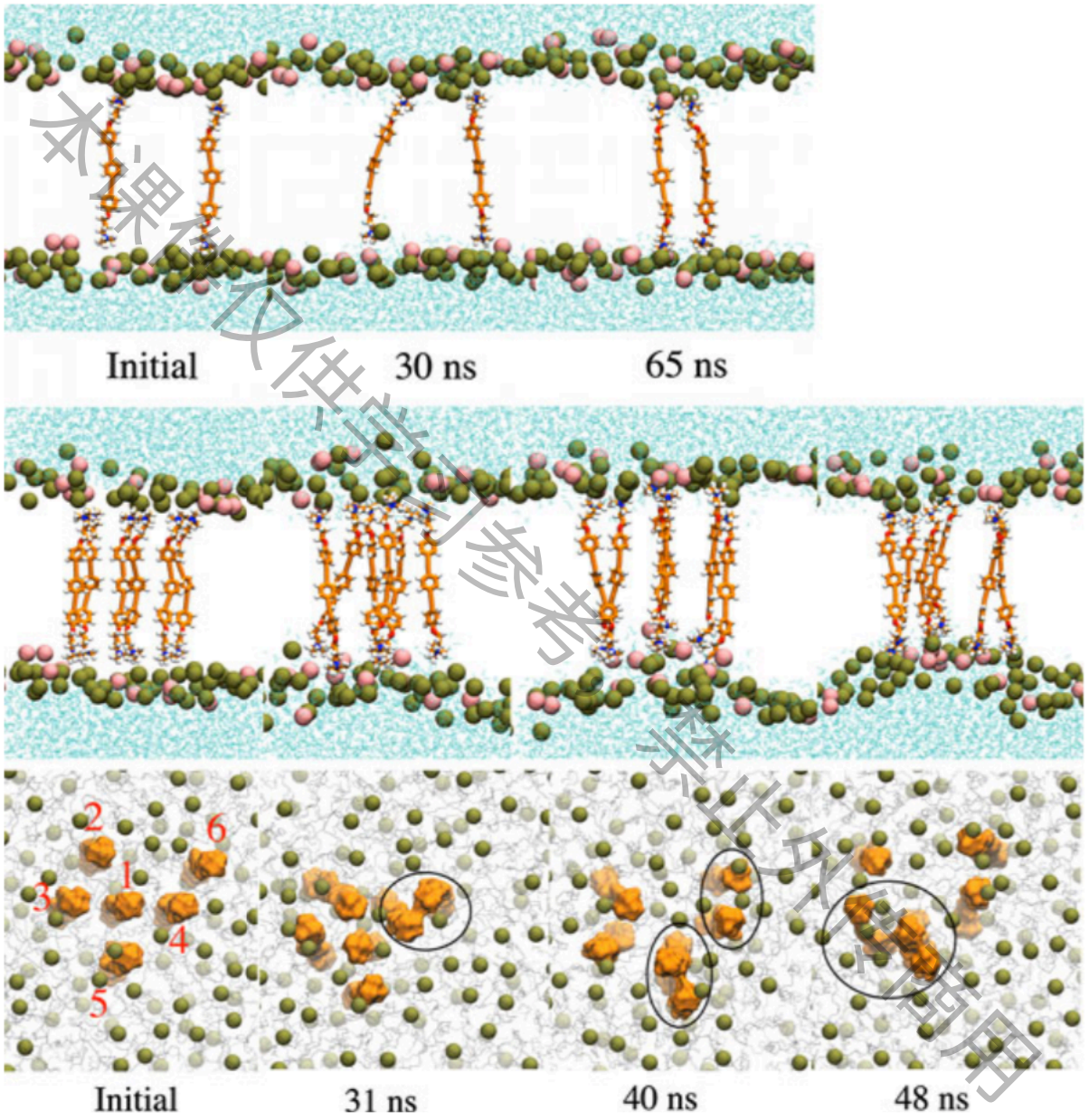


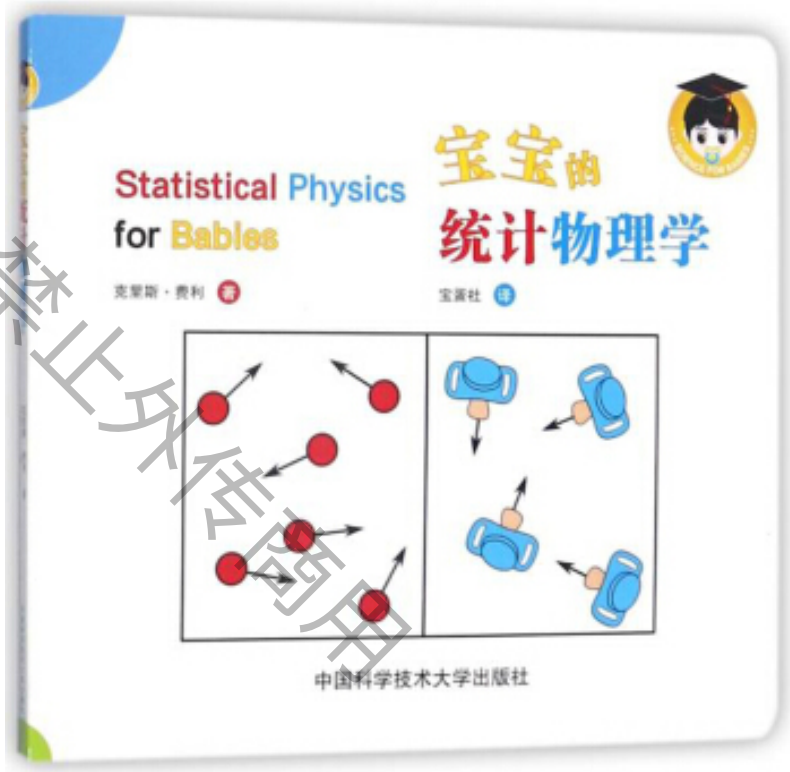
1. Li, Y.; Guo, H. Atomistic simulations of an antimicrobial molecule interacting with a model bacterial membrane. *Theor Chem Acc* **2012,** *132* (1), 1-8.

Distraction: Ergodic hypothesis

$$\langle A \rangle = \int A \exp(-\beta E)\, d\Gamma = \frac{1}{T}\int_0^{\infty} A(t)\, dt$$

$$= \lim_{N_{step}\to\infty} \frac{1}{N_{\text{step}}} \sum_{i=1}^{N\text{step}} A(i\Delta t),$$

Ensemble average =
Time average



Ergodic hypothesis

$$\langle A \rangle = \int A \exp(-\beta E) d\Gamma$$

$$= \int d\boldsymbol{p}_1 \int d\boldsymbol{p}_2 \cdots \int d\boldsymbol{p}_N \int d\boldsymbol{q}_1 \int \boldsymbol{q}_2 \cdots \int \boldsymbol{q}_N A(\boldsymbol{p},\boldsymbol{q}) \exp\left(-\beta E(\boldsymbol{p},\boldsymbol{q})\right)$$

$$\boldsymbol{p} = (\boldsymbol{p}_1, \boldsymbol{p}_2, \cdots \boldsymbol{p}_N), \qquad \boldsymbol{q} = (\boldsymbol{q}_1, \boldsymbol{q}_2, \cdots \boldsymbol{q}_N)$$

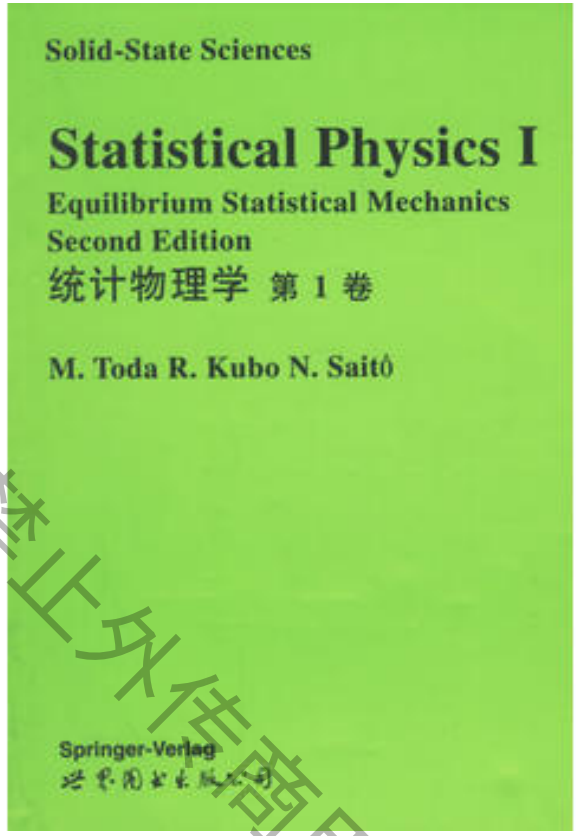
$$= \frac{1}{N_{\text{step}}} \sum_{i=1}^{N\text{step}} A(i\Delta t),$$

