中国科学院物理研究所
Institute of Physics CAS
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软物质计算机模拟导论

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软物质实验室八组

Outline

- 背景介绍：
  软物质与计算机模拟

- 模拟方法介绍：
  - 分子动力学模拟

Lecture 1

- 蒙特卡罗模拟

Lecture 2

- 布朗动力学模拟
- 介观流体力学模拟

Lecture 3

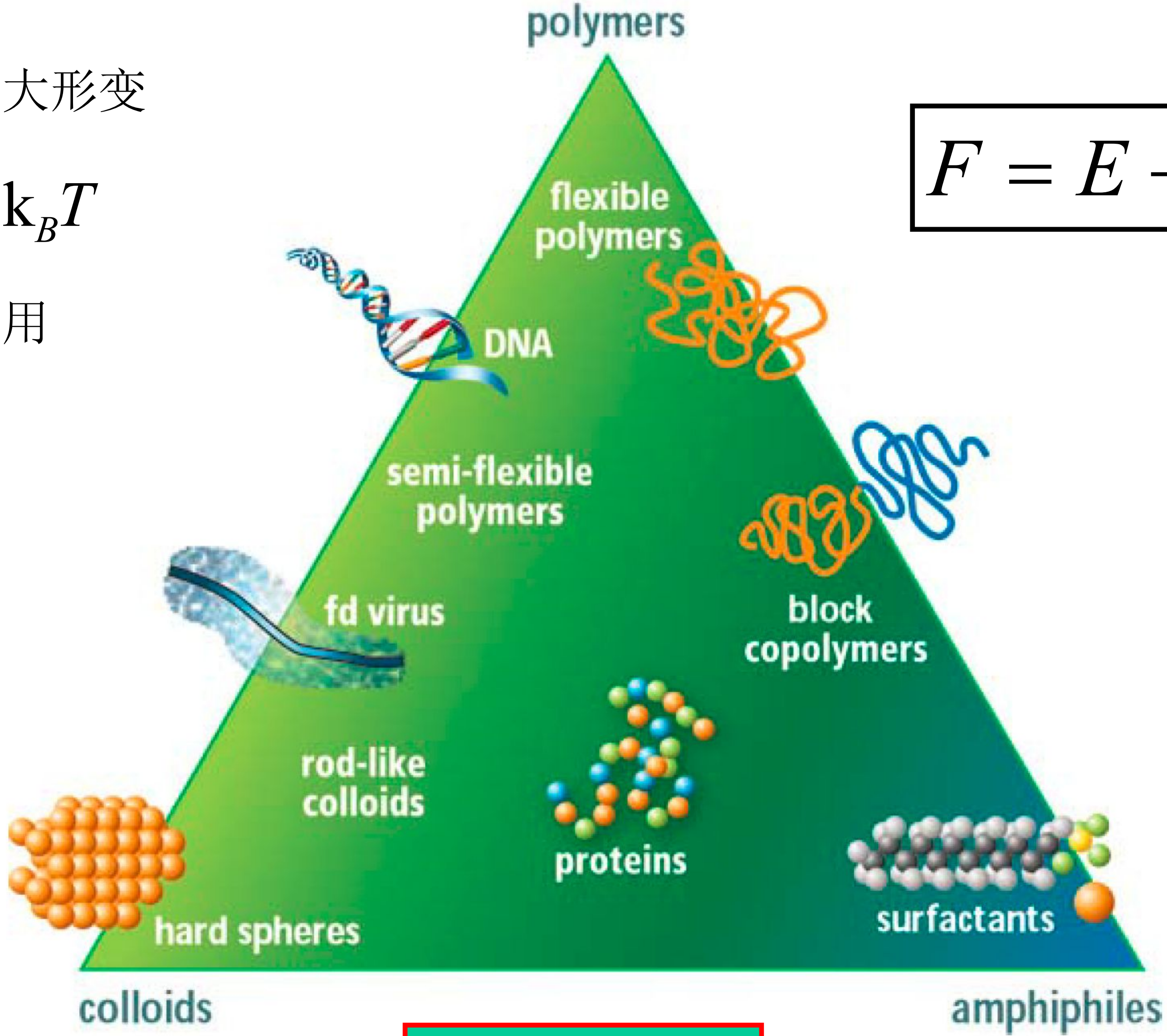
Lecture 1

- 软物质与计算机模拟

- 分子动力学模拟

软物质 (soft matter)

- 小扰动导致大形变
- 特征能量　k_BT
- 熵起重要作用
- 多尺度性
- 宏观流动性
- 介观有序性
- 处于溶剂中

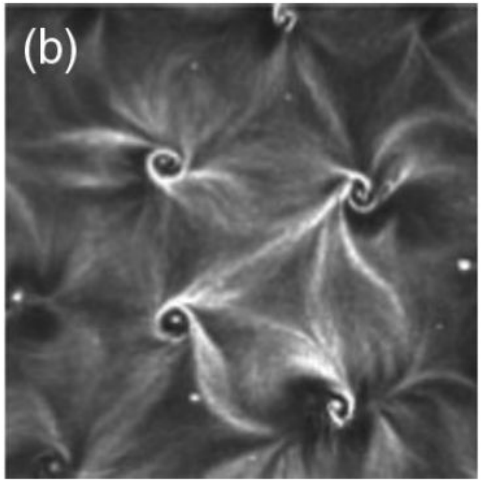


$$\boxed{F = E + TS}$$

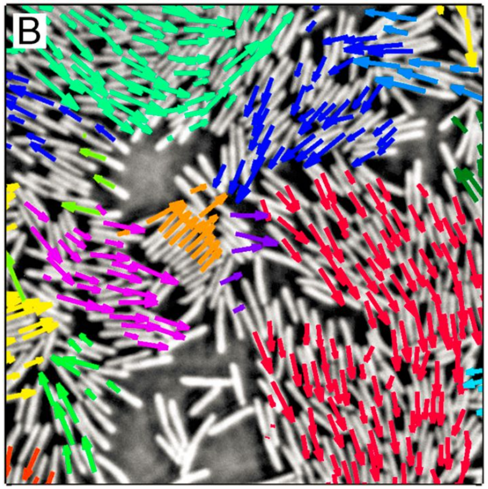
复杂流体

活力物质 (active matter)

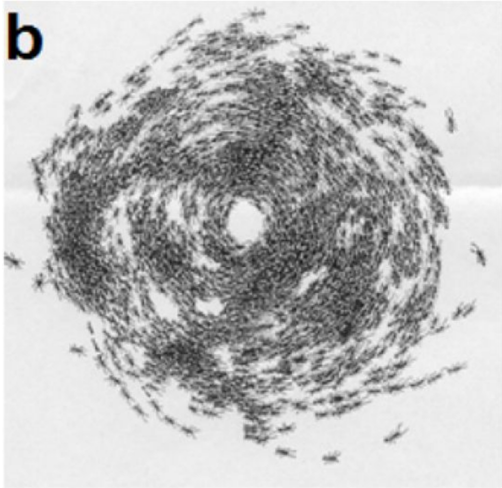
length scale 10^{-9} 10^{-6} 10^{-3} 10^{0} (m)



马达蛋白和微管



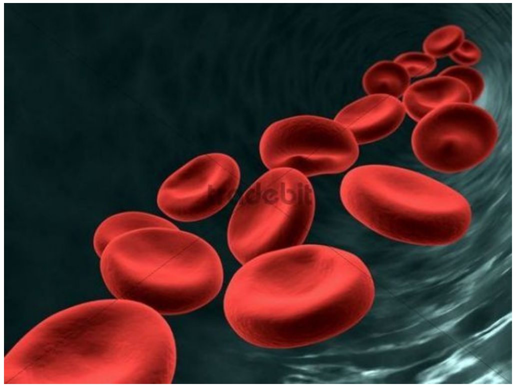
细菌



蚂蚁

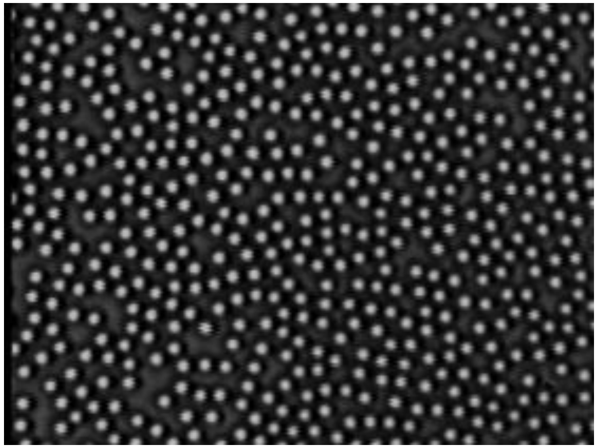
胶体 (colloid) — 最简单的软物质

- 微观颗粒散布在分散介质中所形成的系统
- 颗粒尺寸为 纳米至微米
- 分散介质可以是气体、液体和固体



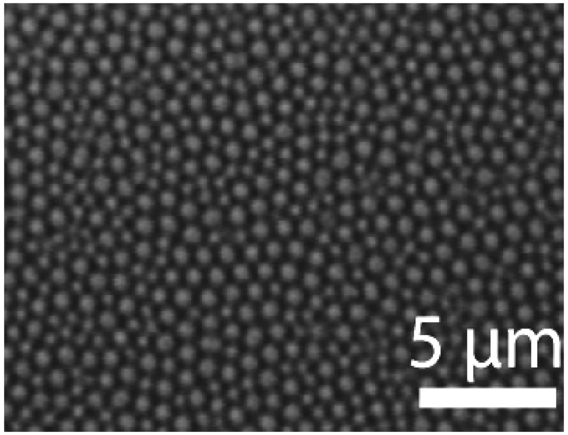

胶体 — 宏观的原子模型

微米大小的胶体粒子，运动的特征时间为秒，可以用通常的显微镜直接的观测研究。



胶体液体

胶体晶体



胶体玻璃

计算机模拟

- 广义上：利用可计算的模型或方程，以计算机为工具，对真实的系统进行研究。

- 狭义上：计算机实验（虚拟的实验室），建立一个虚拟系统，组成系统的单元（"粒子"）以一定的规则演化。

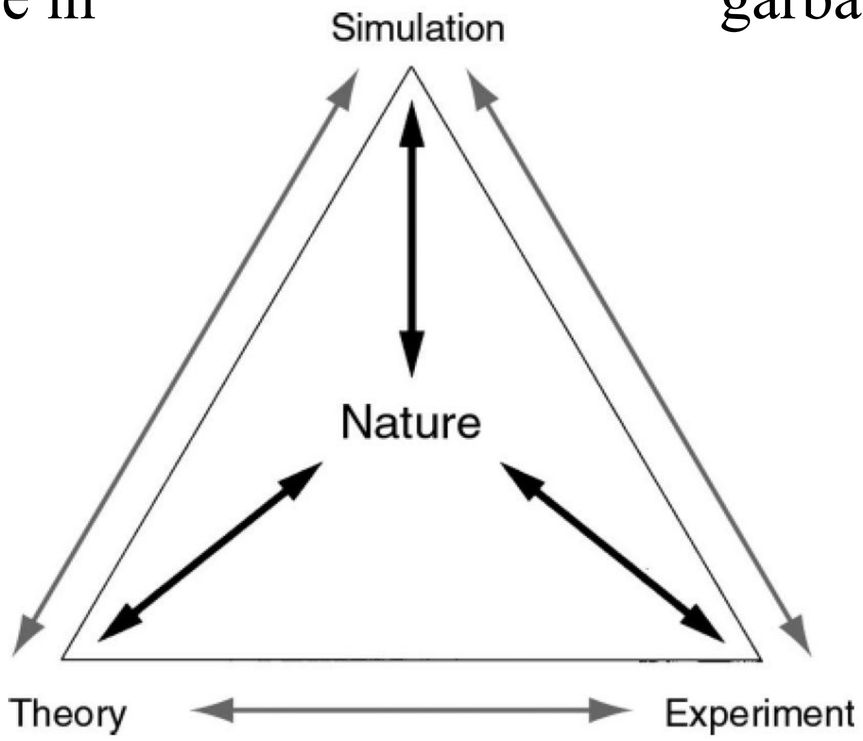
  - 分子动力学模拟
  - 蒙特卡罗模拟
  - 布朗动力学模拟
  - 介观流体力学模拟
  - 密度泛函

  … …

计算机模拟

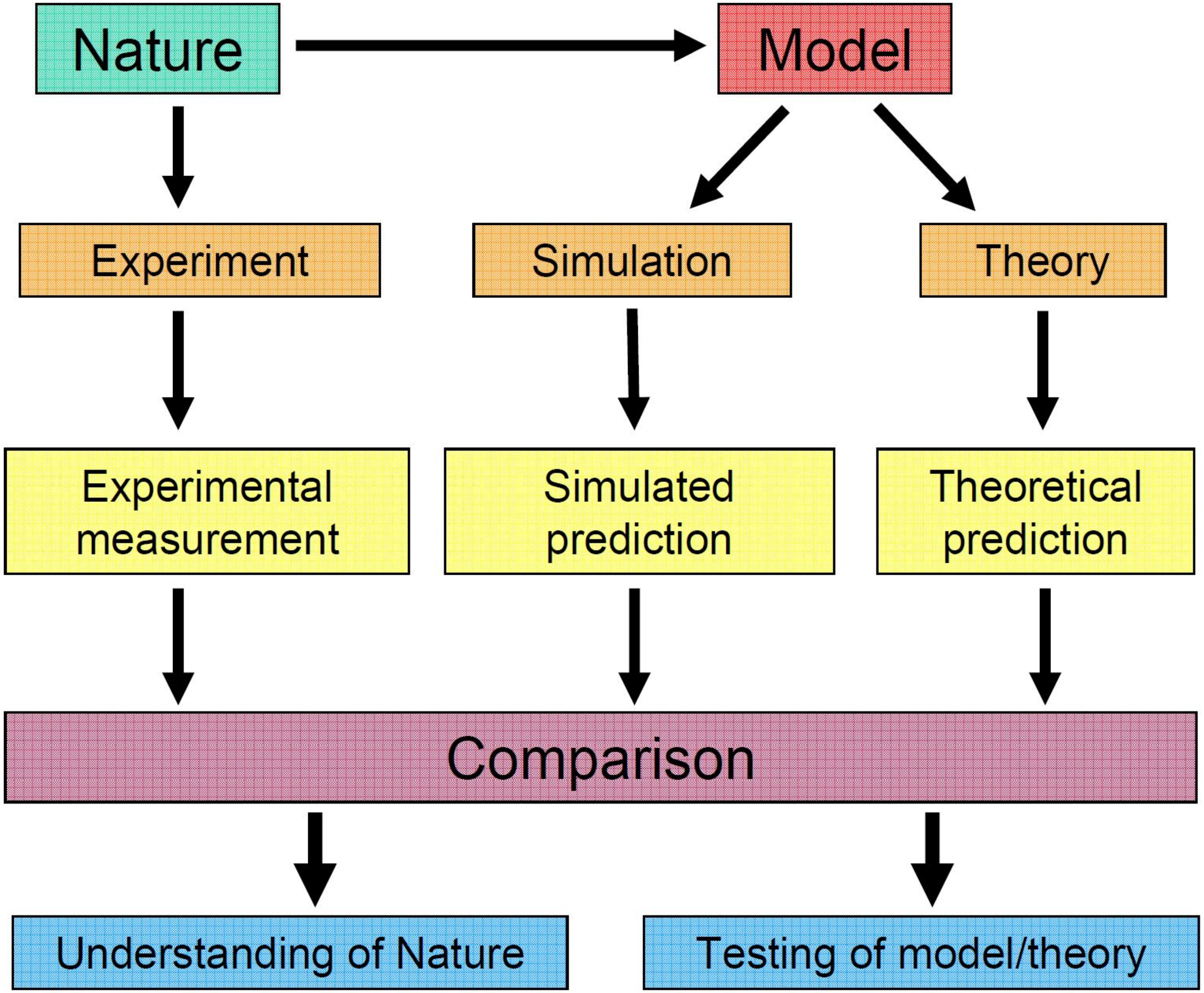
- 发展于上世纪50年代，对液体的理论处理。

garbage in　　　　garbage out



检验理论 （原则上无近似）
解释实验（微观细节和干净）

计算机模拟



Nature

Model

Experiment

Simulation

Theory

Experimental measurement

Simulated prediction

Theoretical prediction

Comparison

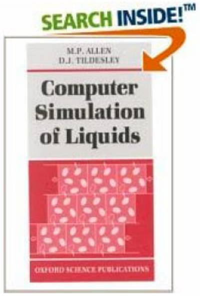
Understanding of Nature

Testing of model/theory

计算机模拟

- 软物质模拟：仅考虑经典力学，忽略量子效应
- 统计力学：模拟系统的信息为粒子的位置、速度和力，因此需要统计力学计算宏观量（压强、温度、能量、粘度...）
- 计算机编程语言：C, C++ 或 Fortran

参考书



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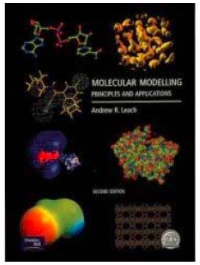

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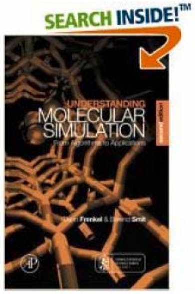

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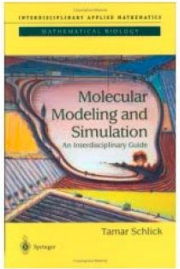

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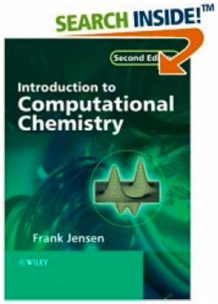

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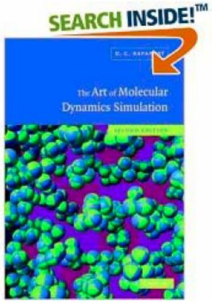

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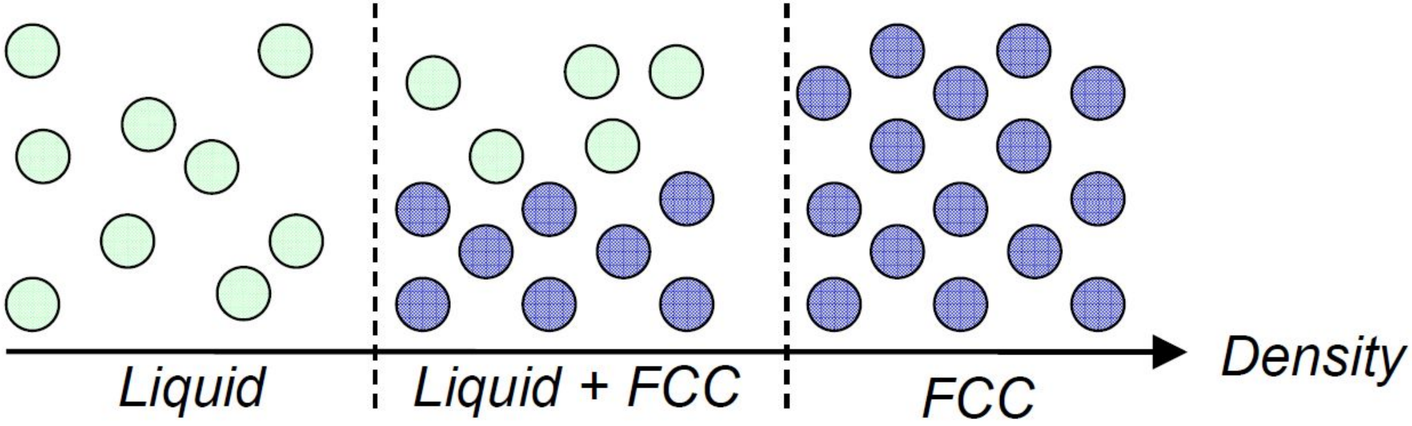
(Cambridge University Press, 2004)

分子动力学模拟（MD）

MD的基本思想：

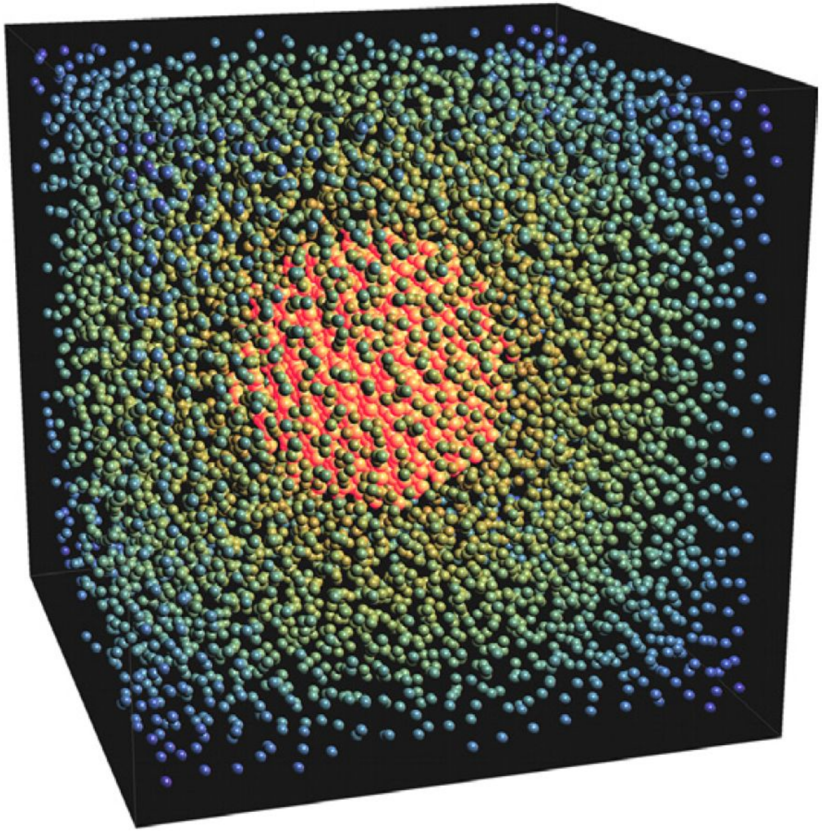
用计算机来求解多粒子系统在相空间的运动轨迹，其中粒子的运动满足牛顿方程；从而获得系统随时间的演化过程；进一步通过统计方法得到想要的物理量。

The first molecular dynamics simulations were carried out by B.J. Alder and T.E. Wainwright, ”*Phase transition for a hard-sphere system*”, J. Chem. Phys. **27** (1957) 1208.

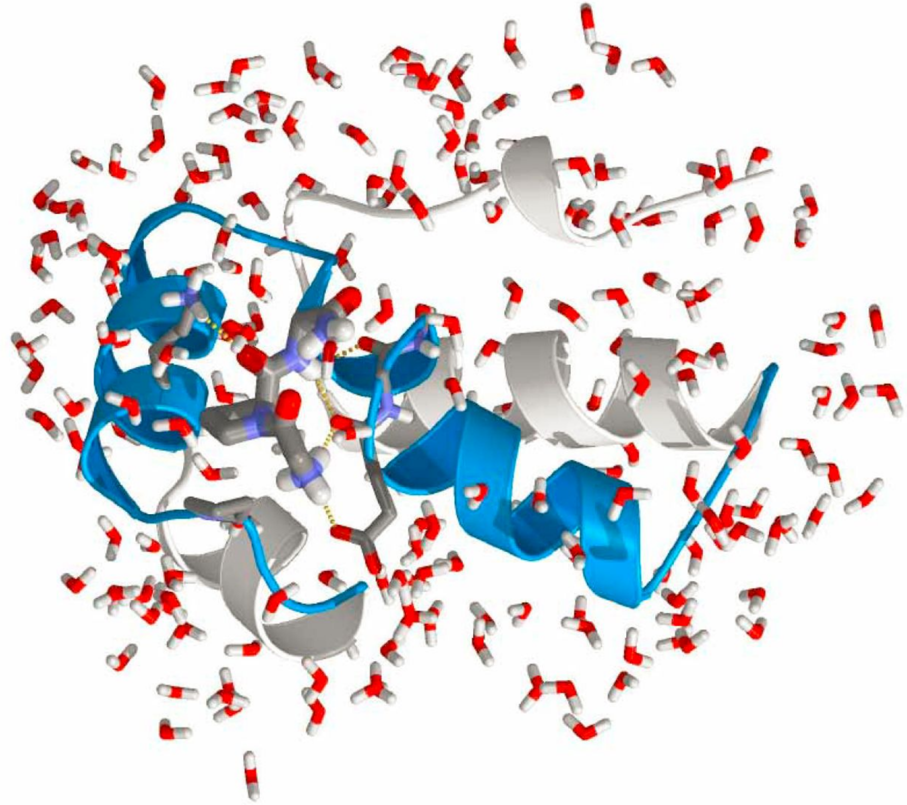


几个MD例子

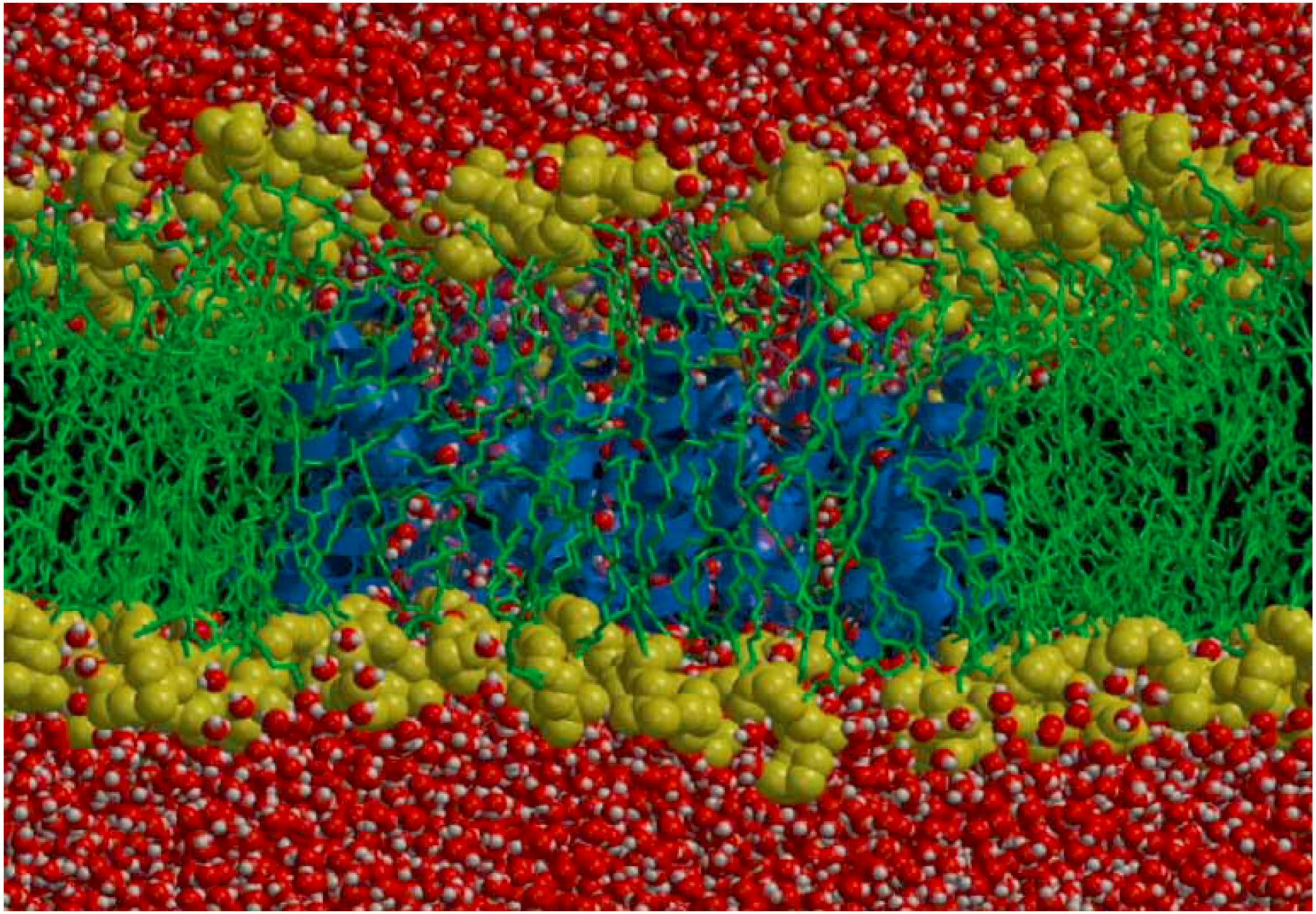
热胶体球的运动行为



蛋白质折叠

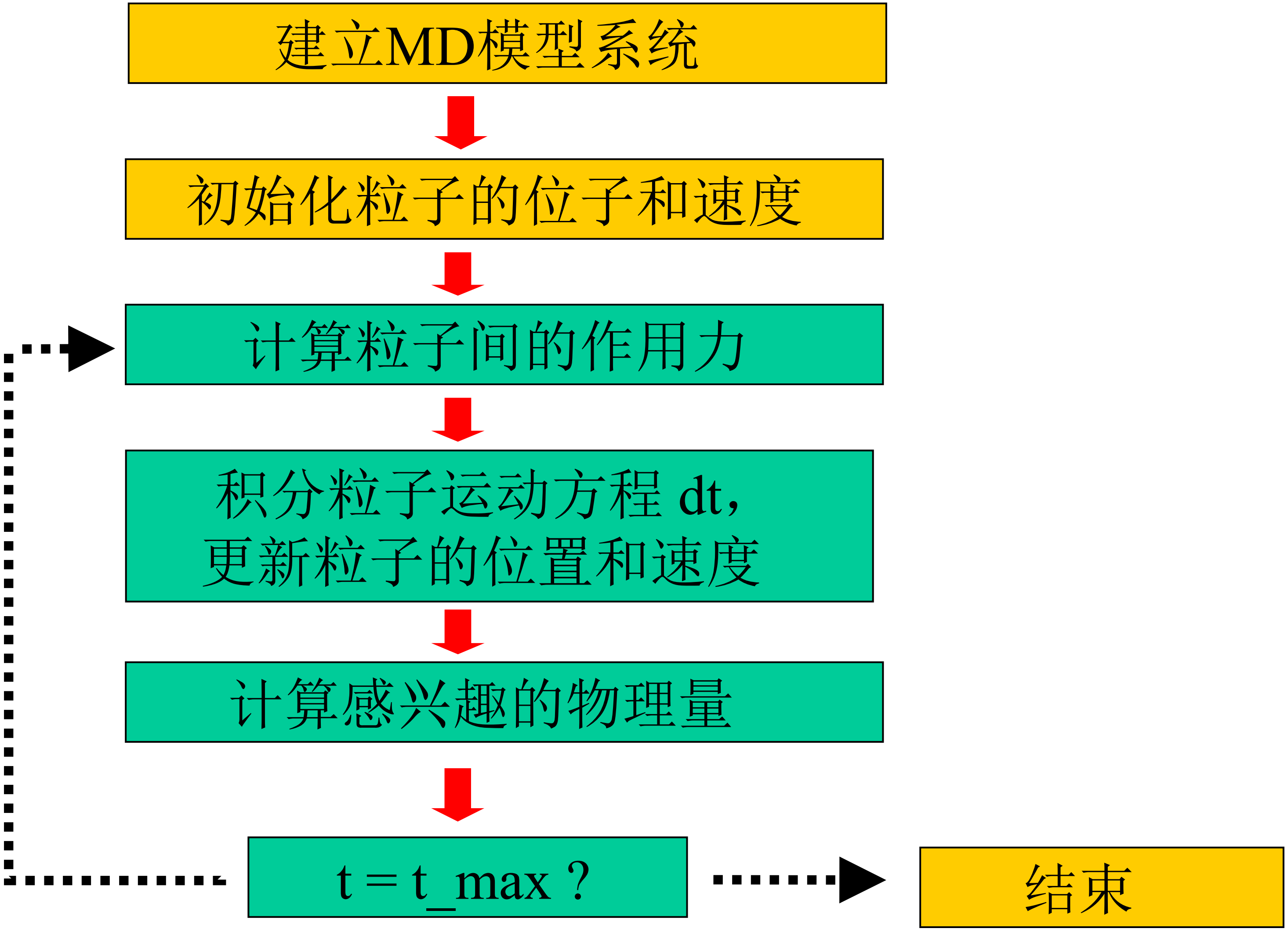


Selective translocation of water across a membrane



Hub and Bert L. de Groot. Mechanism of selectivity in aquaporins and aquaglyceroporins PNAS. 105:1198-1203 (2008)

MD的基本步骤



建立MD模型系统

初始化粒子的位子和速度

计算粒子间的作用力

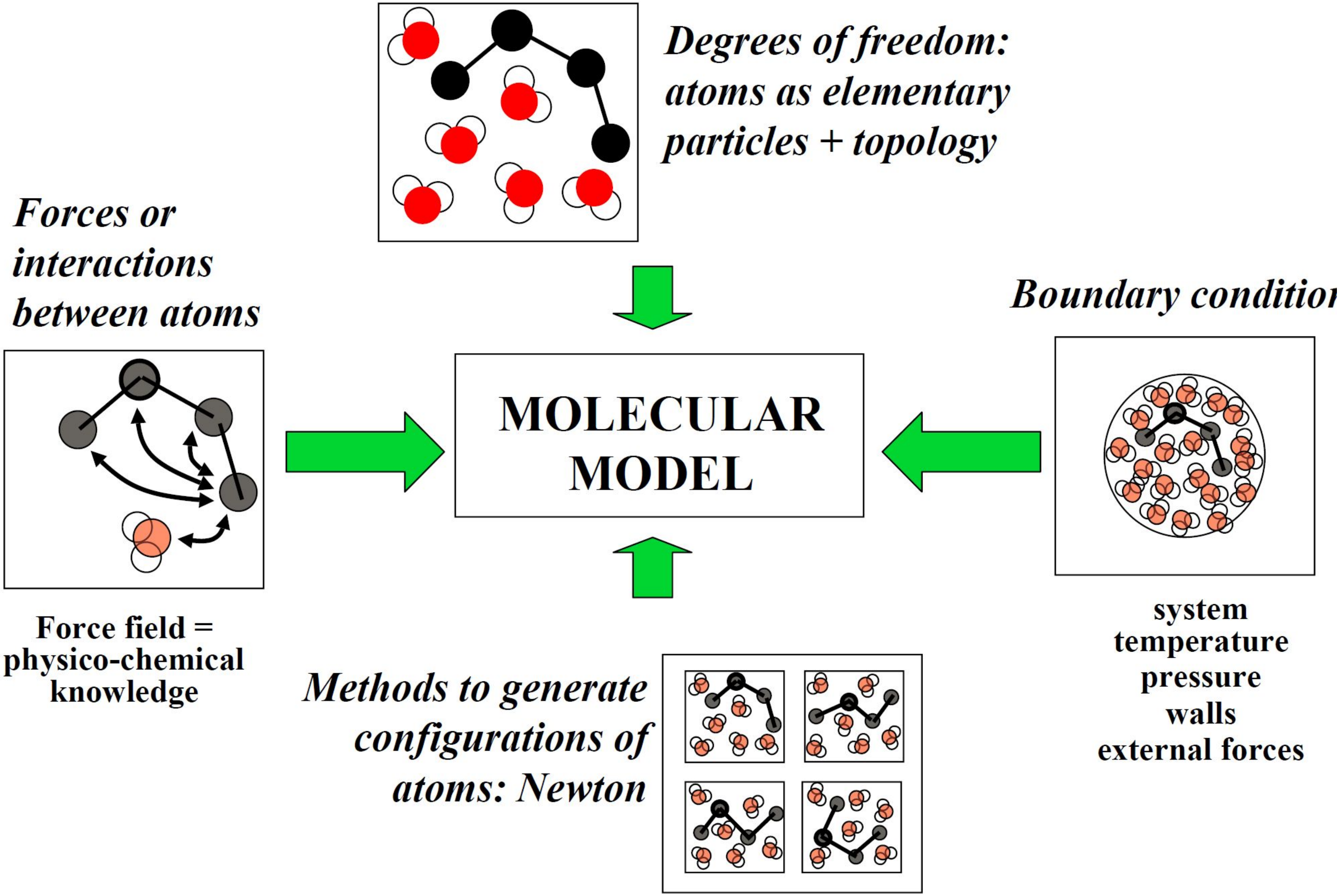
积分粒子运动方程 dt，
更新粒子的位置和速度

计算感兴趣的物理量

t = t_max ?

