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Key Laboratory of Computational Physical Sciences
(Fudan University), Ministry of Education

复旦大学
FUDAN UNIVERSITY

# Thermal Conductivity Calculation of Argon by Molecular Dynamics

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# Introduction

实验目的：

1. 深入理解分子动力学模拟
2. 解热传导过程涉及的基本物理知识，熟悉计算热导率的不同算法。
3. 掌握热传导过程分子动力学模拟的核心控制参数与模拟步骤。
4. 分析影响热导的物理因素（声子平均自由程、温度效应、尺寸等）。

本课程共8次课： 1-3次课为周阳讲授，4-8节为动手实验环节

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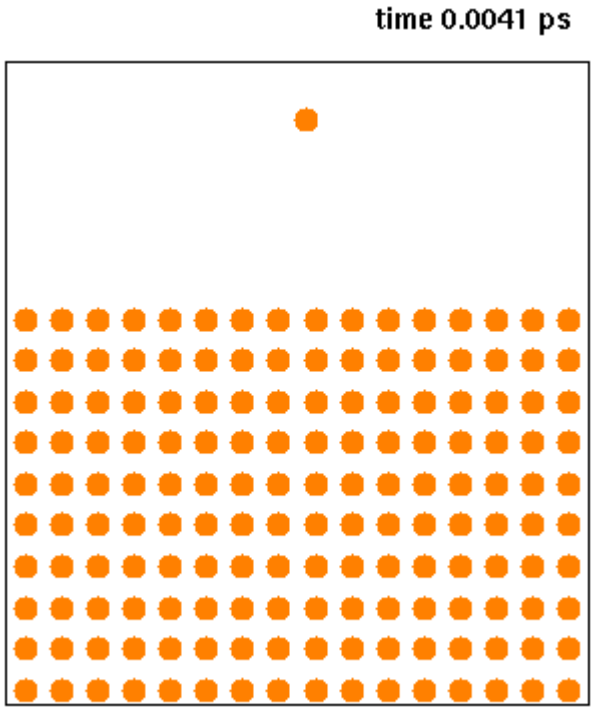
# Basic Methods: Molecular Dynamical Simulation

# What & Why




Molecular Dynamics(MD) is a commonly used method to study N-body systems.

It can be used to study

- Solar systems or universe
- Atoms groups or solid, gas and liquid, DNA and even plasma under classical assumption.
- Birds or other cluster systems

- Equilibrium systems
- Highly non-equilibrium systems

- Statics
- Correlation
- Evolution

# Conceptions

§ Dynamical Equation

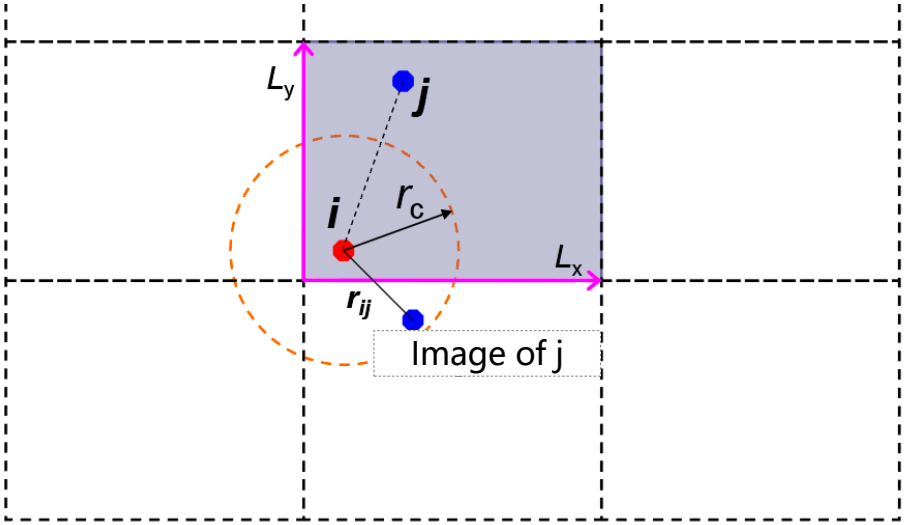
$$\mathbf{F}_i = m_i \mathbf{a}_i \quad \Rightarrow m\frac{\mathrm{d}^2\mathbf{r}_i}{\mathrm{d}t^2} = -\nabla_i V(\{r_i\})$$