Ergodic hypothesis

对于一般的某一力学体系（动力系统），常常不满足；
但是对于很多力学体系组成的系综，至今应用此假设得到的结论正确！原因：系综中的体系不会完全无相互作用！

Ensemble average equal to time average

Toda, Kubo, Saito, *Statistical Physics I*, Springer-Velarg,1983

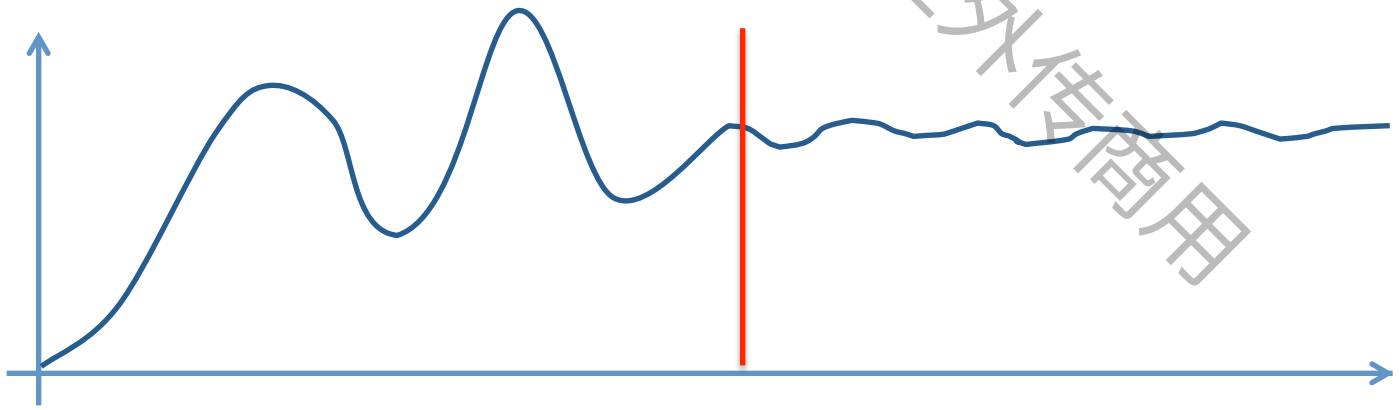


Time average of physical variables

$$\langle E \rangle = \frac{1}{N_{\text{step}}} \sum_{i=1}^{N\text{step}} E_i$$

$$\langle T \rangle = \frac{m\langle \upsilon^2 \rangle}{3k_{\text{B}}} = \frac{1}{N_{\text{step}}} \frac{m}{3k_{\text{B}}} \sum_{i=1}^{N\text{step}} \frac{1}{N_{\text{particle}}} \sum_{j=1}^{N\text{particle}} \upsilon_j^2$$

In general, *i*=1 is not the *initial* time!
Must discard all non-equilibrium trajectories



Mean value and fluctuation

$$\mathrm{STD}(E) = \sqrt{\frac{1}{N_{\mathrm{step}}} \sum_{i=1}^{N\mathrm{step}} \left(E_i - \langle E \rangle\right)^2}$$

标量!

$$= \sqrt{\frac{1}{N_{\mathrm{step}}} \left(\langle E^2 \rangle - \langle E \rangle^2\right)}$$

Mean value and fluctuation

$$\frac{\left\langle (\Delta K)^2 \right\rangle}{\left\langle K \right\rangle^2} = \frac{2}{3N}\left(1 - \frac{3N}{2C_V}\right)$$

Phys. Rev. 153: 250 (1967)

$$P_{\text{int}} = Nk_BT - \frac{1}{3}\left\langle \sum_{i<j} r_{ij} \frac{\partial U(R)}{\partial r_{ij}} \right\rangle$$

J. P. Hansen, I. R. McDonald, *Theories of simple liquid*, 3rd ed. 2.2.9

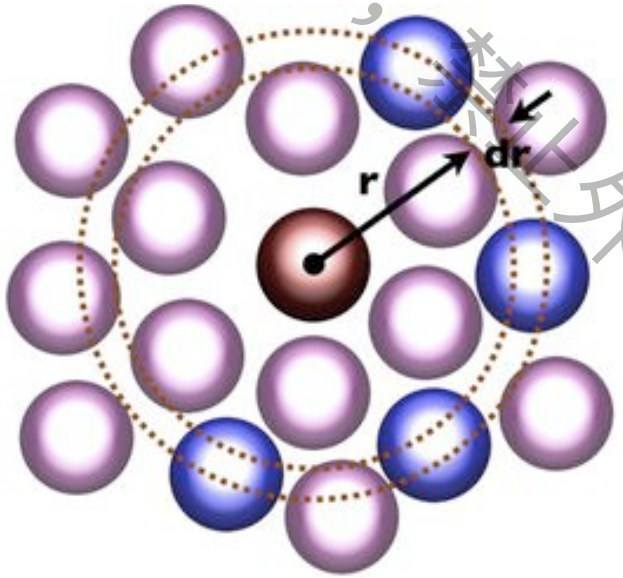
Radial distribution: $g(r)$

1. histogram

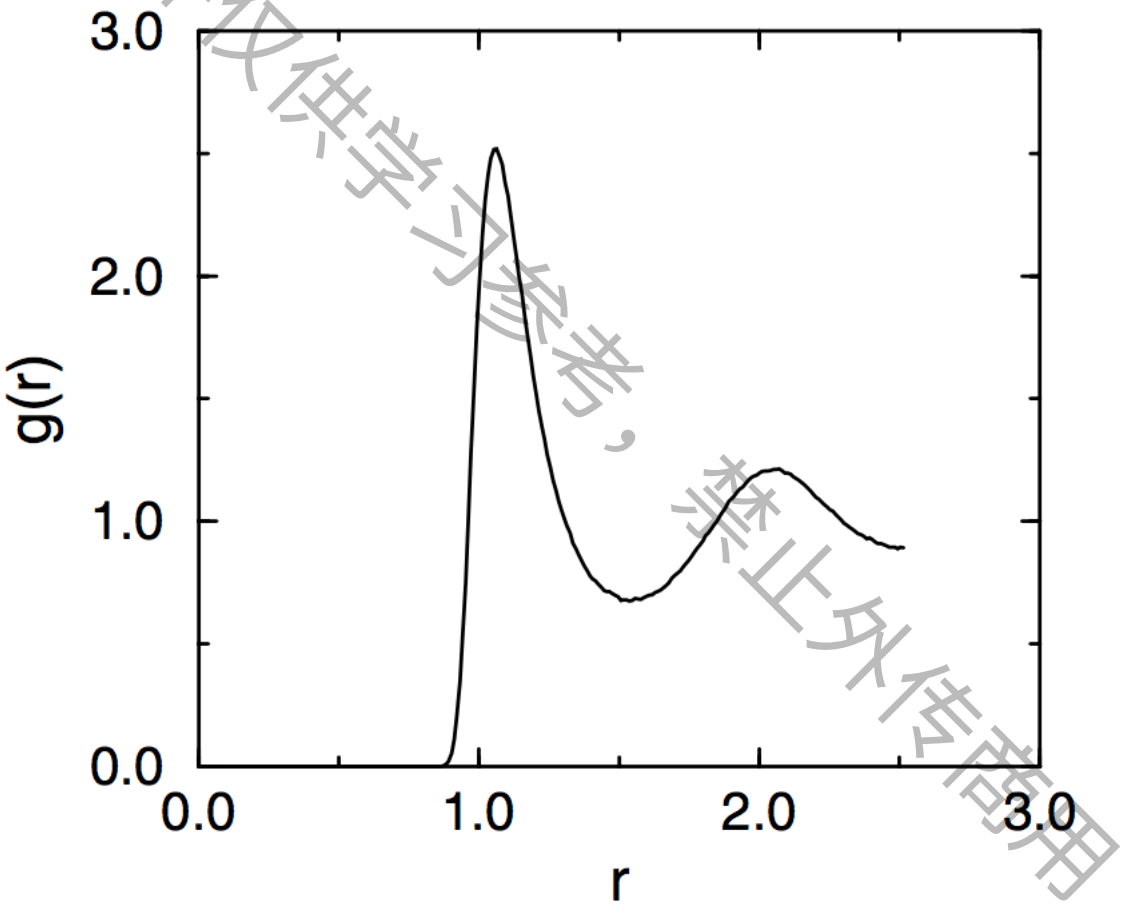
$$n(r) = hist(XX)$$

2. $g(r)$

$$g(r) = \frac{2V}{N(N-1)}\left[\frac{\langle n(r)\rangle}{4\pi r^2(\Delta r)}\right]$$