结束

建立MD模型系统



Degrees of freedom: atoms as elementary particles + topology

Forces or interactions between atoms

MOLECULAR MODEL

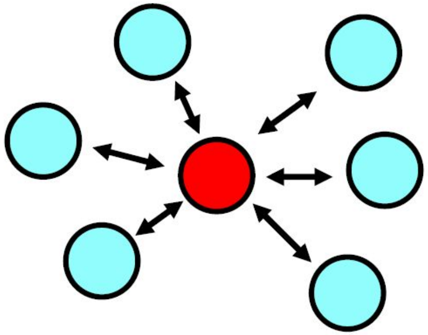
Boundary conditio

Force field = physico-chemical knowledge

system
temperature
pressure
walls
external forces

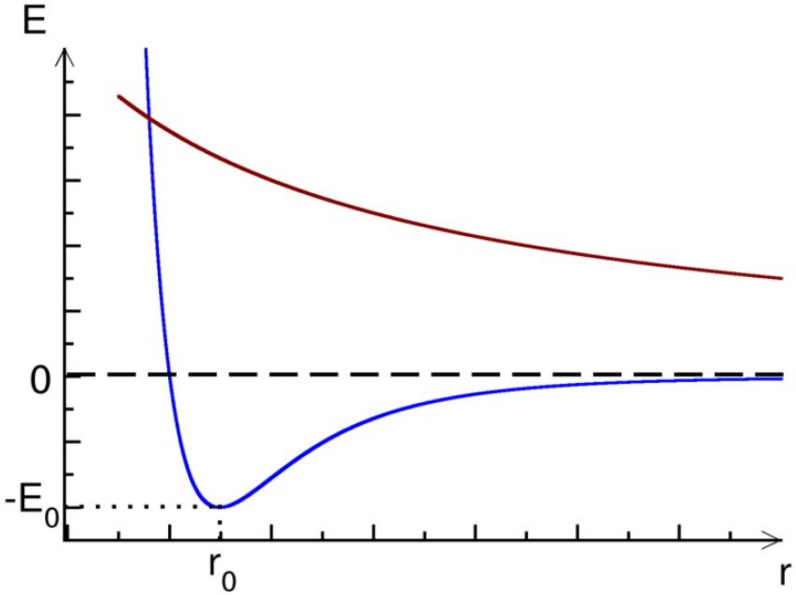
Methods to generate configurations of atoms: Newton

粒子的相互作用



$$\overrightarrow{F_i}(t) = m_i\overrightarrow{a_i}(t) = -\overrightarrow{\nabla_i}U\big(\vec{r}(t)\big)$$

Forcefield



$$V_{coul}(r) = \frac{q_i q_j}{4\pi\varepsilon_0 r}$$

Charge-charge interactions

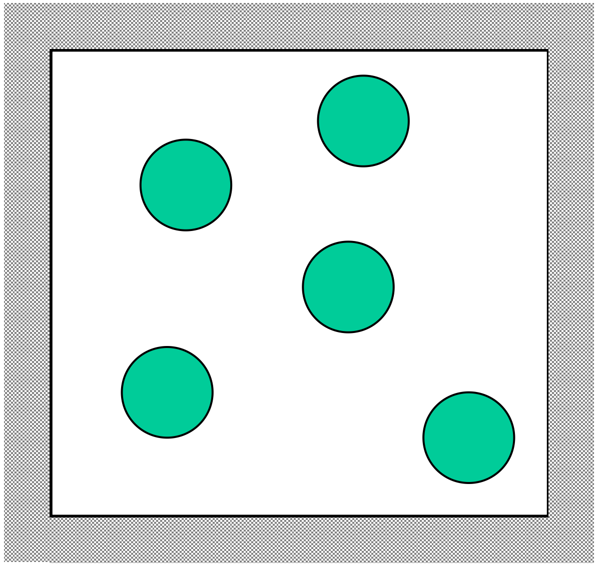
$$V_{LJ}(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$

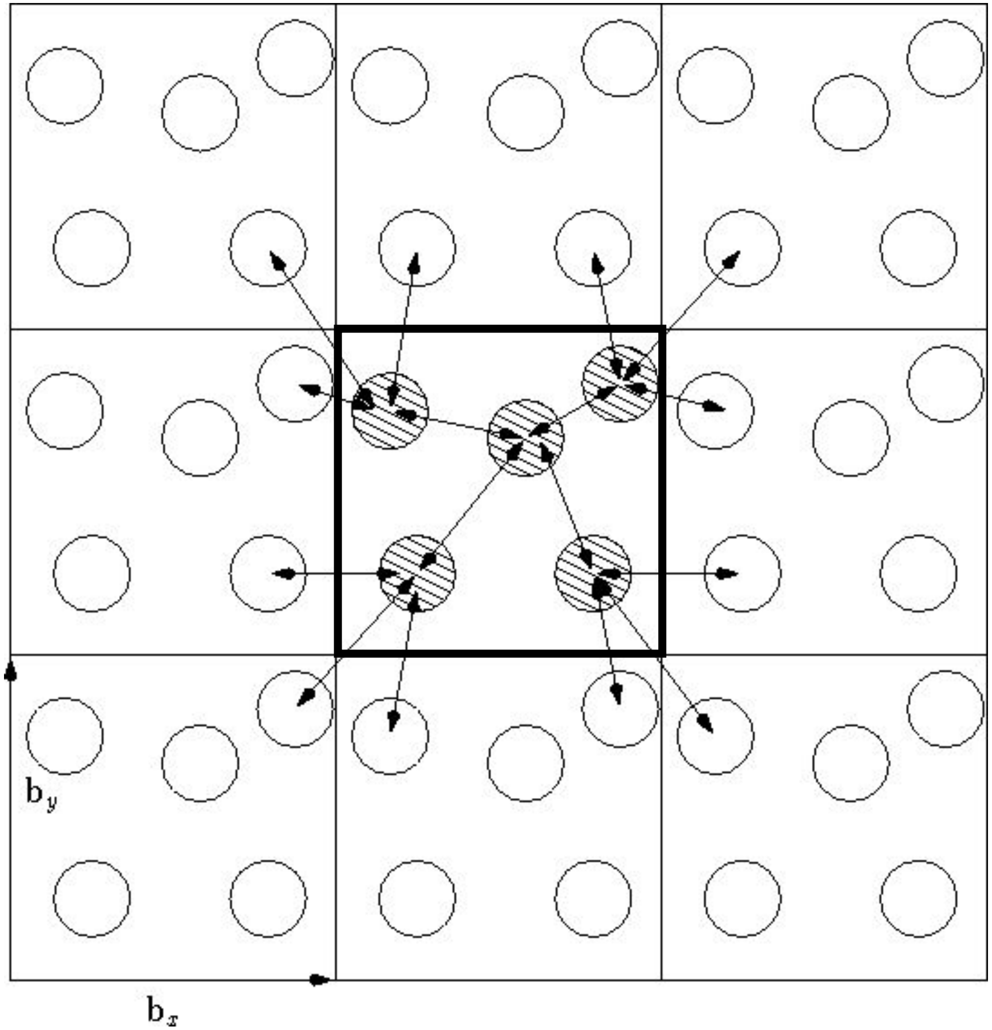
Dipole-dipole interactions

边界条件

墙边界

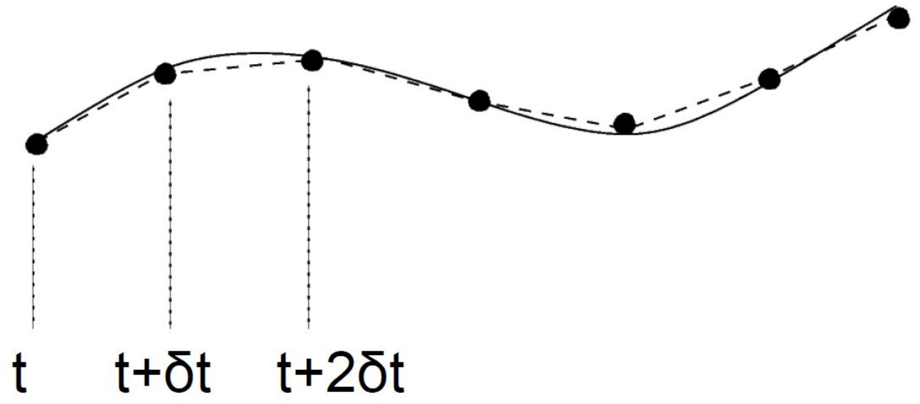
周期边界





求解粒子运动方程的算法

有限差分方法（多体问题）：轨迹离散化和数值积分



$$\vec{r}(t+\delta t)=\vec{r}(t)+\delta t\,\vec{v}(t)+\frac{1}{2}(\delta t)^2\vec{a}(t)+\ldots$$

$$\vec{v}(t+\delta t)=\vec{v}(t)+\delta t\,\vec{a}(t)+\ldots$$

保留至二阶即为Euler方法（不可取）

Verlet积分算法

$$\vec{r}(t+\delta t)=\vec{r}(t)+\delta t\vec{v}(t)+\frac{1}{2}(\delta t)^2\vec{a}(t)$$

$$\vec{r}(t-\delta t)=\vec{r}(t)-\delta t\vec{v}(t)+\frac{1}{2}(\delta t)^2\vec{a}(t)$$

$$\vec{a}(t)=-\vec{\nabla}U(t)$$

$$\vec{r}(t+\delta t)=2\vec{r}(t)-\vec{r}(t-\delta t)+(\delta t)^2\vec{a}(t)$$

$$\vec{v}(t)=[\vec{r}(t+\delta t)-\vec{r}(t-\delta t)]/2\,\delta t$$

Velocity-Verlet algorithm

$$\vec{r}(t+\delta t)=\vec{r}(t)+\delta t\vec{v}(t)+\frac{1}{2}(\delta t)^2\vec{a}(t)$$

$$\vec{v}(t+\delta t)=\vec{v}(t)+\frac{\delta t}{2}[\vec{a}(t)+\vec{a}(t+\delta t)]$$

积分算法

- 选择哪种积分算法

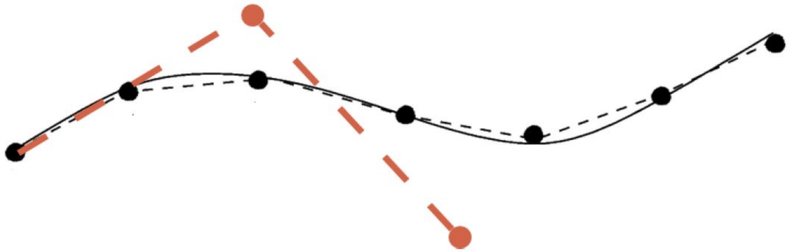
  \- 较好地保证能量守恒

  \- 同样时间步长，有更好精度

- 如何选取时间步长

  短：精度高，但耗时

  长：精度低，但高效



权衡计算精度和计算效率

时间步长的具体选取

- 不能太小，也不能太大
- 一般取作粒子最快的运动模式周期的十分之一

Example 1: argon atoms

Caracteristic distance: $d \approx 0.3nm$

Caracteristic speed:

$$v \approx \sqrt{\frac{3k_BT}{m}} \approx 350m.s^{-1}$$

Caracteristic time: $\tau \approx \frac{d}{v} \approx 10^{-13}s$

→ **Time step $\delta t \approx 10^{-14}$ s**

Example 2: water molecules

Fastest motion:
vibration of O-H bond

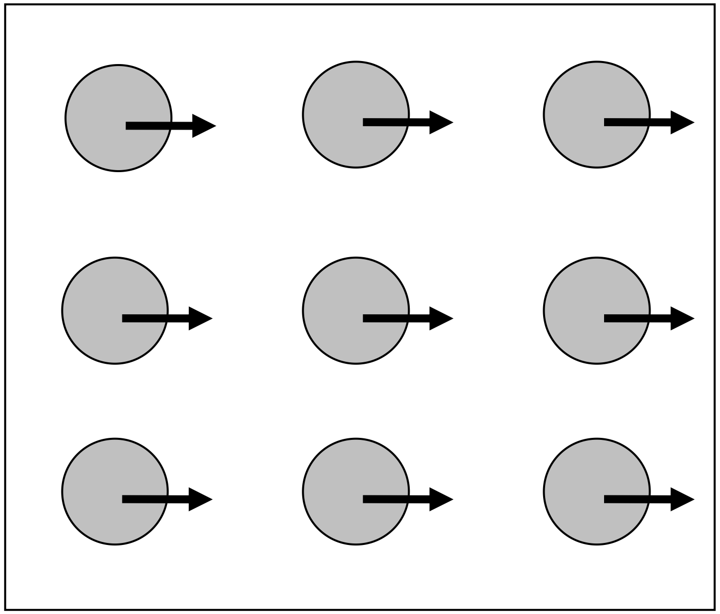
Period of the vibration:

$$\nu \approx 4000cm^{-1} \Rightarrow T \approx 10^{-14}s$$

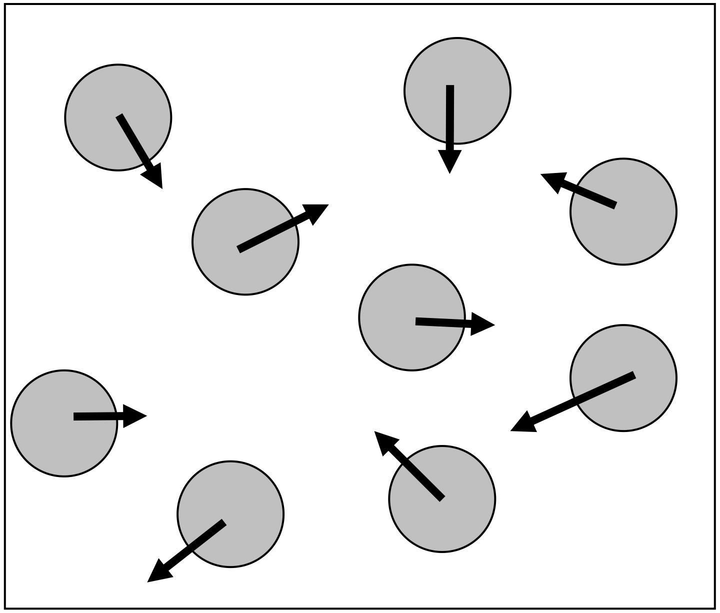
→ **Time step $\delta t \approx 10^{-15}$ s**

初始化

规则的初始化



随机的初始化



物理量的测量

粒子间的力为保守力

→ 系统总能量为常数（NVE）微正则系综

保证个态历经条件

→ 时间平均等价于系综平均

$$\overline{\rho_i(r)} = \langle \rho_i(r) \rangle_{NVE}$$

$$\overline{\rho_i(r)} = \lim_{t\to\infty} \frac{1}{t}\int_0^t dt'\, \rho_i(r;t')$$

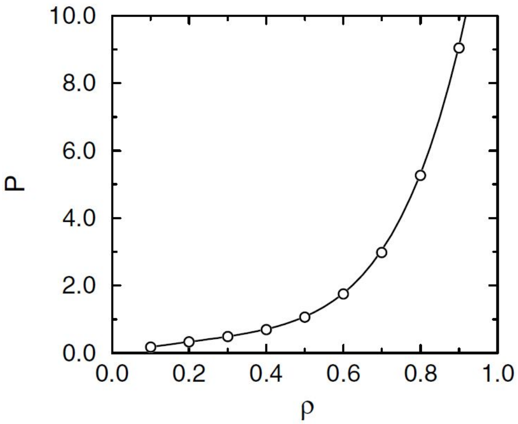
其他系综的MD模拟（如 NVT，NPE）也可实现。

物理量的测量

LJ流体的压力

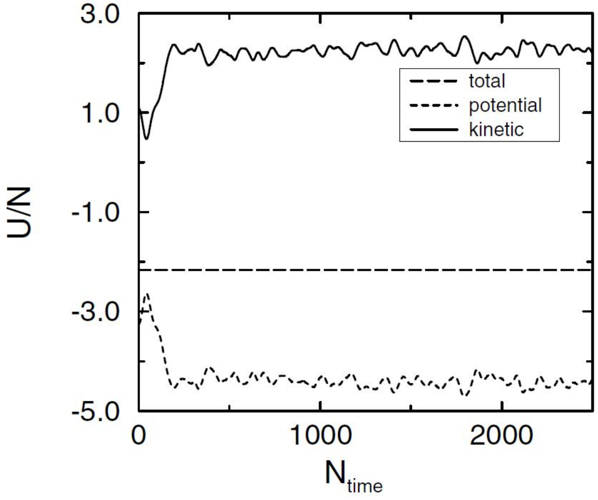
$$P = \frac{\rho}{\beta} + \frac{\mathrm{vir}}{V}$$

$$\mathrm{vir} = \frac{1}{3} \sum_{i} \sum_{j>i} \mathbf{f}(\mathbf{r}_{ij}) \cdot \mathbf{r}_{ij}$$



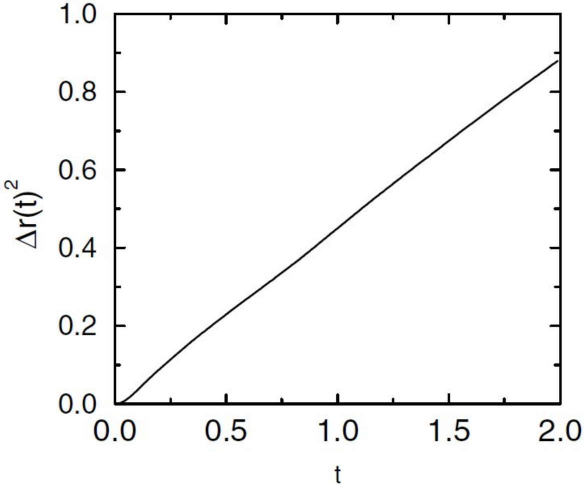
温度和能量

$$\left\langle \frac{1}{2} m v_{\alpha}^{2} \right\rangle = \frac{1}{2} k_B T$$



粒子均方位移

$$\left\langle \Delta r(t)^2 \right\rangle = \frac{1}{N} \sum_{i=1}^{N} \Delta \mathbf{r}_i(t)^2$$



物理量的测量 - 输运量

通过 Green-Kubo 关系：

$$D = \int_0^\infty d\tau \ \langle v_x(\tau) v_x(0) \rangle$$

- 扩散系数

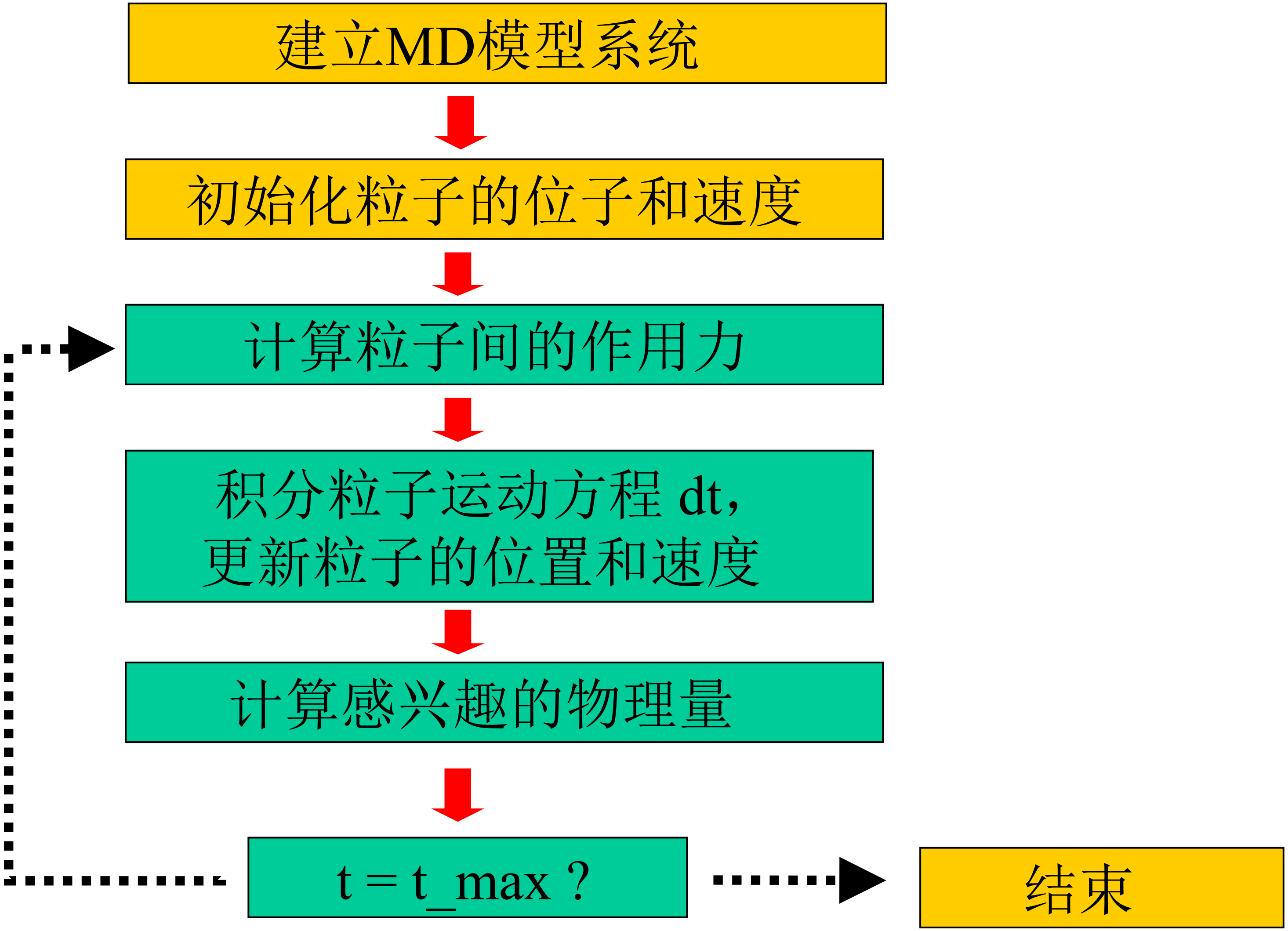
$$\eta = \frac{1}{Vk_BT}\int_0^\infty dt \ \langle \sigma^{xy}(0)\sigma^{xy}(t) \rangle$$

- 剪切粘度

$$\sigma^{xy} = \sum_{i=1}^{N} \left(m_i v_i^x v_i^y + \frac{1}{2}\sum_{j\neq i} x_{ij} f_y(r_{ij}) \right)$$

……

MD的基本步骤



建立MD模型系统

初始化粒子的位子和速度

计算粒子间的作用力

积分粒子运动方程 dt，
更新粒子的位置和速度

计算感兴趣的物理量

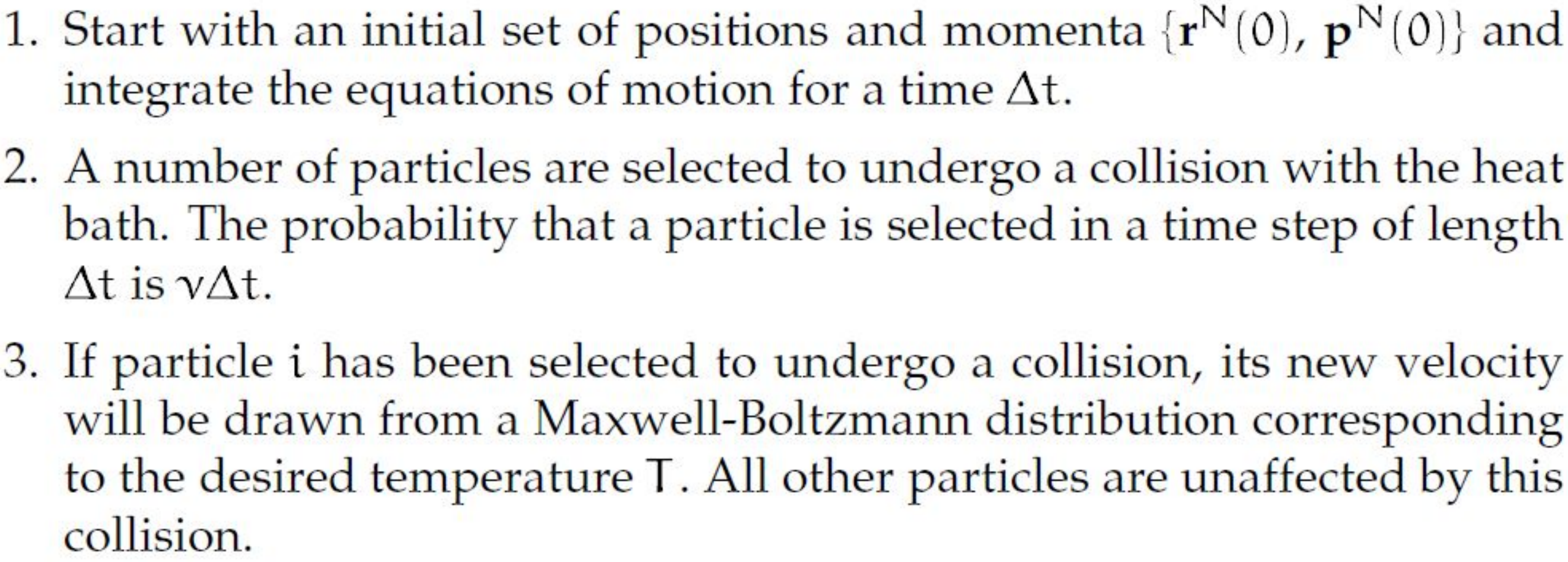
t = t_max ?

结束

常温MD - 控温

- Andersen thermostat

粒子速度每隔一段时间被重新赋值，新速度选自于给定温度的Maxwell速度分布（等价于与thermal bath碰撞）。



1. Start with an initial set of positions and momenta $\{\mathbf{r}^N(0), \mathbf{p}^N(0)\}$ and integrate the equations of motion for a time Δt.
2. A number of particles are selected to undergo a collision with the heat bath. The probability that a particle is selected in a time step of length Δt is $\nu \Delta t$.
3. If particle i has been selected to undergo a collision, its new velocity will be drawn from a Maxwell-Boltzmann distribution corresponding to the desired temperature T. All other particles are unaffected by this collision.

控温

- Berendsen thermostat

每一个MD步，所有粒子的速度乘以一个修正因子$v' = \chi v$,驱动系统向着指定的温度演化。

指定的温度

$$\chi = \left(1 + \frac{\delta t}{t_T}\left(\frac{T}{\mathcal{T}} - 1\right)\right)^{1/2}$$

弛豫率

当前的瞬时温度

- Extended system method
- Constraint method

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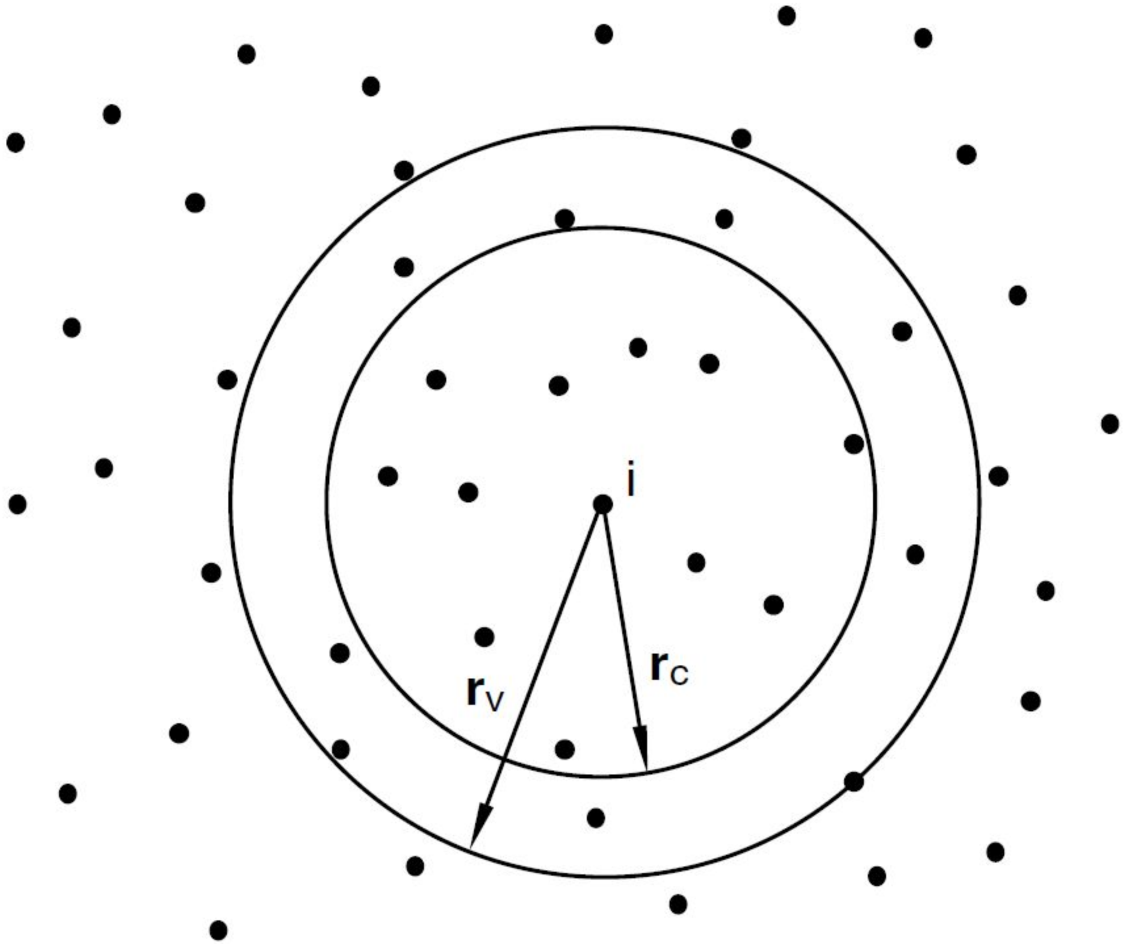
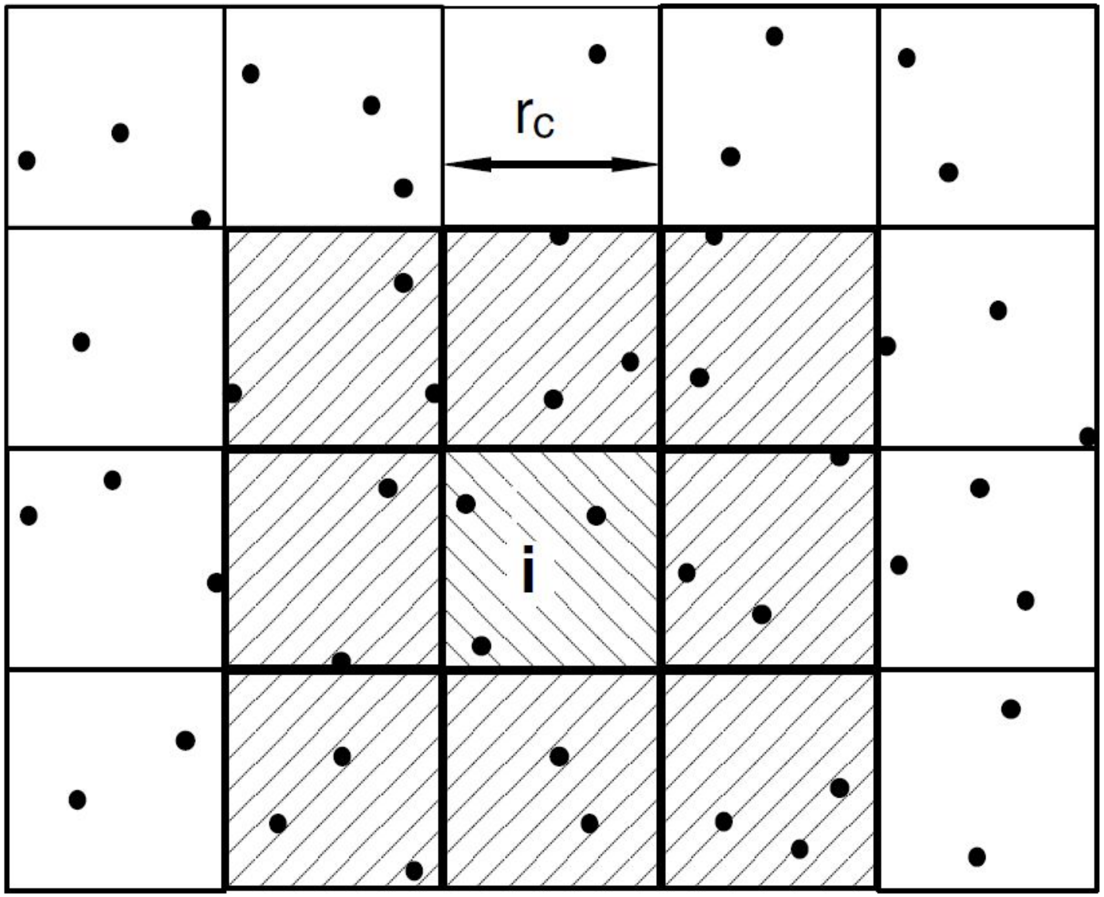
提高模拟效率 - Verlet 列表



r_c 相互作用范， r_v近邻范围

Cell 列表



No list

$$\tau = cN(N-1)/2$$

Verlet list

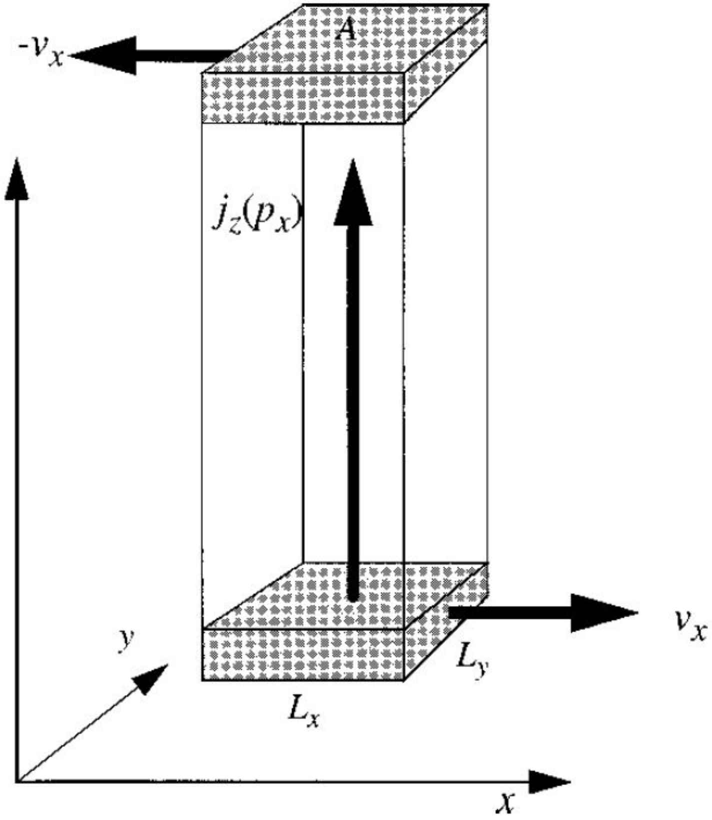
$$\tau_v = cn_v N + \frac{c_v}{n_u} N^2$$