§ Verlet algorithm

$$\begin{aligned}
\mathbf{r}(t+\Delta t) &= \mathbf{r}(t) + \mathbf{v}(t)\cdot\Delta t + \frac{1}{2}\mathbf{a}(t)\cdot(\Delta t)^2 + \frac{1}{6}\mathbf{b}(t)\cdot(\Delta t)^3 + o[(\Delta t)^4] \\
\mathbf{r}(t-\Delta t) &= \mathbf{r}(t) - \mathbf{v}(t)\cdot\Delta t + \frac{1}{2}\mathbf{a}(t)\cdot(\Delta t)^2 - \frac{1}{6}\mathbf{b}(t)\cdot(\Delta t)^3 + o[(\Delta t)^4]
\end{aligned}$$

$$\mathbf{r}(t+\Delta t) = 2\mathbf{r}(t) - \mathbf{r}(t-\Delta t) + \mathbf{a}(t)\cdot(\Delta t)^2 + o[(\Delta t)^4]$$

§ Structure & Boundary



# Conceptions

§ Neighbor list

In order to reduce the calculation complexity of force from O(N^2) to O(N) , these could be done:

1. cut off the potential, so we can only calculate the summation over the atoms within the sphere.
2. save the atoms within the sphere and there’ s no need to search the spheres for M steps.
3. when search for spheres after the M steps, there’ s no need to find all the atoms within the sphere, but remove the atoms leaved and add the atoms get close

find neighbor

build neighbor list

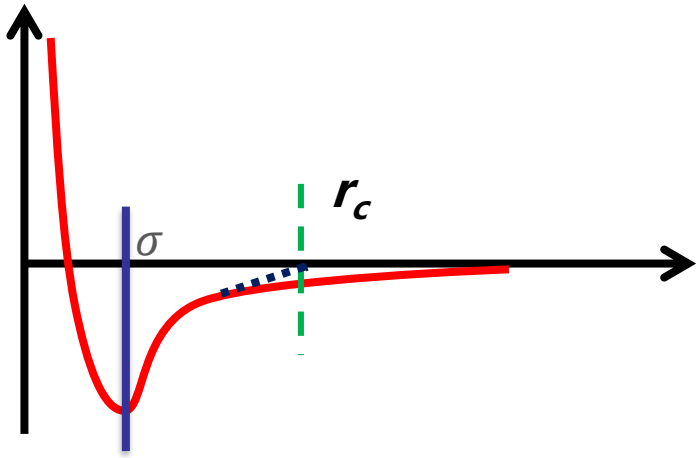
update neighbor list

# Conceptions

§ Potential Lennard-Jones (LJ) Potential

$$V = 4\epsilon\left(\frac{\sigma^{12}}{r^{12}} - \frac{\sigma^{6}}{r^{6}}\right)$$

$r_c$ – *cutting radius*




§ Velocity Distribution Gaussian distribution of Temperature T

Clear out the drift and remaining rotation

# Properties

- Energy $E = \sum_i E_i$ Atomic energy $E_i = \frac{3}{2} m_i v_i^2 + Pot_i$

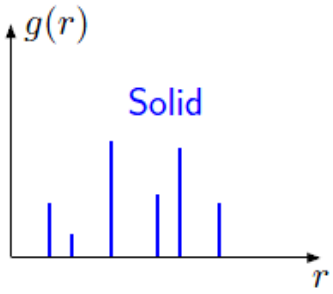
  Atomic Potential $Pot_i = \frac{1}{2!}\sum_j V_{ij} + \frac{1}{3!}\sum_{jk} V_{ijk} + \cdots$