Radial distribution: $g(r)$



T=1.5043; ρ=0.8442

Dynamic information: correlation function

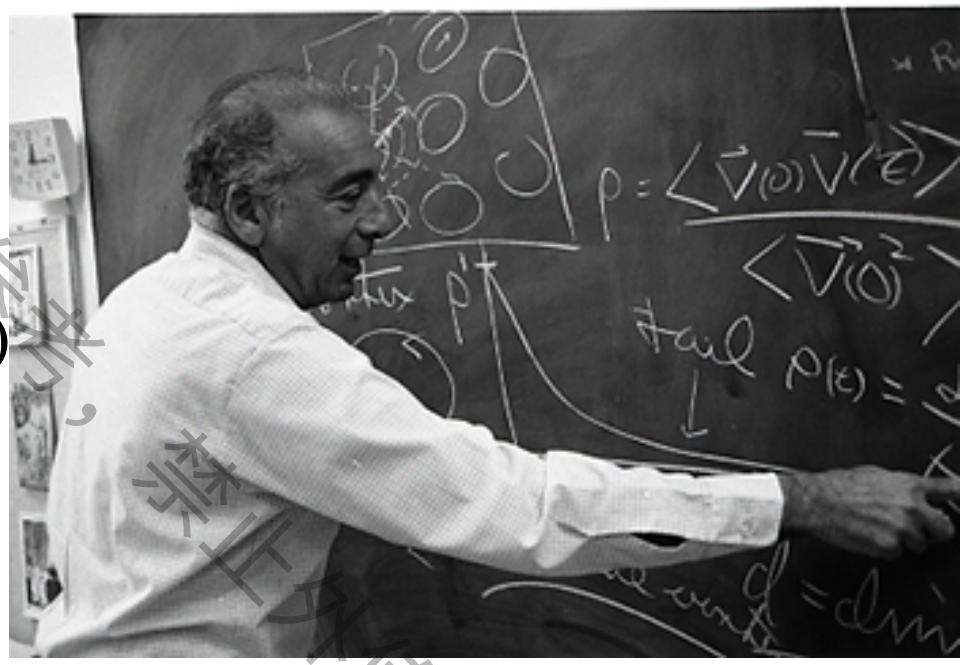
$$C_{AA}(t) = \langle A(t)A(0) \rangle$$

$$= \frac{1}{T}\int A(\tau)A(t-\tau)\,dt$$

$$= \frac{1}{N-m}\sum_{i=1}^{N-m-1} A(i)A(i+t/\Delta t)$$

$$t = m \cdot \Delta t$$

e. g.



$$\langle C_{\mu\mu}(t) \rangle = \frac{1}{N_{\text{step}}}\sum_{i=1}^{N\text{needed}} \boldsymbol{\mu}(i) \bullet \boldsymbol{\mu}(i+t/\Delta t), \qquad \boldsymbol{\mu} = \sum_{j=1}^{N\text{particle}} e_j r_j$$

Correlation function

$$C_{XY}(t) = \langle \delta \boldsymbol{X}(t) \bullet \delta \boldsymbol{Y}(0) \rangle$$

$$= \frac{1}{T} \int (\boldsymbol{X}(\tau) - \langle \boldsymbol{X} \rangle) \bullet (\boldsymbol{Y}(t-\tau) - \langle \boldsymbol{Y} \rangle) dt$$

$$= \frac{1}{N-m} \sum_{i=1}^{N-m-1} (\boldsymbol{X}(m+i) - \langle \boldsymbol{X} \rangle) \bullet (\boldsymbol{Y}(i) - \langle \boldsymbol{Y} \rangle),$$

$$t = m \cdot \Delta t$$

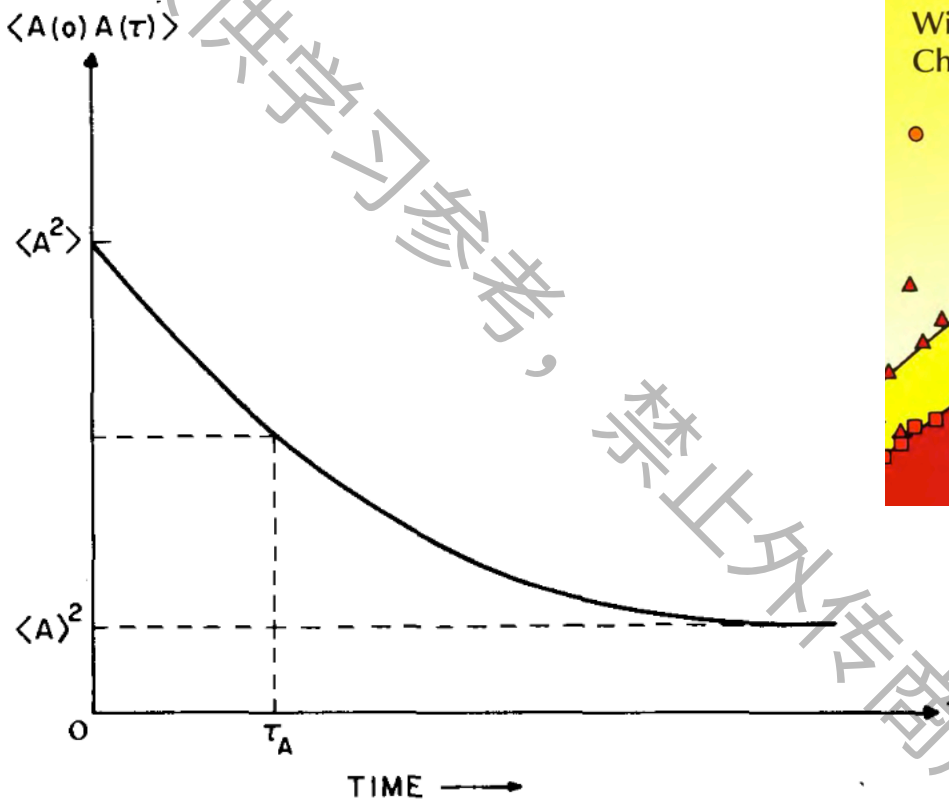
$$c_{XY}(t) = \frac{C_{XY}(t) - \langle \boldsymbol{X} \rangle \bullet \langle \boldsymbol{Y} \rangle}{\mathrm{STD}(X) \cdot \mathrm{STD}(Y)}$$

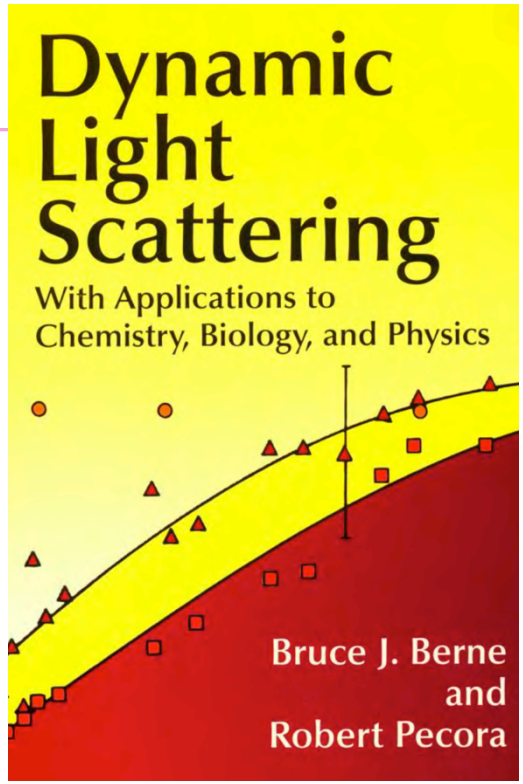
Usage:
（1）Exploration of correlated variables
（2）Validation of the system having reached equilibrium.