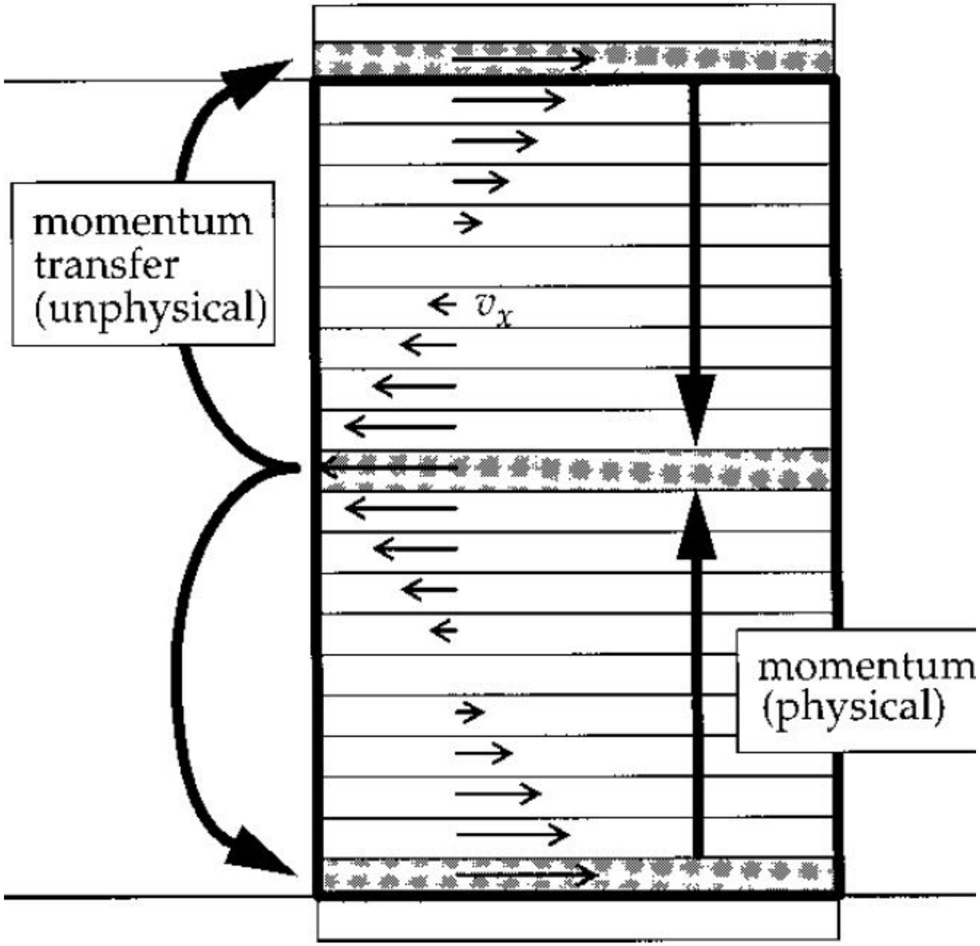
Cell list

$$\tau_l = cn_l N + c_l N$$

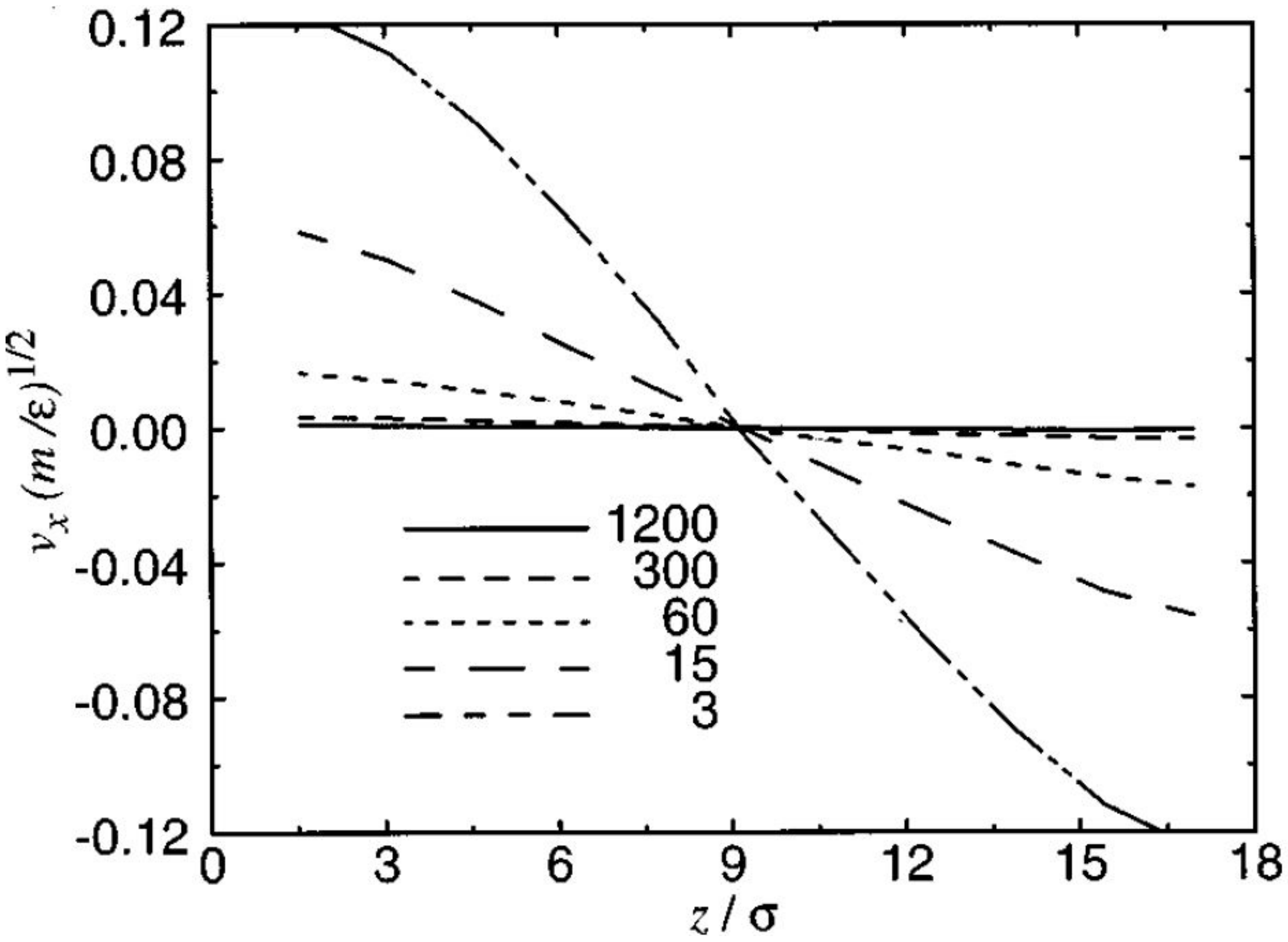
非平衡MD模拟 - 剪切流场

$$j_z(p_x) = -\eta \frac{\partial v_x}{\partial z}.$$





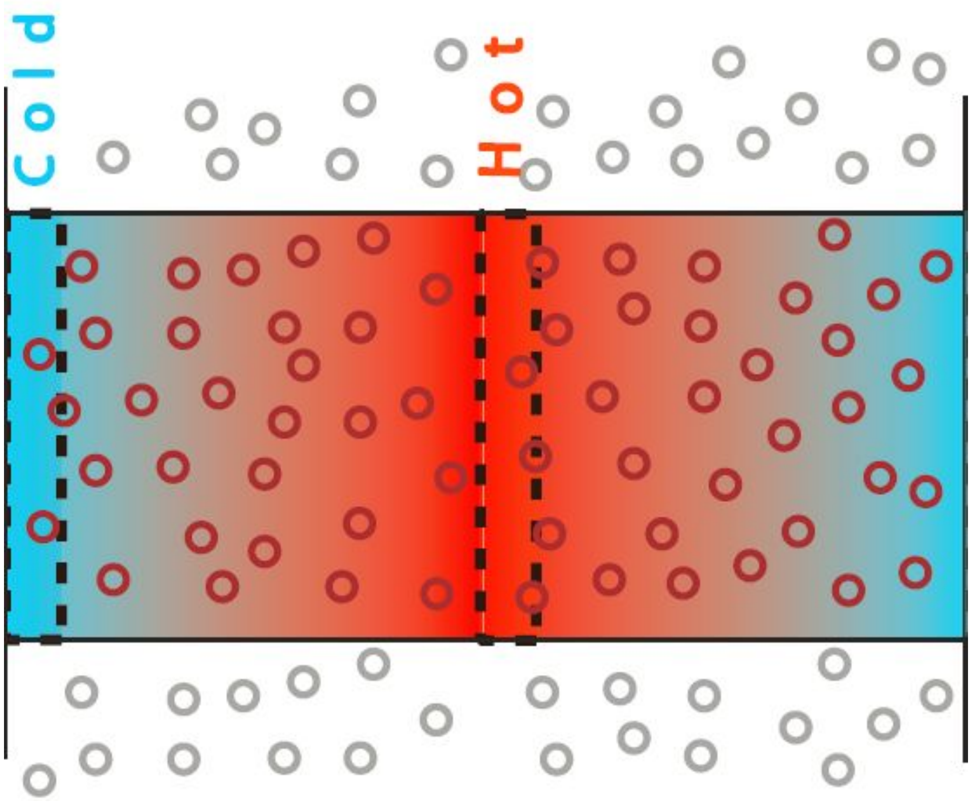
剪切流场

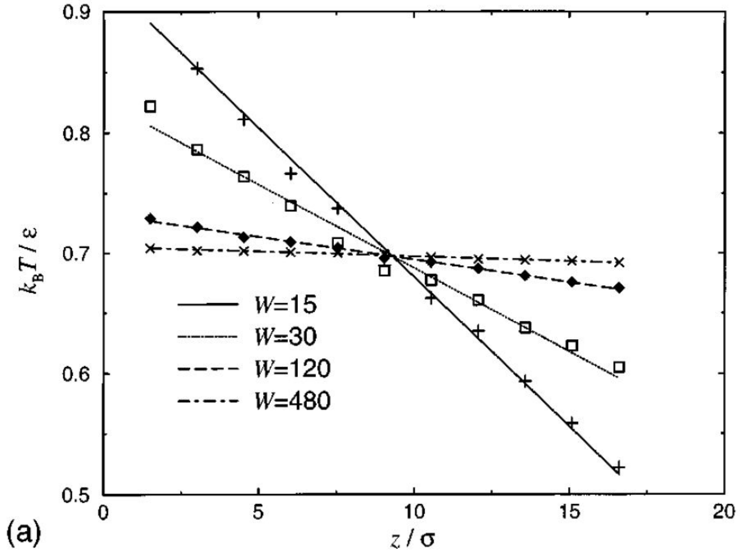


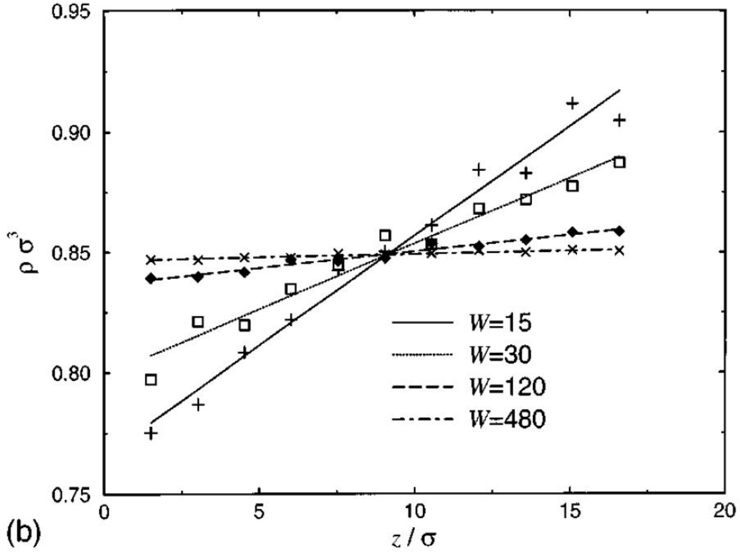
0.12
0.08
0.04
0.00
-0.04
-0.08
-0.12
0
3
6
9
12
15
18
$v_x\ (m/\varepsilon)^{1/2}$
z/σ
1200
300
60
15
3

非平衡MD模拟 - 温度梯度

$$\mathbf{J} = -\lambda \nabla T$$

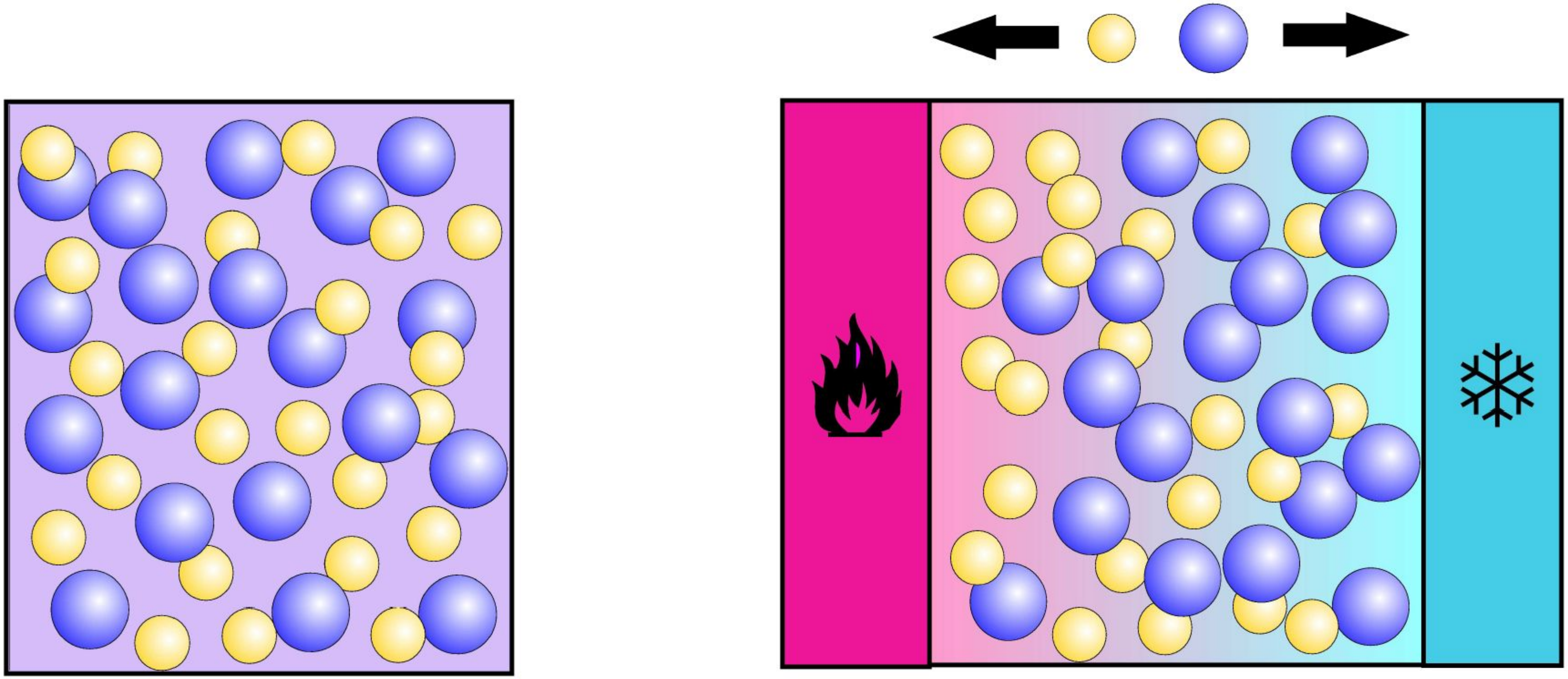






温度梯度 - 热扩散（Thermodiffusion）

温度梯度可以导致质量（物质）输运

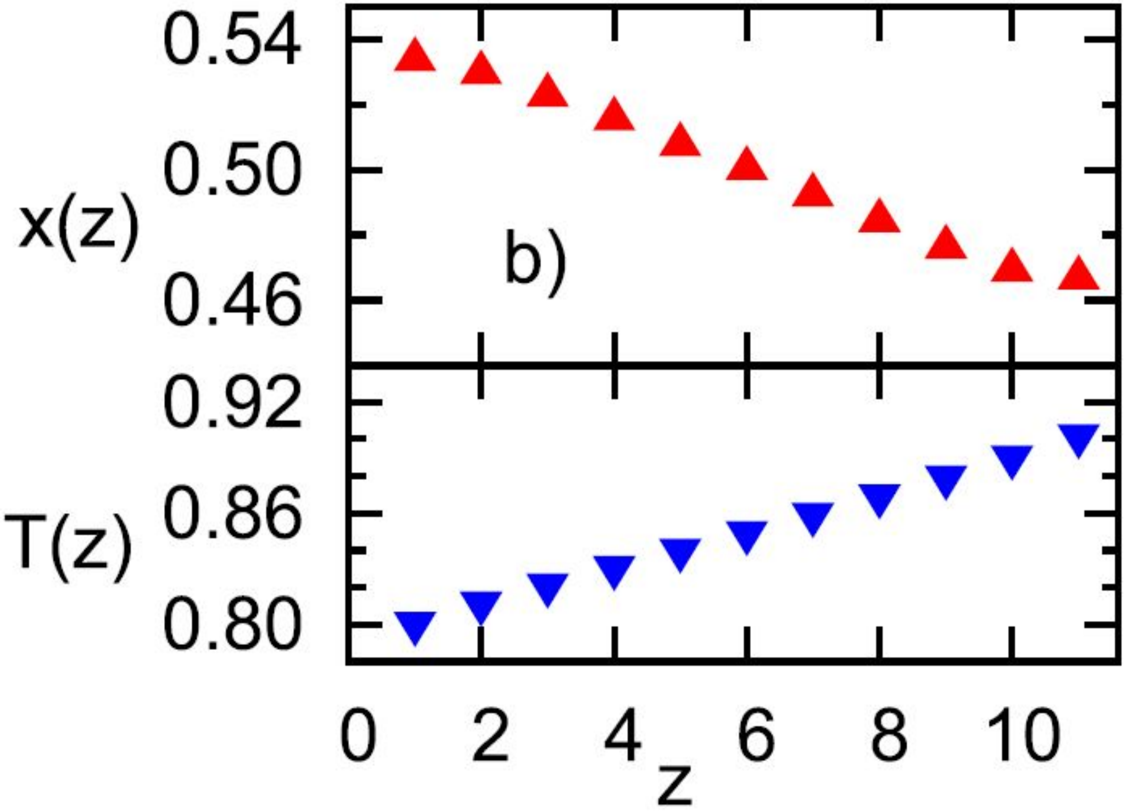


$$\mathbf{J}(\mathbf{r}) = -\tilde{n} D_{\mathrm{m}} \nabla x - \tilde{n} x(1-x) D_{\mathrm{T}} \nabla T$$

$$S_T \equiv \frac{D_{\mathrm{T}}}{D_{\mathrm{m}}}$$

热扩散

$$\left.\begin{aligned} \mathbf{J}(\mathbf{r}) &= -\tilde{n}D_{\mathrm{m}}\nabla x - \tilde{n}x(1-x)D_{\mathrm{T}}\nabla T \\ S_T &\equiv \frac{D_{\mathrm{T}}}{D_{\mathrm{m}}} \end{aligned}\right\} \quad S_T = -\frac{1}{x(1-x)}\frac{\nabla x}{\nabla T}$$



随机数

特点：具有特定的分布，无关联性，不可预测性。
计算机所产生的随机数都是赝随机数。

常用的均匀分布的随机数产生器：

Linear Congruential Generator (LCG)：

$$X_n = (c \times X_{n-1} + a_o)\mathrm{MOD}\, N_{\max}$$

$$X_n = (16807 \times X_{n-1})\mathrm{MOD}(2^{31} - 1)$$

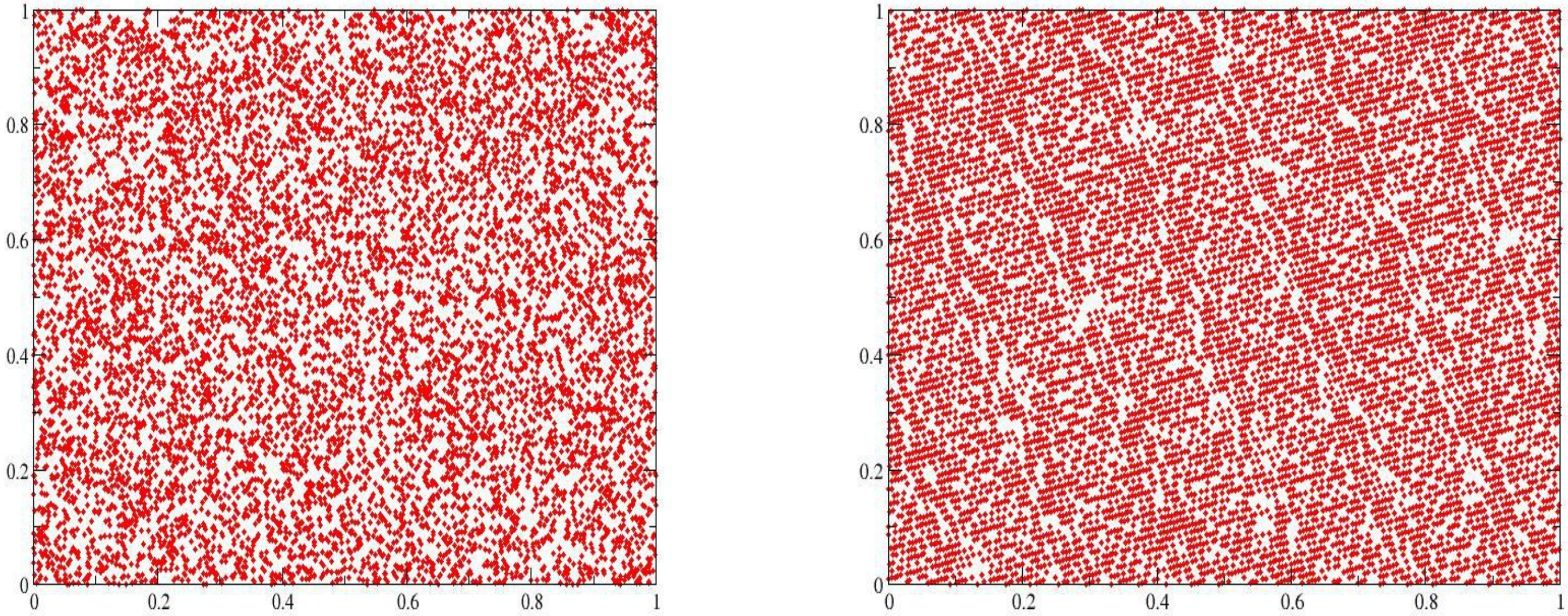
Kirkpatrick-Stoll (R250)（预先产生一些随机数X）：

$$X_n = X_{n-p} \cdot \mathrm{XOR} \cdot X_{n-q}$$

$$p = 250,\ q = 103$$

Mersenne Twister （MT） ... ...

随机数质量检验



相关性检验：左为R250，右为同余法。

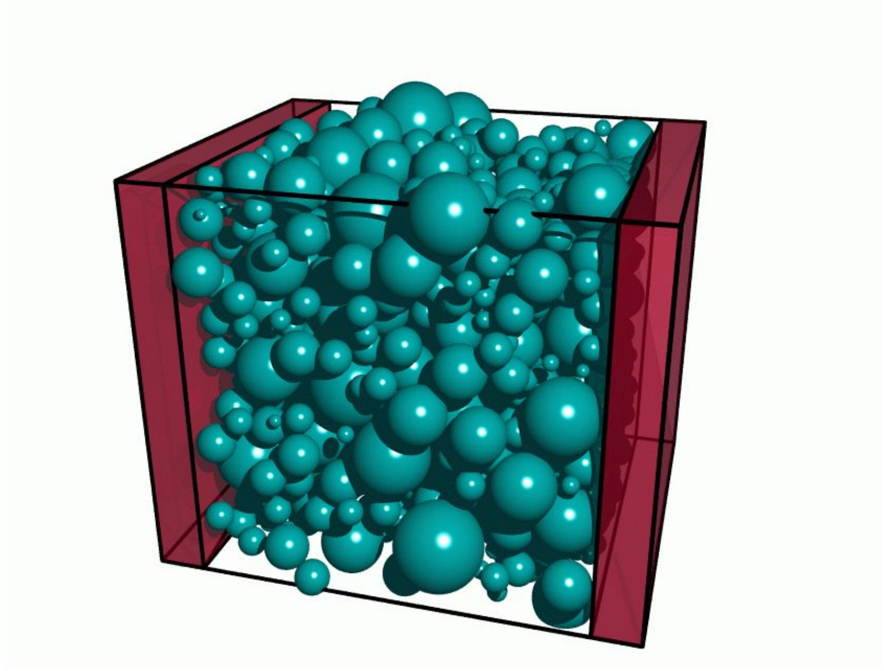
小结

- 软物质与计算机模拟
- 分子动力学模拟
  - 建立模型
  - 积分算法
  - 边界条件
  - 控温
  - 非平衡分子动力学
- 随机数

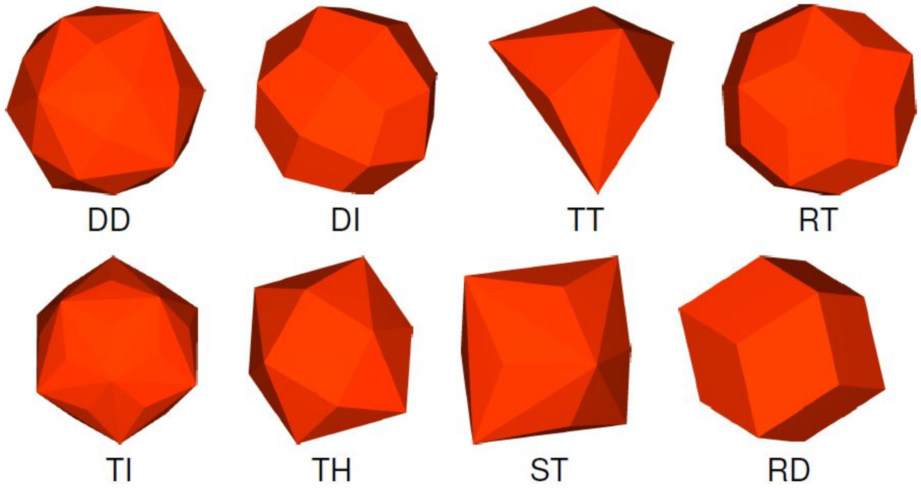
Lecture 2

模特卡罗模拟（Monte Carlo）

MD模拟平衡态的局限性



- 没有自然的动力学过程
- 动力学太慢或存在局域的自由能极小值
- 粒子具有复杂的形状



蒙特卡罗模拟（Monte Carlo）

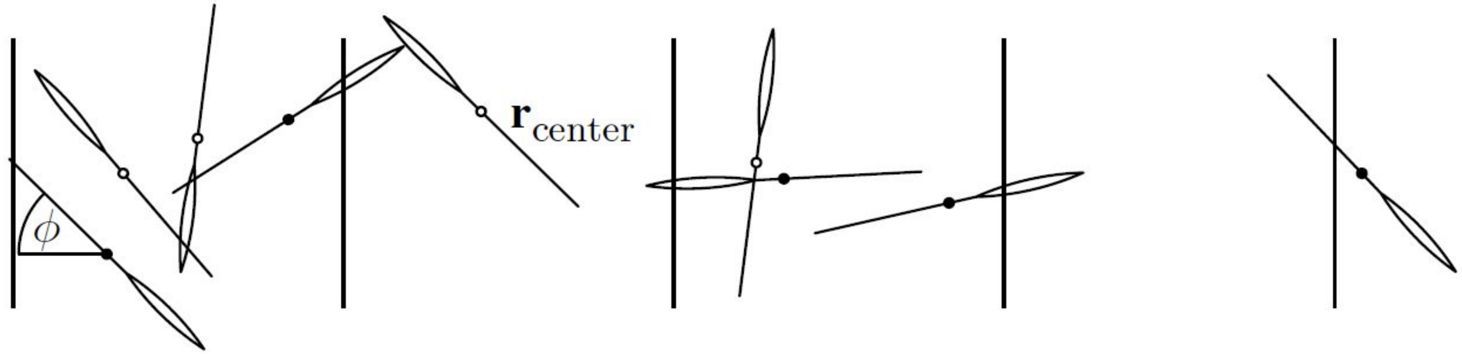
- Monte Carlo methods are a broad class of computational algorithms that rely on repeated random (statistical) sampling to solve mathematical problems.

- They are often used in physical and mathematical problems and are most useful when it is difficult or impossible to use other mathematical methods.

- Monte Carlo methods is particularly suitable for statistical physics problems in equilibrium-state many-body systems.

早期历史起源

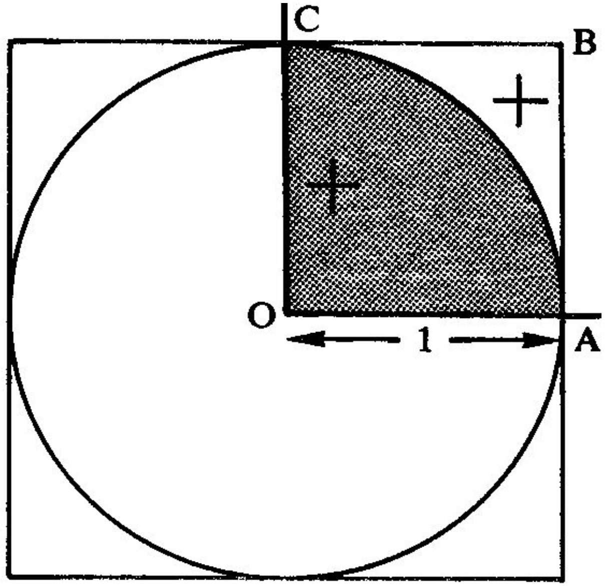
Buffon's needle experiment (1777)

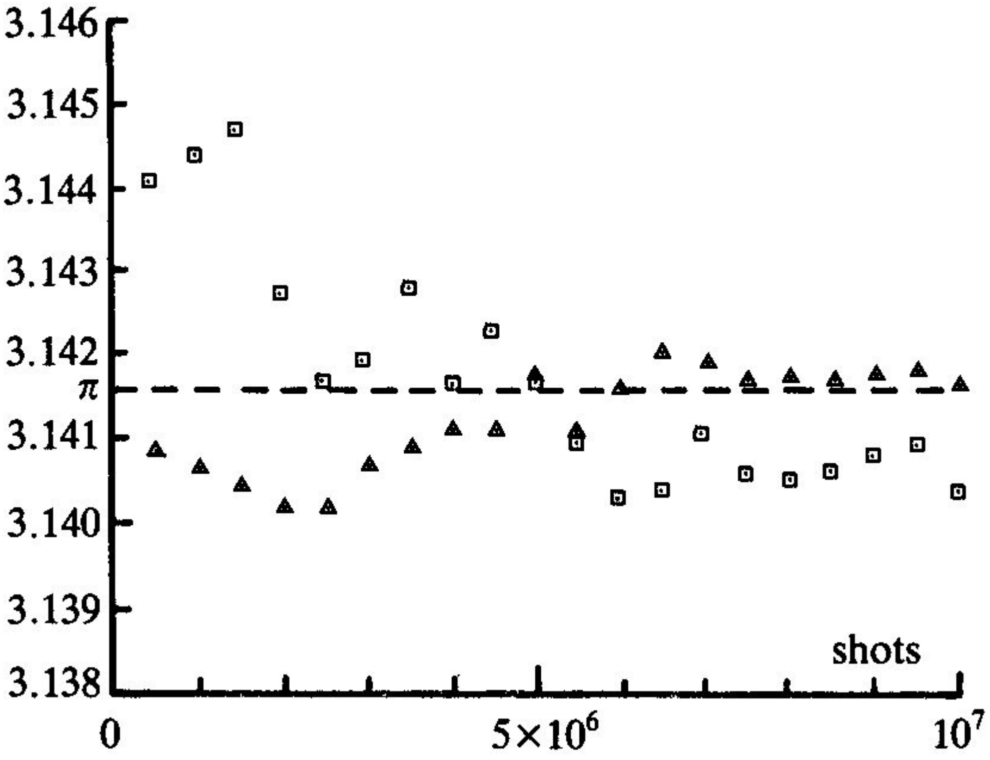


$$p = \frac{2L}{\pi d}$$

简化版本

投点法计算Pi





$$\pi \approx \frac{4 \times \text{Area under the curve CA}}{\text{Area of the square OABC}} = \frac{4\tau_{\text{hit}}}{\tau_{\text{shot}}}$$

当代的蒙特卡罗模拟

- The modern version of the Monte Carlo method was invented in the late 1940s by Stanislaw Ulam, while he was working on nuclear weapons projects at the Los Alamos National Laboratory.
- The novel contribution of Ulam was to realize that derterminate problems could be treated by finding a probabilitic analogue which is then solved by a stochastic sampling experiment.

Stanislaw Ulam (1909-1984)

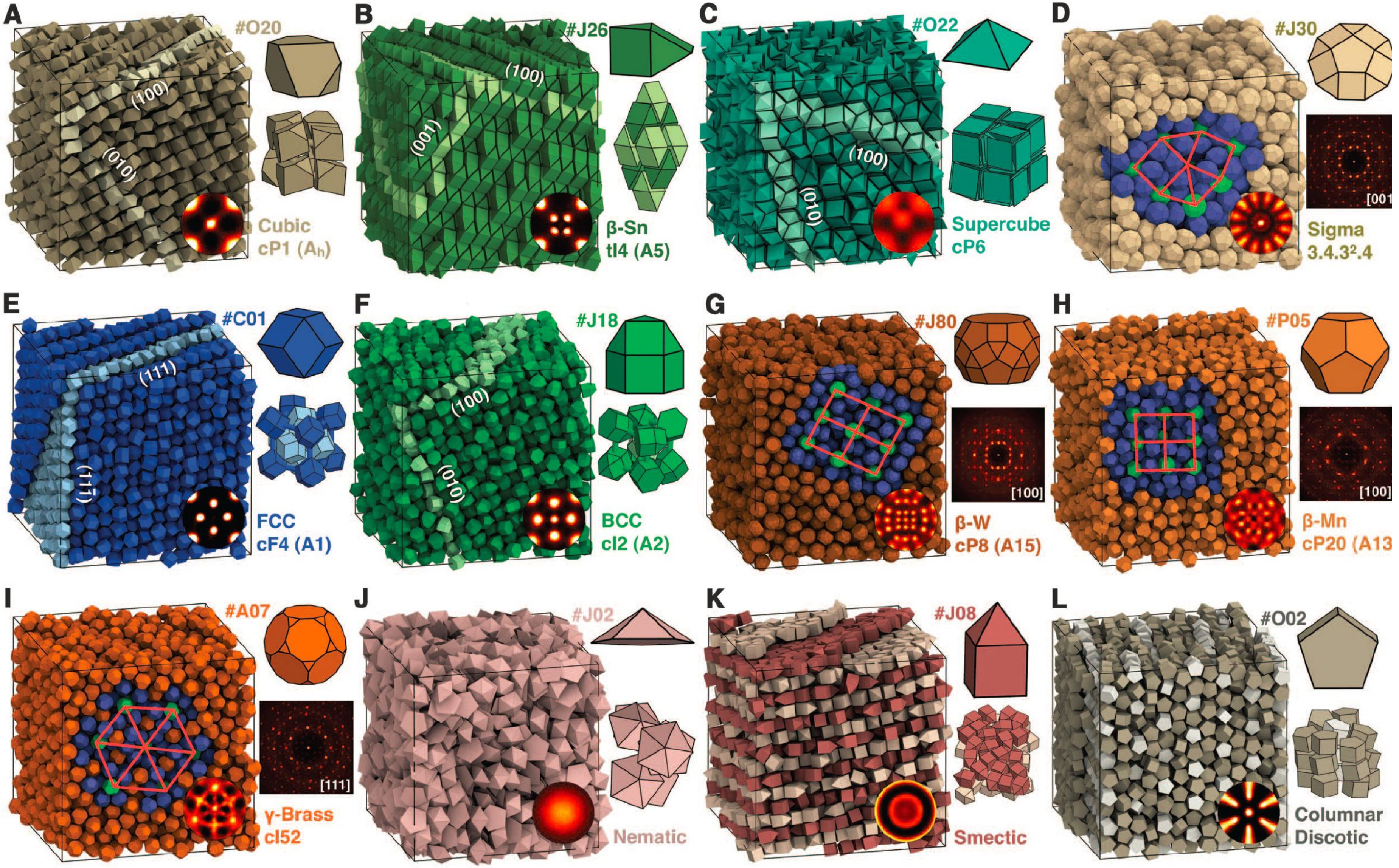
Nicholas Metropolis

Nicholas Metropolis (1915-1999)
The algorithm invented by Metropolis et al (1953) is the most important MC method.
(the first simulation of a liquid)