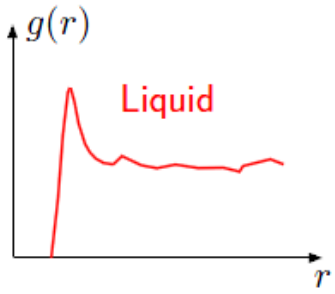
- Temperature $T = \frac{1}{k_B}\frac{1}{N}\sum_i \frac{3}{2} m_i v_i^2$

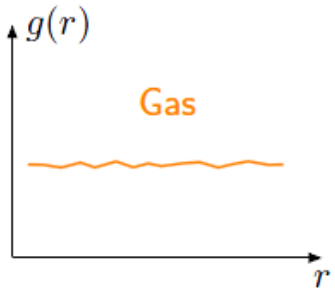
- Pressure Virial Thorem $pV = Nk_BT + \frac{1}{3}\left\langle \sum_i \boldsymbol{r_i} \cdot \boldsymbol{F}_i \right\rangle$

- Radial distribution function(R $G(r) = \frac{1}{N}\left\langle \sum_{i=1}^{N}\sum_{j=1}^{N} \delta(r - r_{ij}) \right\rangle$

  Pair-Correlation function $g(r) = \frac{1}{4\pi r^2} G(r)$



# NVT Ensemble

$$\dot{\boldsymbol{r}}_i = \frac{p_i}{m_i}$$

$$\dot{\boldsymbol{p}}_i = F_i - \frac{p_{\xi_1}}{Q_1} p_i$$

Feedback force

$$\dot{\boldsymbol{\xi}}_k = \frac{p_{\xi_k}}{Q_k} \quad k = 1, \ldots, M$$

$$\dot{p}_{\xi_1} = \left(\sum_i \frac{p_i^2}{m_i} - Lk_BT\right) - \frac{p_{\xi_2}}{Q_2} p_{\xi_1}$$

$$\dot{p}_{\xi_k} = \left(\frac{p_{\xi_{k-1}}^2}{Q_{k-1}} - k_BT\right) - \frac{p_{\xi_{k+1}}}{Q_{k+1}} p_{\xi_k}$$

$$\dot{p}_{\xi_M} = \left(\frac{p_{\xi_{M-1}}^2}{Q_{M-1}} - k_BT\right)$$

Dynamics of Nose-Hoover Chain

L=3N is degree of freedom(dof)

$\mathrm{Q}_1 = Lk_BT\tau^2$ $\mathrm{Q}_k = k_BT\tau^2$ $\tau$ is relaxation time

The power of heatbath:

$$J_i = F_i \cdot \frac{p_i}{m_i} = -\frac{p_{\xi_1}}{Q_1} p_i \cdot \frac{p_i}{m_i} = -\xi_1 \frac{p_i p_i}{m_i}$$

$$= -\xi \sum 2E_{ki} = -2\xi N \frac{3}{2} k_B T_{real} = -3\xi N \, k_B T_{real} = -\xi \, L \, k_B T_{real}$$

# Langevin Ensemble

$$\dot{\boldsymbol{r}}_i = \frac{p_i}{m_i}$$

$$\dot{\boldsymbol{p}}_i = F_i - \gamma_i \frac{p_i}{m_i} + \xi_i(t)$$

$$\langle \xi_i(t_1) \cdot \xi_j(t_2) \rangle = 2\mathrm{k_B T_i} \gamma_i \delta_{ij} \delta(t_1 - t_2)$$

