\mathbf{r}_i(t + \Delta t), \mathbf{v}_i(t + \Delta t)\}$$

● Verlet算法：速度形式

$$\begin{aligned} |x_{n+1} &= x_n + v_n \Delta t + \frac{1}{2} a_n \Delta t^2 \\ |v_{n+1} &= v_n + \left(\frac{1}{2} a_{n+1} + \frac{1}{2} a_n \right) \Delta t \end{aligned}$$

$$|v_{n+\frac{1}{2}} = v_n + \frac{1}{2} a_n \Delta t$$

$$|v_{n+1} = v_{n+\frac{1}{2}} + \frac{1}{2} a_{n+1} \Delta t$$

● Leap-frog算法：

$$v_{n+1/2} = v_{n-1/2} + \Delta t a_n$$

$$x_{n+1} = x_n + \Delta t v_{n+1/2}$$

$$v_n = v_{n-1/2} + \frac{\Delta t}{2} a_n$$

x 的截断误差为 $O(\Delta t^4)$ ， v 的截断误差 $O(\Delta t^2)$

- 微观量

- 温度

根据统计热力学，平衡态下经典系统的能量中的每一个二次项具有平均值 $k_B T/2$ ，即

$$\frac{d}{2} N k_B T = \sum_i \left\langle \frac{1}{2} m_i \dot{\mathbf{v}}_i^2 \right\rangle$$

空间维数 $\frac{d}{2}$ 粒子个数 N $\langle \rangle$: 取时间平均

注意：上式在系统质心速度为 $\mathbf{0}$ 时适用

问题：如何给定系统的初始条件，得到所需要的平衡态温度 T_{eq} ？

解决方法之一：速度标定法

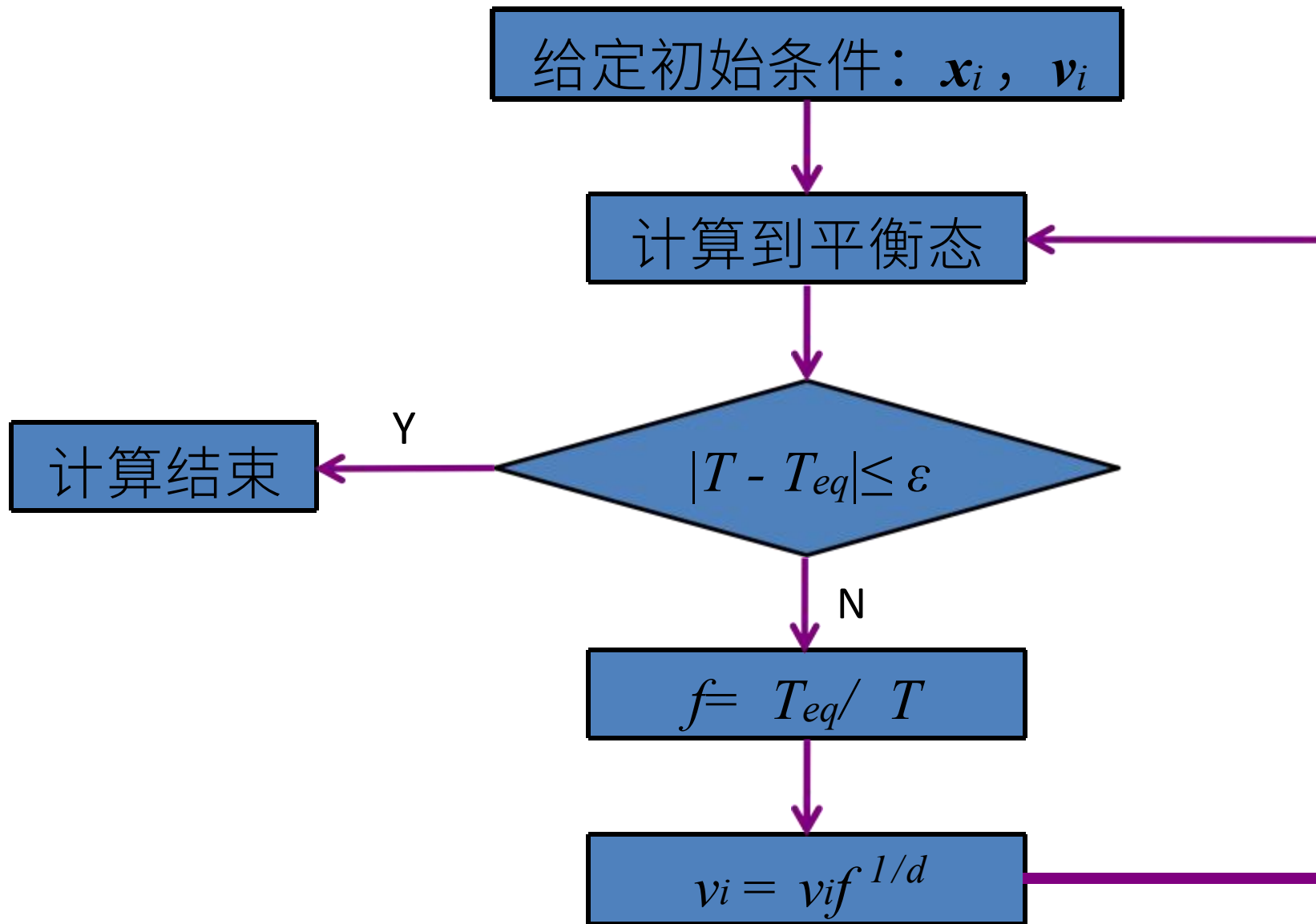
任给初始条件，模拟到平衡，得到系统平衡态温度 T 。一般 $T \neq T_{eq}$ 。令

$$f = T_{eq} / T$$

用速度

$$f^{1/d} v_i \rightarrow v_i$$

再模拟直到平衡，若所得温度仍不等于 T_{eq} ，再进行上述过程

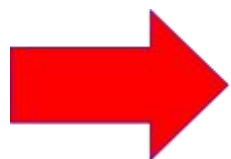


其它方法：Gaussian热浴法 (约束温度调节方法)