Monte Carlo in Monaco

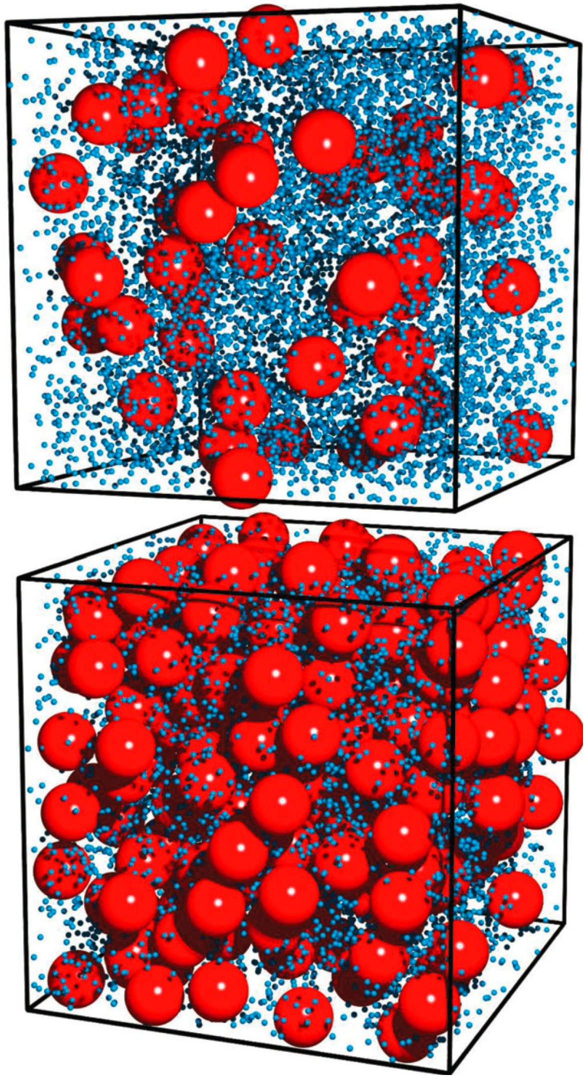
MC模拟的例子

多面体粒子结晶

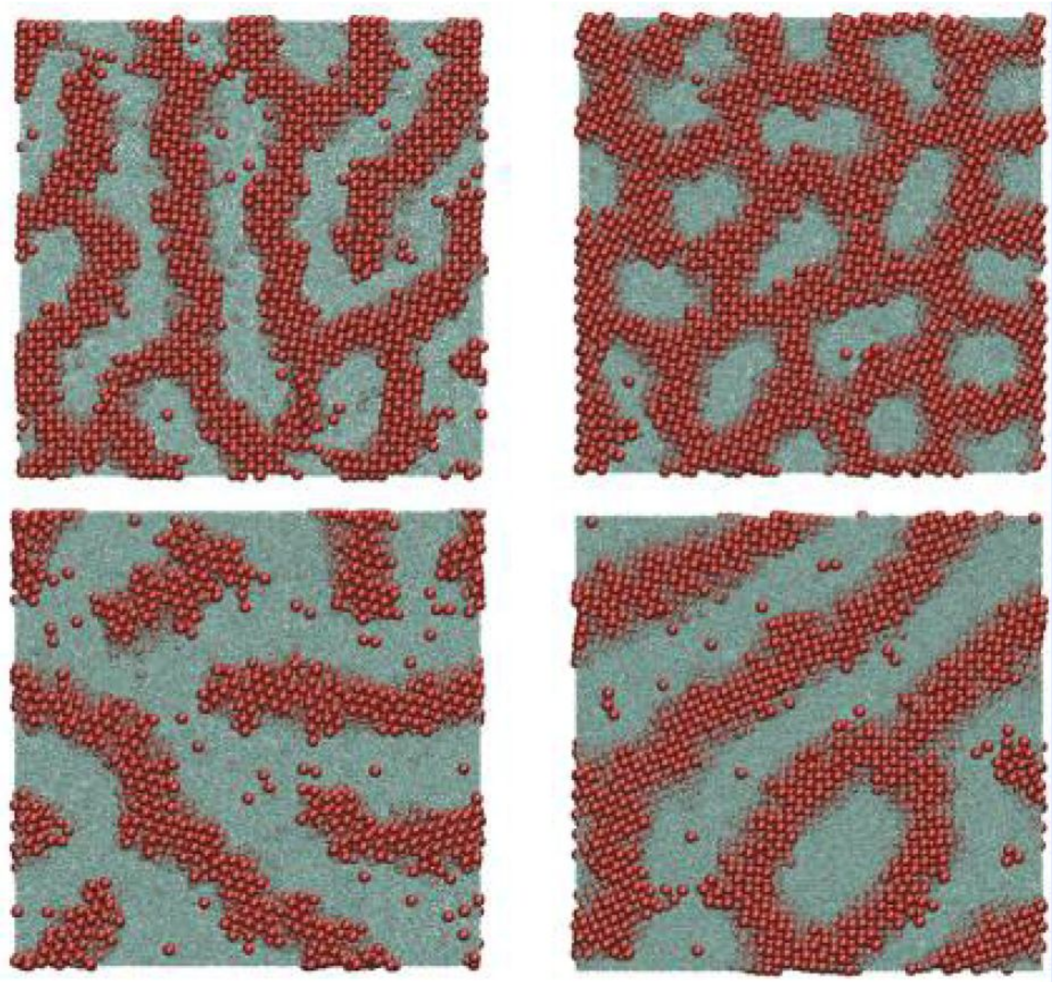


MC模拟的例子

胶体粒子气液相变

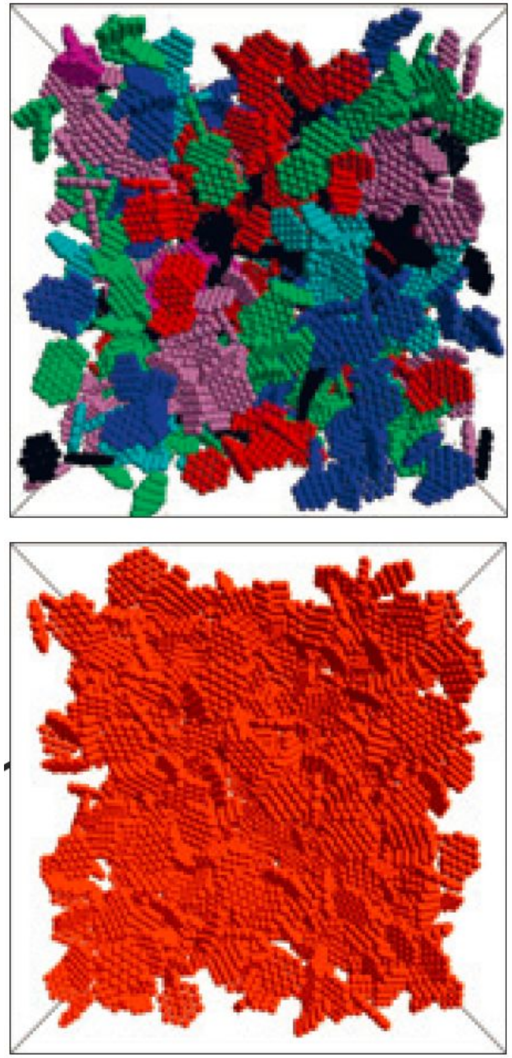


纳米粒子和polymer

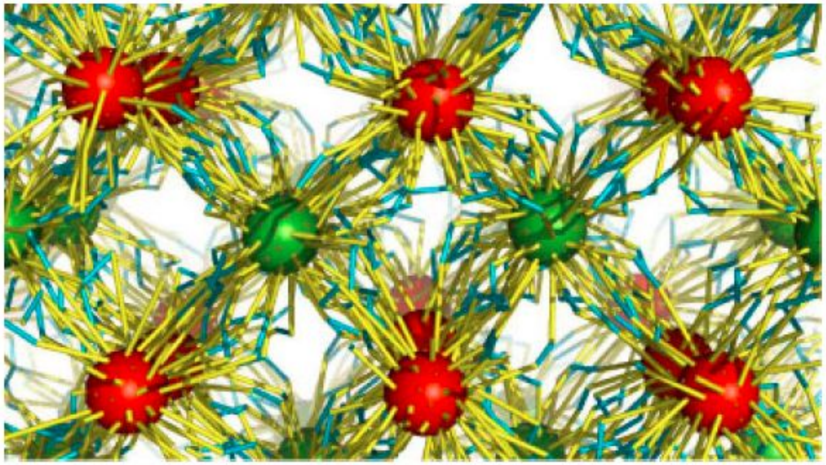


MC模拟的例子

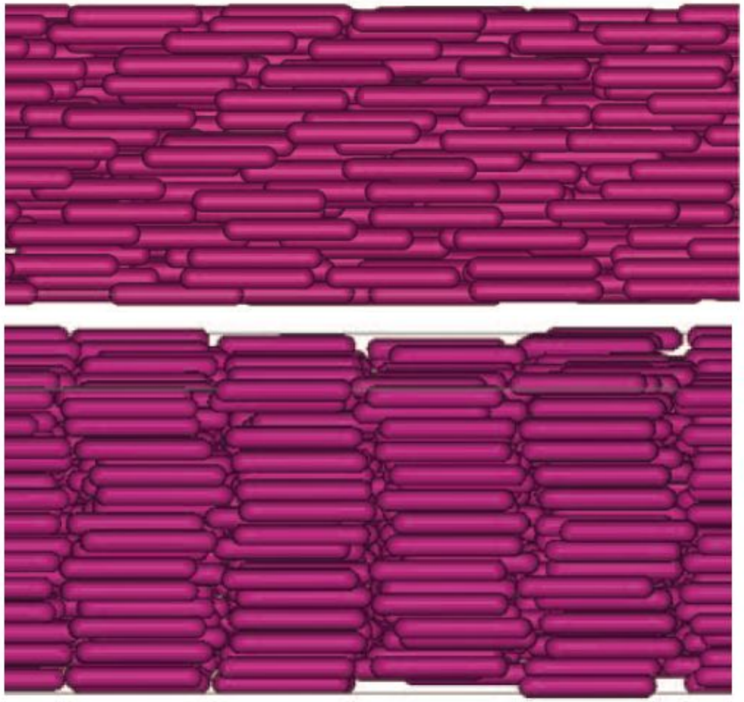
patchy粒子



colloid
with DNA



liquid
crystal



Monte Carlo与平衡态统计物理

Monte Carlo方法特别适合求解复杂的多重积分问题；而统计物理中到处都是复杂的多重积分。

$$Q = c \int d\mathbf{p}^N d\mathbf{r}^N \exp[-\mathcal{H}(\mathbf{r}^N \ \mathbf{p}^N)/k_B T]$$

$$\langle A \rangle = \frac{\int d\mathbf{p}^N d\mathbf{r}^N \ A(\mathbf{p}^N, \mathbf{r}^N) \exp[-\beta \mathcal{H}(\mathbf{p}^N, \mathbf{r}^N)]}{\int d\mathbf{p}^N d\mathbf{r}^N \ \exp[-\beta \mathcal{H}(\mathbf{p}^N, \mathbf{r}^N)]}$$

因此，Monte Carlo模拟就很自然的应用到平衡态的统计物理中。软物质作为一个典型的复杂多体系统，为Monte Carlo模拟提供了非常广阔的应用空间。

MC求积分

$$I = \int_a^b dx\, f(x)$$

数值求积分：(划分很多区间) 梯形法，辛普森法...

用概率的语言改写

$$I = (b-a)\,\langle f(x)\rangle$$

MC求积分：求函数的期望值

其中概率分布为[a,b]区间内的均匀分布 -— 简单抽样 !!!

$$I = \int_a^b dx\, f(x) = (b-a)\frac{1}{N}\sum_{i=1}^{N} f(x_i) = (b-a)\langle f\rangle$$

例子：计算积分 $$I=\int_0^1 dx\frac{1}{1+x^4}$$

精确值是 $$I^{\text{exact}}=0.86697298733991 10\cdots$$

用简单抽样法计算此积分. $$I=\langle f\rangle$$

N	I	$\Delta I/I$
10^2	0.879679	1.47×10^{-2}
10^3	0.871238	4.92×10^{-3}
10^4	0.869603	3.03×10^{-3}
10^5	0.866777	2.26×10^{-4}
10^6	0.866876	1.11×10^{-4}
10^7	0.867004	3.63×10^{-5}
10^8	0.866947	2.97×10^{-5}
10^9	0.866956	1.89×10^{-5}

数值积分与MC积分

数值积分

优点：精度高，算法简单直接

缺点：不适合多重积分

- 设系统由100个粒子构成，每个粒子有6个自由度，所以需要计算600重积分．在每一维取10个点，总共有10^{600}个点!!!
- 对高度震荡的被积函数，这一问题将变的更为严重!!!

MC积分

优点：特别适合多重积分

缺点：精度低，算法复杂

简单抽样MC的缺点

简单抽样：抽样的概率分布是均匀的

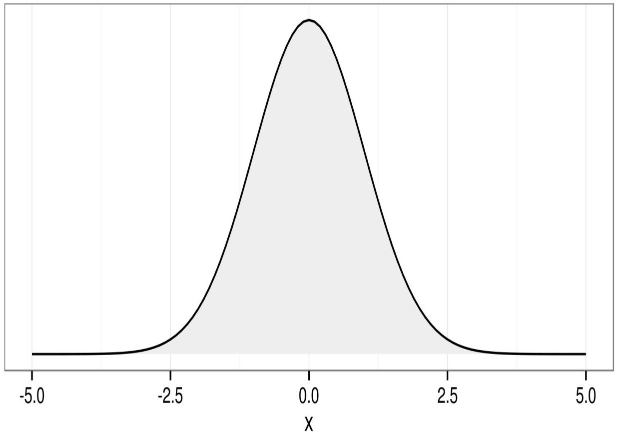
（函数越平滑，结果越准确）

$$\mathrm{I} = \int_a^b dx\mathrm{f}(x) = (b-a)\int_a^b dx\mathrm{f}(x)\rho(x) = (b-a)\langle \mathrm{f} \rangle$$

$$\rho(x) = \frac{1}{b-a}$$

缺点：不适合不平滑的被积函数，或者积分区间内的大部分区域几乎没有贡献。

解决方案：重要的区域多抽样几次（非均匀抽样）



重要性抽样方法

$$I = \int_a^b dx\, f(x)$$

$$I = \int_0^1 dx\, w(x) \frac{f(x)}{w(x)}$$

$w(x)$ [0,1] 区间内非均匀分布的概率密度

$$I = \int_0^1 du\, \frac{f[x(u)]}{w[x(u)]}$$

$$I \approx \frac{1}{L} \sum_{i=1}^{L} \frac{f[x(u_i)]}{w[x(u_i)]}$$

重要性抽样方法

计算 $I \approx \frac{1}{L}\sum_{i=1}^{L}\frac{f[x(u_i)]}{w[x(u_i)]}$的方差

$$\sigma_I^2 = \frac{1}{L^2}\sum_{i=1}^{L}\sum_{j=1}^{L}\left\langle\left(\frac{f[x(u_i)]}{w[x(u_i)]}-\langle f/w\rangle\right)\left(\frac{f[x(u_j)]}{w[x(u_j)]}-\langle f/w\rangle\right)\right\rangle$$

$$= \frac{1}{L^2}\sum_{i=1}^{L}\left\langle\left(\frac{f[x(u_i)]}{w[x(u_i)]}-\langle f/w\rangle\right)^2\right\rangle$$

$$= \frac{1}{L}\left[\langle (f/w)^2\rangle - \langle f/w\rangle^2\right].$$

角括号是系综平均（精确值）

抽样数目越多，结果越准确 $f(x)/w(x)$ 越平滑，结果越准确。

重要性抽样方法

$$I = \int_a^b dx\, f(x) \longrightarrow I = \int_0^1 dx\, w(x) \frac{f(x)}{w(x)}$$

$$I \approx \frac{1}{L} \sum_{i=1}^{L} \frac{f[x(u_i)]}{w[x(u_i)]}$$

当使用MC求积分时，通过概率分布构造,使被积函数 $f(x)/w(x)$ 尽可能的平滑。

统计力学

正则系综配分函数：
$$Q = c\int d\mathbf{p}^N d\mathbf{r}^N \exp[-\mathcal{H}(\mathbf{r}^N \mathbf{p}^N)/k_B T]$$

Helmholtz自由能：
$$F = -k_B T \ln Q$$

内能：
$$E = -T^2 \frac{\partial\left(\frac{F}{T}\right)}{\partial T}$$

熵：
$$S = -\left(\frac{\partial F}{\partial T}\right)_{V,N}$$

动量积分部分：
$$(2\pi m k_B T)^{3N/2}$$

位形积分部分：
$$Z \equiv \int d\mathbf{r}^N \exp[-\beta\mathcal{U}(\mathbf{r}^N)]$$

困难：配分函数求不出来!!! 使用MC方法求积分???

（Boltzmann因子在位形空间剧烈变化（液体））

统计力学

如果不去考虑Boltzmann因子在相空间的剧烈变化，而强行利用简单抽样的MC计算积分

$$Z \equiv \int d\mathbf{r}^N \exp[-\beta \mathcal{U}(\mathbf{r}^N)]$$

步骤如下（假如有100个粒子）：

（1）在一个300维的位形空间中随机的取一点（产生300个均匀分布的随机数，每三个对应于一个粒子的位置）。

（2）计算这个位形的势能，从而得到该位形的Boltzmann因子。

（3）重复这一过程多次，求位形积分。

$$Z \approx \frac{V^N}{L} \sum_{i=1}^{L} \exp[-\beta \mathcal{U}(\mathbf{r}^N)]$$

绝大多数位形贡献为零！

利用重要性抽样MC求配分函数是否可行???

不能构造一个恰当的概率分布使被积函数足够平滑！

统计力学

物理量 A 的期望值：

$$\langle A \rangle = \frac{\int d\mathbf{p}^N d\mathbf{r}^N \, A(\mathbf{p}^N, \mathbf{r}^N) \exp[-\beta \mathcal{H}(\mathbf{p}^N, \mathbf{r}^N)]}{\int d\mathbf{p}^N d\mathbf{r}^N \, \exp[-\beta \mathcal{H}(\mathbf{p}^N, \mathbf{r}^N)]}$$

概率密度

约去动量部分：

$$\langle A \rangle = \frac{\int d\mathbf{r}^N \, \exp[-\beta \mathcal{U}(\mathbf{r}^N)] A(\mathbf{r}^N)}{\int d\mathbf{r}^N \, \exp[-\beta \mathcal{U}(\mathbf{r}^N)]}$$

概率密度： $\mathcal{N}(\mathbf{r}^N) \equiv \frac{\exp[-\beta \mathcal{U}(\mathbf{r}^N)]}{Z}$ $\quad Z \equiv \int d\mathbf{r}^N \, \exp[-\beta \mathcal{U}(\mathbf{r}^N)]$

$$\langle A \rangle = \int d\mathbf{r}^N \mathcal{N}(\mathbf{r}^N) \, A(\mathbf{r}^N) \approx \frac{1}{L} \sum_{i=1}^{L} A(\mathbf{r}_i^N)$$

构造一个具有Boltzman分布的随机过程，进行重要性抽样。

Metropolis方法 - Markov链

构建一个系统状态演化的Markov链（过程），经过长时间的演化，系统的状态达到一个指定的几率分布（Boltzmann分布）。

Markov链：

系统的一序列随机演化的状态，$x_0, x_1, x_2, \ldots, x_i, \ldots$

Markov链特征 - 无记忆：

当前状态进一步的演化行为，仅与当前状态相关，与更早期的状态无关， $P(X_{n+1}|X_0, X_1, \ldots, X_n) = P(X_{n+1}|X_n)$ 。

$P(X_{n+1}|X_n)$也叫做转移概率 $\pi(X_n\text{->}X_{n+1})$，确定了Markov过程，因此系统状态的几率分布。

个态历经要求：

经过有限步的演化，系统的任意两个态可以相互到达。

Metropolis方法 - 细致平衡

- 如何构造转移概率 $\pi(o \rightarrow n)$ 使得进行Markov演化的系统的状态分布满足指定的概率分布（Boltzmann）？

- 一旦系统达到了平衡分布，按照转移概率 $\pi(o \rightarrow n)$ 进行演化不应该破坏该平衡分布。

- 细致平衡条件：

$$\mathcal{N}(o)\pi(o \rightarrow n) = \mathcal{N}(n)\pi(n \rightarrow o)$$

（ $\mathcal{N}(n)$和 $\mathcal{N}(o)$与新旧位形几率分布） $\mathcal{N}(\mathbf{r}^N) \equiv \frac{\exp[-\beta \mathcal{U}(\mathbf{r}^N)]}{Z}$

满足细致平衡的转移概率确保系统收敛到指定的概率分布。

Metropolis方法 - 构造转移概率

- 转移概率 $\pi(o \rightarrow n)$实际上包括两部分：

  状态选择概率$\alpha(o \rightarrow n)$和 状态接受概率 $acc(o \rightarrow n)$

  $$\pi(o \rightarrow n) = \alpha(o \rightarrow n) \times acc(o \rightarrow n)$$

- 通常选取 $\alpha(o \rightarrow n) = \alpha(n \rightarrow o)$

- 细致平衡条件 $\mathcal{N}(o)\pi(o \rightarrow n) = \mathcal{N}(n)\pi(n \rightarrow o)$

$$\Downarrow$$

$$\mathcal{N}(o) \times acc(o \rightarrow n) = \mathcal{N}(n) \times acc(n \rightarrow o)$$

$$\Downarrow$$

$$\frac{acc(o \rightarrow n)}{acc(n \rightarrow o)} = \frac{\mathcal{N}(n)}{\mathcal{N}(o)} = \exp\{-\beta[\mathcal{U}(n) - \mathcal{U}(o)]\}$$

构造接受几率

$$\frac{\mathrm{acc}(o \to n)}{\mathrm{acc}(n \to o)} = \frac{\mathcal{N}(n)}{\mathcal{N}(o)} = \exp\{-\beta[\mathcal{U}(n) - \mathcal{U}(o)]\}$$

一个简单的接受几率构造（Metropolis）：

$$\begin{aligned} \mathrm{acc}(o \to n) &= \mathcal{N}(n)/\mathcal{N}(o) \quad && \text{if } \mathcal{N}(n) < \mathcal{N}(o) \\ &= 1 && \text{if } \mathcal{N}(n) \geq \mathcal{N}(o) \end{aligned}$$

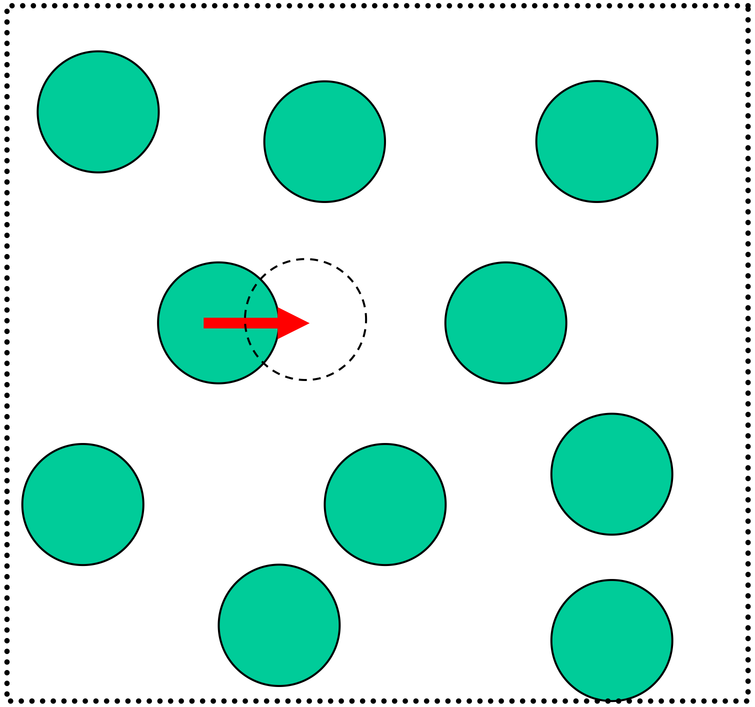
$$\mathrm{acc}(o \to n) = \min\left(1, \exp\{-\beta[\mathcal{U}(\mathbf{r}'^N) - \mathcal{U}(\mathbf{r}^N)]\}\right)$$

当新态的能量大旧态的能量 $\mathcal{U}(n) > \mathcal{U}(o)$

$$\mathrm{acc}(o \to n) = \exp\{-\beta[\mathcal{U}(n) - \mathcal{U}(o)]\} < 1$$

产生一个[0,1]之间均匀分布的随机数，判断是否接受

一个基本的MC模拟



粒子间具有势能作用

步骤：

1. 随机的选择一个粒子，计算它的势能 $\mathcal{U}(\mathbf{r}^N)$

2. 随机的移动一下该粒子的位置 $r' = r + \Delta$ ，计算它的新势能 $\mathcal{U}(\mathbf{r}'^N)$（Markov链）

3. 接受这个试探性的随机移动 $\mathbf{r}^N$ to $\mathbf{r}'^N$ 以如下概率：

$$\mathrm{acc}(o \to n) = \min\left(1, \exp\{-\beta[\mathcal{U}(\mathbf{r}'^N) - \mathcal{U}(\mathbf{r}^N)]\}\right)$$

4. 重复（1 - 3），收集结果。

一个Monte Carlo步对应着所有的粒子循环一边。

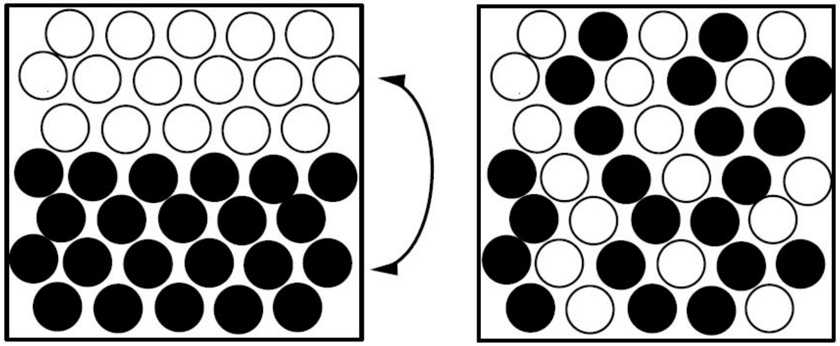
试探性移动

MC中所发生的移动是随机的，不满足微观的运动方程；且移动的方式多种多样（弛豫快！）。

局域移动
- 平移
- 旋转
- 改变粒子属性，如粒子尺寸

$$x_i' \rightarrow x_i + \Delta(\mathrm{Ranf} - 0.5)$$
$$y_i' \rightarrow y_i + \Delta(\mathrm{Ranf} - 0.5)$$
$$z_i' \rightarrow z_i + \Delta(\mathrm{Ranf} - 0.5)$$

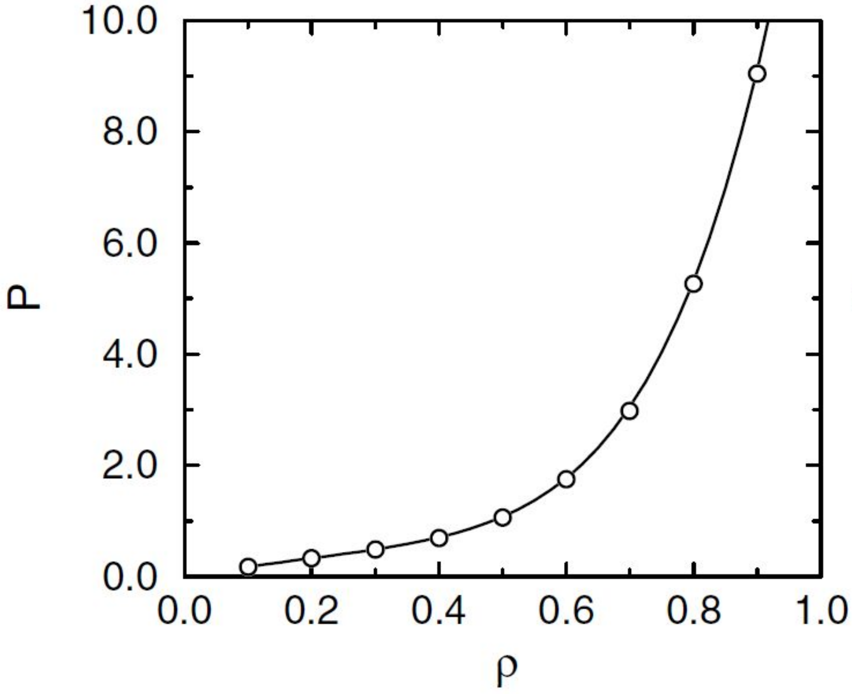
非局域移动
- 交换粒子位置
- 粒子集团运动
- 改变系统属性，如体积、温度

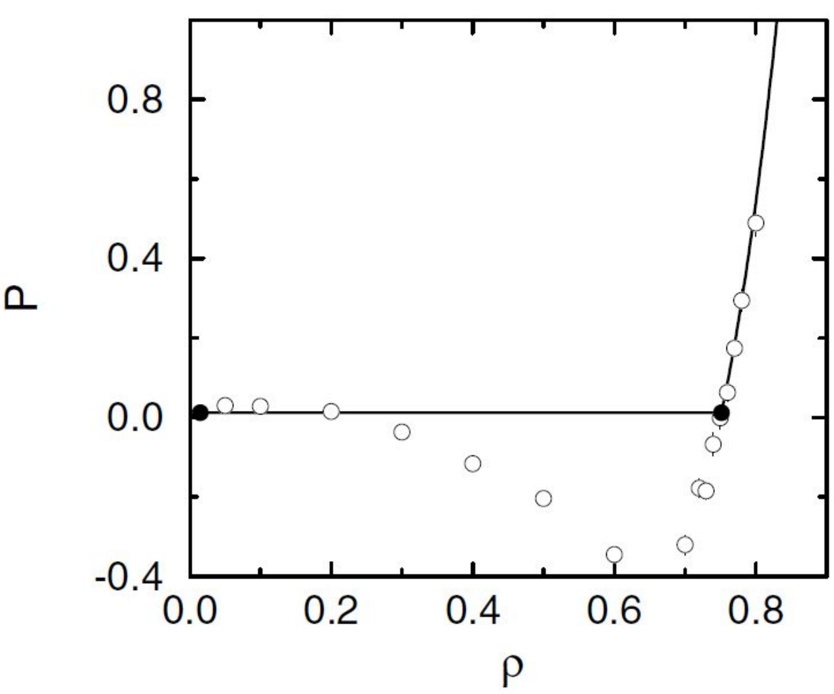


一个MC例子

计算状态方程

$$u^{lj}(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$





温度高于临界点 温度低于

临界点

$$P = \frac{\rho}{\beta} + \frac{vir}{V} \qquad vir = \frac{1}{3}\sum_{i}\sum_{j>i} \mathbf{f}(\mathbf{r}_{ij}) \cdot \mathbf{r}_{ij}$$

计算自由能

MC模拟不能直接地计算自由能，需要一些额外的技巧。一个常用的方法是沿着可逆路径进行热力学积分。

- 物理的路径： $\left(\frac{\partial F}{\partial V}\right)_{NT} = -P$ $\left(\frac{\partial F/T}{\partial 1/T}\right)_{VN} = E$
- 非物理的路径：

$$\begin{aligned} \mathcal{U}(\lambda) &= (1-\lambda)\mathcal{U}_{\mathrm{I}} + \lambda\mathcal{U}_{\mathrm{II}} \\ &= \mathcal{U}_{\mathrm{I}} + \lambda(\mathcal{U}_{\mathrm{II}} - \mathcal{U}_{\mathrm{I}}) \end{aligned}$$

$$Q(N,V,T,\lambda) = \frac{1}{\Lambda^{3N}N!}\int d\mathbf{r}^N \exp[-\beta\mathcal{U}(\lambda)]$$

$$\Rightarrow \quad \left(\frac{\partial F(\lambda)}{\partial \lambda}\right)_{N,V,T} = \left\langle \frac{\partial \mathcal{U}(\lambda)}{\partial \lambda} \right\rangle_{\lambda}$$

$$\Rightarrow \quad F(\lambda=1) - F(\lambda=0) = \int_{\lambda=0}^{\lambda=1} d\lambda \left\langle \frac{\partial \mathcal{U}(\lambda)}{\partial \lambda} \right\rangle_{\lambda}$$

巨正则系综MC模拟

粒子的数目不固定，Markov随机过程须包括粒子数目的涨落

配分函数：

$$Q(\mu,V,T) \equiv \sum_{N=0}^{\infty} \frac{\exp(\beta\mu N)V^{N}}{\Lambda^{3N}N!}\int d\mathbf{s}^{N} \exp[-\beta\mathcal{U}(\mathbf{s}^{N})]$$

概率分布：

$$\mathcal{N}_{\mu VT}(\mathbf{s}^{N};N) \propto \frac{\exp(\beta\mu N)V^{N}}{\Lambda^{3N}N!}\exp[-\beta\mathcal{U}(\mathbf{s}^{N})]$$

细致平衡条件：

$$\mathcal{N}(o)\times \mathrm{acc}(o\to n) = \mathcal{N}(n)\times \mathrm{acc}(n\to o)$$

试探移动：

位置平移

$$\mathrm{acc}(s\to s') = \min\left(1,\exp\{-\beta[\mathcal{U}(\mathbf{s}'^{N})-\mathcal{U}(\mathbf{s}^{N})]\}\right)$$

插入粒子

$$\mathrm{acc}(N\to N+1)=\min\left[1,\frac{V}{\Lambda^{3}(N+1)}\exp\{\beta[\mu-\mathcal{U}(N+1)+\mathcal{U}(N)]\}\right]$$

删除粒子

$$\mathrm{acc}(N\to N-1)=\min\left[1,\frac{\Lambda^{3}N}{V}\exp\{-\beta[\mu+\mathcal{U}(N-1)-\mathcal{U}(N)]\}\right]$$

小结

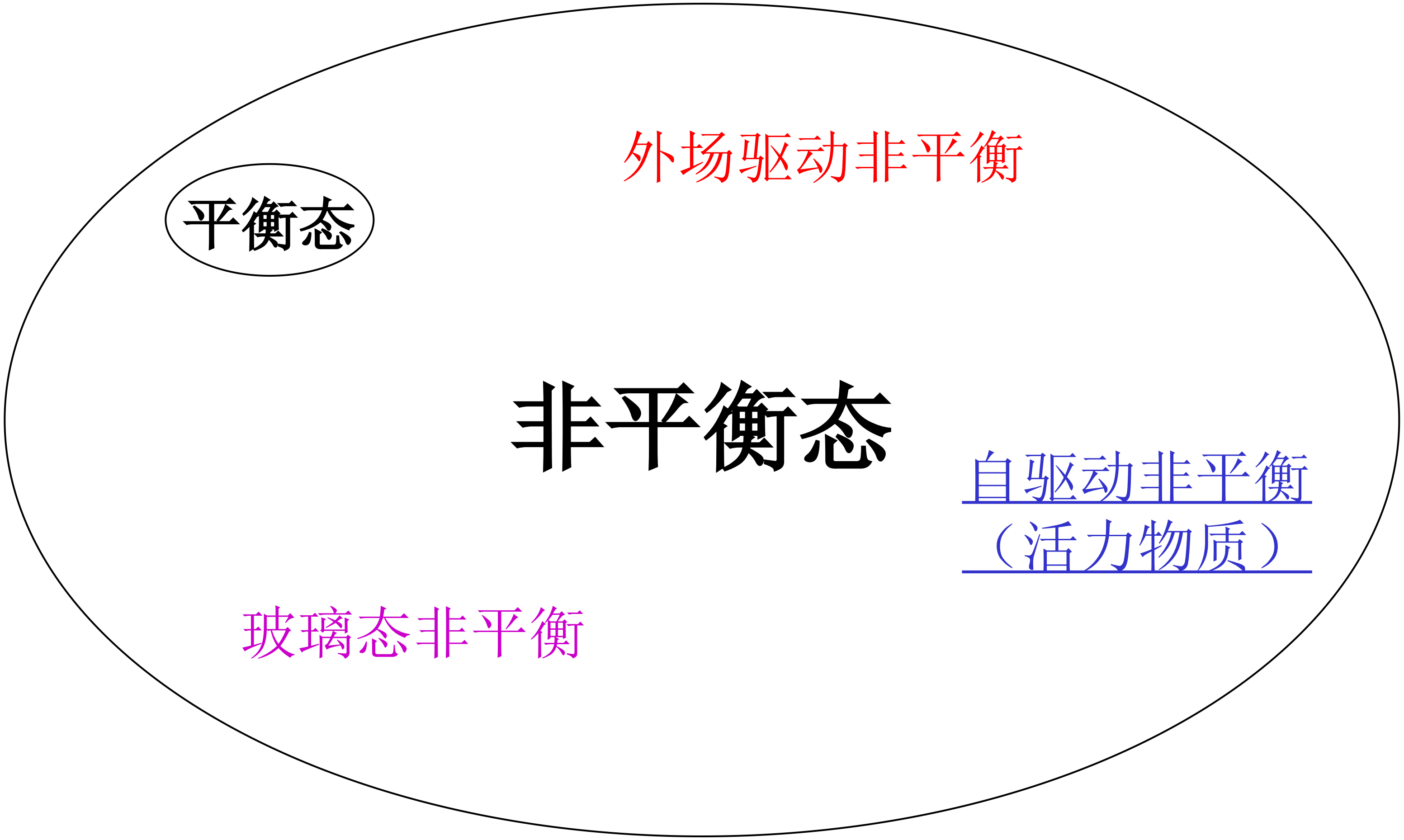
- MC方法的历史起源
- MC计算积分
- 简单抽样（均匀分布）
- 重要抽样（非均匀分布）
- Metropolis方法
- 细致平衡条件
- 计算自由能
- 巨正系综MC模拟