Plank-Fokker Equation

$$\frac{\partial \rho(r_i, p_i)}{\partial t} = \sum_i -\left[\frac{\partial}{\partial r_i}\left(\frac{p_i}{m_i}\rho\right) + \frac{\partial}{\partial p_i}\left(\left(F_i - \gamma_i \frac{p_i}{m_i}\right)\rho\right)\right] + \frac{\partial}{\partial p_i^2}(\mathrm{k_B T_i} \gamma_i \rho)$$

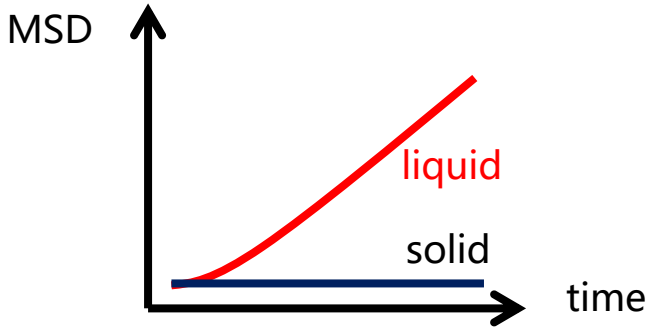
If $\gamma_i = 0$ $\quad \frac{\partial \rho(r_i, p_i)}{\partial t} = \sum_i -\left[\frac{\partial}{\partial r_i}\left(\frac{p_i}{m_i}\rho\right) + \frac{\partial}{\partial p_i}(F_i \rho)\right]$

Liouville Equation

# Properties

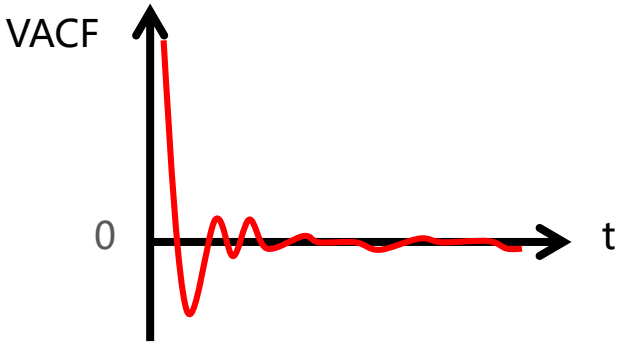
$$R(t) = <|\vec{r}(t) - \vec{r}(0)|^2> = \frac{\sum_{i=1}^{N} \sum_{t_0=1}^{t_{max}} (\vec{r}_i(t_0 + t) - \vec{r}_i(t_0))^2}{N \times t_{max}}$$

§ Mean square displacement(MSD)