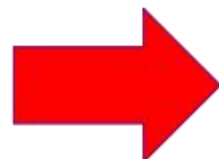
其基本原理在运动方程中加入“摩擦力”项，并将其与粒子速度联系起来。

$$f_i = ma_i + \xi mv_i$$

平衡态时，系统温度不变，因此 $dEk/dt=0$



$$\sum_i v_i a_i = 0$$



$$\xi = \frac{\sum_i f_i v_i}{m \sum_i v_i^2}$$

宏观性质的统计

- 系统的势能

$$E_p = \sum_{1 \leq i < j \leq N} V_{ij}$$

- 系统的内能

$$E_k = \sum_i \frac{p_i^2}{2m_i}$$

- 系统的总能 $E = E_p + E_k$


- 系统的温度

$$T = \frac{1}{dNk_B} \sum_i \frac{m_i v_i^2}{2}$$

— 热容

定义热容

E: 系统总能

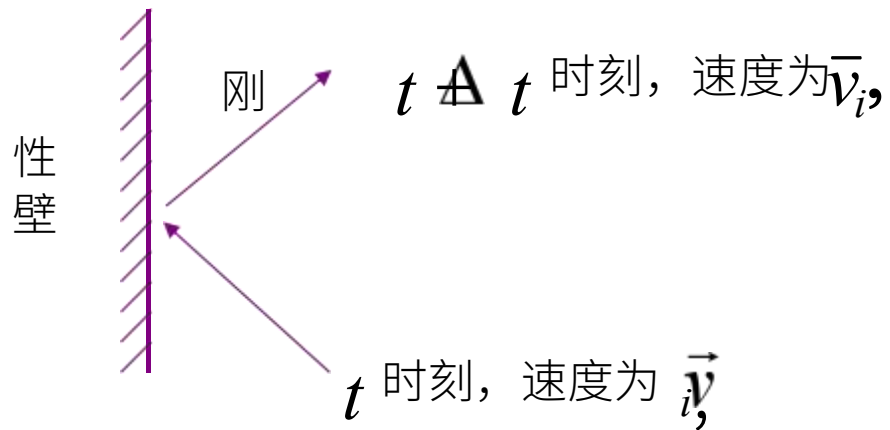
$$C_v = \left(\frac{\partial E}{\partial T} \right)_V$$


计算系统在温度T和T+编T时的总能E_T、E_{T+编T},

$$C_v = \frac{E_{T+\text{编}T} - E_T}{\text{编}T}$$

— 压强

· 对壁面的压强



$$p = \frac{1}{dA} \sum_i m \left\langle \frac{\bar{v}_{i,2} - \bar{v}_{i,1}}{\Delta t} \right\rangle$$

Δt 时间里作用在单位面积壁上的压力

系综的选择

NVE

NPT

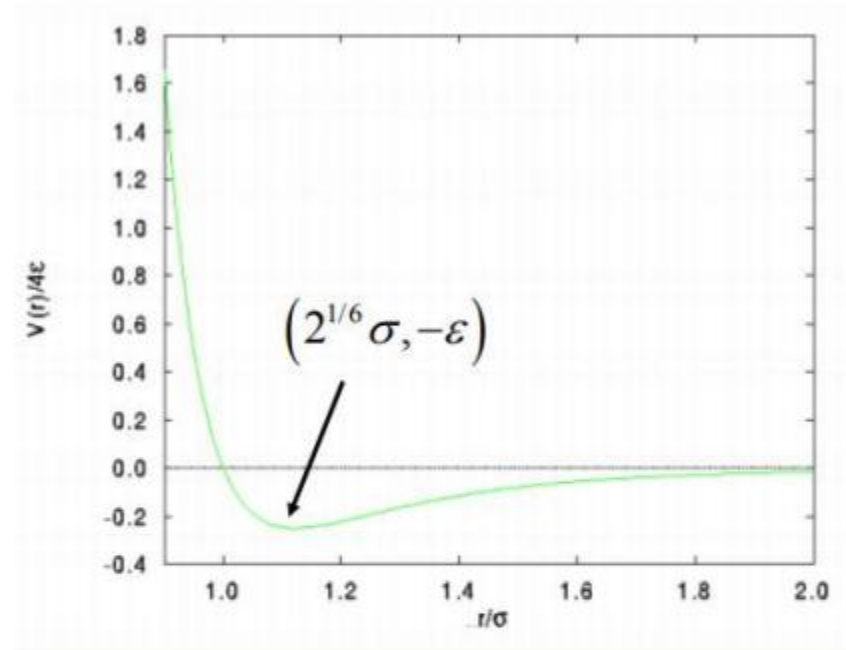
NVT

NPH

做拉伸的时候为什么用NVT?

势函数

The Lennard-Jones potential



The two-parameter function

$$V(r_{ij}) = 4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right]$$

Lorentz-Berthelot mixing rules

Atom	Source	$\epsilon/k_B(\text{K})$	$\sigma(\text{nm})$
H	[Murad and Gubbins 1978]	8.6	0.281
He	[Maitland <i>et al.</i> 1981]	10.2	0.228
C	[Tildesley and Madden 1981]	51.2	0.335
N	[Cheung and Powles 1975]	37.3	0.331
O	[English and Venables 1974]	61.6	0.295
F	[Singer <i>et al.</i> 1977]	52.8	0.283
Ne	[Maitland <i>et al.</i> 1981]	47.0	0.272
S	[Tildesley and Madden, 1981]	183.0	0.352
Cl	[Singer <i>et al.</i> 1977]	173.5	0.335
Ar	[Maitland <i>et al.</i> 1981]	119.8	0.341
Br	[Singer <i>et al.</i> 1977]	257.2	0.354
Kr	[Maitland <i>et al.</i> 1981]	164.0	0.383

$$\sigma_{AB} = \sigma_A + \sigma_B$$

$$\epsilon_{AB} = \sqrt{\epsilon_A \epsilon_B}$$

Potential functions for metal, semi-conductor and polymers

1. Metals

EAM potential: in addition to pairs of atoms have contribution due to environment of atoms, expressed through electron density (which is a pair potential)

$$\phi_i = \sum_{j=1 \dots N_{\text{neigh}}} \frac{1}{2} \phi(r_{ij}) + F(\rho_i(r_{ij}))$$

depends on all neighbors of i (multi-body)