Lecture 3

布朗动力学模拟

介观流体力学模拟

统计物理



外场驱动非平衡

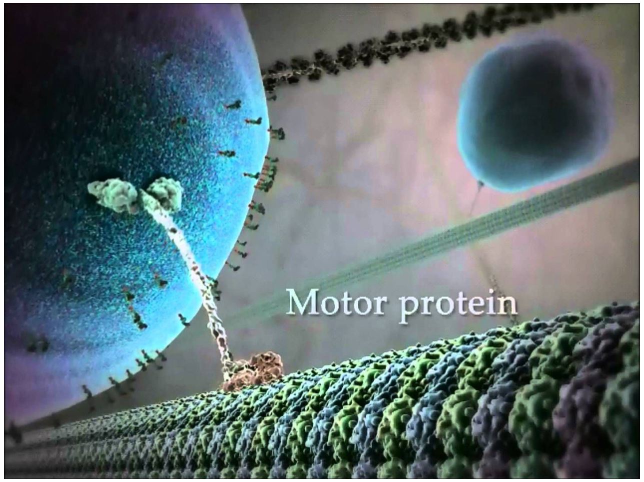
平衡态

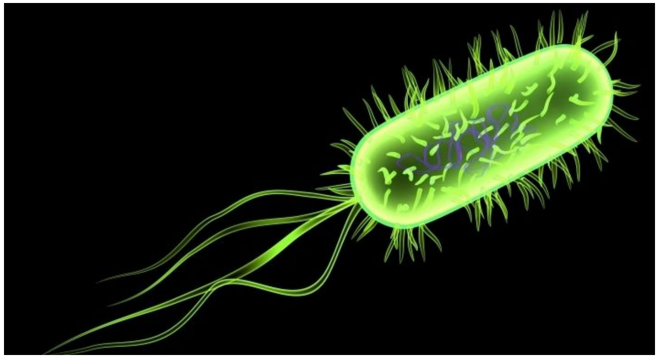
非平衡态

自驱动非平衡
（活力物质）

玻璃态非平衡

活力物质的组成单元



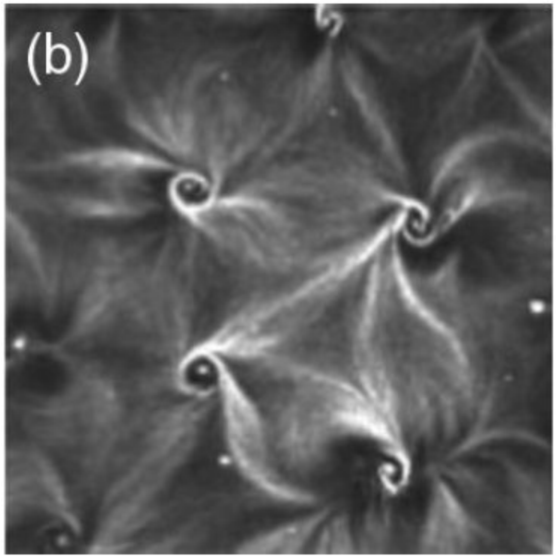


基本物理特征：

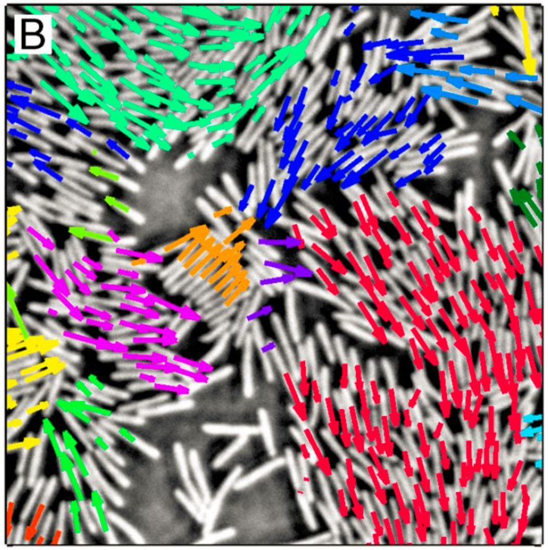
单体
- 自推进运动
- 能量消耗（非平衡态、时间反演不可逆）
- 空间结构非对称

群体
- 集体运动行为
- 动态结构图案
- 奇异密度涨落
- 反常流变性质

活力物质的集体行为



马达蛋白和微管

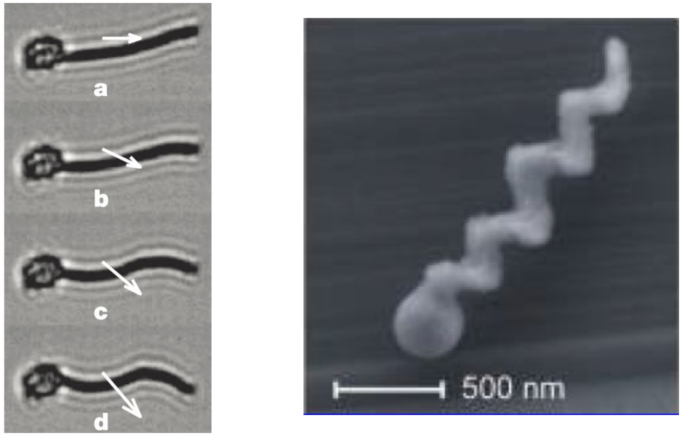


细菌

鸟群

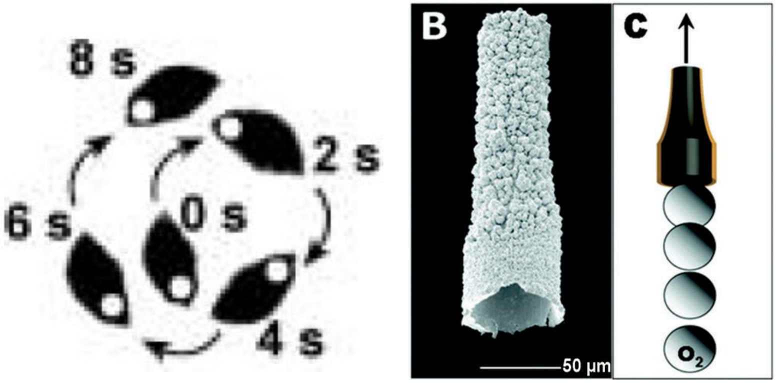
人造 (synthetic) 活力物质

外磁场



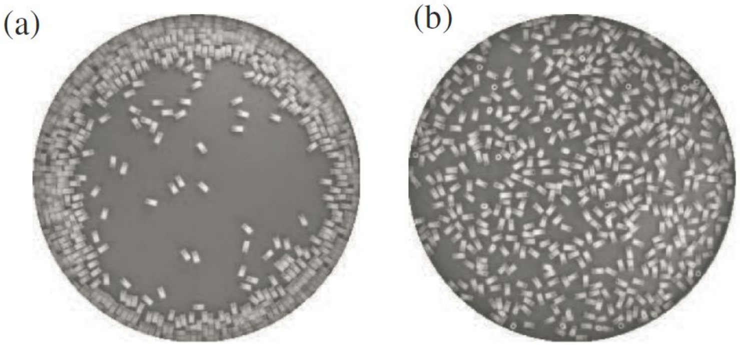
Dreyfus et al (2005) Nature, Ghosh et al (2009) Nanolett

气泡释放



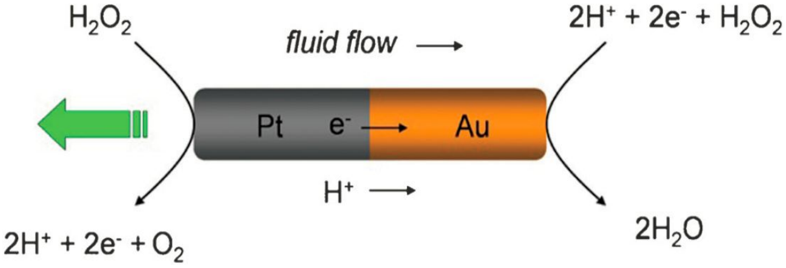
Ismagilov et al (2002) Angew. Chem,Manesh et al (2010) ACS Nano

震动的颗粒



Kudrolli et al (2008) PRL

自泳效应



Paxton et al (2004) JACS

人造活力物质的设计原理

设计的基本规则：

（一）非平衡条件（破坏时间反演对称）
（二）非对称结构 （破坏空间对称性）

驱动机制：

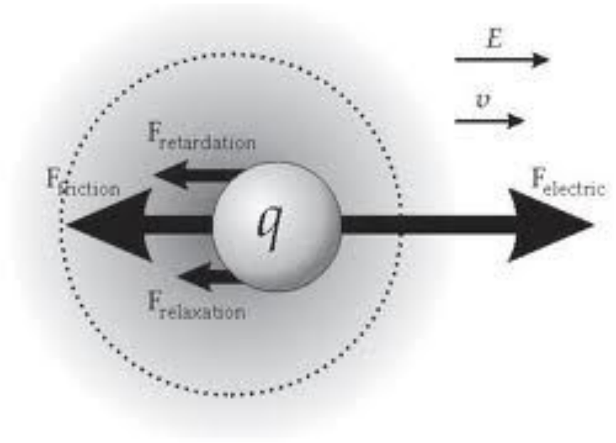
- ✓ 磁场
- ✓ 气泡释放
- ✓ 机械振动
- ✓ 自泳效应 ...

自泳机制的优点：

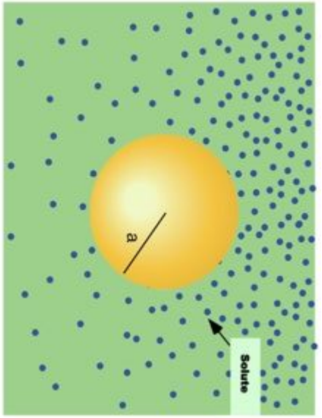
- 单体粒子易于制作（可批量）
- 粒子易于小尺寸化
- 无需变化的外场 ...

泳效应（Phoresis）

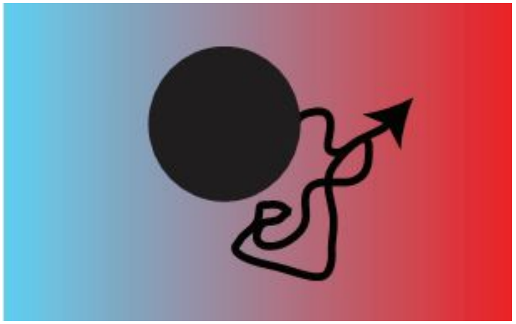
电泳



扩散泳

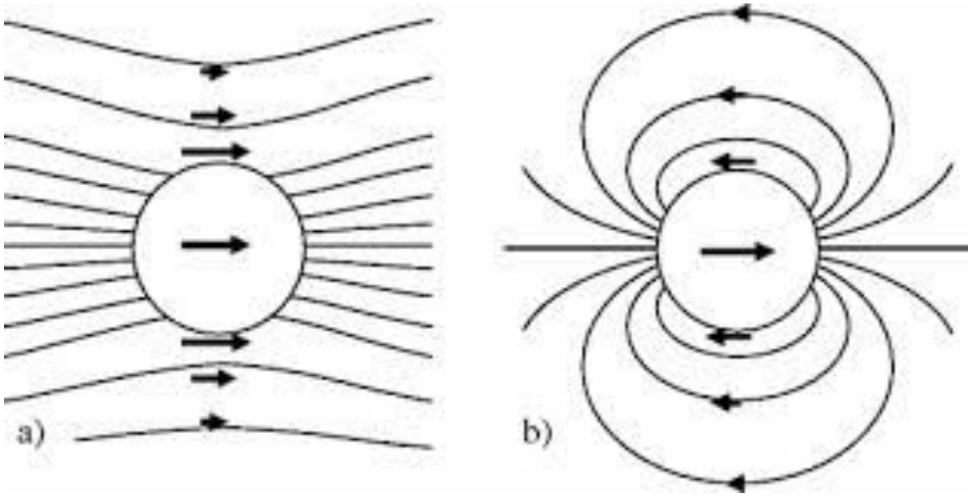


热泳



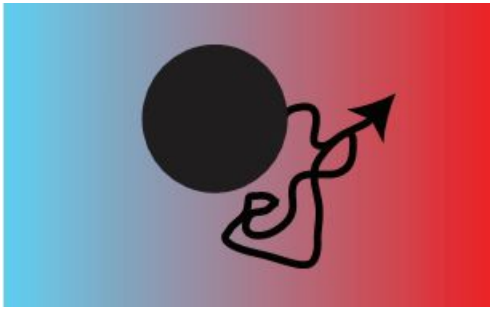
泳力为内力，
正比于梯度场：

$$f = -\alpha \nabla \phi$$

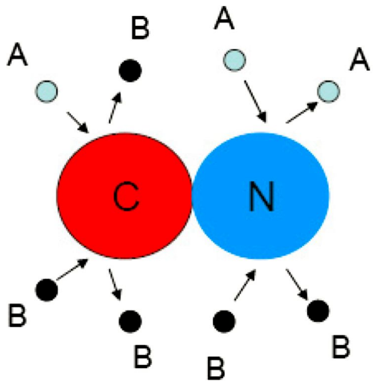


泳效应 → 自泳效应

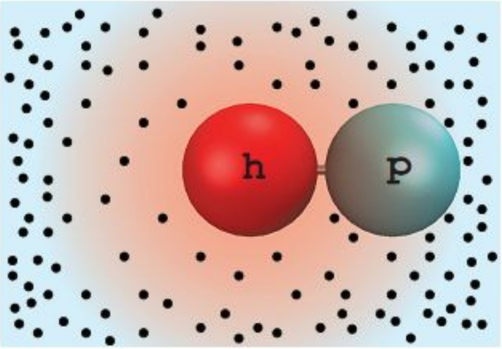
外加梯度场



自产生梯度场



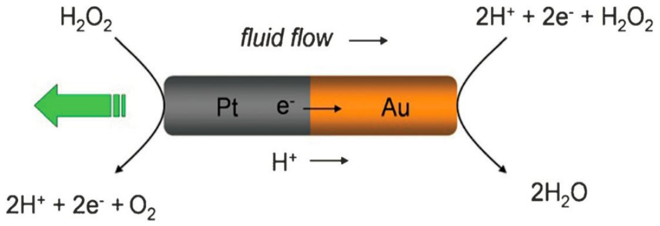
（化学反应）



（吸热）

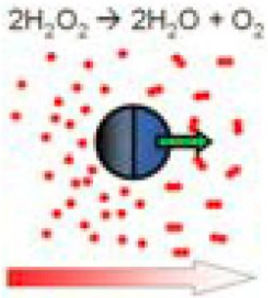
Synthetic self-phoretic microswimmers

self-electrophoresis



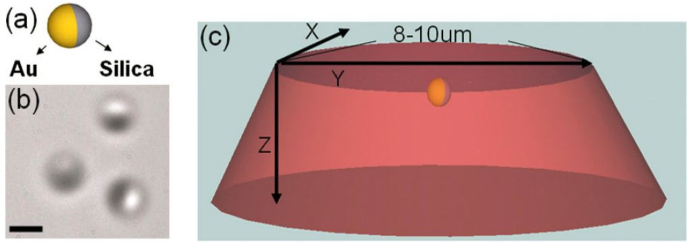
Paxton et al (2004) JACS

self-diffusiophoresis



Howse et al (2007) PRL

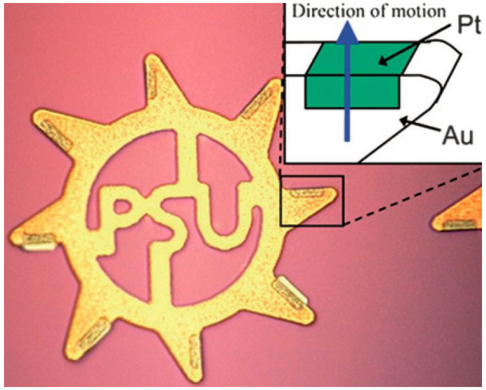
self-thermophoresis



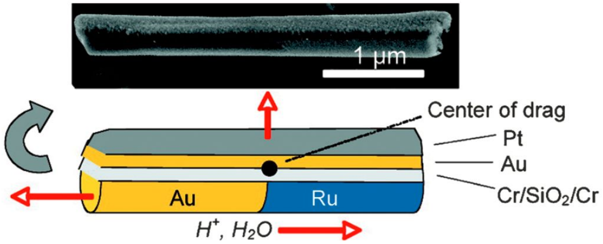
Jiang et al (2010) PRL

Synthetic self-phoretic microrotors

self-electrophoresis

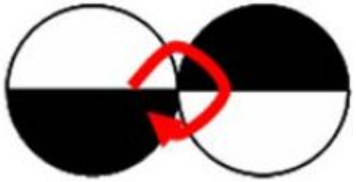


Catchmark et al (2005) Small



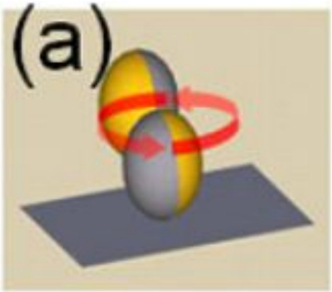
Wang et al (2009) JACS

self-diffusiophoresis



Ebbens et al (2010) PRE

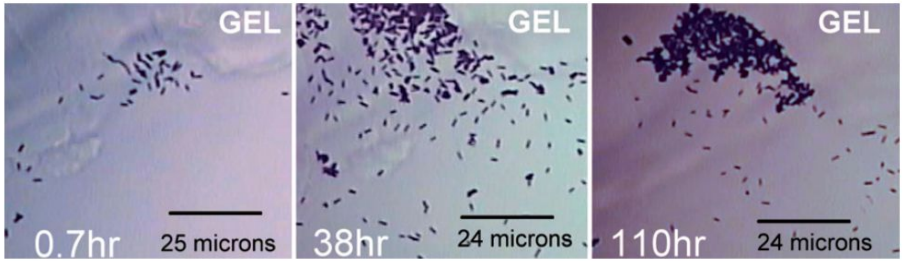
self-thermophoresis



Jiang et al (2010) PRL

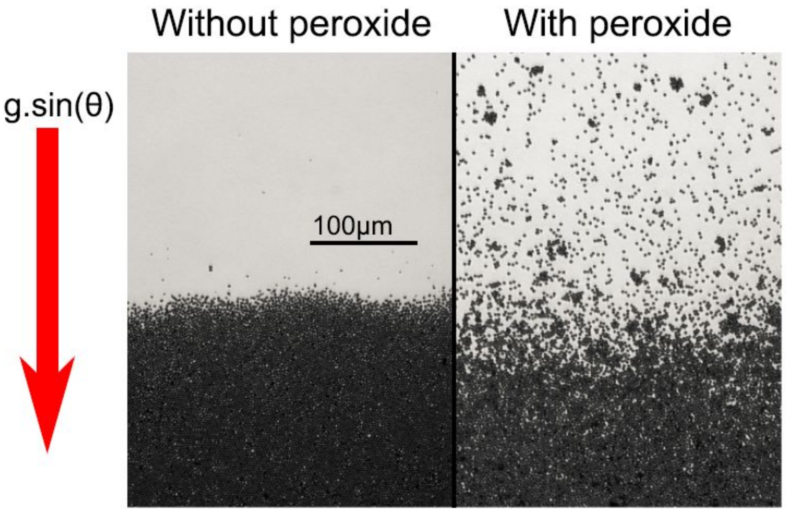
活力胶体溶液

chemotaxis



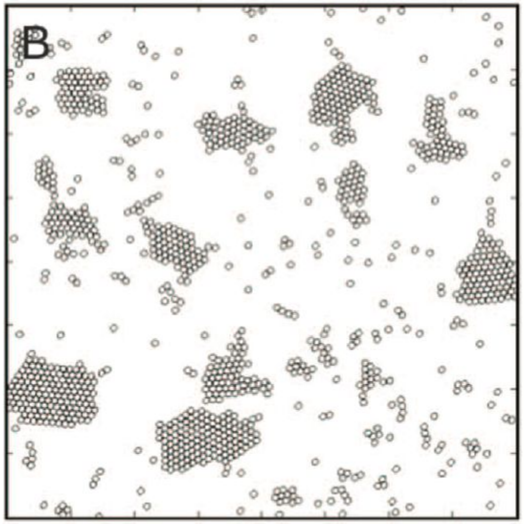
Hong et al (2007) PRL

sedimentation



Theurkauff et al (2012) PRL

living crysical



Palacci et al (2013) Science

Two movies

dilute.mov

concentrate.mov

Palacci et al (2013) Science

What we need in simulation?

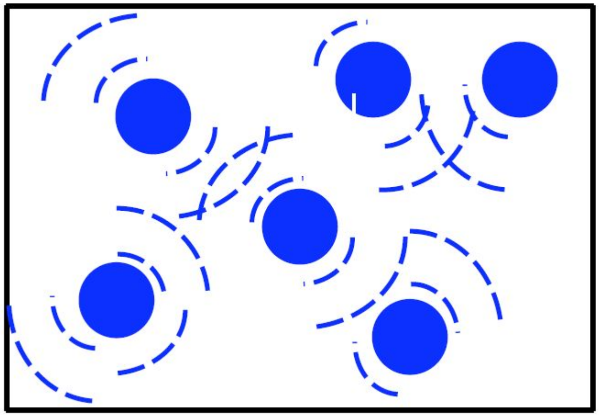
- Colloid-colloid direct interactions

- Colloid-solvent direct interactions
- Thermal fluctuation
- Dissapation
- Mass diffussion
- Heat conduction
- Hydrodynamic interactions

→ Explicit liquid solvent

Hydrodynamic interactions

Mediated by solvent



Continuum limit:

Navier-stokes equation

$$\rho\overbrace{\Bigg(\underbrace{\frac{\partial \mathbf{v}}{\partial t}}_{\text{Unsteady acceleration}} + \underbrace{\mathbf{v}\cdot\nabla\mathbf{v}}_{\text{Convective acceleration}}\Bigg)}^{\text{Inertia (per volume)}} = \overbrace{\underbrace{-\nabla p}_{\text{Pressure gradient}} + \underbrace{\mu\nabla^2\mathbf{v}}_{\text{Viscosity}}}^{\text{Divergence of stress}} + \underbrace{\mathbf{f}}_{\text{Other body forces}}.$$

imcompressible condition

$$\nabla\cdot\mathbf{v} = 0$$

$$\frac{\partial \rho}{\partial t} + \nabla\cdot(\rho\mathbf{v}) = 0$$

Low Reynolds number hydrodynamics

$$\overbrace{\rho\Big(\underbrace{\frac{\partial \mathbf{v}}{\partial t}}_{\text{Unsteady acceleration}} + \underbrace{\mathbf{v}\cdot\nabla\mathbf{v}}_{\text{Convective acceleration}}\Big)}^{\text{Inertia (per volume)}} = \overbrace{\underbrace{-\nabla p}_{\text{Pressure gradient}} + \underbrace{\mu\nabla^2\mathbf{v}}_{\text{Viscosity}}}^{\text{Divergence of stress}} + \underbrace{\mathbf{f}}_{\text{Other body forces}}.$$

Re = $lV\rho/\mu$ << 1, external-force free

Stokes equation $$\nabla^2\mathbf{v} = \frac{1}{\mu}\nabla p$$

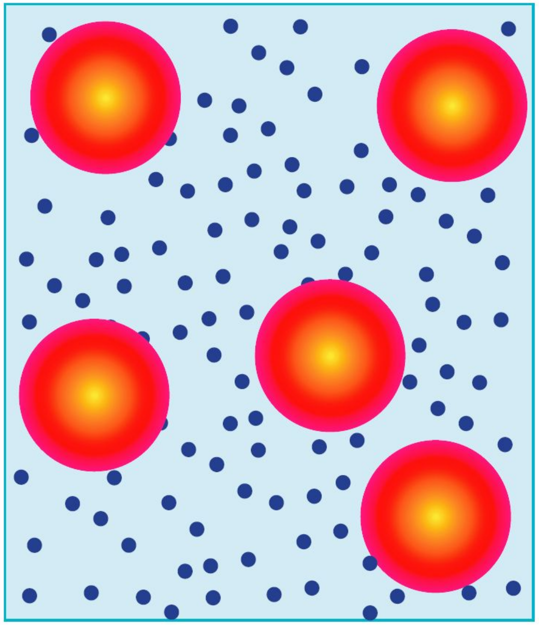
$$\nabla\cdot\mathbf{v} = 0$$

Simulation scheme

Challenge:

Separation of relevant scales

→ Coarse grained solvents



LENGTH SCALES

colloid: 10-1000 nm

solvent: 0.2 nm

TIME SCALES

characteristic time t*

$2Dt^* = a^2$

$t^* \sim \eta a^3/kT$

colloid: $t^* \sim 10^{-7} - 10^{-3}$s

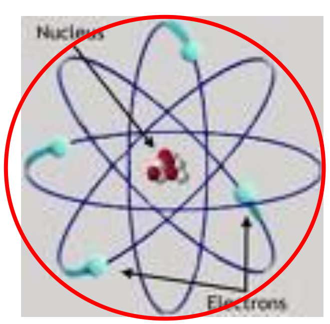
solvent: $t^* \sim 10^{-12}$ s

Hybrid mesoscopic simulation:

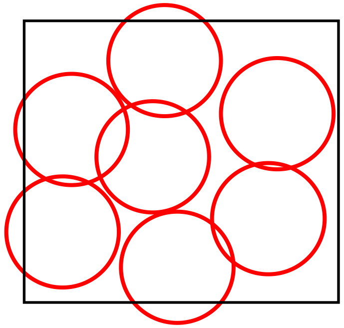
Solvent: Coarse graining method

Colloid: Molecular dynamics (MD)

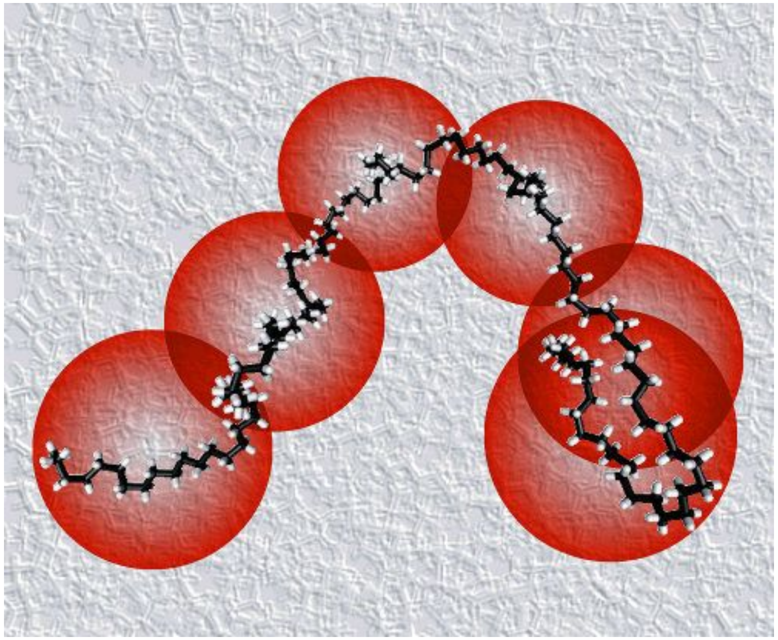
Coarse graining



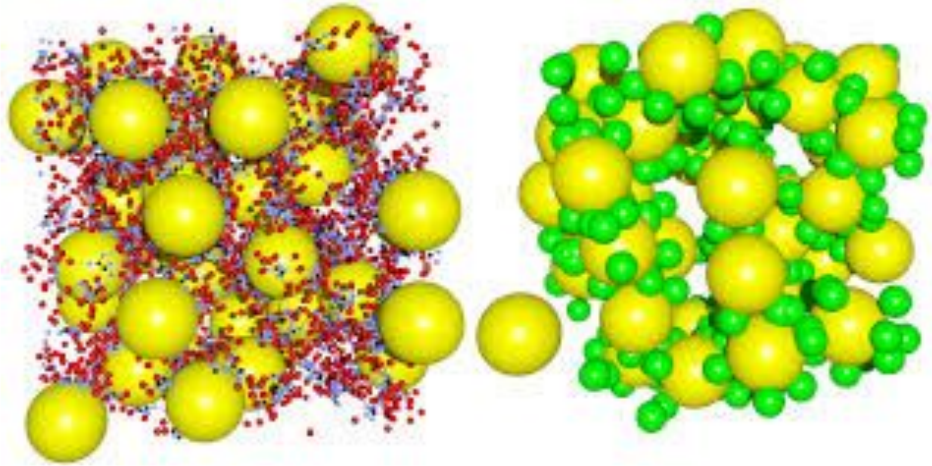
量子模拟



经典模拟



高分子



胶体粒子

Coarse graining solvent

Colloid-solvent direct interactions
Thermal fluctuation
Dissapation
Mass diffussion
Heat conduction
Hydrodynamic interactions

} Local conservation of mass, energy and momentum

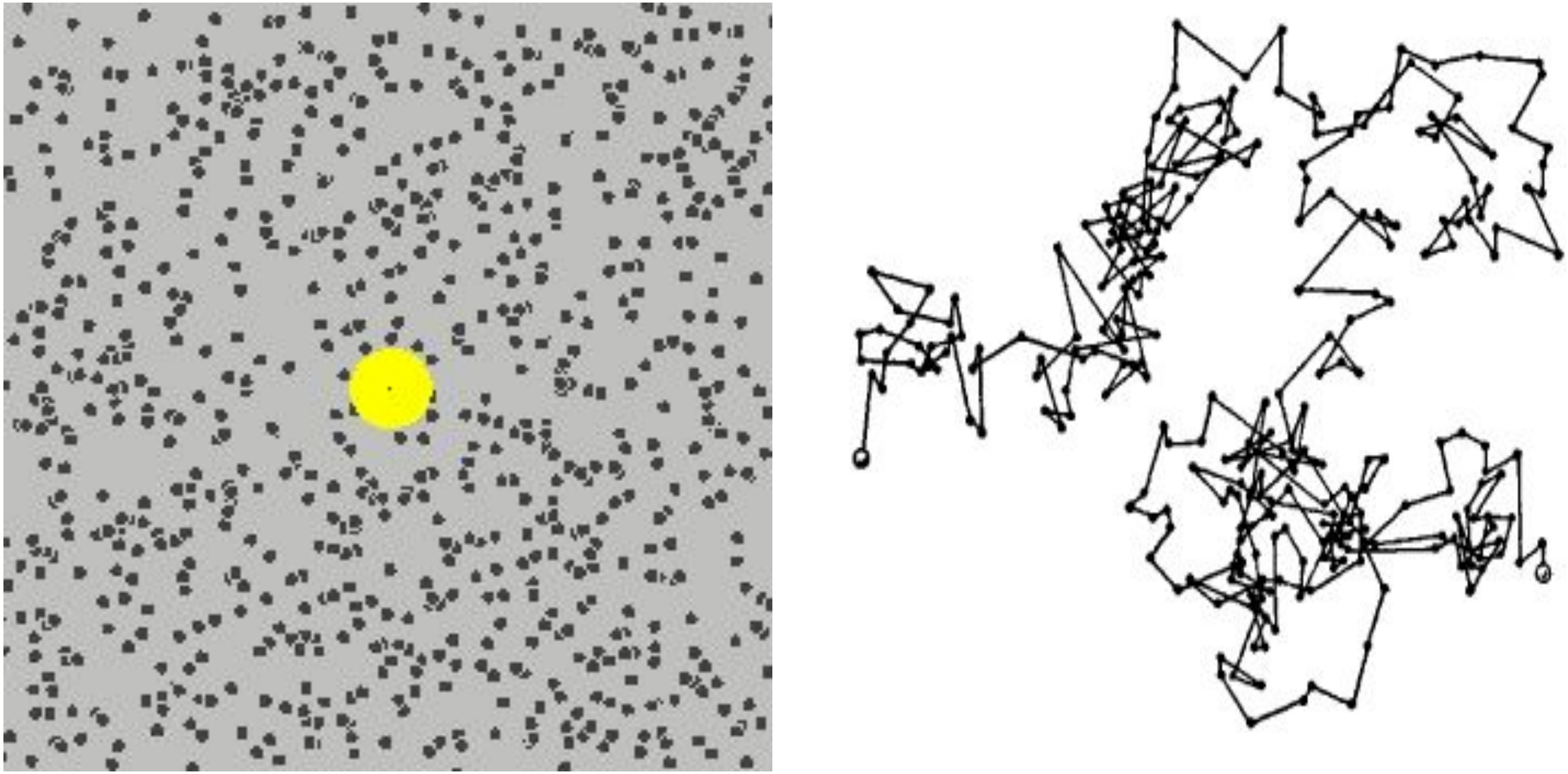
Correct equilibrium description
H-theorem
Galilean invariance
Isotropy
High efficiency

Starting point for construction: basic conserved quantities

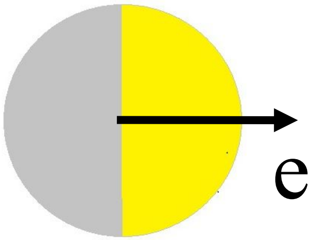
Important coarse graining methods

- Brownian dynamics
- Lattice Boltzmann method
- Dissapative particle dynamics
- Direct simulation monte carlo
- Multiparticle collision particle dynamics

Brownian motion



Brownian dynamics simulation



translational Langevin equation

driving stochastic

（underdamped）

$$m\ddot{\mathbf{r}} = -\gamma_t\dot{\mathbf{r}} + F_d\mathbf{e} + \mathbf{F} + \gamma_t\eta$$

friction interparticle

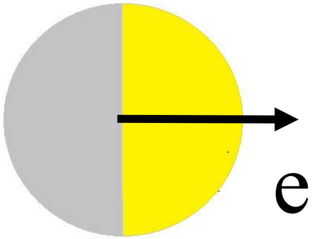
$$\langle \boldsymbol{\eta} \rangle = 0 \qquad \langle \boldsymbol{\eta}_i(t)\boldsymbol{\eta}_j(t') \rangle = 2D_t\mathbf{1}\delta_{ij}\delta(t-t')$$

Einstein relation $D_t = k_B T/\gamma_t$

（overdamped）
long-time scale

$$\dot{\mathbf{r}} = F_d\mathbf{e}/\gamma_t + \mathbf{F}/\gamma_t + \eta$$

Brownian dynamics simulation



<u>rotational Langevin equation</u>

（underdamped）

$$\dot{\mathbf{I}} = \underset{\text{friction}}{\boxed{-\gamma_r \omega}} + \underset{\text{stochastic}}{\boxed{\gamma_r \xi}}$$

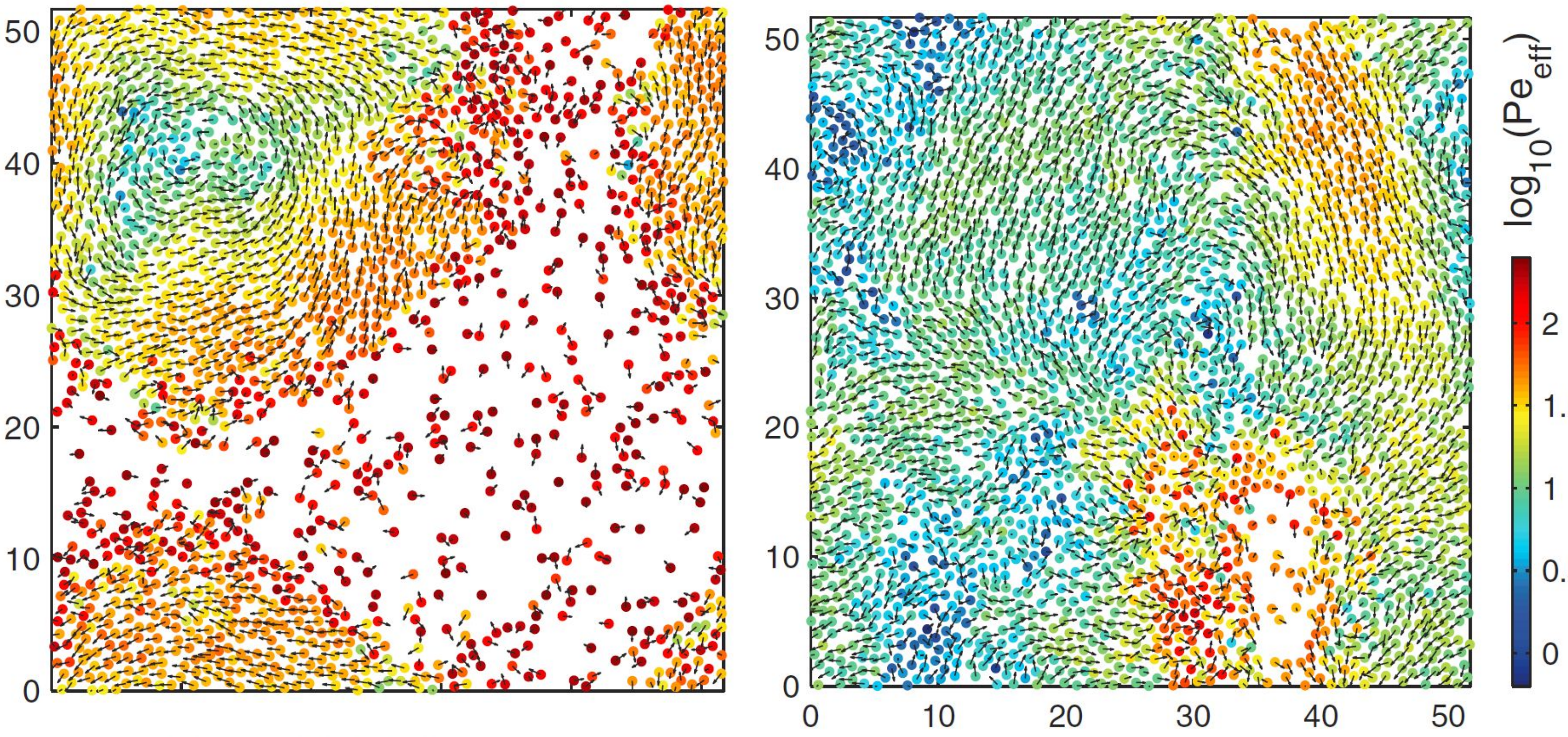
$$\langle \boldsymbol{\xi} \rangle = 0 \qquad \langle \boldsymbol{\xi}_i(t) \boldsymbol{\xi}_j(t') \rangle = 2D_r \mathbf{1} \delta_{ij} \delta(t - t')$$

（overdamped）
long-time scale

$$\dot{\mathbf{e}} = \boldsymbol{\xi} \times \mathbf{e}$$

Brownian dynamics simulation

self-propelled Brownian particle



$(\phi = 0.3375)$

$(\phi = 0.6)$

Coarse graining solvent

Colloid-solvent direct interactions
Thermal fluctuation
Dissapation
Mass diffussion
Heat conduction
Hydrodynamic interactions

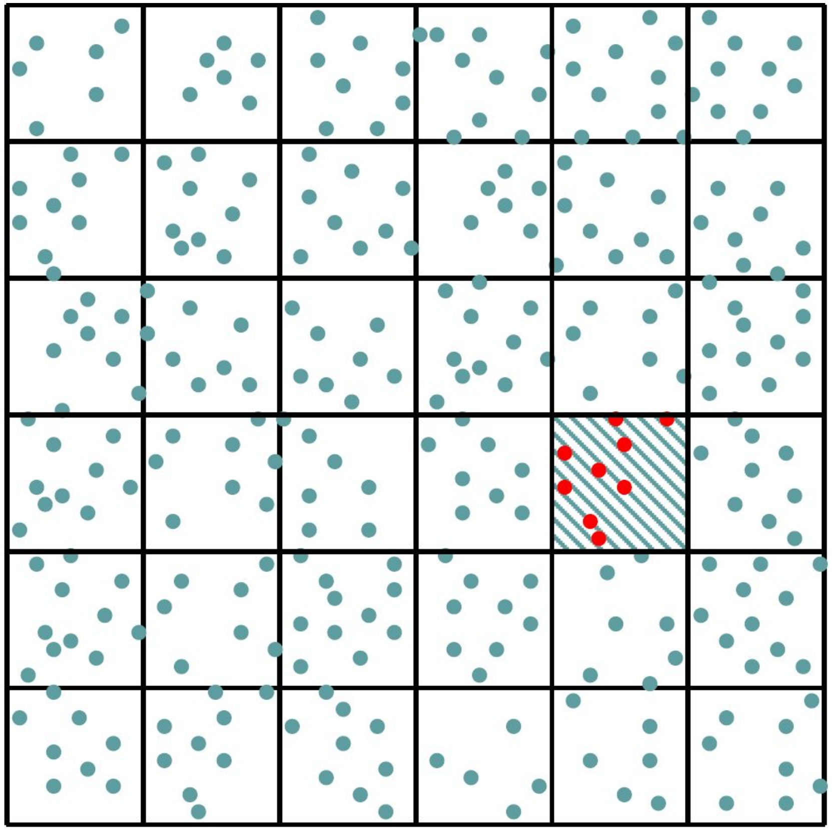
Local conservation of mass, energy and momentum

Correct equilibrium description
H-theorem
Galilean invariance
Isotropy
High efficiency

Starting point for construction: basic conserved quantities

Multiparticle collision dynamics method

N point particles {
- continuous positions $\boxed{\mathbf{r}_i(t)}$
- continuous velocities $\boxed{\mathbf{v}_i(t)}$
- discrete time increment $\boxed{h}$



Dynamics in two steps:
- ➢ Streaming
- ➢ Collision

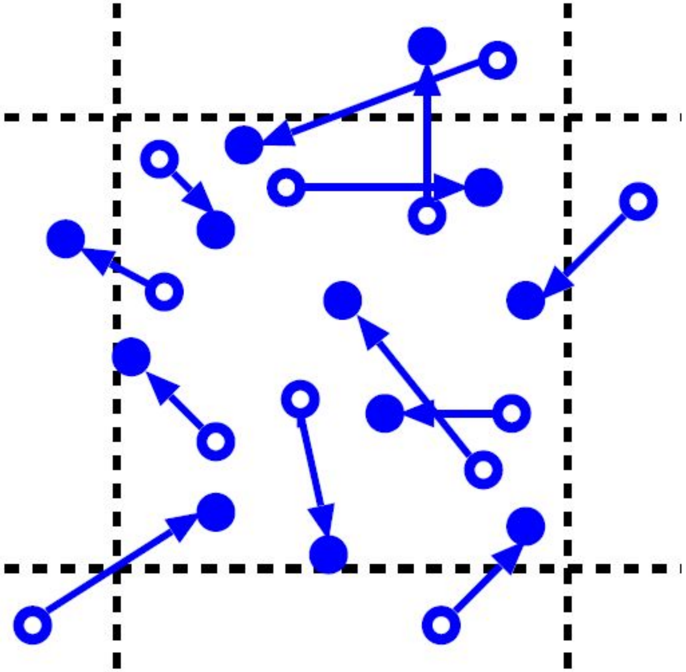
Malevanets, Kapral (1999) JCP

Kapral (2008) Adv. Chem. Phys.