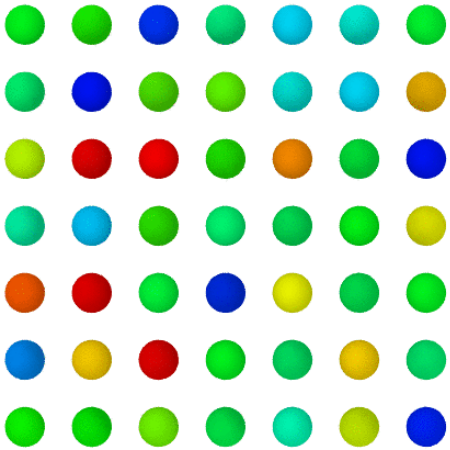


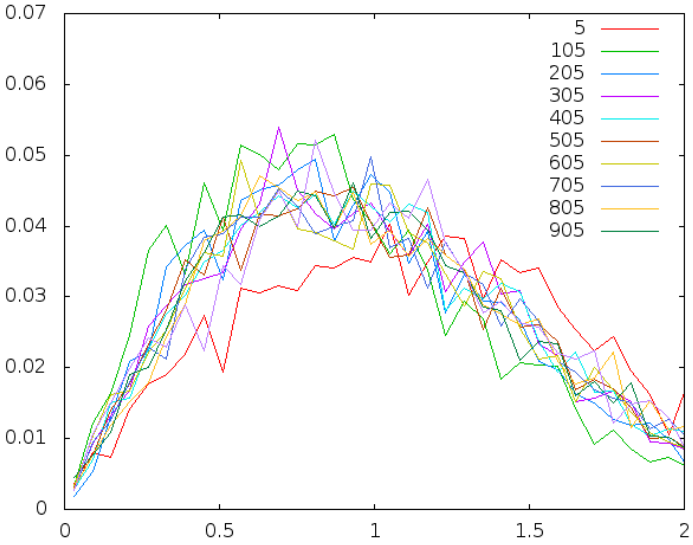

§ Velocity autocorrelation function(VACF)

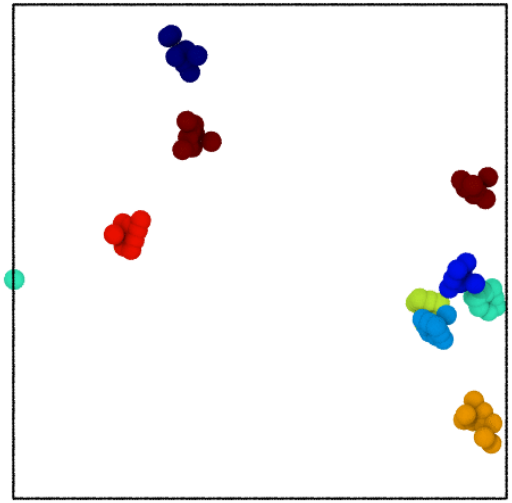
$$C_v(t) = <\mathbf{v}(t) \cdot \mathbf{v}(0)> = \frac{\sum_{i=1}^{N} \sum_{t_0=1}^{t_{max}} \mathbf{v}_i(t_0) \cdot \mathbf{v}_i(t_0 + t)}{N \times t_{max}}$$