Onsager's *regression of spontaneous fluctuations*:
A consequence of Fluctuation-Dissipation Theorem.

$$C_{AA}(t \to 0) = \left\langle A^2 \right\rangle$$

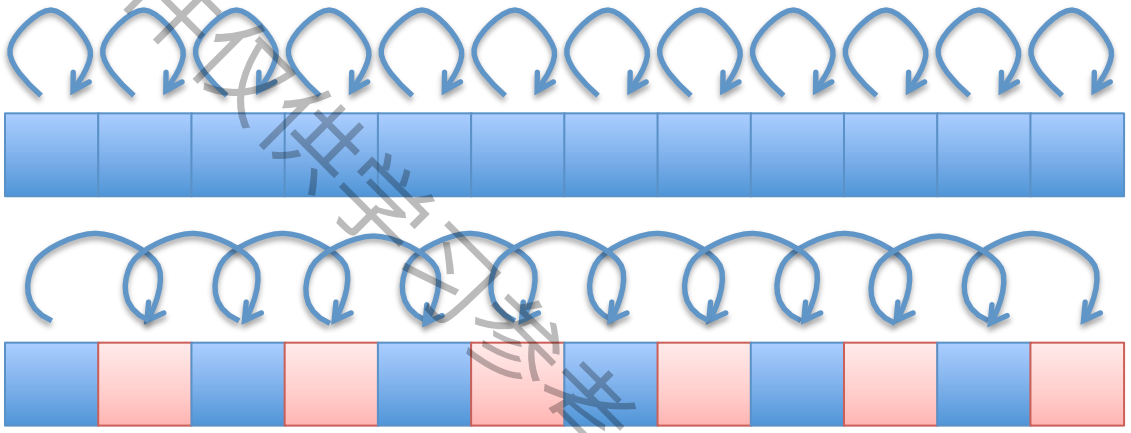
$$C_{AA}(t \to \infty) = \left\langle A \right\rangle^2$$





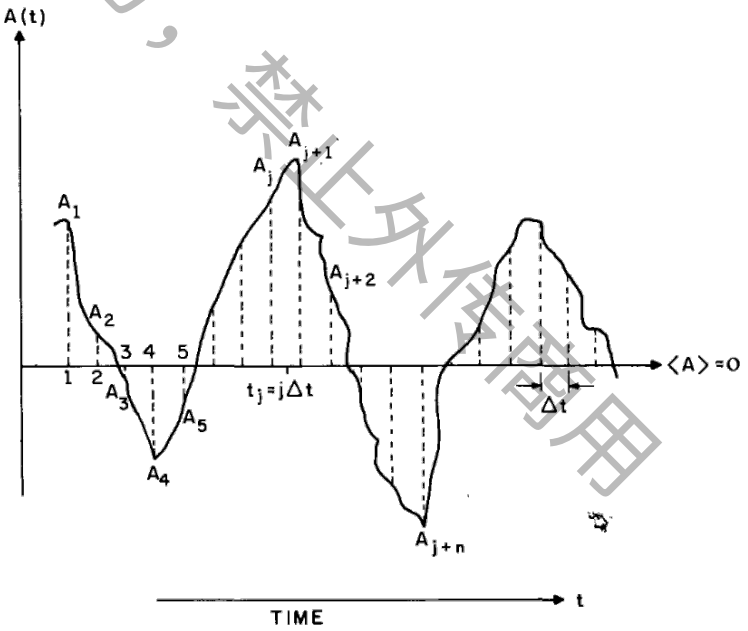
Calculation of auto-correlation

$C_{AA}(1)$



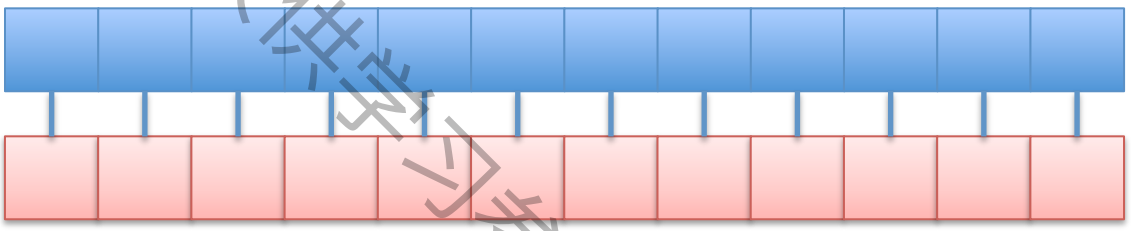
$C_{AA}(2)$

.....

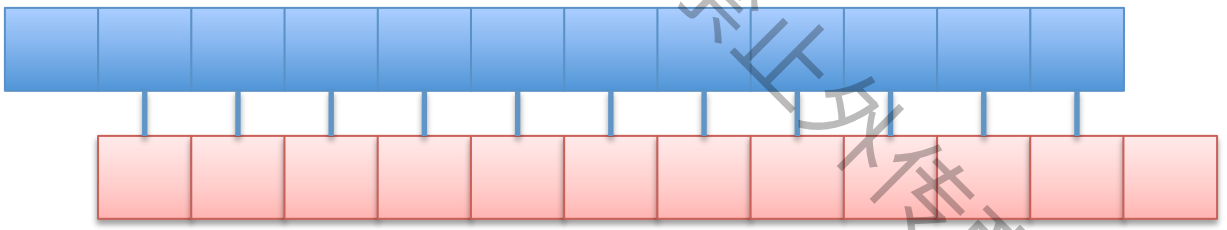


Calculation of cross-correlation

$C_{AB}(1)$



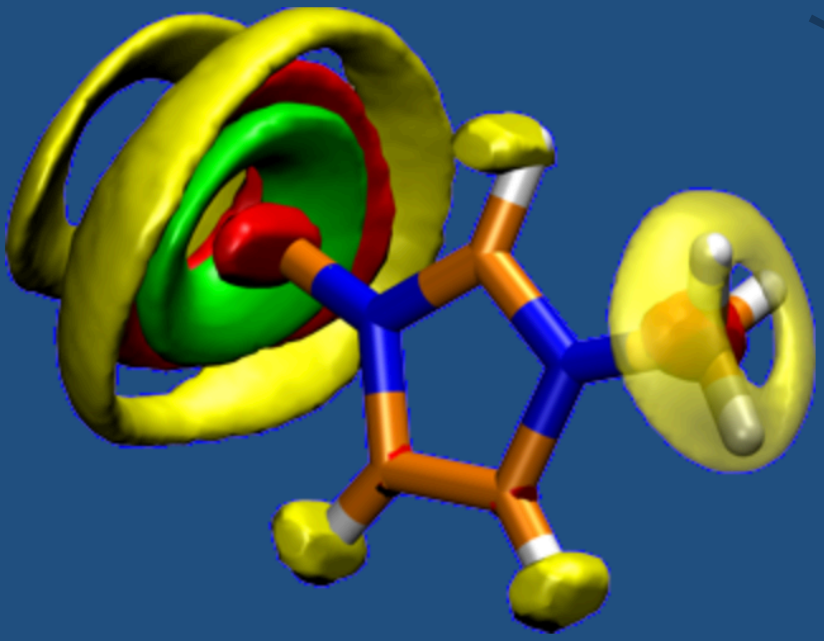
$C_{AB}(2)$



……

Software of obtaining $C(t)$: Travis

TRAVIS - Trajectory Analyzer and Visualizer



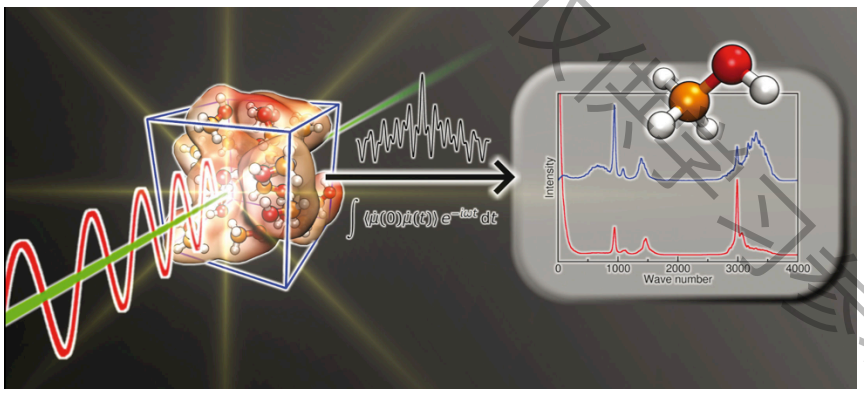
The homepage has moved:
http://www.travis-analyzer.de

Last page update: **Oct 13 2016**
Last program update: **Oct 13 2016**
(current version: 1.14.0)

>> Critical bug fix <<

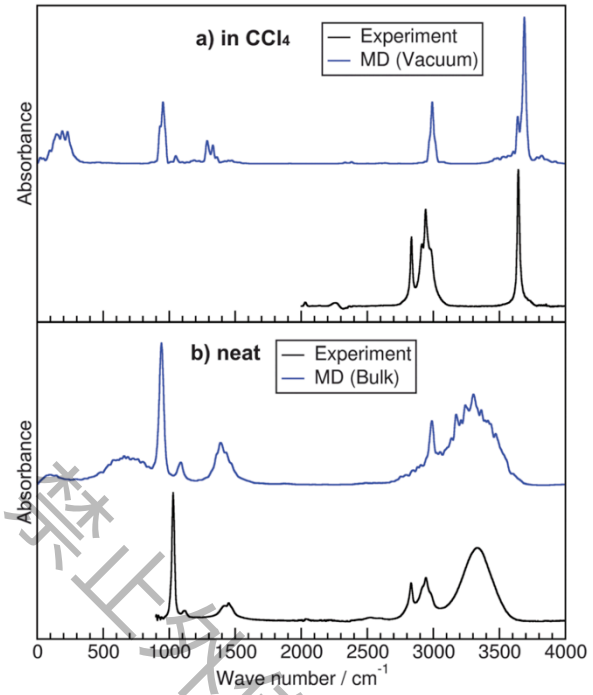
What is TRAVIS?