Gompper et al (2009) Adv. Polym. Sci.

Padding and Louis (2006) PRE

Streaming step

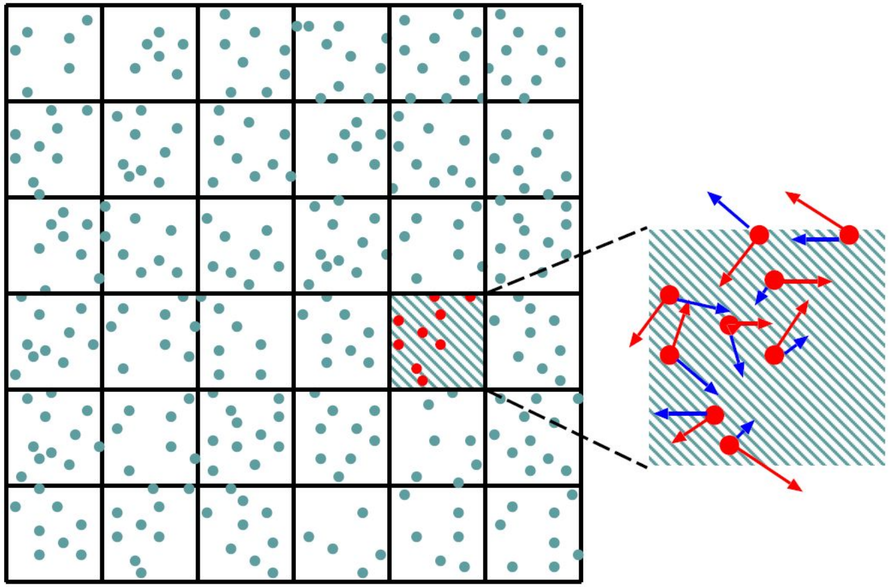


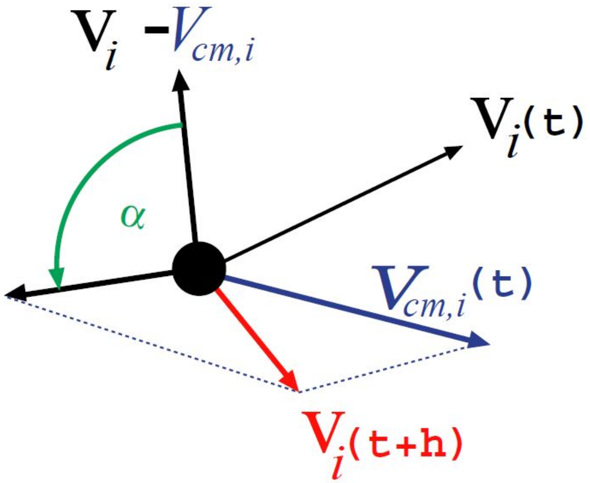
- ballistic motion

$$\boxed{\mathbf{r}_i(t+h) = \mathbf{r}_i(t) + h\mathbf{v}_i(t)}$$

Collision step

- Particles are sorted into collision boxes
- Interchange momentum within the particles of the box.





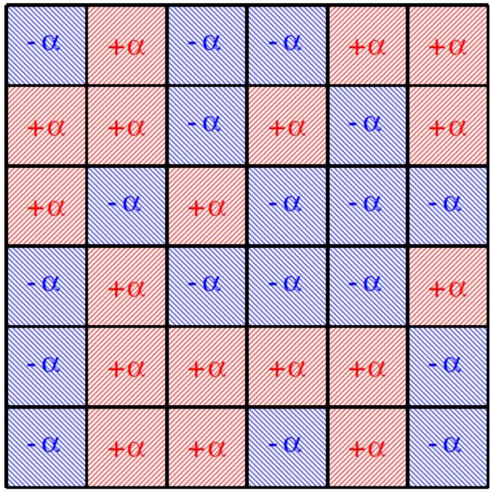
- center of mass velocity

$$\mathbf{v}_{cm,i}(t) = \frac{\sum_{j\in C_i}^{n_i} m\mathbf{v}_j(t)}{\sum_{j\in C_i}^{n_i} m}$$

- stochastic rotation by angle α

$$\boxed{\mathbf{v}_i(t+h) = \mathbf{v}_{cm,i}(t) + \mathcal{R}(\alpha)\left[\mathbf{v}_i(t) - \mathbf{v}_{cm,i}(t)\right]}$$

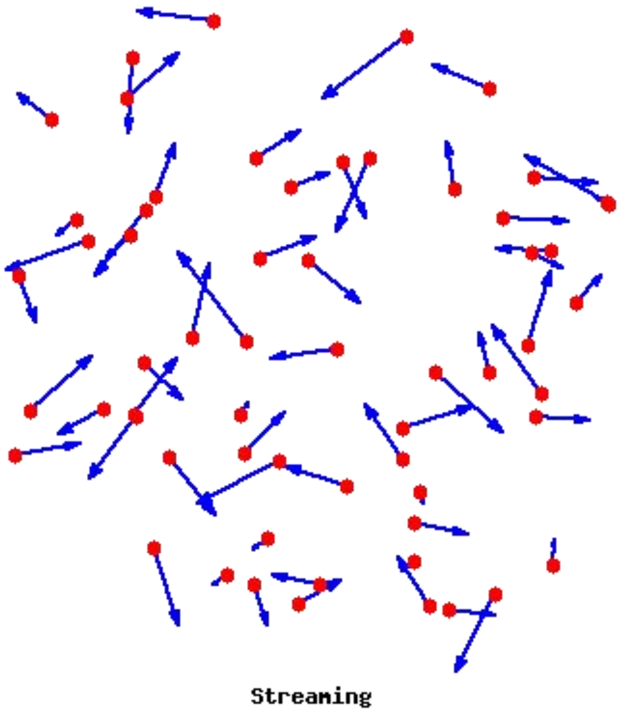
Rotational collisin in 2D



-α	+α	-α	-α	+α	+α
+α	+α	-α	+α	-α	+α
+α	-α	+α	-α	-α	-α
-α	+α	-α	-α	-α	+α
-α	+α	+α	+α	+α	-α
-α	+α	+α	-α	+α	-α

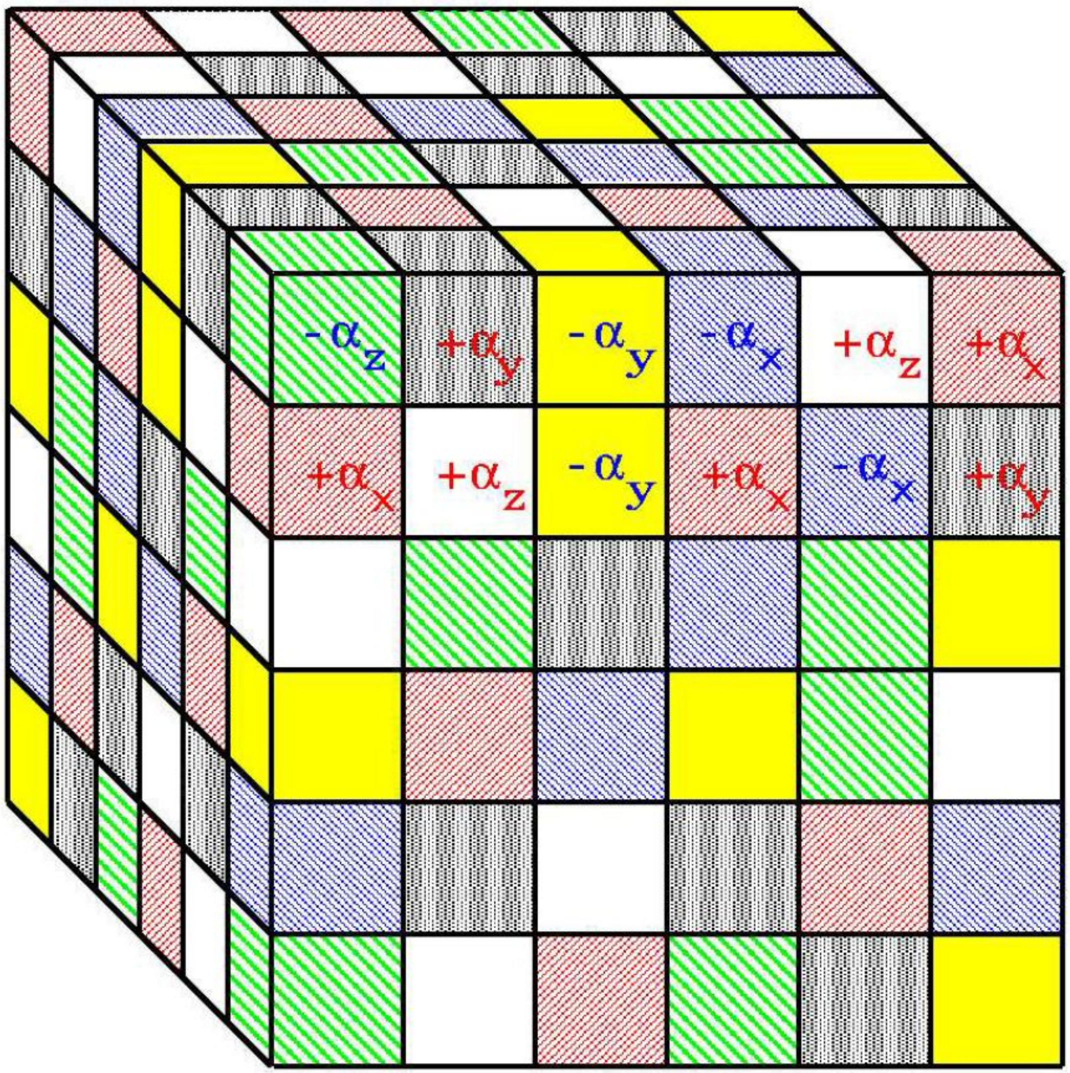
$$\mathcal{R}(\alpha) \equiv \begin{pmatrix} \cos\alpha & \pm\sin\alpha \\ \mp\sin\alpha & \cos\alpha \end{pmatrix}$$

$$\mathbf{v}_i(t+h) = \mathbf{v}_{cm,i}(t) + \mathcal{R}(\alpha)\left[\mathbf{v}_i(t) - \mathbf{v}_{cm,i}(t)\right]$$



Stochastic rotation dynamics — SRD

Rotational collisin in 3D



Rotational collisin in 3D

- Random direction $\mathbf{R} = (R_x, R_y, R_z)$

random numbers r_1, $r_2\ \epsilon[0,1]$

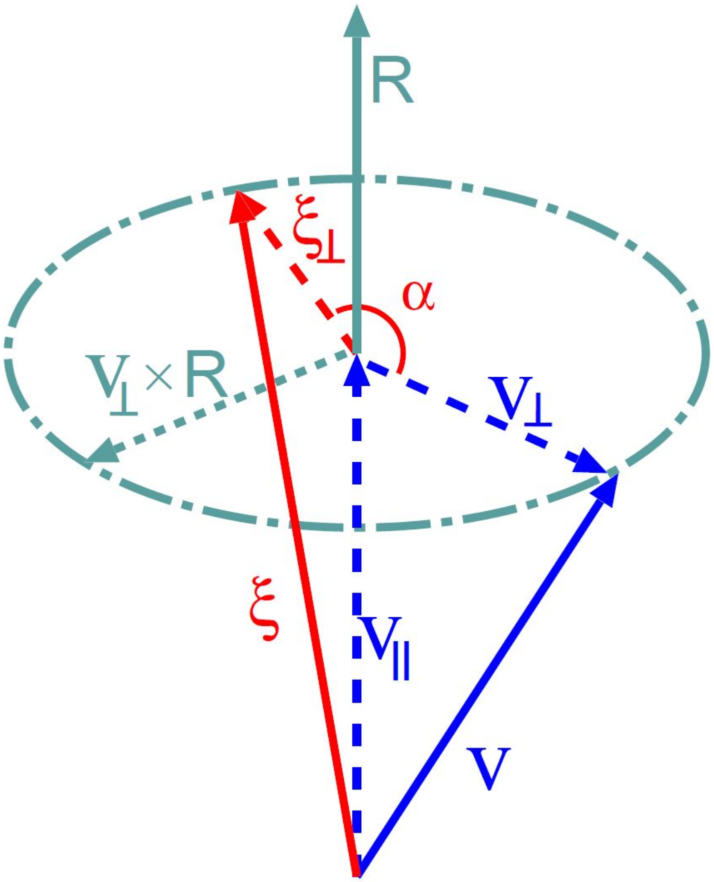
$$\left.\begin{array}{l}\varphi_1 = 2r_1 - 1\\ \varphi_2 = 2\pi r_2\end{array}\right\} \leftrightarrow \left\{\begin{array}{lcl}R_x &=& \sqrt{1-\varphi_1^2}\ \cos\varphi_2\\ R_y &=& \sqrt{1-\varphi_1^2}\ \sin\varphi_2\\ R_z &=& \varphi_1\end{array}\right.$$

- Rotation of $\mathbf{v}$ around $\mathbf{R}$ by an angle α

$$\boxed{\mathbf{v} \longrightarrow \xi \equiv \mathcal{R}(\alpha)\mathbf{v}}$$

$$\mathbf{v} = \mathbf{v}_{||} + \mathbf{v}_{\perp} \left\{\begin{array}{l}\mathbf{v}_{||} = (\mathbf{R}\cdot\mathbf{v})\mathbf{R}\\ \mathbf{v}_{\perp} = \mathbf{v} - \mathbf{v}_{||}\end{array}\right.$$

$$\boxed{\xi = \mathbf{v}_{||} + \mathbf{v}_{\perp}\cos\alpha + (\mathbf{v}_{\perp}\times\mathbf{R})\sin\alpha}$$



Conservation of mass, momentum and energy

- Streaming step locally conserves everything!
- Collision step locally conserves mass
- In cell level, collision locally conserves momentum

$$\sum_{j}^{(i,t)} m\mathbf{v}_j(t+h) = \sum_{j}^{(i,t)} m\left(\mathbf{v}_{cm,i}(t) + \mathcal{R}(\alpha)\left[\mathbf{v}_j(t) - \mathbf{v}_{cm,i}(t)\right]\right) = \sum_{j}^{(i,t)} m\mathbf{v}_j(t)$$

- In cell level, collision locally conserves energy

$$\sum_{j}^{(i,t)} \frac{m}{2} v_j^2(t+h) = \sum_{j}^{(i,t)} \frac{m}{2}\left(\mathbf{v}_{cm,i}(t) + \mathcal{R}(\alpha)\left[\mathbf{v}_j(t) - \mathbf{v}_{cm,i}(t)\right]\right)^2 = \sum_{j}^{(i,t)} \frac{m}{2} v_j^2(t)$$

→ {
Hydrodynamic behaviors
Heat conduction
Mass transport
Thermal fluction (intrinsic)

(microcanonical ensemble)

Anderson thermostat MPC

Collision rule:

$$\mathbf{v}_i(t+h) = \mathbf{v}_{cm,i}(t) + \mathbf{v}_i^{ran} - \frac{1}{N_C}\sum_{j\in cell} \mathbf{v}_j^{ran}$$

$\mathbf{v}_i^{ran}$	random number from Maxwellian distribution
N_C	the number of particles in collision cell

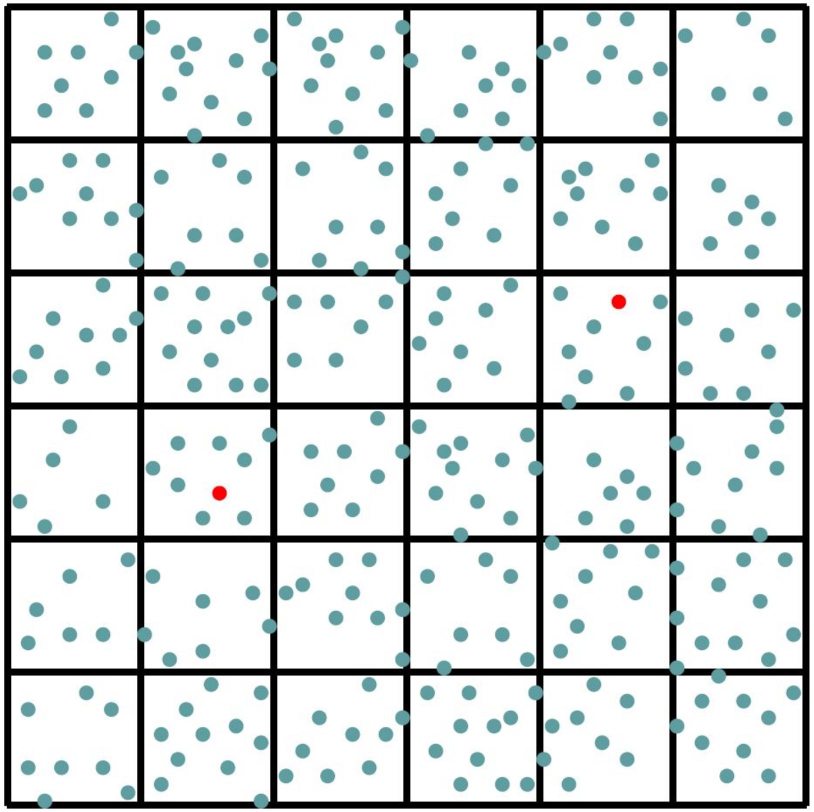
Locally conserve mass and momentum, but not energy (canonical ensemble)

Coarse graining solvent

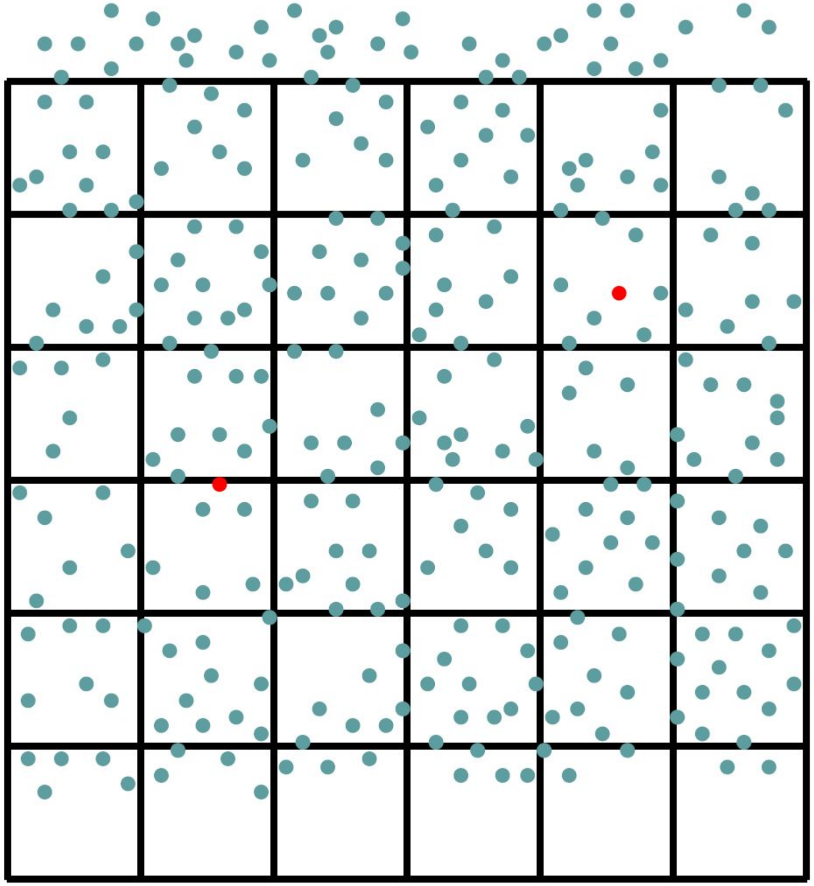
Thermal fluctuation
Dissapation
Mass diffussion
Heat conduction
Hydrodynamic interactions
Correct equilibrium description
H-theorem
Galilean invariance
Isotropy
High efficiency

Galilean invariance

System with $\mathbf{v} = 0$

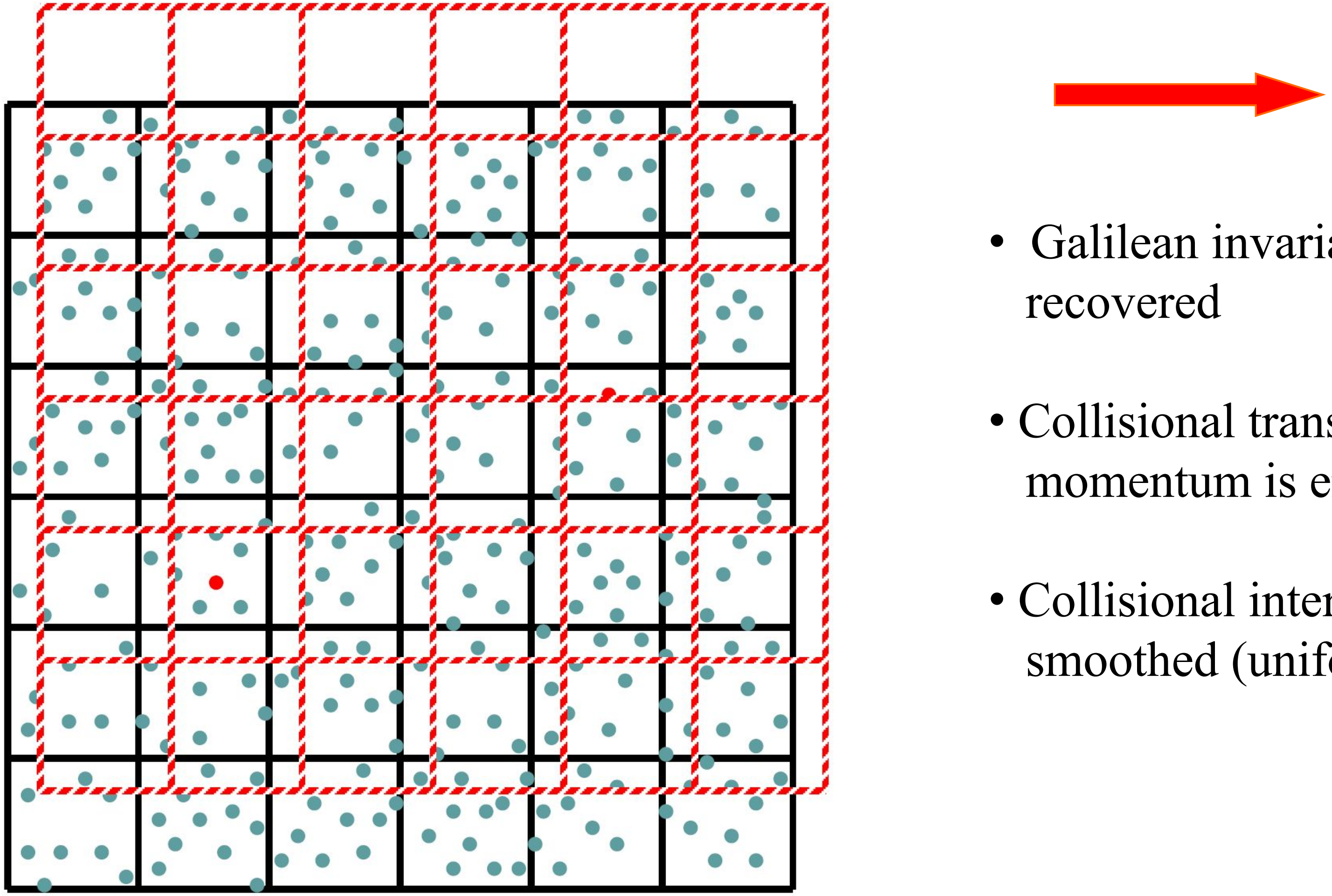


System with $\mathbf{v} \neq 0$



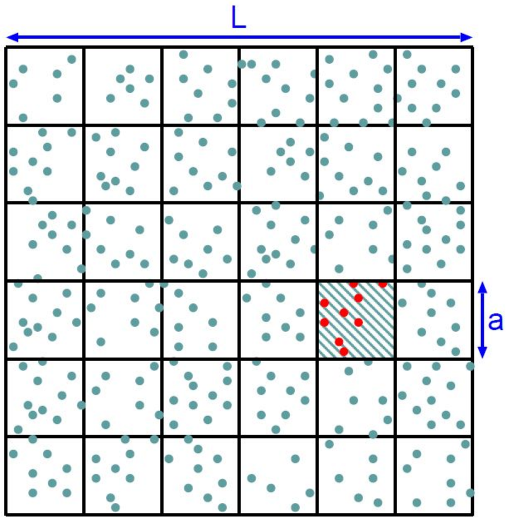
Breakdown of Galilean invariance

Random shift



- Galilean invariance is recovered
- Collisional transfer of momentum is enhanced
- Collisional interaction is smoothed (uniform)

MPC units and parameters



Mass unit: $m \equiv$ particle mass

Length unit: $a \equiv$ collision box size

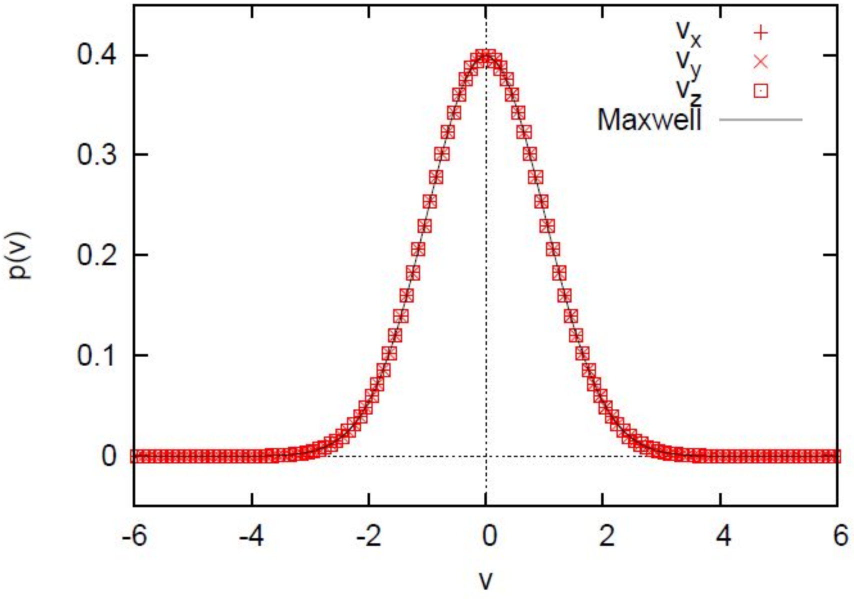
Energy units: $k_B T \equiv$ system temperature

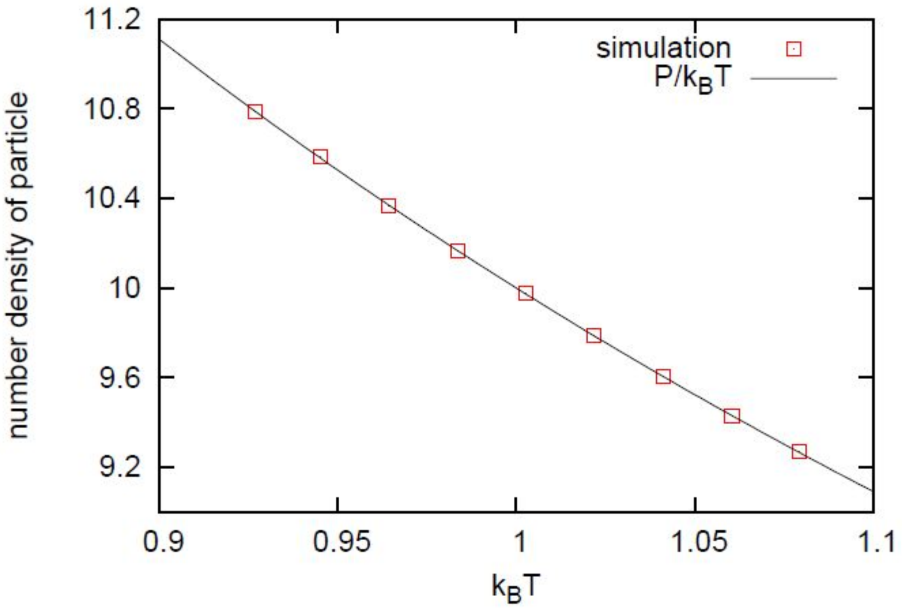
$\Rightarrow$ Time units $\hat{t} \sim t\, a\sqrt{k_B T/m}$

$$\left.\begin{array}{ll}\text{Streaming:} & \mathbf{r}_i(t+h) = \mathbf{r}_i(t) + h\mathbf{v}_i(t) \\ \text{Collision:} & \mathbf{v}_i(t+h) = \mathbf{v}_{cm,i}(t) + \mathcal{R}(\alpha)\left[\mathbf{v}_i(t) - \mathbf{v}_{cm,i}(t)\right]\end{array}\right\} \leftrightarrow \left\{\begin{array}{rl}\text{Collision time:} & \boxed{h} \\ \text{Rotation angle:} & \boxed{\alpha}\end{array}\right.$$

- Number density $\boxed{\rho} = \dfrac{N}{a^d}$
- Mean free path $\lambda = h\sqrt{\dfrac{k_B T}{m a^2}}$

Velocity distribution and equation of state



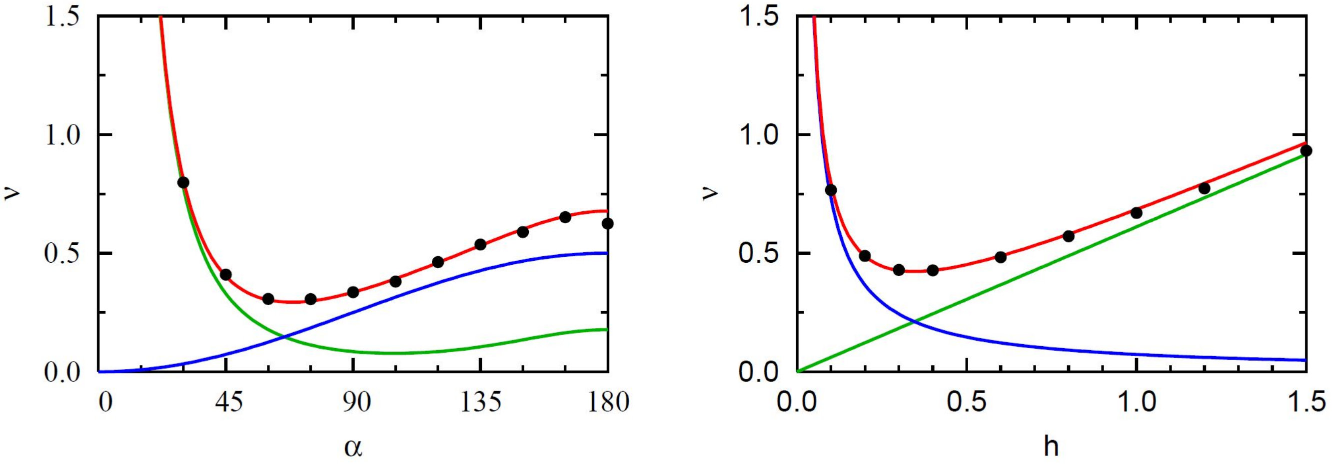


MPC: liquid-like dynamics, but gas-like thermodynamics

Viscosity and diffusion

Transport coefficient	Dimension (d)	Kinetic (terms below to be multiplied by $k_B T\tau/2m$)	Collisional (terms below to be multiplied by a^2/τ)
Shear viscosity, ν	2	$\dfrac{M}{(M-1+e^{-M})\sin^2(\alpha)}-1$	$\dfrac{1}{6dM}(M-1+e^{-M})[1-\cos(\alpha)]$
	3	$\dfrac{5M}{(M-1+e^{-M})[2-\cos(\alpha)-\cos(2\alpha)]}-1$	
Thermal diffusivity, D_T	2	$\dfrac{d}{1-\cos(\alpha)}-1+\dfrac{2d}{M}\left(\dfrac{7-d}{5}-\dfrac{1}{4}\csc^2(\alpha/2)\right)$	$\dfrac{1}{3(d+2)M}\left(1-\dfrac{1}{M}\right)[1-\cos(\alpha)]$
	3		
Self-diffusion coefficient, D	2	$\dfrac{dM}{[1-\cos(\alpha)](M-1+e^{-M})}-1$	—
	3		