2. Semi-conductors

Tersoff potential

$$U = \frac{1}{2} \left(\sum_{i,j,i \neq j} \phi_{ij} \right) = \frac{1}{2} \left(\sum_{i,j,i \neq j} f_c(r_{ij}) (\phi_R(r_{ij}) + b_{ij} \phi_A(r_{ij})) \right)$$

Cutoff function (beyond immediate bonding neighbor)
 Repulsive pair potential
 Attractive pair potential
 Bond environment term

3. Polymers

CHARMM/DREIDING potential (forcefield)

$$U_{\text{total}} = U_{\text{Elec}} + U_{\text{Covalent}} + U_{\text{Metallic}} + U_{\text{vdW}} + U_{\text{H-bond}}$$

=0 for organics (e.g. protein)

$$U_{\text{Covalent}} = U_{\text{stretch}} + U_{\text{bend}} + U_{\text{rot}}$$

Charge on atoms

Common forcefields in molecular dynamics simulations

- AMBER (Peter Kollman, UCSF; David Case, Scripps)
- CHARMM (Martin Karplus, Harvard)
- OPLS (Bill Jorgensen, Yale)
- MM2/MM3/MM4 (Norman Allinger, U. Georgia)
- GROMOS (Van Gunsteren, ETH, Zurich)
- GROMACS
- CVFF, PCFF, COMPASS (for polymers)

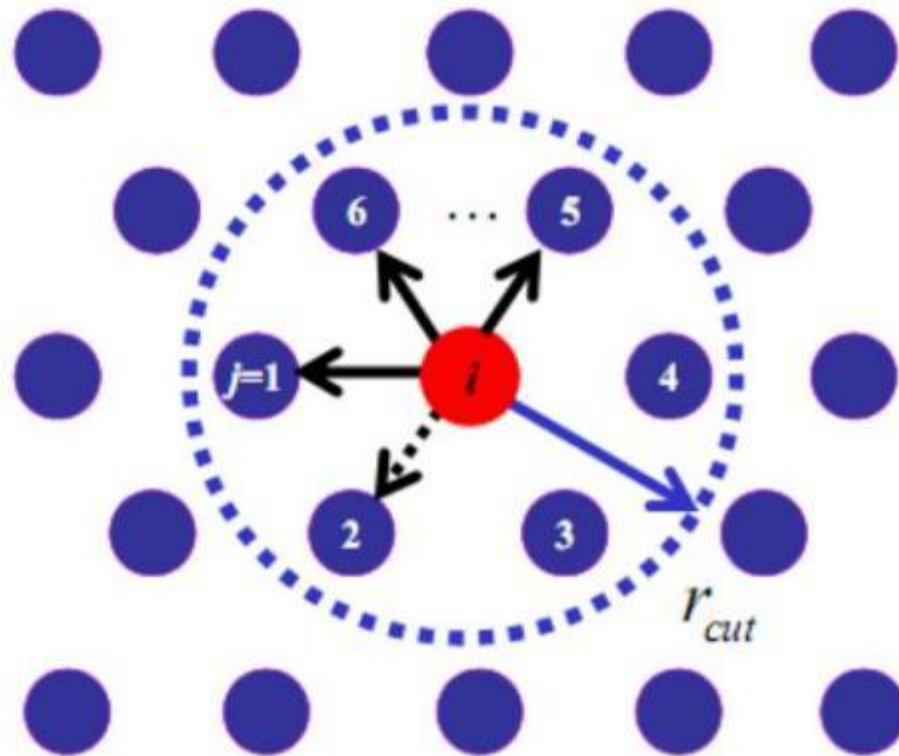
- MARTINI (coarse-grained force fields)