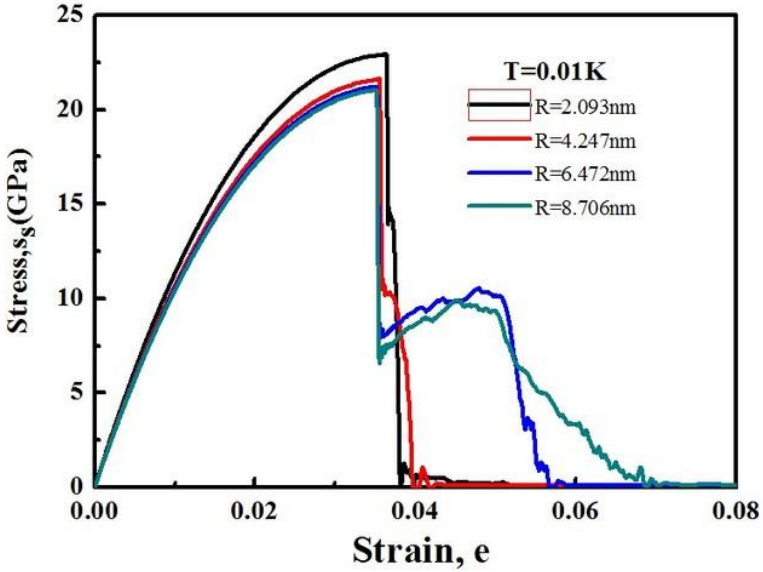


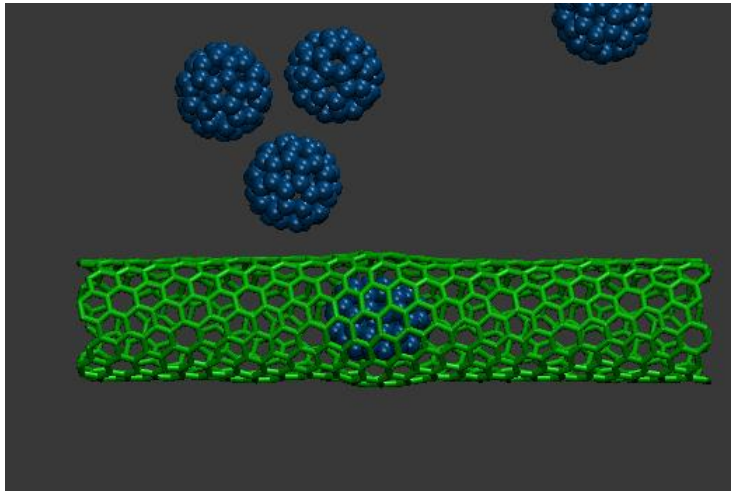
# Examples



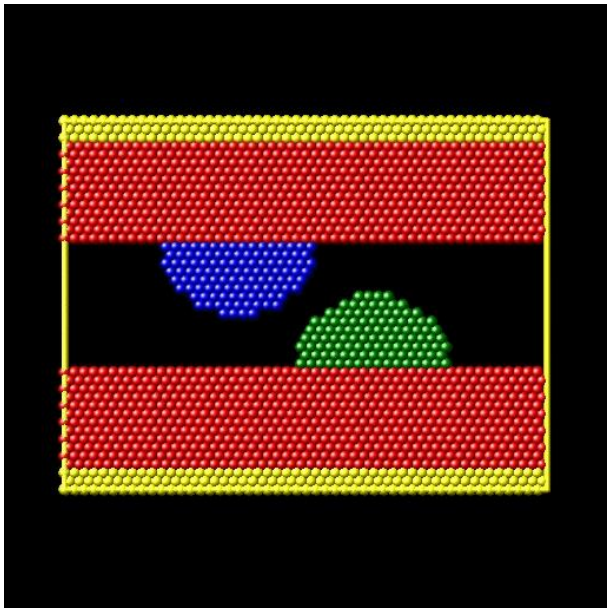

0.07
0.06
0.05
0.04
0.03
0.02
0.01
0
0
0.5
1
1.5
2
5
105
205
305
405
505
605
705
805
905

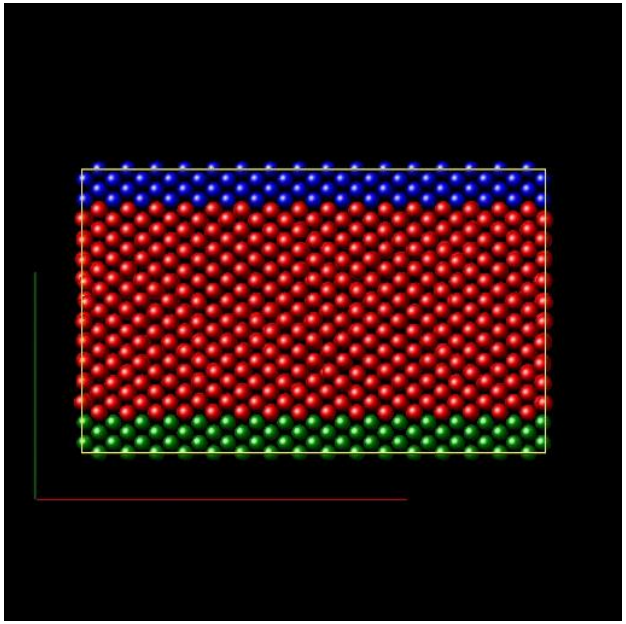



T=0.01K
R=2.093nm
R=4.247nm
R=6.472nm
R=8.706nm
Stress,s$_s$(GPa)
Strain, e
25
20
15
10
5
0
0.00
0.02
0.04
0.06
0.08



# Examples





# Homework

- 编写一个代码，用Verlet算法数值求解N个Ar理想气体原子的牛顿方程
- 验证玻尔兹曼速率分布

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# THANK FOR YOUR ATTENTION!

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