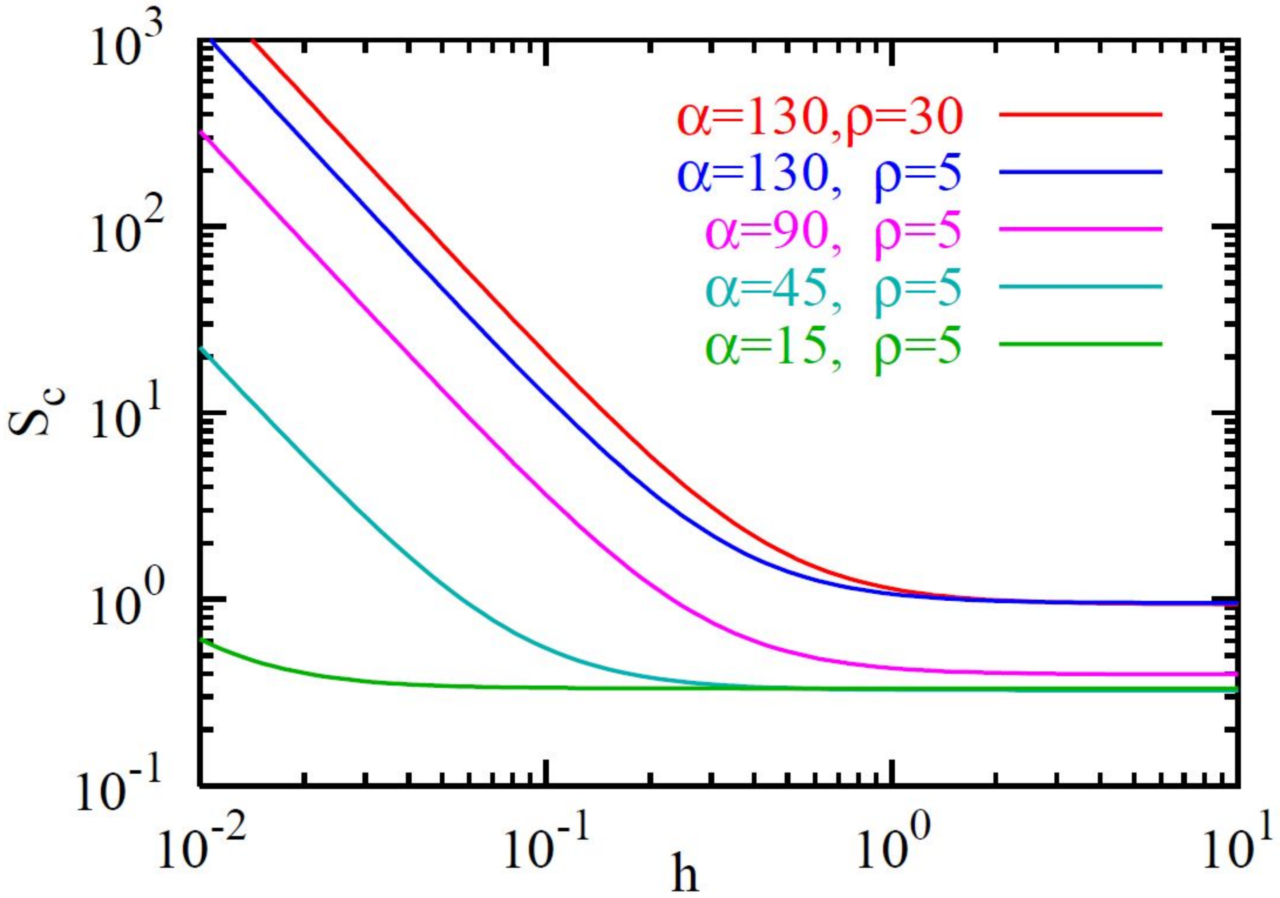
viscosity



Important dimensionless number (I)

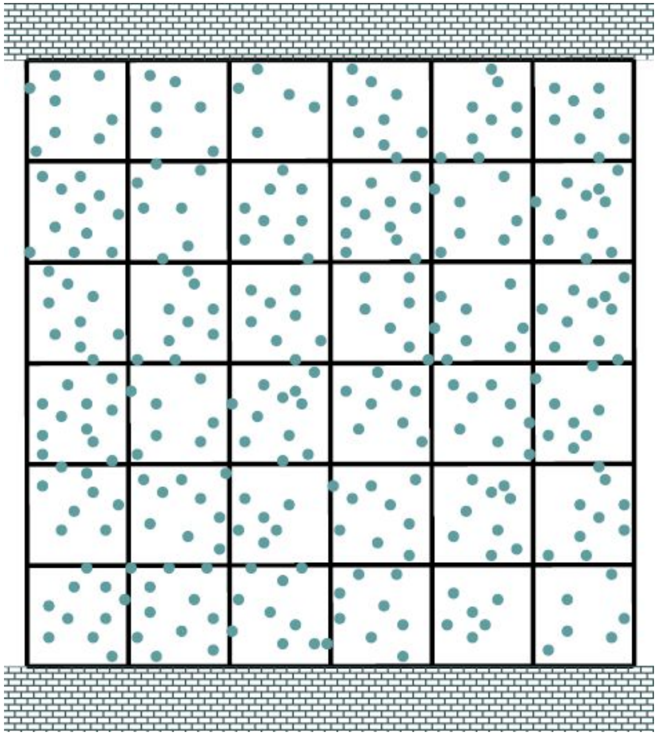
- Schmidt number $\mathrm{Sc} = \dfrac{\nu}{D_f}$ diffusive momentum transfer / diffusive mass transfer

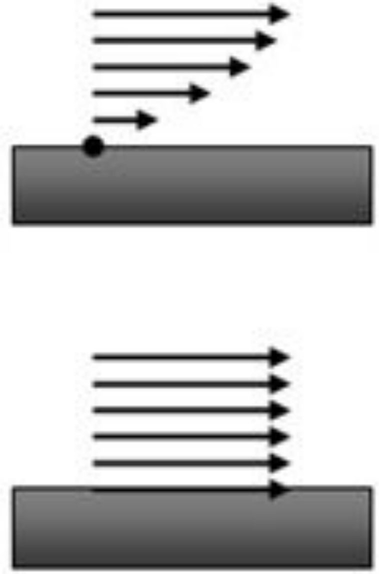
Liquid: $\mathrm{Sc} \gg 1$ (simulation ~ 10)



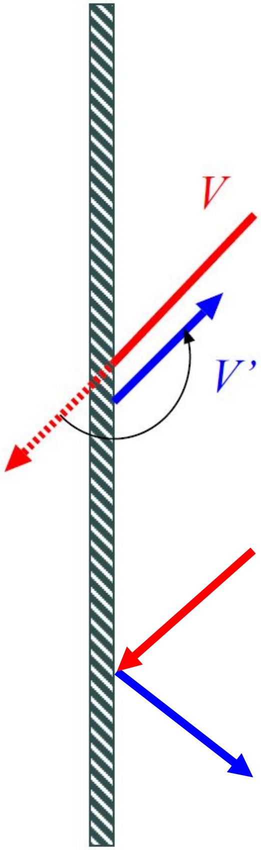
Boundary conditions

- Periodic boundary
- Stick (noslip) wall boundary
- Slip wall boundary



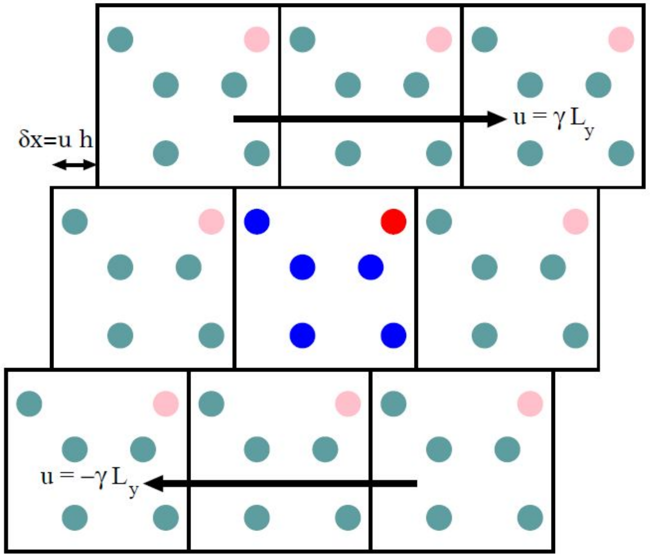


streaming step



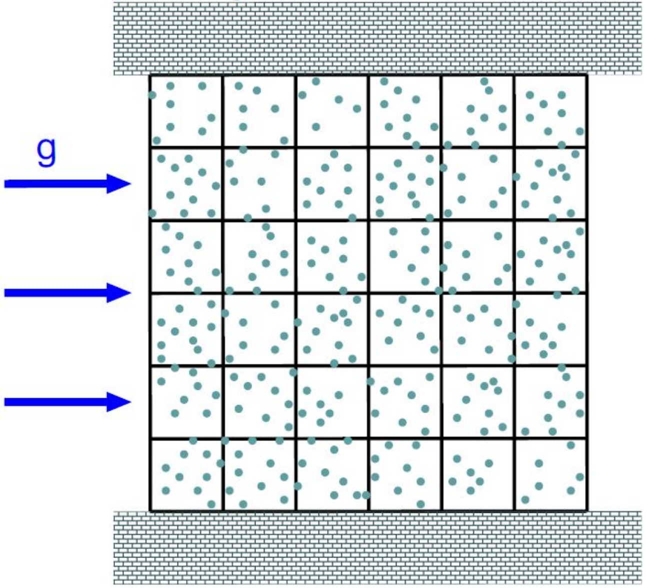
External flow: shear and capillary

Shear flow

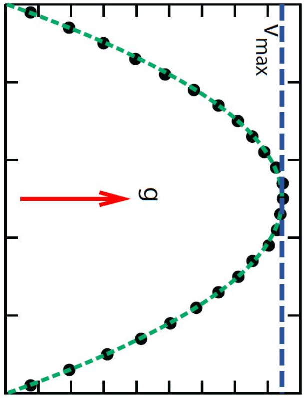


Lees Edwalds

Capillary flow

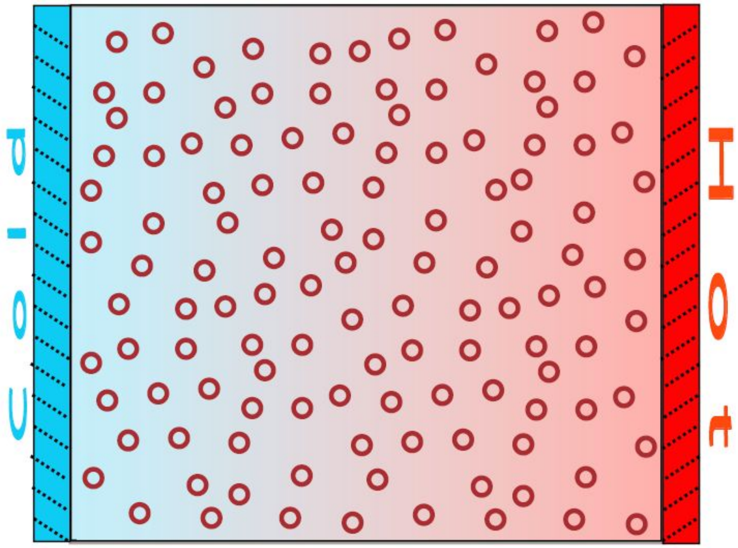


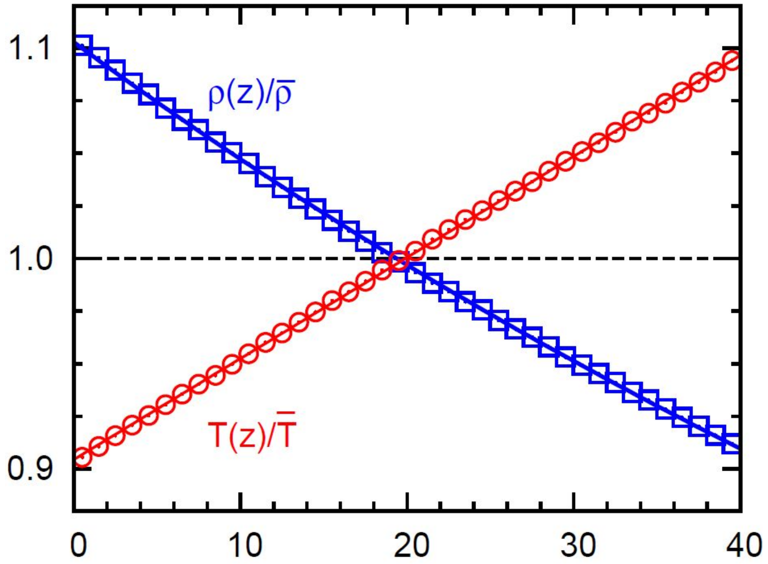
external force+stick boundary



Thermostat and temperature gardient

Define hot and cold layers; rescale particle thermal energy



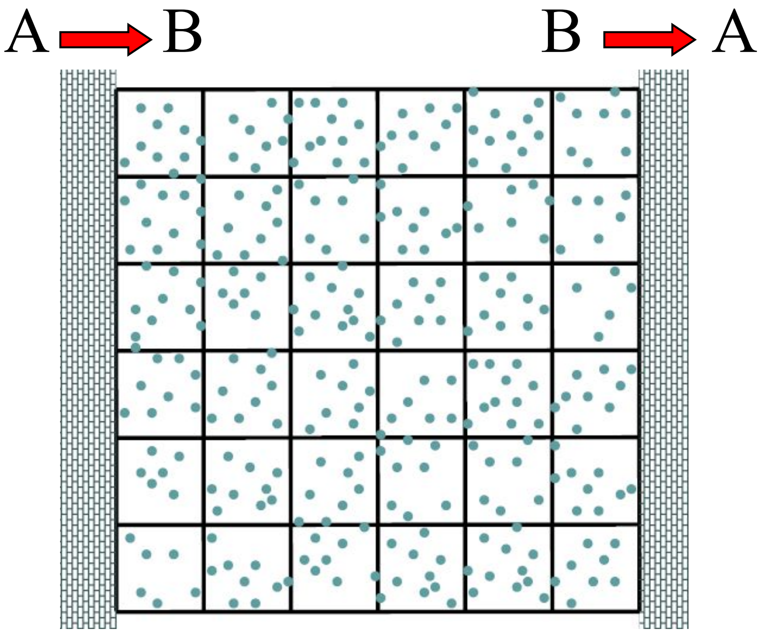


boundary thermostat

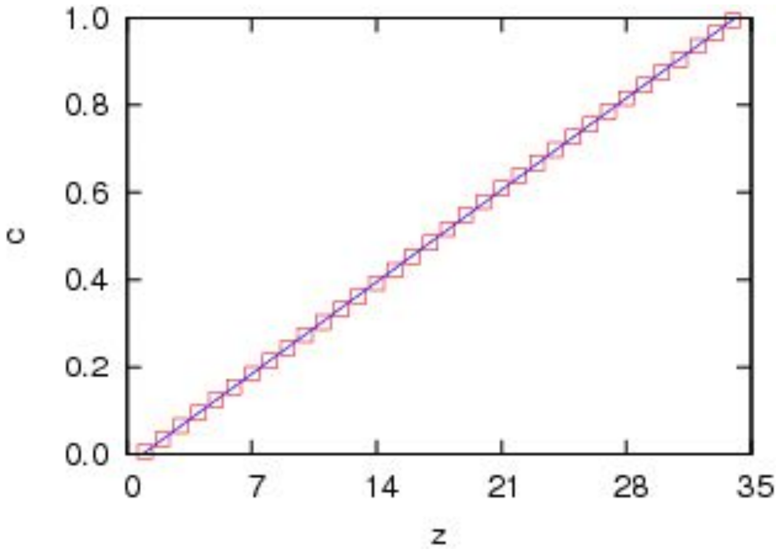
temperature and density distribution

Chemical reaction and concentration gardient

Define reaction layers; change particle's species

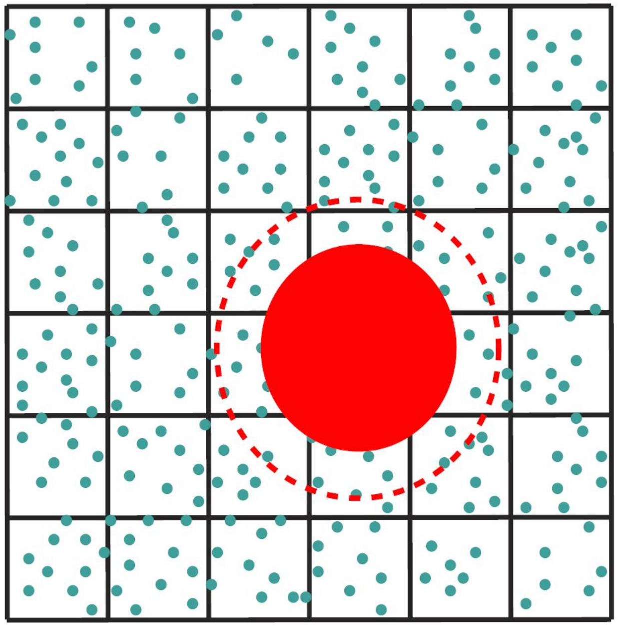


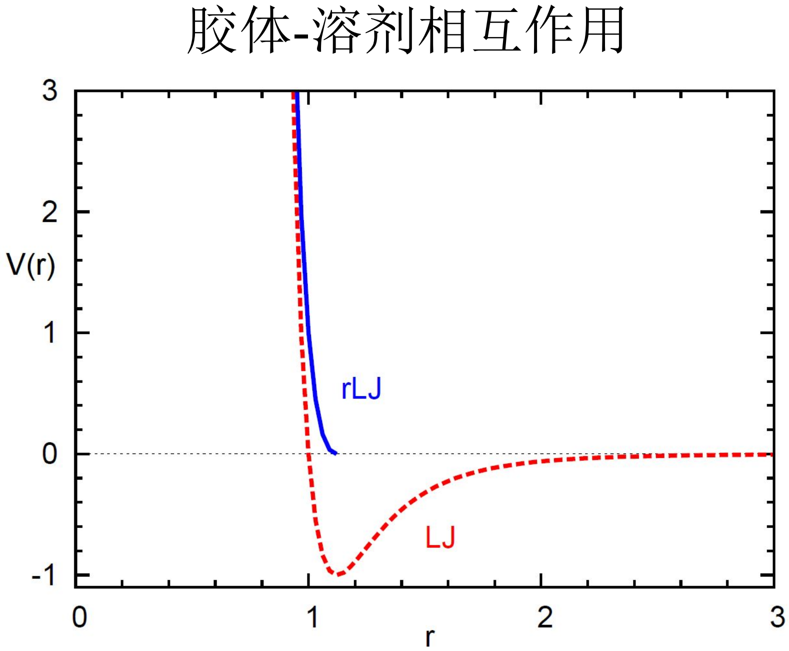
boundary reaction



concentration distribution of species A

Colloid-solvent coupling: molecular dynamics

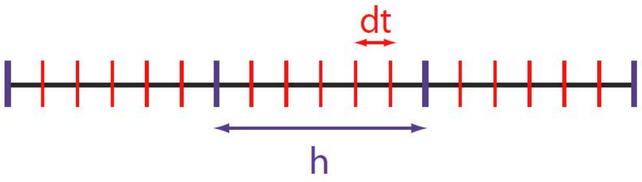




$$U(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{2k} - \left(\frac{\sigma}{r}\right)^{k}\right] + C, r \le r_c$$

Combine MPC with MD

- Solvent - solvent interactions: MPC
- Solute - solute interactions: MD
- Solute - Solvent interactions: MD



dt MD time integration: solute & solvent

h MPC interaction: only solvent-solvent collisions

Important time scales

Heat conduction: $\tau_\kappa = \sigma^2/\kappa$ κ.- heat diffusivity

Colloid mass diffusion : $\tau_D = \sigma^2/D$ D.- diffusion coefficient

Momentum diffusion: $\tau_\nu = \sigma^2/\nu$ ν.- kinematic viscosity

In experiments $\tau_D \gg \tau_\kappa > \tau_\nu$

In simulations $\frac{\tau_D}{\tau_\kappa} \simeq 10^2$ $\frac{\tau_\kappa}{\tau_\nu} \simeq 5$

Important dimensionless number (II)

- Reynolds number $\mathrm{Re} = \frac{v_s a}{\nu}$ inertial force / viscous force

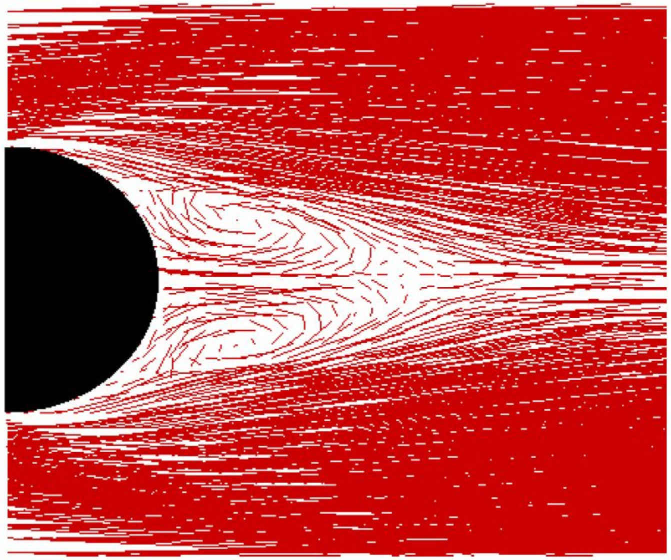
Low Re region $\mathrm{Re} \ll 1$ (simulation < 0.1)

- Knudsen number $\mathrm{Kn} = \frac{\lambda_{\mathrm{free}}}{a}$ mean free path / particle size

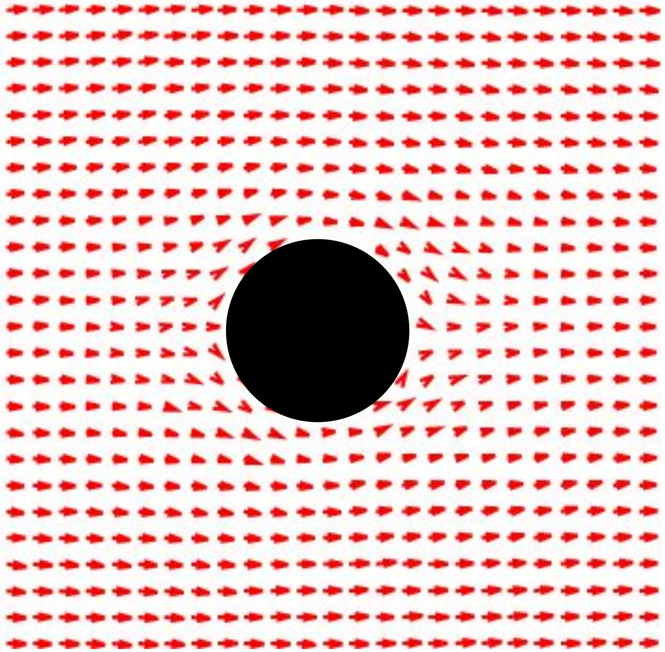
Liquid (continuum) $\mathrm{Kn} \ll 1$ (simulation < 0.05)

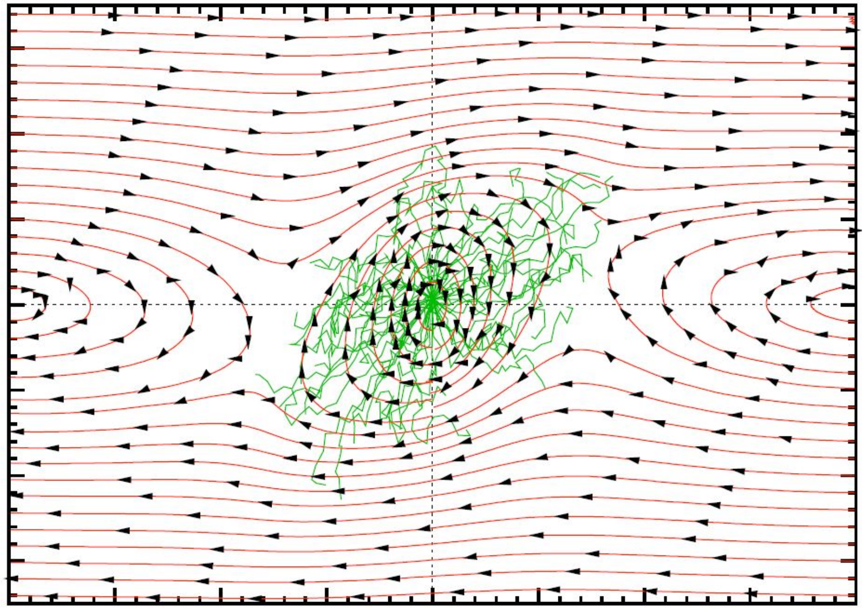
Examples of flow field

flow past sphere with high Re



with low Re

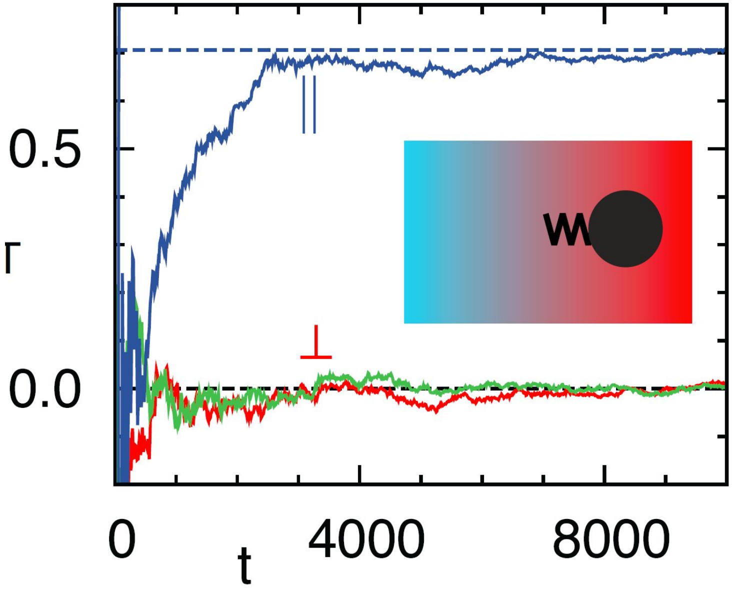




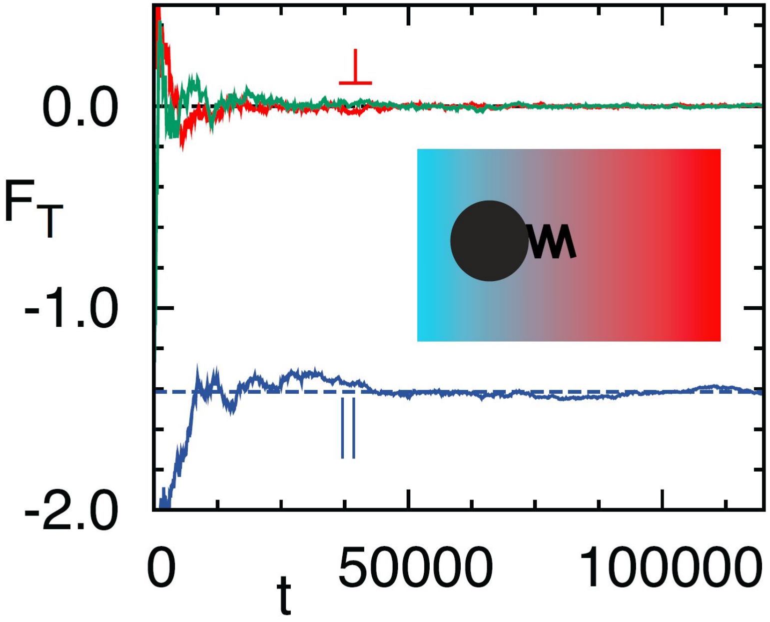
polymer in shear

（1）Colloidal thermophoresis

Repulsive → thermophilic



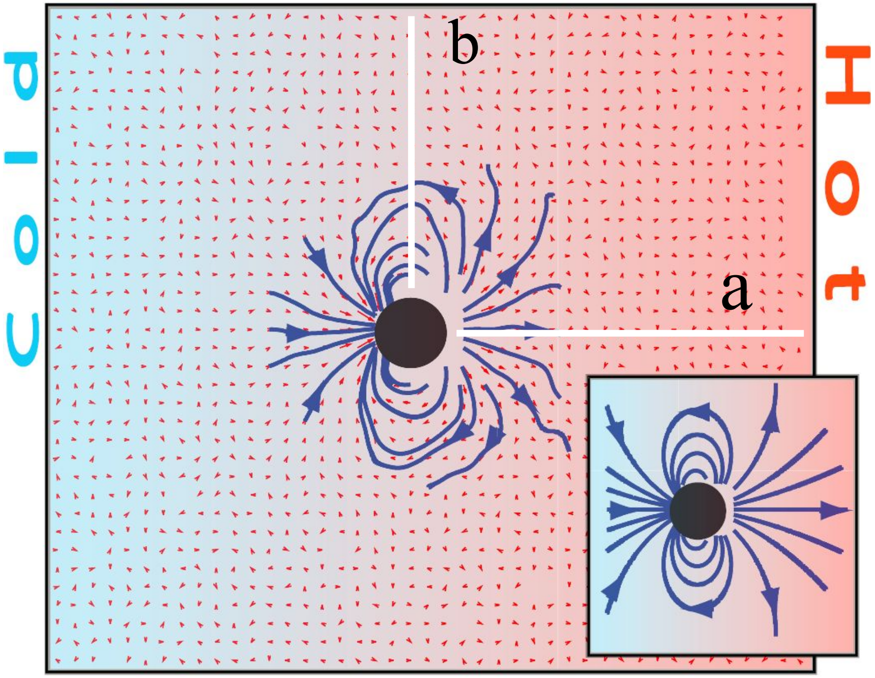
Attractive → thermophobic



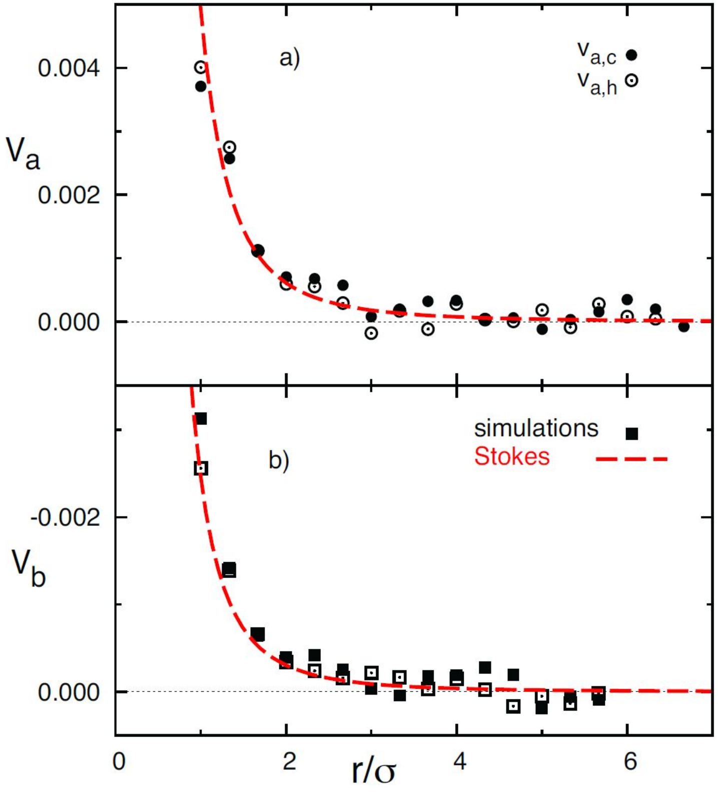
boundary thermostat

Luesebrink, Yang, Ripoll (2012) JPCM

Thermophoretic flow field



flow around thermophoretic colloid

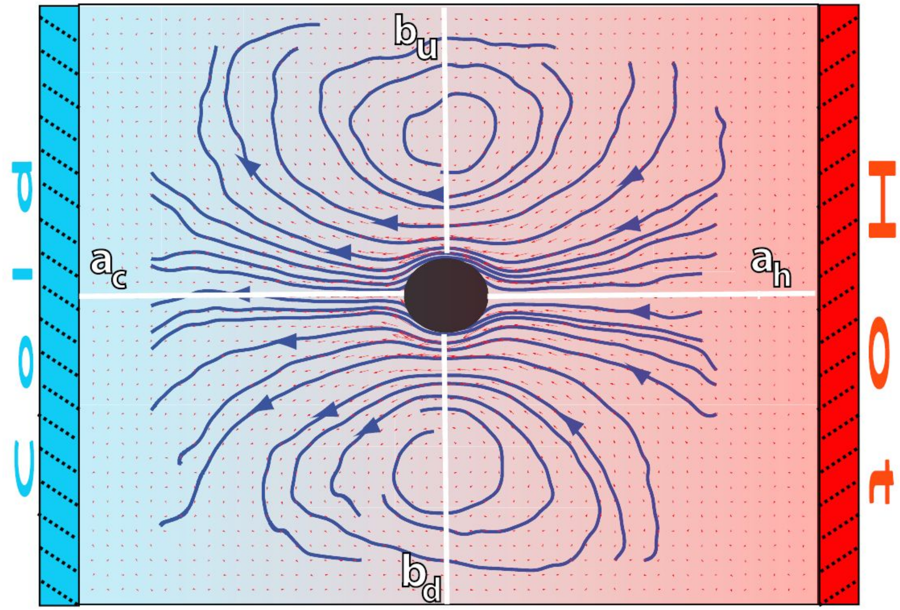


comparison with theory

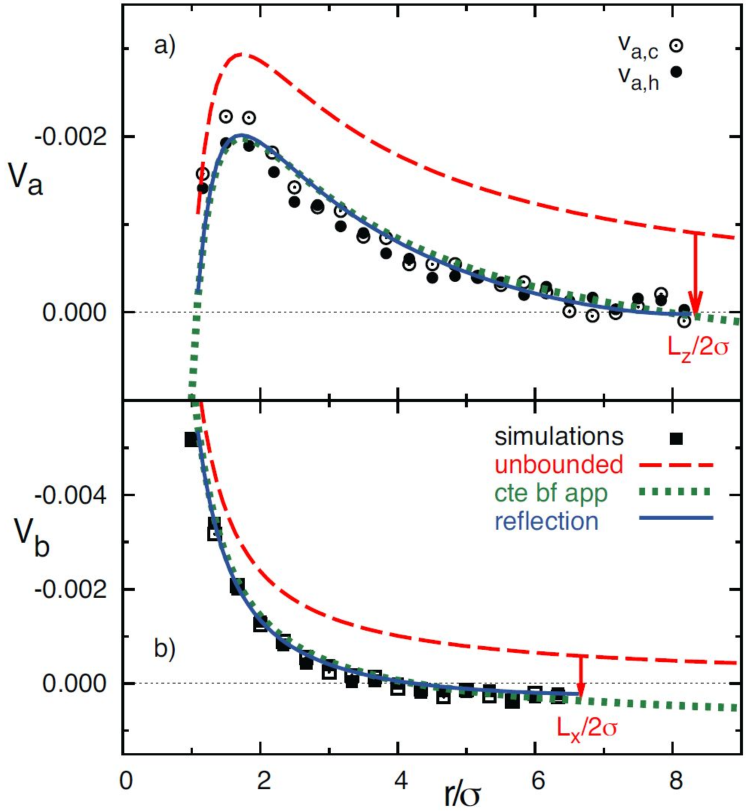
thermophoretic force = friction

→ $$\mathbf{v}(\mathbf{r}) = \frac{R^3}{2r^3}(3\hat{\mathbf{r}}\hat{\mathbf{r}} - \mathbf{I}) \cdot \mathbf{u}_T$$