Application of $C(t)$: spectra



$$\left\langle C_{\dot{\mu}\dot{\mu}}(t)\right\rangle = \frac{1}{N_{\text{step}}} \sum_{i=1}^{N\text{needed}} \dot{\boldsymbol{\mu}}(i) \bullet \dot{\boldsymbol{\mu}}(i + t/\Delta t)$$

$$A(\omega) \propto \int \left\langle C_{\dot{\mu}\dot{\mu}}(t)\right\rangle e^{-i\omega t} dt$$



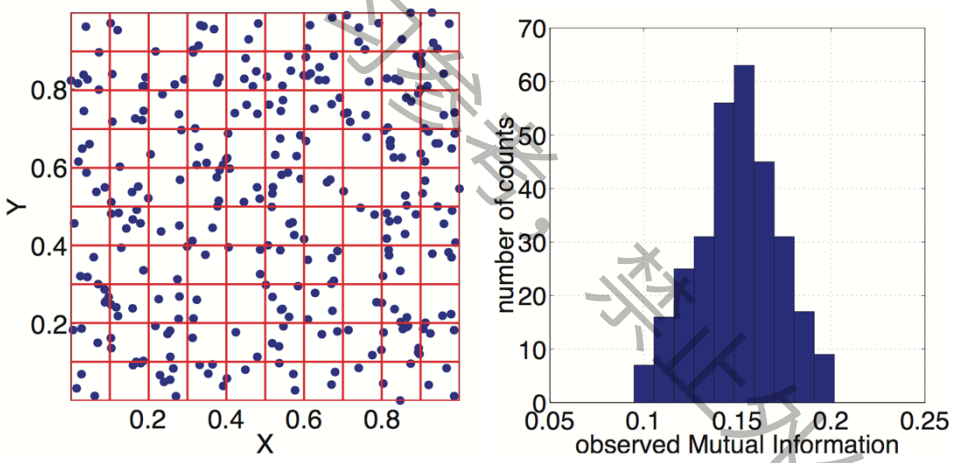
Computing vibrational spectra from *ab initio* molecular dynamics
Phys. Chem. Chem. Phys., 2013, 15, 6608--6622

Dynamic information: MI

Mutual Information

$$MI = \sum_{ij} p(a_i, b_j) \log \frac{p(a_i, b_j)}{p(a_i) p(b_j)}$$

Pro: Can show the correlations between orthogonal variables, and non-linear correlations.
Con: Can show correlation only, but not causality. (One can use **Transfer Entropy** to explore causality)



$$p(a_i) = n(a_i) / N$$
$$p(b_j) = n(b_j) / N$$
$$p(a_i, b_j) = n(a_i, b_j) / N$$

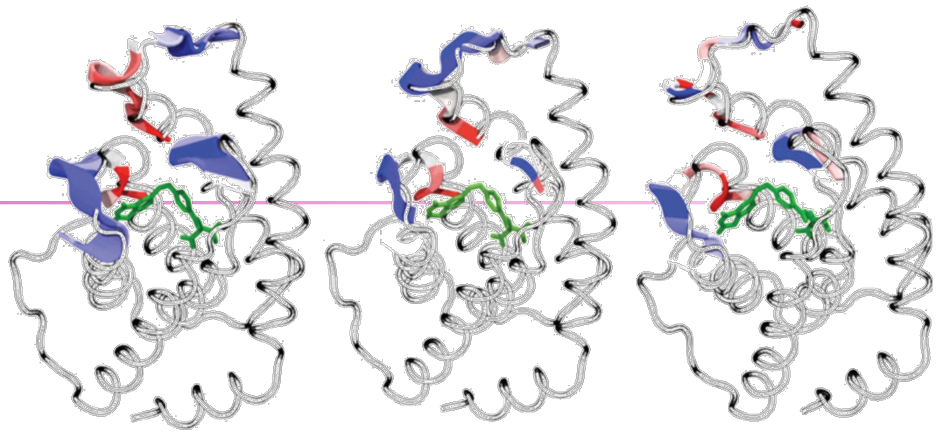
$$MI^{\text{observed}} \approx MI + error$$

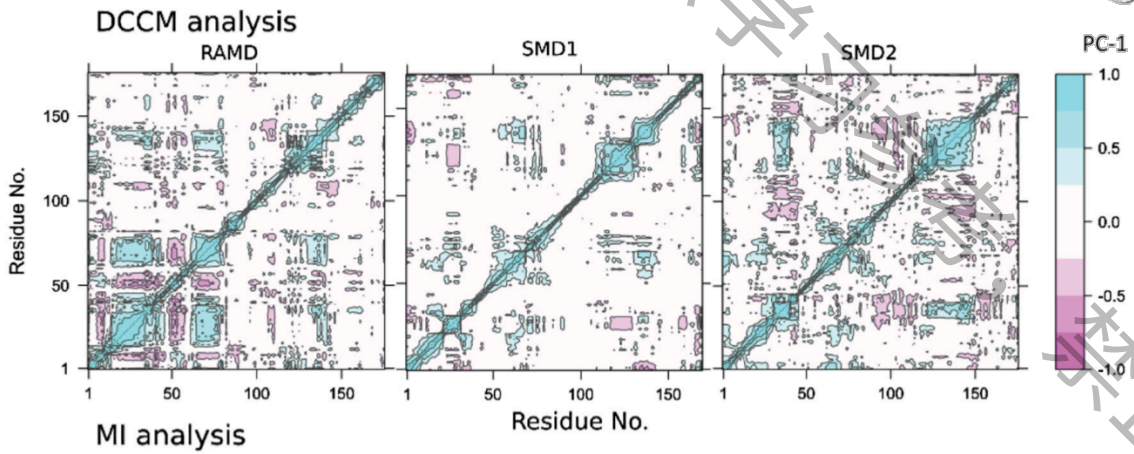
$$error = \frac{M_{ab} - M_a - M_b + 1}{2N}$$

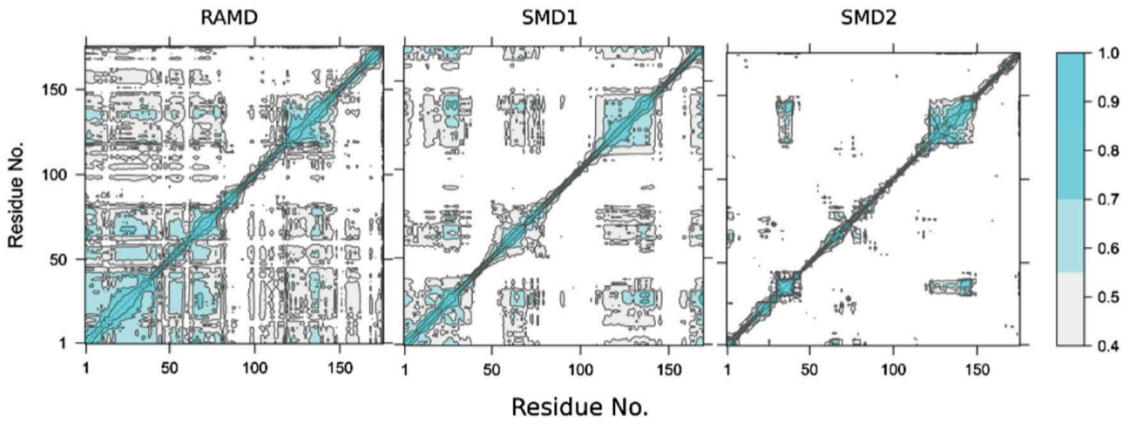
Exploring the correlation among different parts in MD

Application of MI:

L. Q. Qiu, C. Shen, J. N. Song, Y. K. Zhang and J. Z. H. Zhang, *Molecular Physics* **116** (19-20), 2613-2621 (2018).







Challenges of MD

$$\langle F \rangle = -k_B T \ln Q$$

$$\Delta \langle F \rangle = -k_B T \ln \frac{Q_{\text{final}}}{Q_{\text{strart}}}$$

$Q = ???$

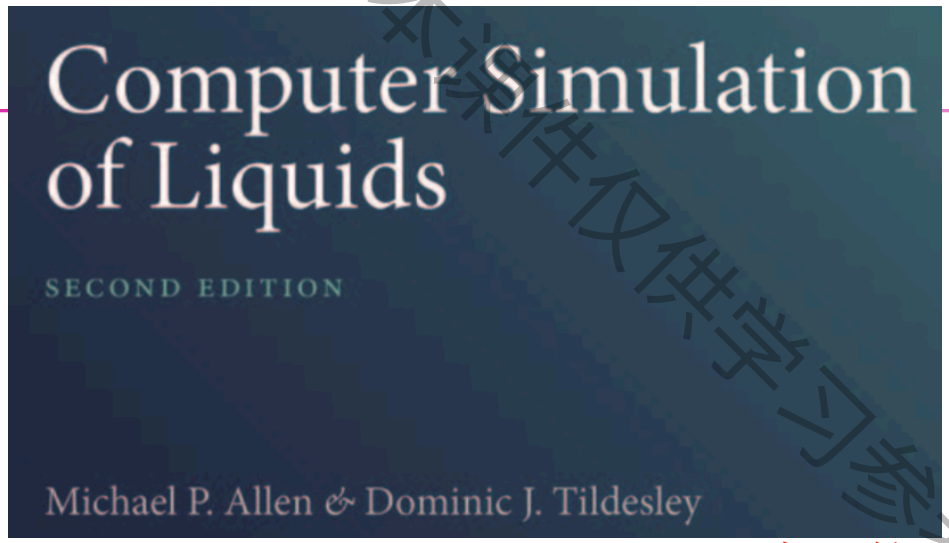
$F = ???$

$S = ???$

Brief summary

- 牛顿力学／量子力学的轨迹
- 轨迹的时间平均获得物理量
- 可获得体系的动态信息
- 挑战依然存在

Classics

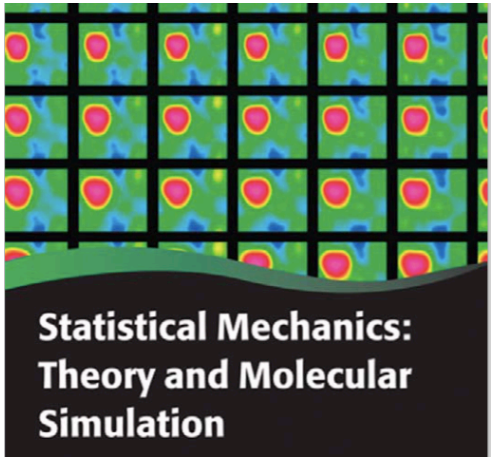


Oxford University Press, 2017, 30年后第二版！

Understanding Molecular Simulation

From Algorithms to Applications

D. Frenkel and B. Smit,
Academic Press, 2002



Mark E. Tuckerman
Oxford University Press, 2010

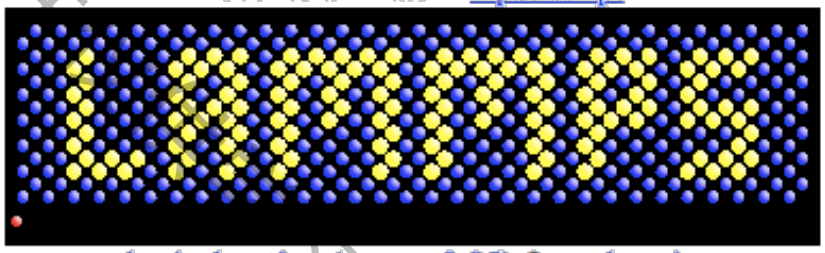
Elements of Molecular Dynamics

W. Smith
https://epubs.stfc.ac.uk/work/20477621

2014年最新版！ 免费！

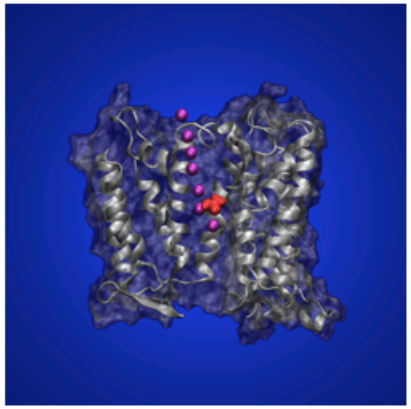
Softwares

hover to animate -- input script



physical analog (start at 3:25) & explanation

D E Shaw Research



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To obtain the current version of Desmond (including source code, if you would like to have it) for non-commercial use, you will need to register by filling out the form that appears below. After confirming your status as a non-commercial user, the information you provide will, among other things, allow us to inform you of any Desmond updates.

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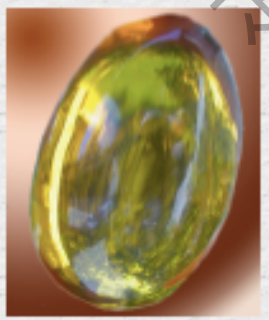
Amber Home Page



"insert clever motto here"

(Learn more about real Amber)

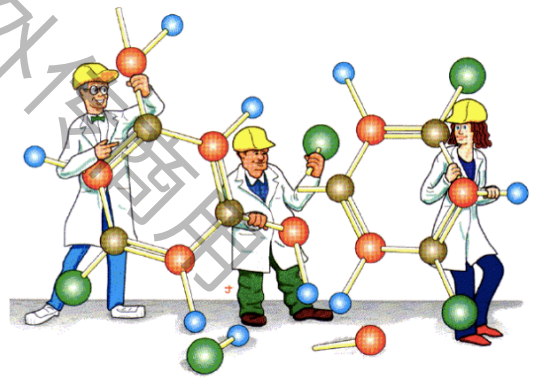
Softwares

GROMACS FAST. FLEXIBLE. FREE.

NAMD
Scalable Molecular Dynamics

CHARMM
Chemistry at HARvard Macromolecular Mechanics

TINKER Molecular Modeling



STFC DL_POLY
Scientific Computing Department

STFC Home > SCD Home > Research and Development > Applications Division > Compu
The DL_POLY Molecular Simulation Package