Algorithm of (pair) force calculation

for $i=1..N$

for $j=1..N (i \neq j)$

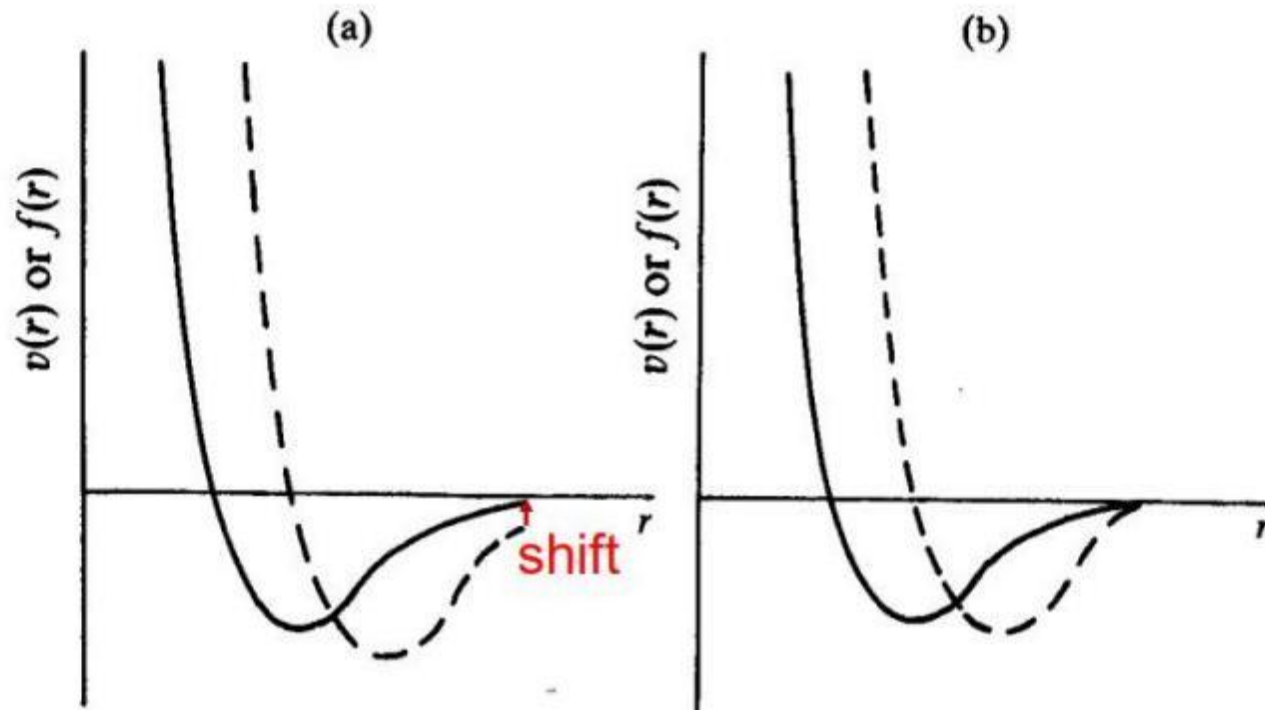
[add force
contributions]



Cutoff and shift

Potential functions are commonly cut over a certain range to reduce the computation to evaluate the interatomic forces.

After the cutoff ($f = 0$ beyond r_{cut}) operation, discontinuity appears in the potential profile, that could lead to energy shift for a long-time run.



Strategies for more efficient computation

Two approaches

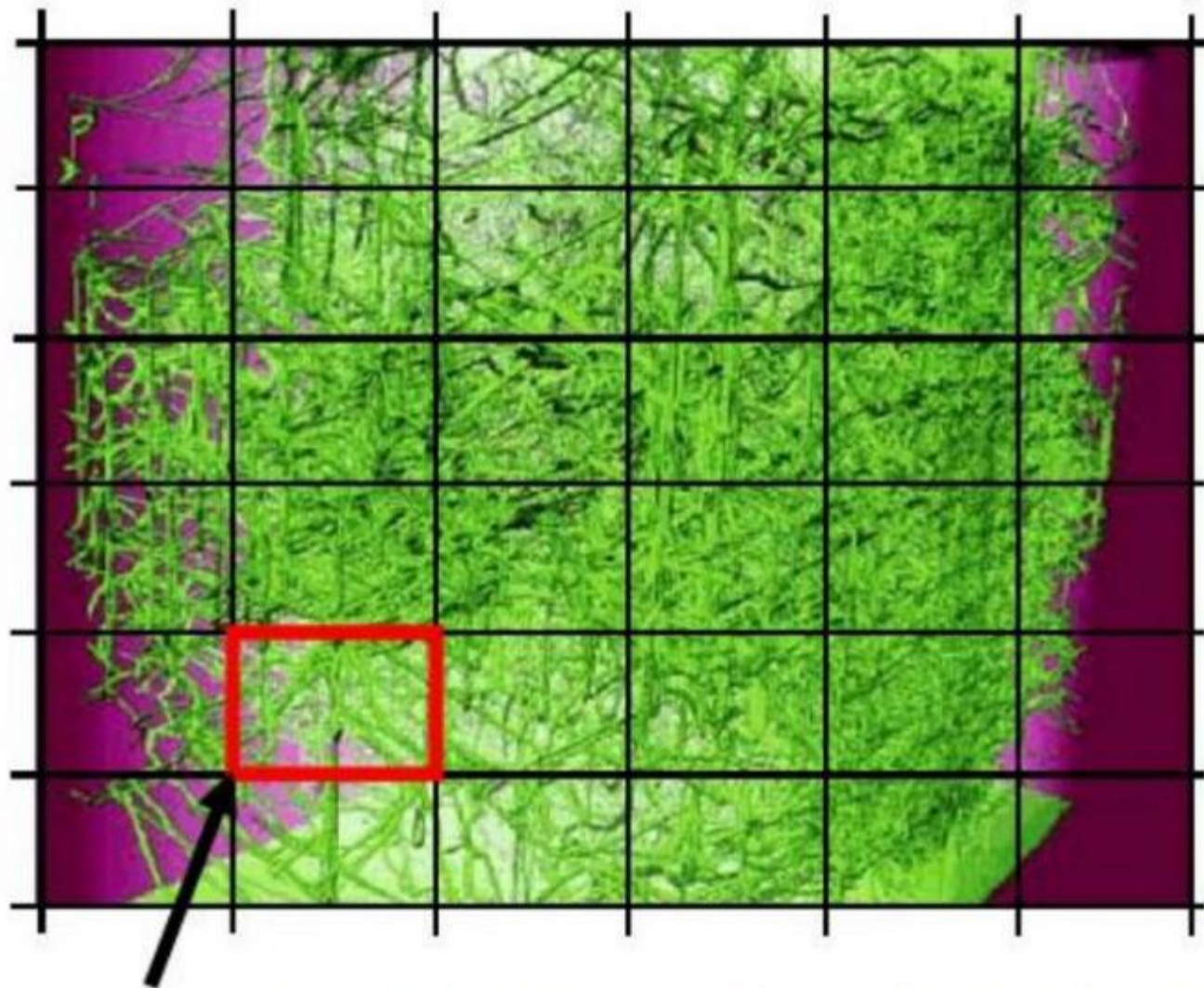
1. **Neighbor lists:** Store information about atoms in vicinity, calculated in an N^2 effort, and keep information for 10..20 steps

Concept: Store information of neighbors of each atom within vicinity of cutoff radius (e.g. list in a vector); update list only every 10..20 steps

2. **Domain decomposition into bins:** Decompose system into small bins; force calculation only between atoms in local neighboring bins

Concept: Even overall system grows, calculation is done only in a local environment (have two nested loops but # of atoms does not increase locally)

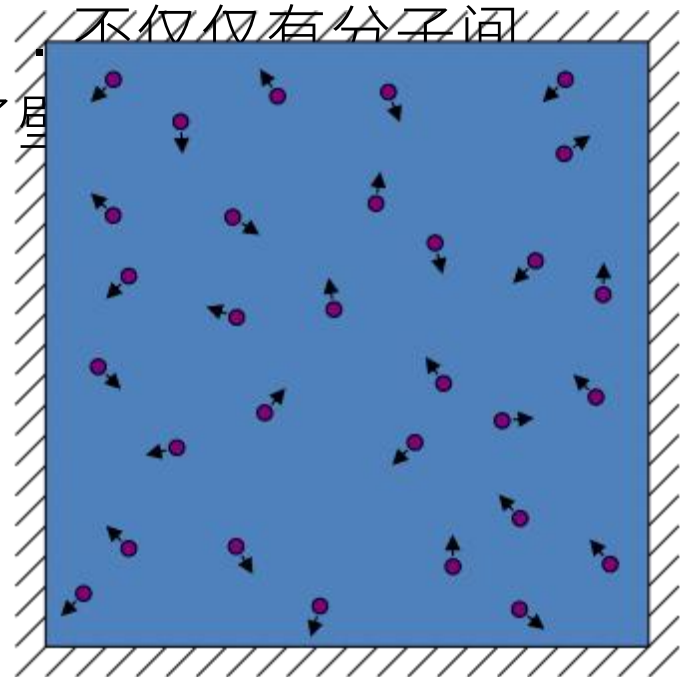
Domain decomposition into bins



Each piece worked on by one of the computers in the supercomputer

边界条件

- 模拟能力限制，不能模拟大量分子，只能模拟有限空间中的有限个分子：有限空间→边界
- 固体 (刚性) 边界条件的相互作用，还引入了壁面作用势。分子量小时，壁面作用可忽略；分子量小时，壁面作用可忽略；分子量小时，壁面作用可忽略。