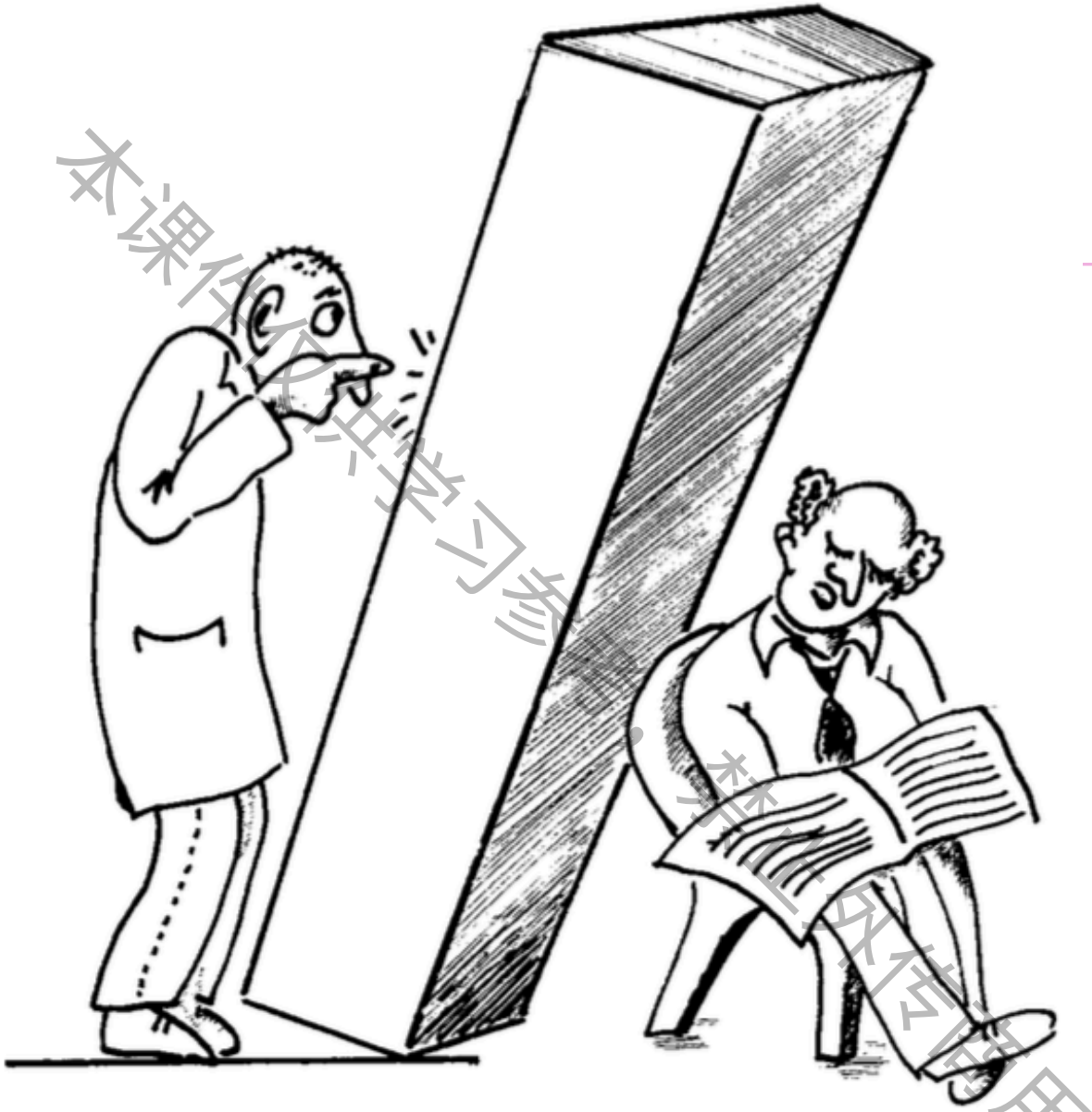
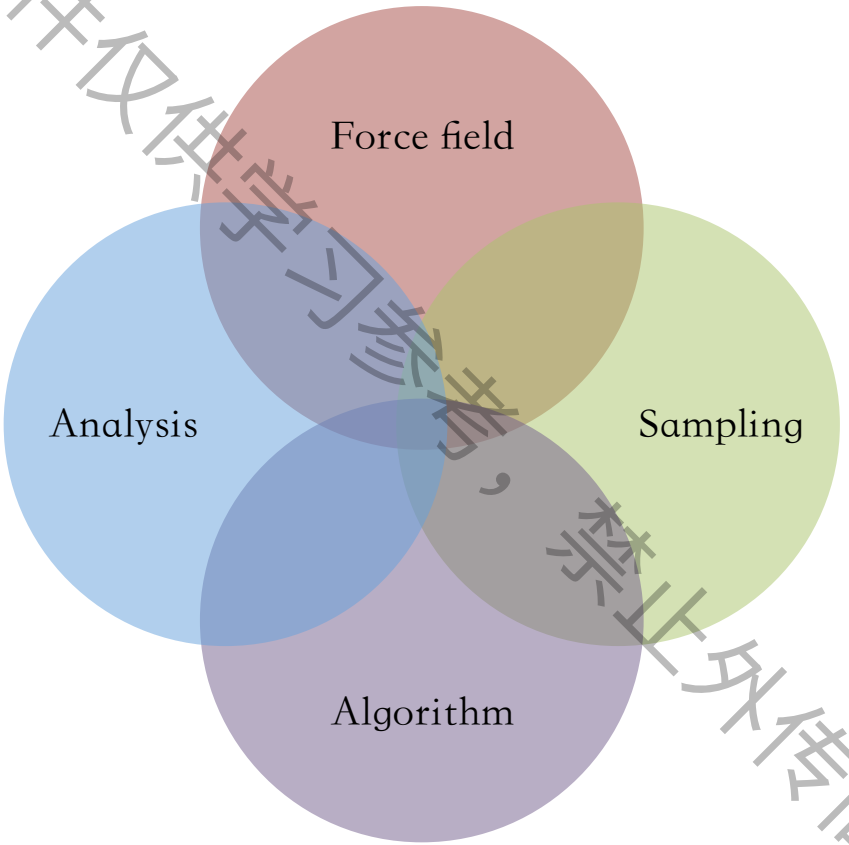


Figure 1.2. Studying responses of a 'black box'.

Alexei M. Tsvelik, *Quantum Field Theory in Condensed Matter Physics*, 2003

Frontiers of MD



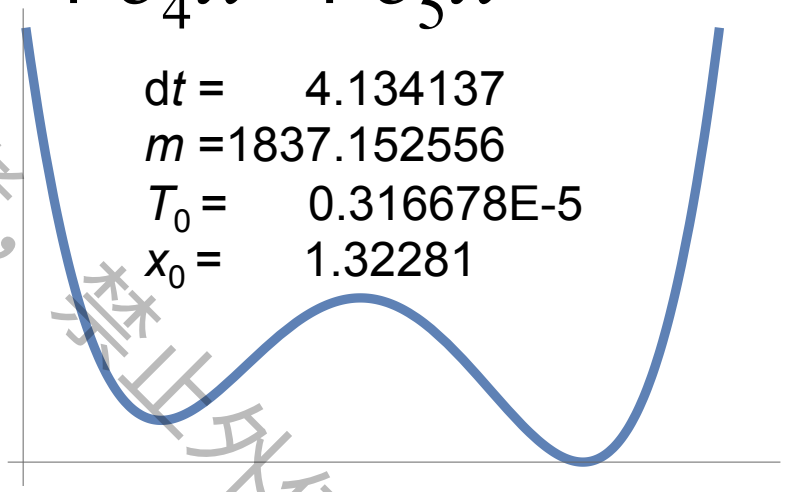
Niels Hansen and Wilfred F. van Gunsteren *J. Chem. Theory Comput.* **2014**, 10, 2632−2647

作业

1. 一维双势阱问题：

$$V(x) = c_1 + c_2 x + c_3 x^2 + c_4 x^3 + c_5 x^4$$

c_1	9.134
c_2	-10.201
c_3	4.542
c_4	-0.744
c_5	0.04



请编写程序，运行，并修改以模拟自己感兴趣的问题

作业

Ar流体

$$U(r)=4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12}-\left(\frac{\sigma}{r}\right)^{6}\right]$$

程序中使用约化单位，保证数值在0附近，不会过大 / 过小

$$U^{*}(r^{*})=4\left[\left(\frac{1}{r^{*}}\right)^{12}-\left(\frac{1}{r^{*}}\right)^{6}\right]$$

能量单位用 ε 、长度单位用 σ，质量单位用1个原子的质量，这样时间单位、温度也都化为约化单位：

$$t^{*}=t/\left(\sigma\sqrt{\frac{m}{\varepsilon}}\right),\qquad T^{*}=T/\left(\frac{\varepsilon}{k_B}\right)$$