总分子数 $N \propto a^3$

和壁面作用分子数 \propto 壁面积

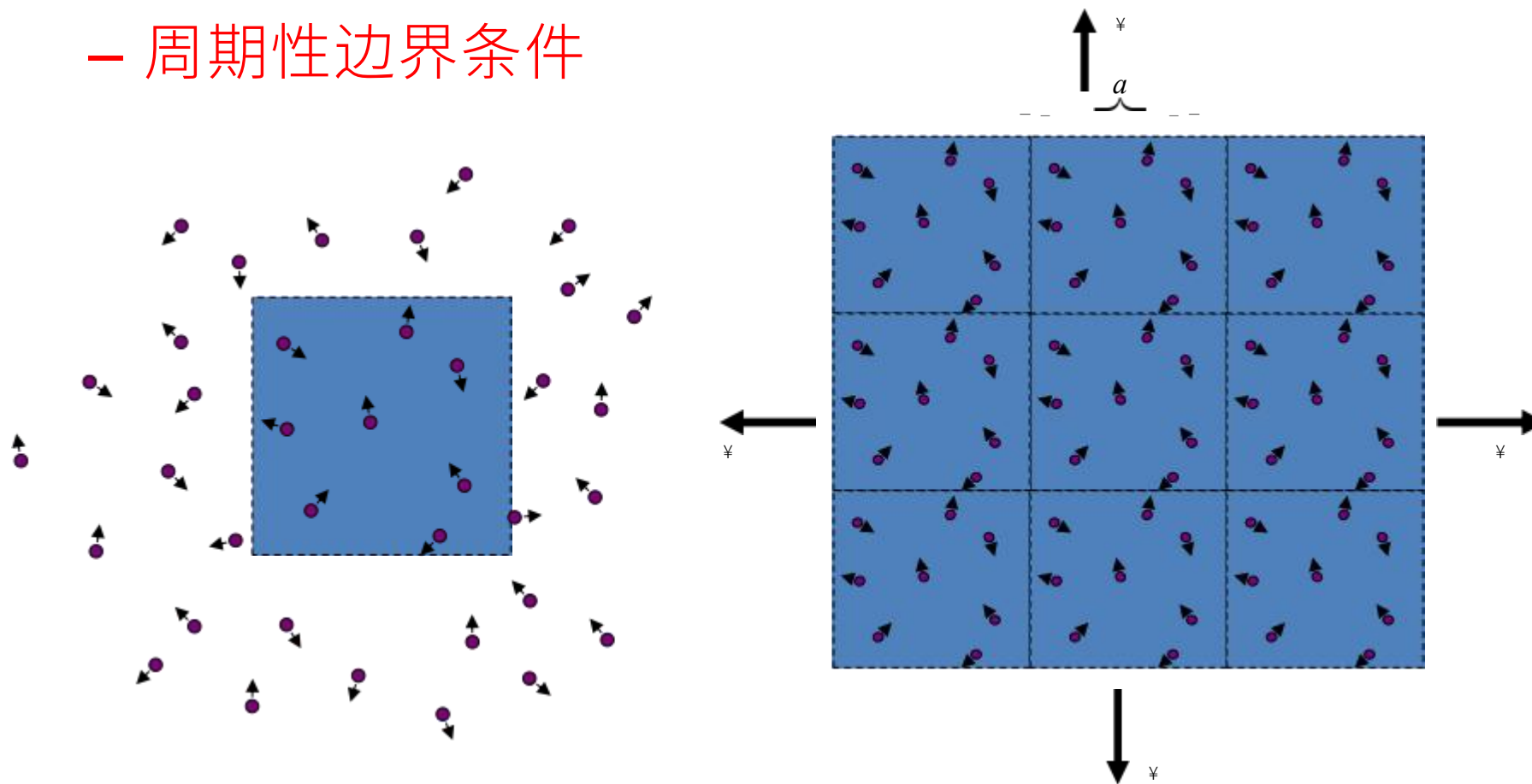
和壁面作用势 \propto 壁面积

和壁面作用势 \propto 壁面积

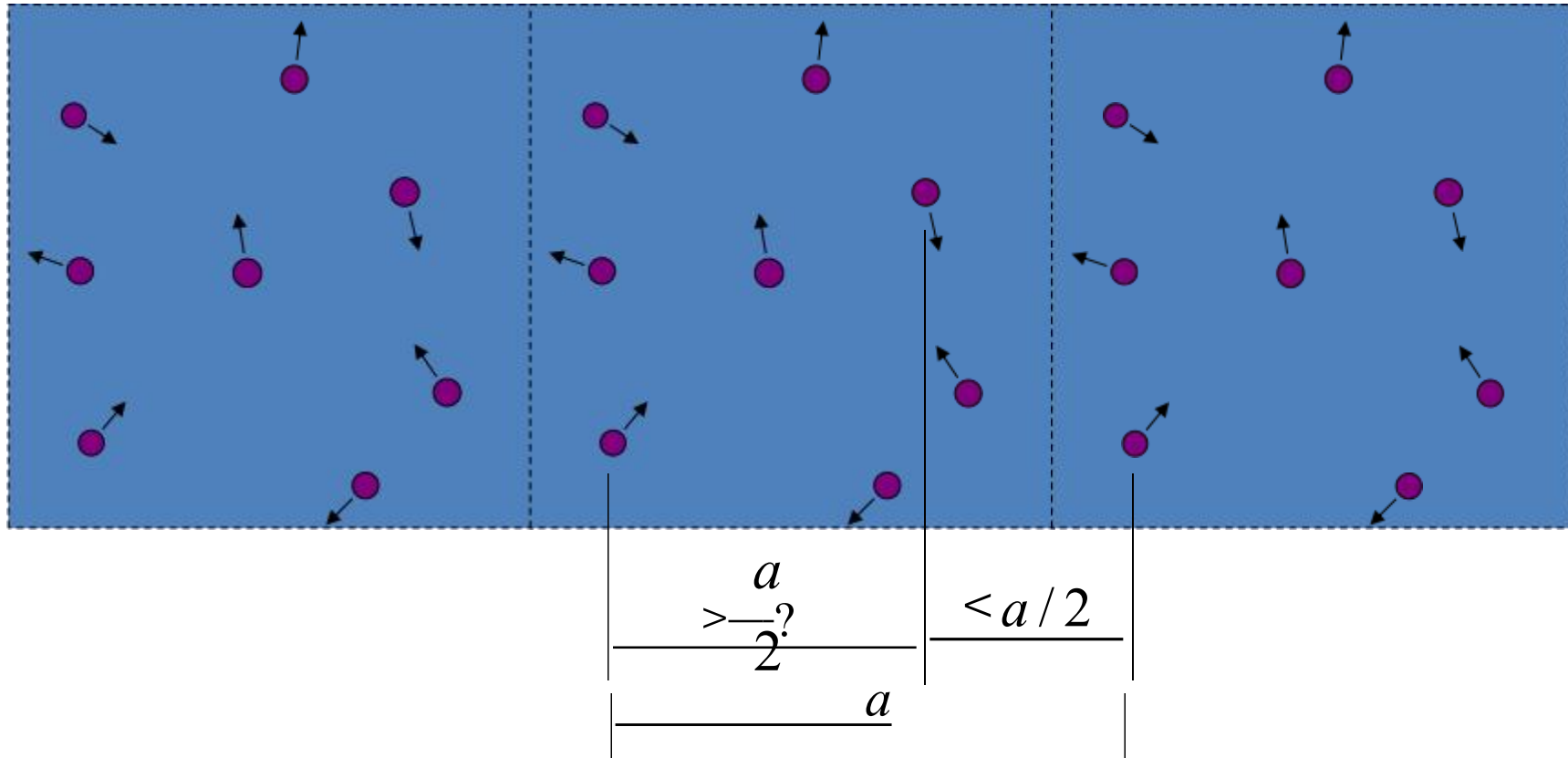
$$\frac{\text{和壁面作用势}}{\text{总分子数}} \propto \frac{\text{壁面积}}{\text{体积}} \propto \frac{6a^2}{a^3} \propto \frac{1}{a} \propto \frac{1}{\sqrt[3]{N}}$$