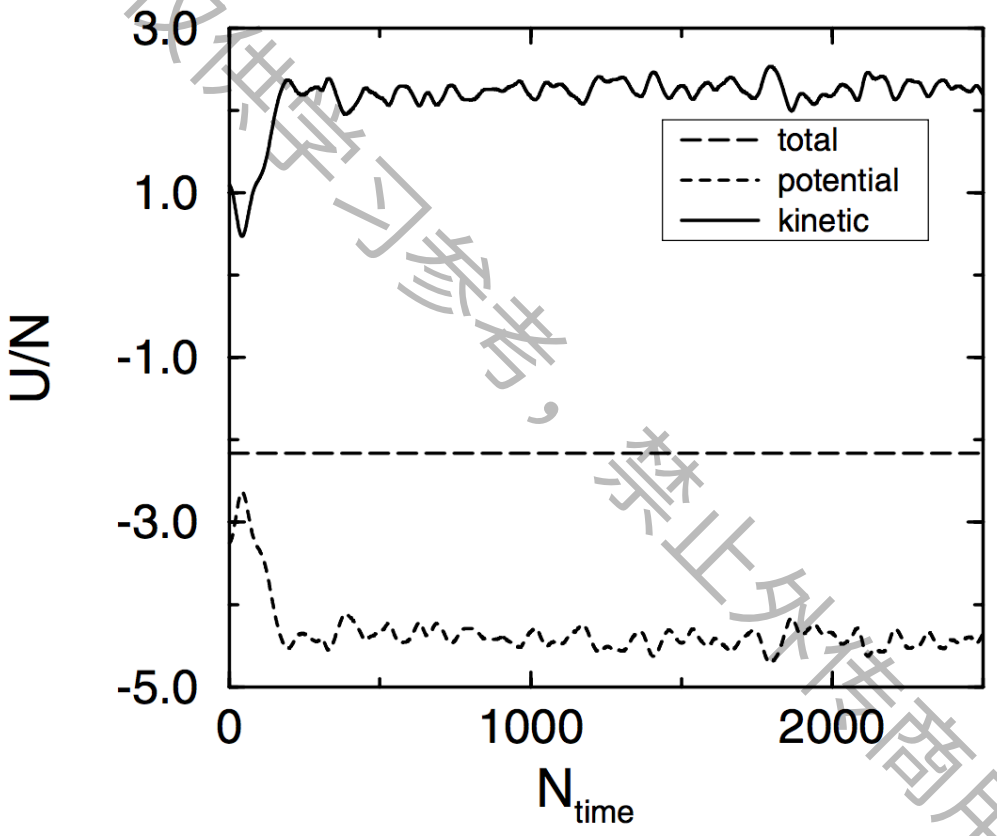
作业

Ar流体

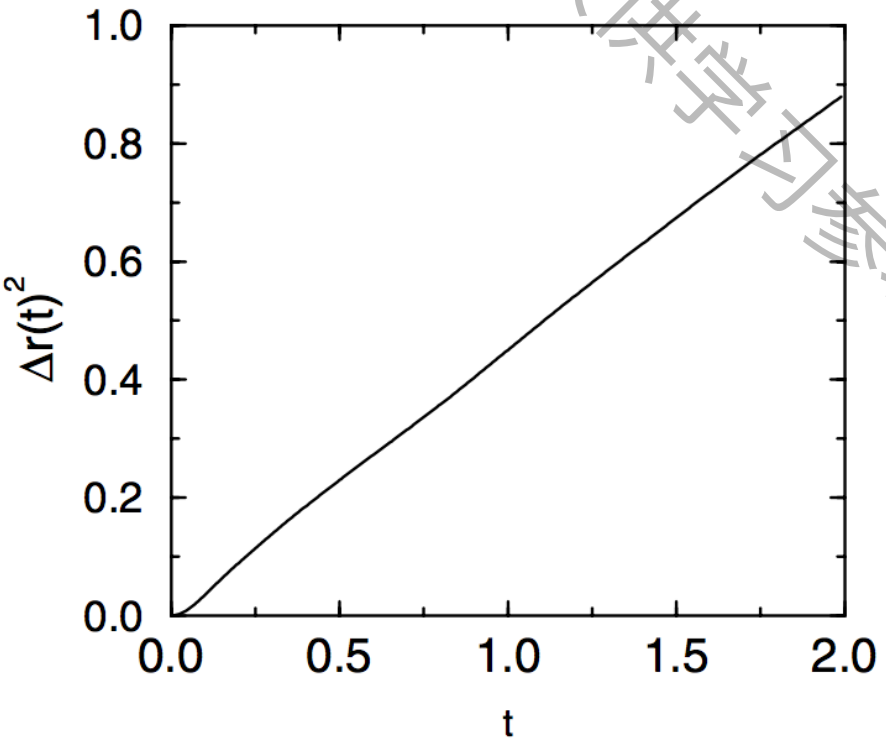
Quantity	Reduced units		Real units
temperature	$T^* = 1$	$\leftrightarrow$	$T = 119.8\ \mathrm{K}$
density	$\rho^* = 1.0$	$\leftrightarrow$	$\rho = 1680\ \mathrm{kg/m^3}$
time	$\Delta t^* = 0.005$	$\leftrightarrow$	$\Delta t = 1.09 \times 10^{-14}\ \mathrm{s}$
pressure	$P^* = 1$	$\leftrightarrow$	$P = 41.9\ \mathrm{MPa}$

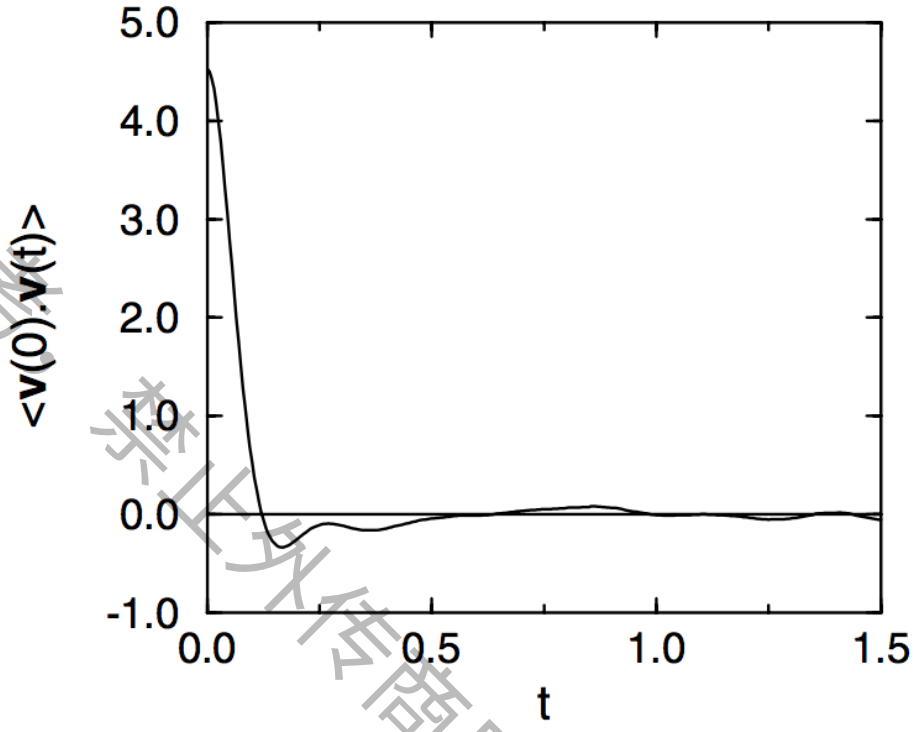
ε/k_B=119.8 K、长度单位用 σ=3.405 Å，质量0.03994 kg/mol，864个原子。

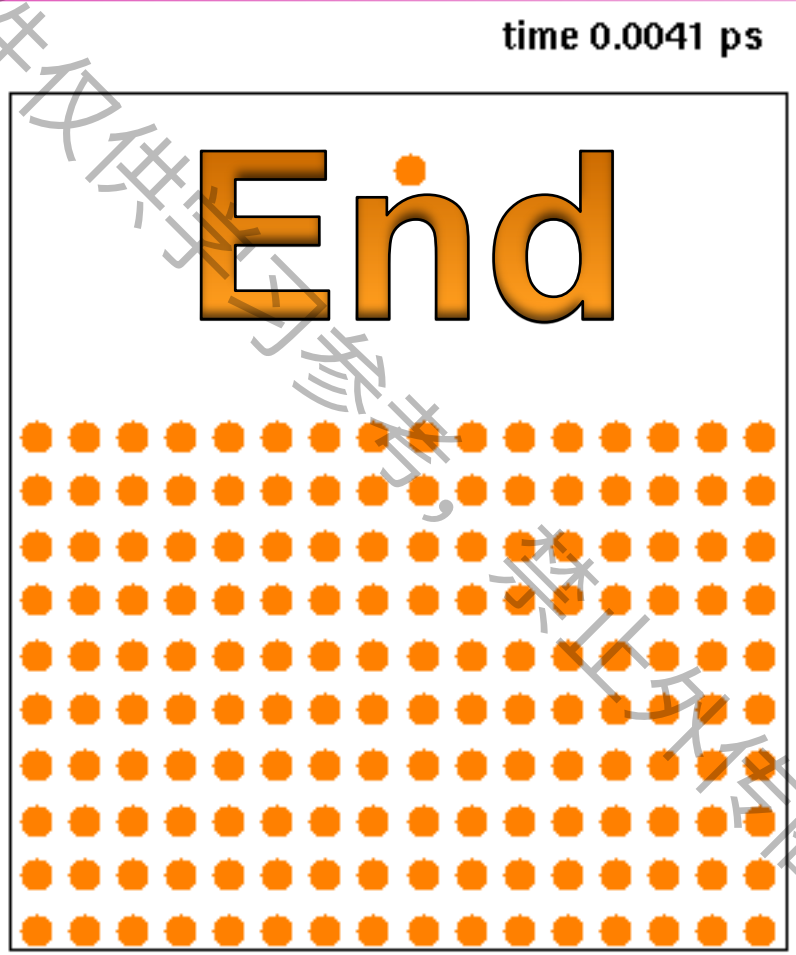
作业：Ar体系能量随时间变化



作业：Ar体系的均方位移与速度关联函数







办公室：E楼121，电话：021-66136131；邮箱：yongleli@shu.edu.cn