取 $N = 10^2 \sim 10^6$ 前比值为 $0.2 \sim 0.01$ 。取前值，模拟粗糙；取后值，模拟计算量太大
处理方法：使用周期性边界条件

— 周期性边界条件



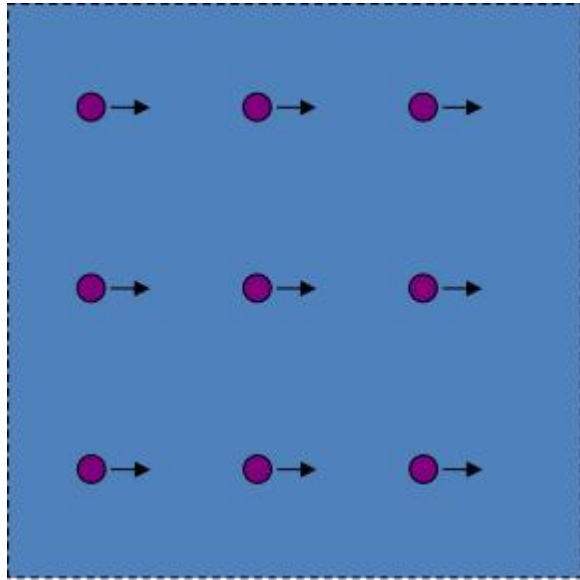
两个不同粒子在x或y方向上的最大分离距离为 $a/2$



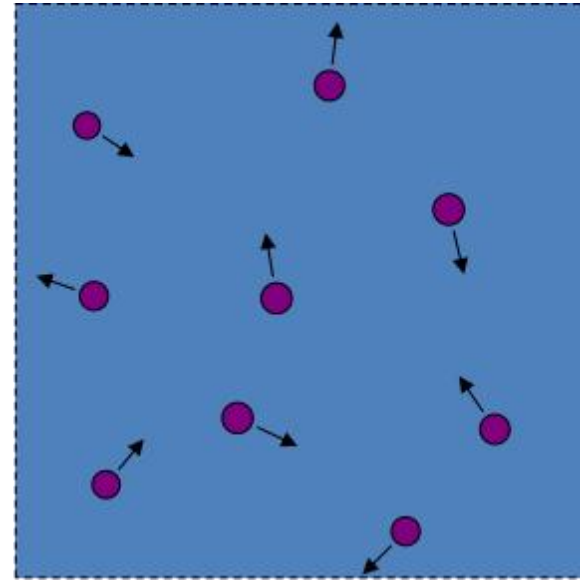
- 最小像约定：两粒子分离距离 $>$ 最大分离距离，相互作用力可以忽略，而加入其中像粒子之一相互作用力来考虑

考虑的粒子总数不变

- 初始条件



条件一:
规则给法



条件二:
随机给法

— 随机初始条件给法之一
要求

大小: $|v| < V_{\max}$

$$v = V_{\max} (2 \times \text{random} - 1)$$

第一天 下午 (14: 00-17: 00)

LAMMPS软件进阶

1. in文件命令设置、调试和注意事项
2. data结构文件及其构建方法
3. MEAM势函数和REAXFF反应势函数简介

units metal

boundary p p p

atom_style atomic

neighbor 2.0 bin

neigh_modify every 1 delay 5 check yes

timestep 0.001

#-----

lattice fcc 4.05 orient x 1 1 0 orient y 0 0 1 orient z 1 - 1 0

region AA block 0 86 0 120 0 2 units box

create_box 1 AA

create_atoms 1 region AA

#read_data **data.xyz** / data.lammps /data.cfg

#=====

pair_style eam/alloy

pair_coeff * * **AlCu.eam.alloy** Al

#=====

thermo 100

thermo_style custom step temp ke pe etotal lx ly lz vol pxx pyy pzz press

#=====

reset_timestep 0

#=====

velocity all create **300 64938**

fix 2 all npt temp **300 300 1.0** iso 0.0 0.0 10.0

fix 3 all print 100 file AlVoid_equi.txt screen no

dump 1 all cfg 100000 AlVoid_equi_*.cfg mass type xs ys zs type

restart 100000 run_equi_restart.*

run 100000

一个简单的分子动力学计算in文件

两大核心文件

1. in文件-----控制/设置计算
2. 势函数文件-----太大了，单独放一个文件
3. (结构文件，如果太大，就单独放)

----- Initialization基本模拟系统设置-----

units (lj) ** 单位系统
boundary (ppp) ** 边界条件 p p p / s p p / s s s
atom_style (atomic) ** 粒子类型

atom_modify * 粒子类型调整，，，凡是后面带一个modify的，都是对头命令的补充修改
newton (on)
processors
dimension (3) * 维数

----- Atom definition---这一组命令主要用来构建模拟模型的-----

lattice ** 晶格参数
region ** 选择一个区域
create_box ** 创建一个盒子
create_atoms ** 创建原子
group, ** 给原子分组
delete_atoms, ** 删除某些原子

delete_bonds,
displace_atoms, * 移动某些原子
replicate* 将已经构建的模型在三维重复复制放大
read_data***这个命令就是用来读取其他软件建的模型的
read_restart* 以之前运行的结果作为这次计算的初始构型

----- Potencial---定义粒子相互作用势-----

pair_style** 势函数类型

pair_coeff,** 势函数文件名 (一般这个文件放在与此in文件的同一个目录下)

pair_modify**

-----Seting-----

neighbor, ** 截断半径相关的设置

neigh_modify, **

timestep,** 模拟的步长

compute, *** ! 定义计算, 一般我们需要的输出数据就需要这个命令来定义

uncompute * 取消某个compute设置

variable**这个命令可以多次使用, 定义一个变量

reset_timestep, ** 步长计数器清零, 有多个run命令的需注意这个

run_style, 配套run的, 不一定需要

compute_modify * 配套compute 的

----- Minimize-----

结构优化, 注意和热力学平衡区分开来

minimize,**

min_style, **

min_modify **

-----Fix-----

fix*** 这个命令相当重要 多的不说，看手册
unfix 取消某个**fix**设置

fix_modify,

-----Output-----

dump, ** 输出数据，输出的为单个原子的信息，可视化就用它

undump,* 取消某个**dump**设置

thermo, ** 输出全局数据，比如温度，压强，长度，总能量等

thermo_style,* 配套**thermo**的

thermo_modify,*

(后面的都是输出一些数据类型，我一般没怎么用，具体需要的可以单独自己了解)

dump image,

dump_modify,

dump movie,

restart,*输出**restart**文件，对应前面**read-restart**，**data**文件只有原子坐标，**restart**含有部分计算信息

write_data,*将当前模型输出为一个**data**文件，对应之前的**read-data**，

write_dump,

write _restart*

-----Run a simulation-----

run, ***这个命令出现之后，模拟才开始进行计算，前面的都是在设置计算过程

结构文件

注释	# Fcc Ni oriented X=[100] Y=[010] Z=[001].
原子个数	400000 atoms
原子种类	5 atom types
模拟空间范围	0.00000000 352.00000000 xlo xhi
	0.00000000 353.26659733 ylo yhi
	0.00000000 35.20000000 zlo zhi
质量	Masses
	1 55.84500000 # Fe
	2 58.93319500 # Co
	3 54.93804500 # Mn
	4 51.99610000 # Cr
	5 58.69340000 # Ni
原子坐标	Atoms # atomic
	1 1 0.85758968 -1.01613907 0.00000000
	2 2 2.61375492 0.75673180 0.00000000
	3 1 0.85319334 0.74735301 1.76000000
	4 3 2.61814404 -1.00681369 1.76000000
	5 3 4.37867211 -0.99752754 0.00000000
	6 3 6.13479812 0.77536903 0.00000000
7 1 4.37428979 0.76607103 1.76000000	

- 1. In文件自带功能编写
- 2. 根据格式自己编程
- 3. 其他软件，如stomsk

REAXFF

pair_style **reax/c** NULL

pair_coeff * * mffield.reax.Si Li Si Li

Reactive MD-force field: Li/Si force field Ostadhossein et al. PCCP 2015

```
39      ! Number of general parameters
50.0000 !Overcoordination parameter
9.5469  !Overcoordination parameter
26.5405 !Valency angle conjugation parameter
1.7224  !Triple bond stabilisation parameter
6.8702  !Triple bond stabilisation parameter
60.4850 !C2-correction
1.0588  ! Undercoordination parameter
4.6000  !Triple bond stabilisation parameter
12.1176 ! Undercoordination parameter
13.3056 !Undercoordination parameter
-70.5044 !Triple bond stabilization energy
0.0000  !Lower Taper-radius
10.0000 ! Upper Taper-radius
2.8793  ! Not used
33.8667 !Valency undercoordination
6.0891  !Valency angle/lone pair parameter
1.0563  !Valency angle
2.0384  !Valency angle parameter

2      ! Nr of atoms; cov.r; valency;a.m;Rvdw;Evdw;gammaEEM;cov.r2;#
      alfa; gammavdW; valency; Eunder; Eover; chiEEM; etaEEM; n. u.
      cov r3;Elp;Heat inc.;n.u.;n.u.;n.u.;n.u.
      ov/un;val 1;n.u.;val3,vval4
Si 2.1932 4.0000 28.0600 1.8951 0.1737 0.5947 1.2962 4.0000
.....
Li 1.6908 1.0000 6.9410 1.6121 0.2459 1.0000 -0.1000 1.0000
.....
3      ! Nr of bonds; Edis1;LPpen;n.u.;pbe1;pbo5;13corr;pbo6
      pbe2;pbo3;pbo4;n.u.;pbo1;pbo2;ovcorr
1 1 70.9120 54.0531 30.0000 0.4931 -0.3000 1.0000 16.0000 0.0392
0.2476 -0.8055 7.1248 1.0000 -0.1009 8.7229 0.0000 0.0000
1 2 0.0000 0.0000 0.0000 1.0000 0.3000 0.0000 26.0000 1.0000
0.5000 0.0000 12.0000 1.0000 -0.2000 10.0000 0.0000 0.0000
2 2 42.9780 0.0000 0.0000 0.3228 0.3000 0.0000 26.0000 0.6003
1.7161 0.0000 12.0000 1.0000 -0.1015 4.0000 0.0000 0.0000
1      ! Nr of off-diagonal terms; Ediss;Ro;gamma;rsigma;rpi;rpi2
1 2 0.0200 1.5000 10.0529 -1.0000 1.0000 1.0000
1      ! Nr of angles;at1;at2;at3;Thetao,o;ka;kb;pv1;pv2;val(bo)
1 1 1 78.5339 36.4328 1.0067 0.0000 0.1694 0.0000 1.6608
0      ! Nr of torsions;at1;at2;at3;at4;;V1;V2;V3;V2(BO);vconj;n.u;n
0      ! Nr of hydrogen bonds;at1;at2;at3;Rhb;Dehb;vhb1
```

MEAM

pair_style **meam**

pair_coeff * * **librarhea.meam** Fe Co Mn Cr Ni **hea.meam** Fe Co Mn Cr Ni

librarhea.meam

'Co'	'hcp'	12	1	58.933				
5.2356147485		3.50	0.00	0.00	4.00	2.5000000000	4.41	0.90
1	3.00	5.00	-1.00	1.00	3			
'Ni'	'fcc'	12	1	58.690				
5.0842175782		2.56	1.50	6.00	1.50	3.5213917703	4.45	0.94
1	3.10	1.80	4.36	1.00	3			
'Cr'	'bcc'	8	1	51.960				
5.5800716432		6.49	1.00	6.00	1.00	2.8809778433	4.10	0.52
1	2.00	6.80	-8.00	1.00	3			
'Fe'	'bcc'	8	1	55.847				
5.1571615396		4.15	1.00	1.00	1.00	2.8636573352	4.29	0.56
1	2.60	1.80	-7.20	1.00	3			
'Mn'	'bcc'	8	1	54.940				
5.7345791984		4.30	1.00	2.00	6.50	2.9213923621	2.90	0.70
1	4.00	-3.00	-4.00	1.00	3			

hea.meam

rc = 4.5
delr = 0.1
augt 1 = 0
erose_form = 2
ialloy = 2
zbl(1,1) = 0
nn2(1,1) = 1
attrac(1,1) = 0
repuls(1,1) = 0
Cmin(1,1,1) = 0.49
Cmax(1,1,1) = 2
Ec(1,1) = 4.41
re(1,1) = 2.5
zbl(2,2) = 0
nn2(2,2) = 1
attrac(2,2) = 0.05
repuls(2,2) = 0.05