Yang, Ripoll (2013) Soft Matter



flow around fixed thermophoretic colloid



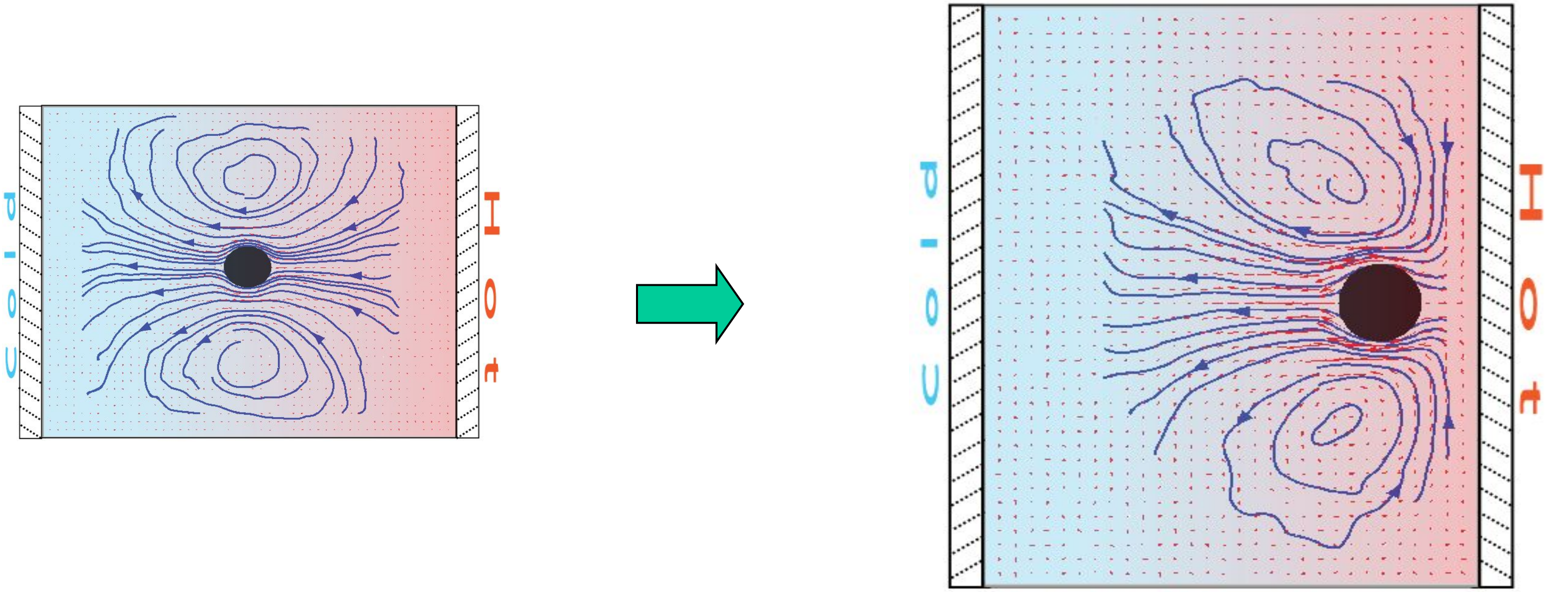
comparison with theory

nonvanishing thermophoretic force

$$\longrightarrow \quad \mathbf{v}(\mathbf{r}) = -\frac{1}{8\pi\eta r}(\hat{\mathbf{r}}\hat{\mathbf{r}} + \mathbf{I}) \cdot \mathbf{f}_T + \frac{R^2}{8\pi\eta r^3}(3\hat{\mathbf{r}}\hat{\mathbf{r}} - \mathbf{I}) \cdot \mathbf{f}_T$$

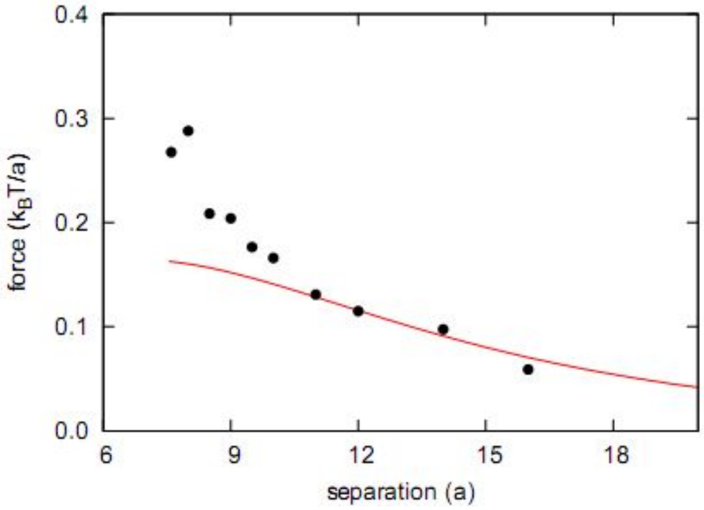
(for infinite system)

Hydrodynamic attraction

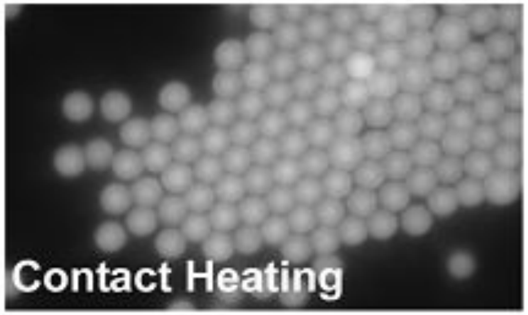


boundary wall effect

<u>**Yang**, Ripoll (2013) Soft Matter</u>



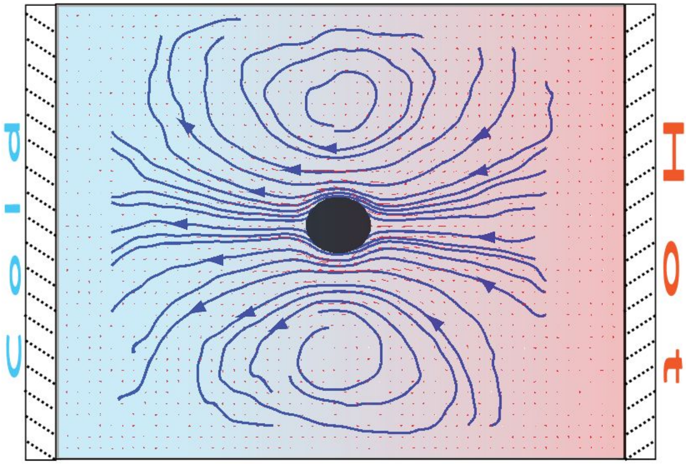
hydrodynamic attraction between particles



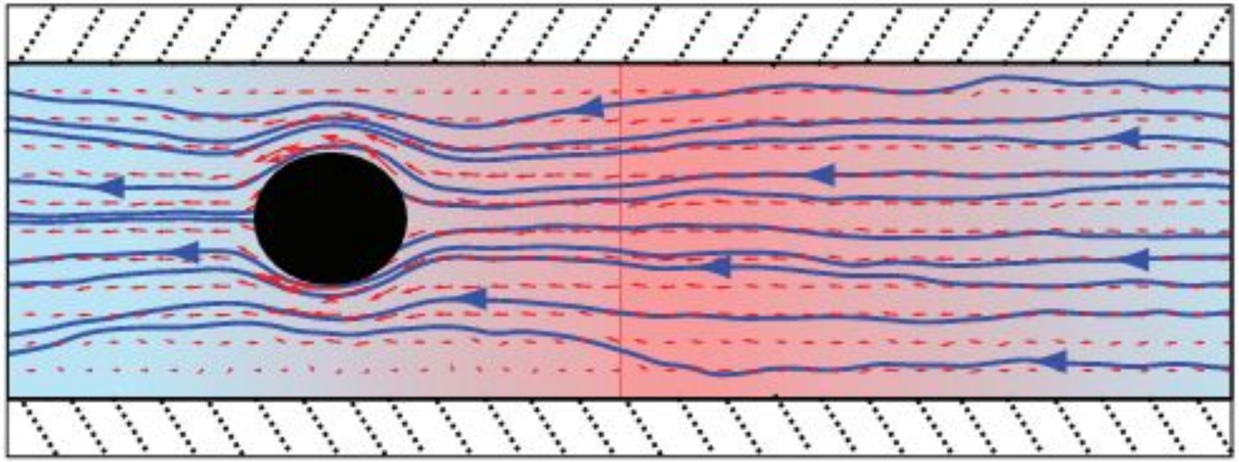
2D colloidal crystal

<u>Weinert, Braun (2008) PRL</u>

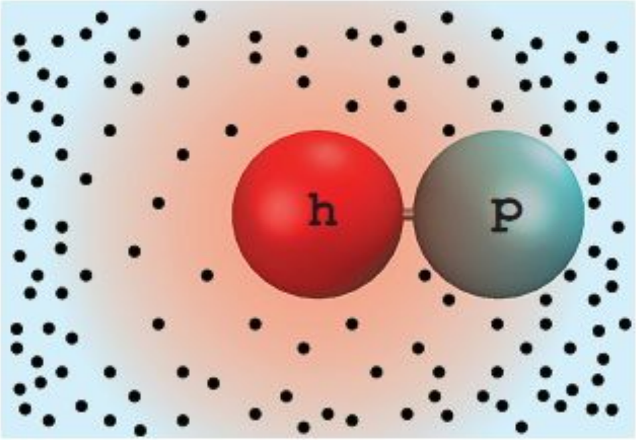
Single-particle microfluidic pump

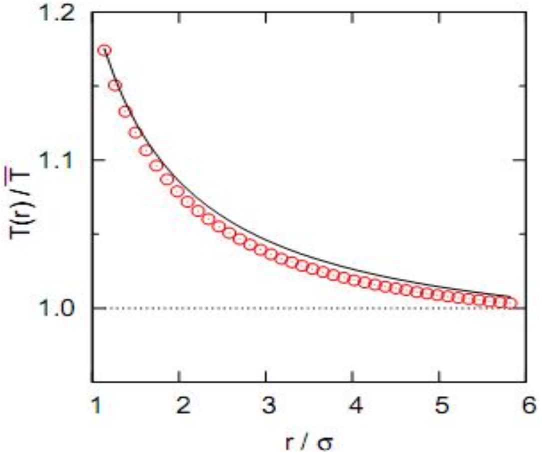


remove the walls



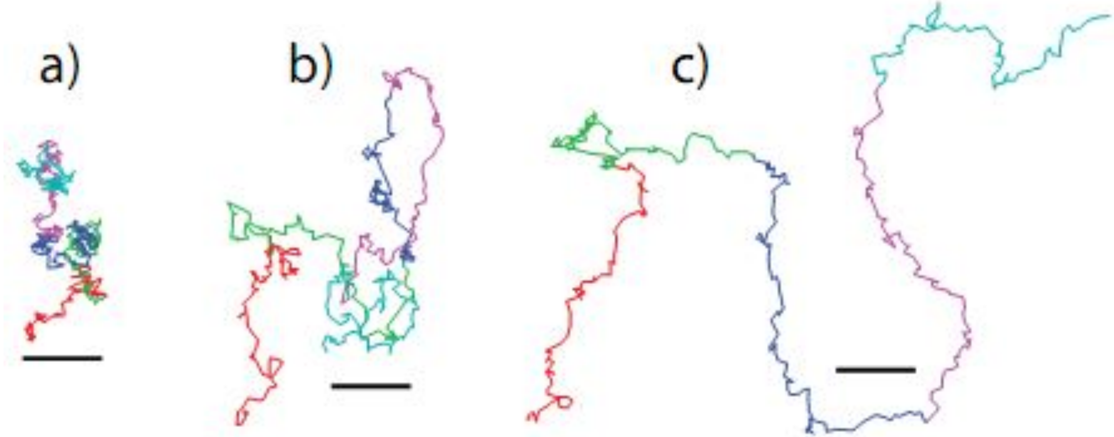
（2）Self-thermophoretic microdimer





温度分布

质心轨迹

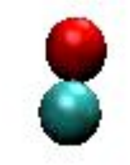


$\nabla T \uparrow$

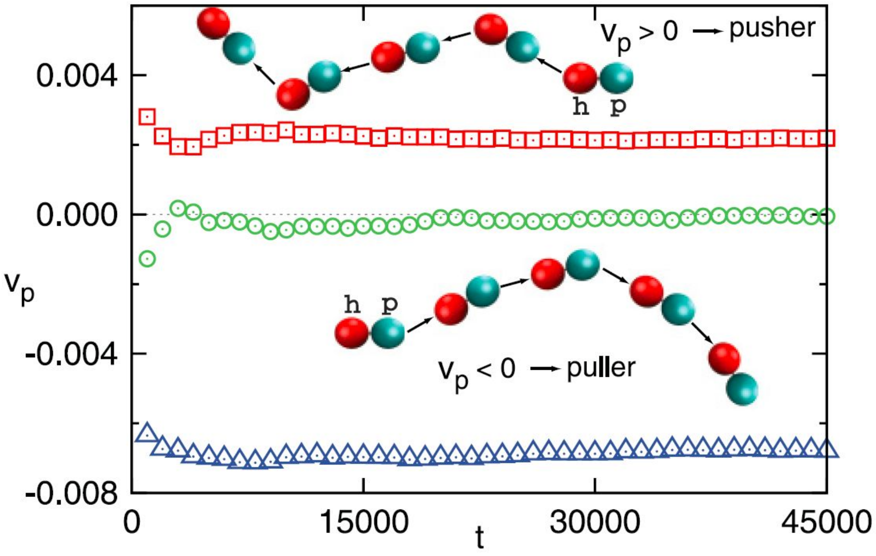
Yang, Ripoll (2011) PRE

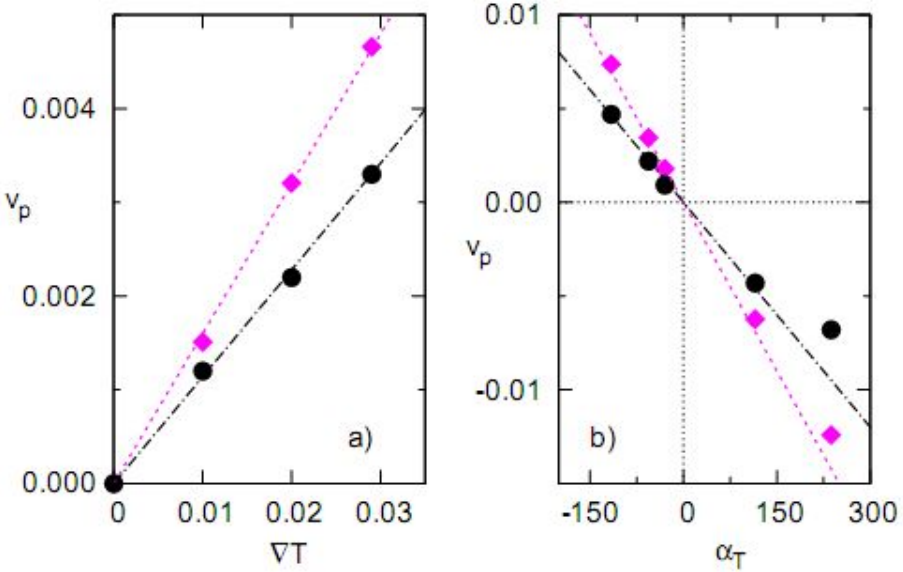
Puller

Pusher



自推进速度

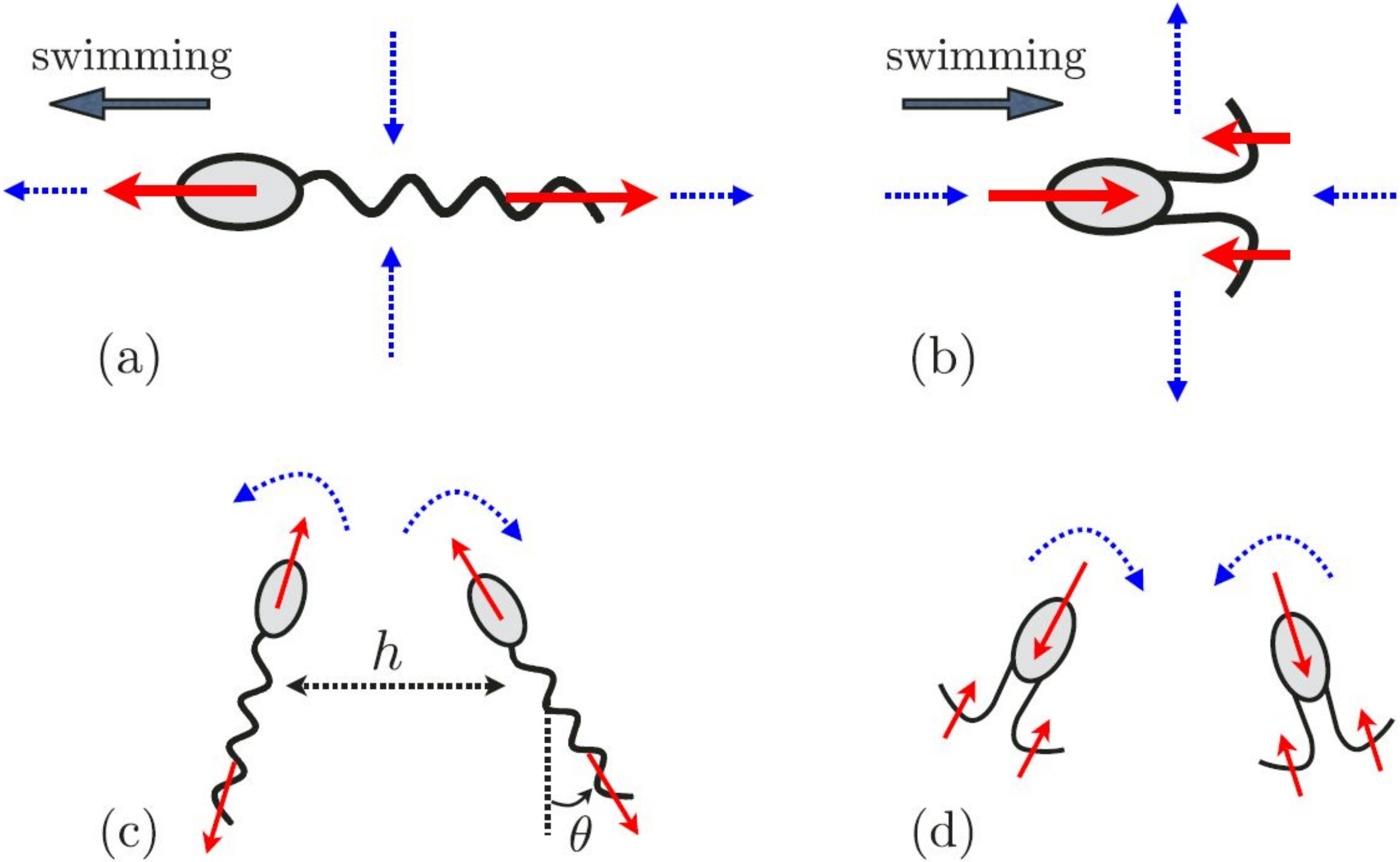

$v_p > 0$ → pusher
h p
h p
$v_p < 0$ → puller
0.004
0.000
-0.004
-0.008
v_p
0
15000
t
30000
45000

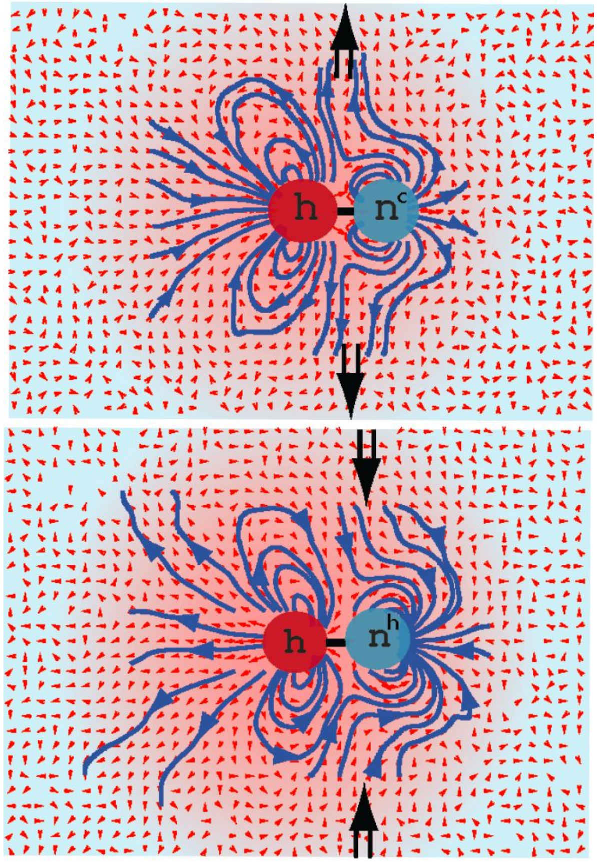

0.004
0.002
0.000
v_p
0
0.01
0.02
0.03
∇T
a)
0.01
0.00
-0.01
v_p
-150
0
150
300
α_T
b)

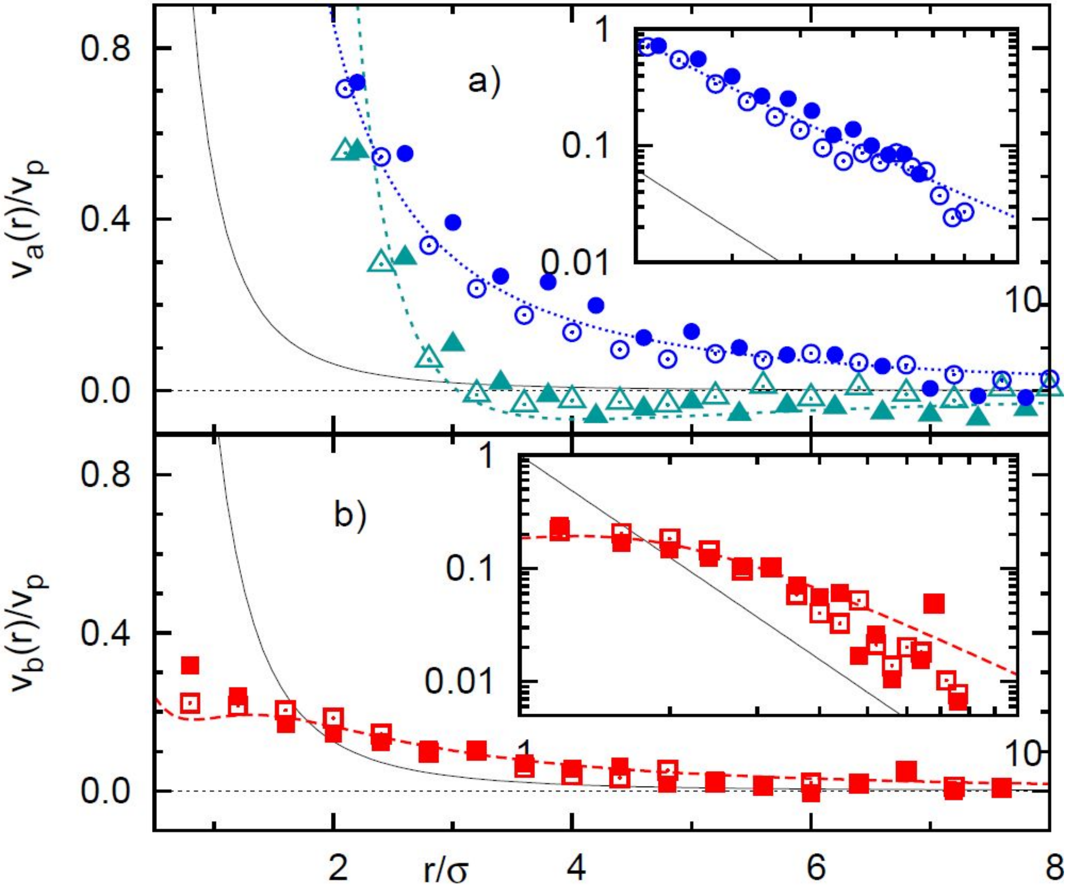
Pusher与puller的流场

pusher

puller







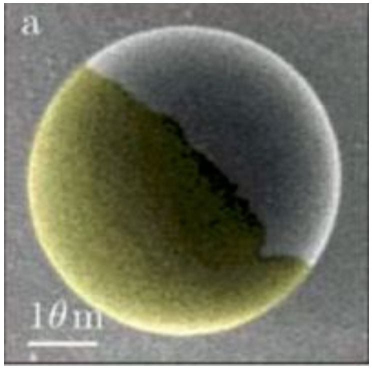
force dipole r^{-2}

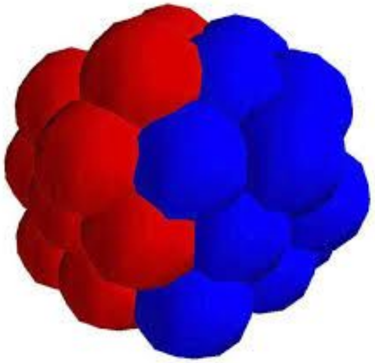
$$\mathbf{v}(\mathbf{r}) = \mathbf{v}_{active}(\mathbf{r}) + \mathbf{v}_{passive}(\mathbf{r})$$

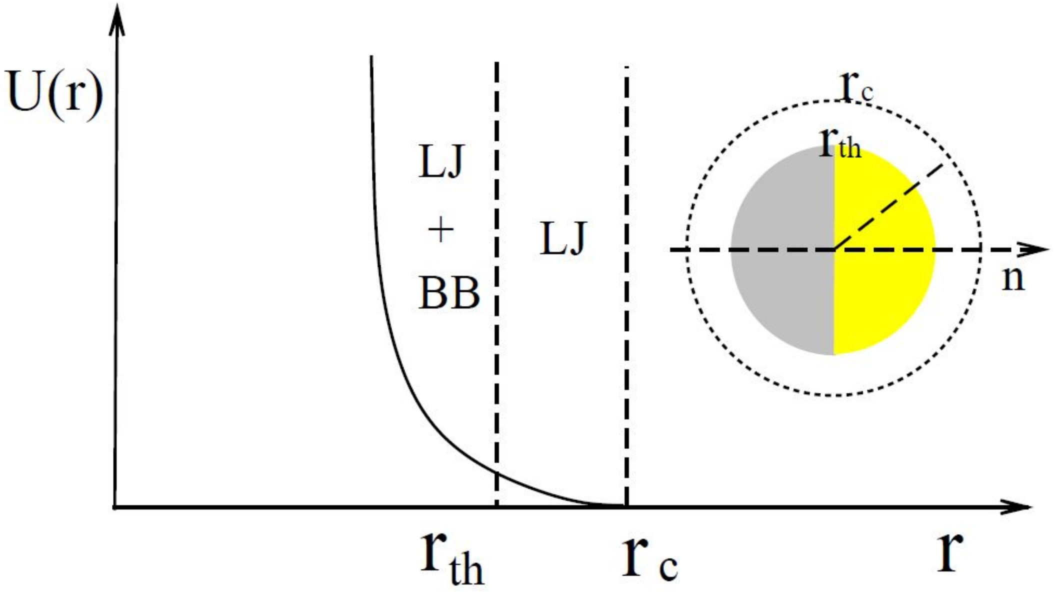
$$\mathbf{v}_{active}(\mathbf{r}) = \frac{R}{2\mid \mathbf{r}-\mathbf{r}_1 \mid}\left(\frac{(\mathbf{r}-\mathbf{r}_1)(\mathbf{r}-\mathbf{r}_1)}{\mid \mathbf{r}-\mathbf{r}_1 \mid^2} + \mathbf{I}\right)\cdot \mathbf{v}_p$$

$$\mathbf{v}_{passive}(\mathbf{r}) = -\frac{R}{2\mid \mathbf{r}-\mathbf{r}_2 \mid}\left(\frac{(\mathbf{r}-\mathbf{r}_2)(\mathbf{r}-\mathbf{r}_2)}{\mid \mathbf{r}-\mathbf{r}_2 \mid^2} + \mathbf{I}\right)\cdot \mathbf{v}_p + \frac{R^3}{\mid \mathbf{r}-\mathbf{r}_2 \mid^3}\left(\frac{3(\mathbf{r}-\mathbf{r}_2)(\mathbf{r}-\mathbf{r}_2)}{\mid \mathbf{r}-\mathbf{r}_2 \mid^2} - \mathbf{I}\right)\cdot \mathbf{v}_p.$$

（3）Self-phoretic Janus particle







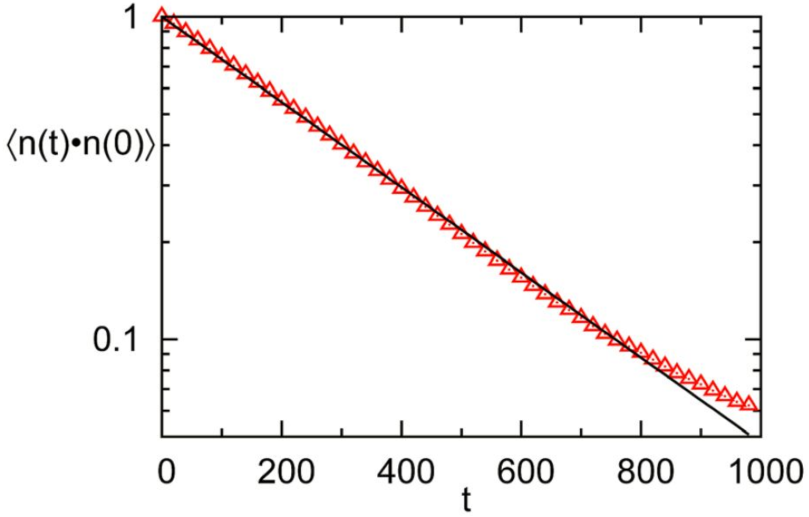
转动扩散
泳效应

→

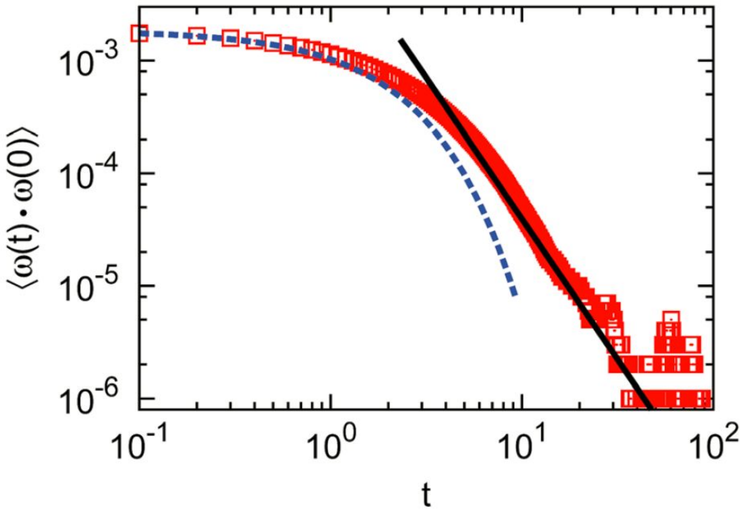
粘性边界
势能相互作用

Yang et al, (2014) Soft Matter

Rotational dynamics of passive particle



$$\langle \mathbf{n}(t)\cdot\mathbf{n}(0)\rangle = \exp(-2D_{\mathrm{r}}t)$$

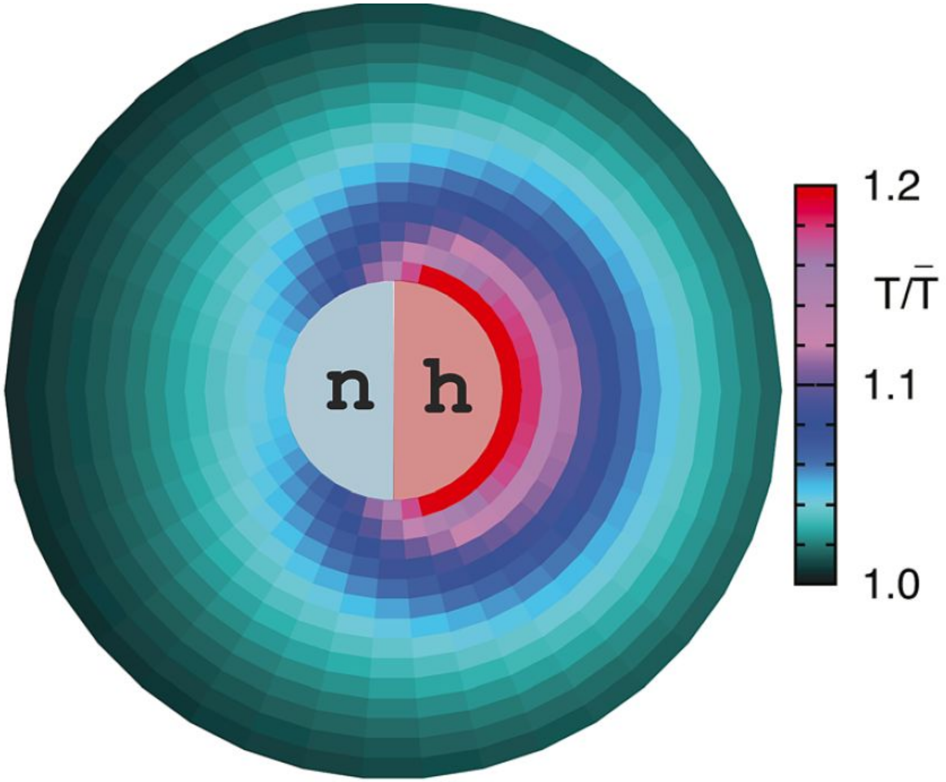


$$\lim_{t\to 0}\langle\omega(t)\cdot\omega(0)\rangle = \langle\omega^2\rangle\exp(-\zeta_{\mathrm{E}}t/I)$$

$$\zeta_{\mathrm{E}} = \frac{8}{3}\sqrt{2\pi k_{\mathrm{B}}T\mu}\,\rho_\sigma\sigma^4\frac{\chi M}{\mu+\chi M}$$

$$\lim_{t\to\infty}\langle\omega(t)\cdot\omega(0)\rangle = \frac{\pi k_B T}{m\rho(r_b)(4\pi\nu t)^{5/2}}$$

Self-thermophoretic Janus particle

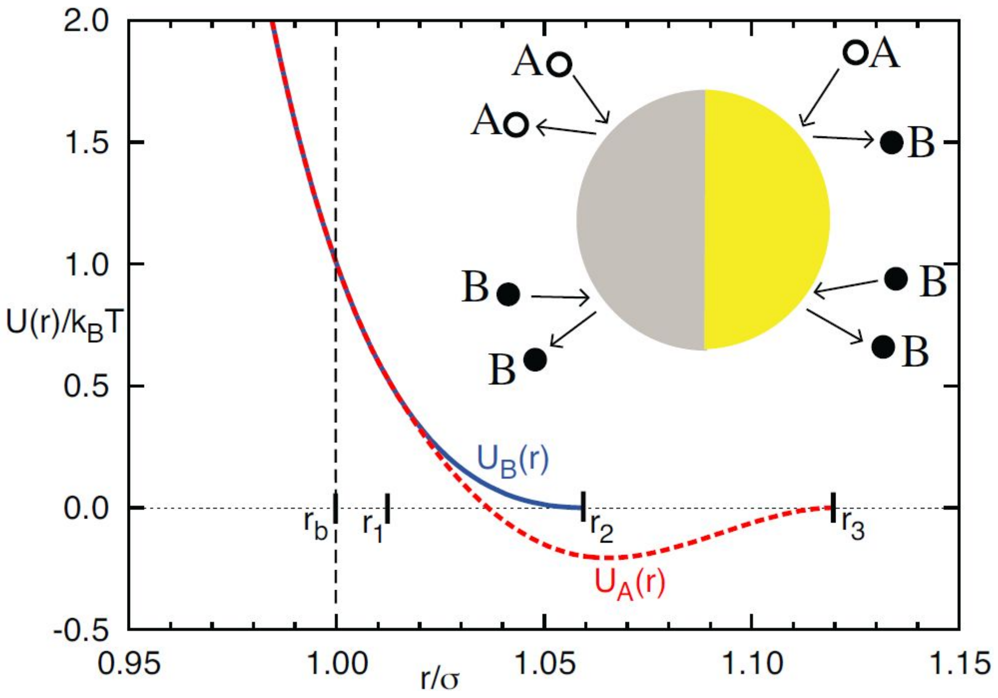


温度分布

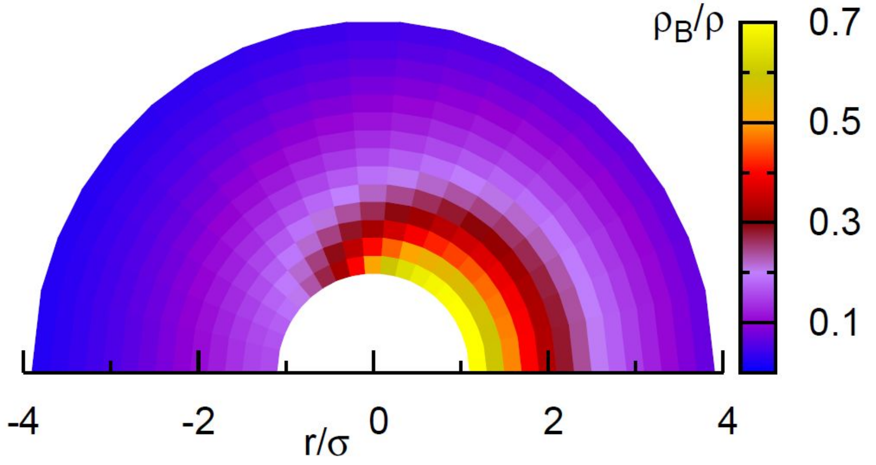
加热粒子：

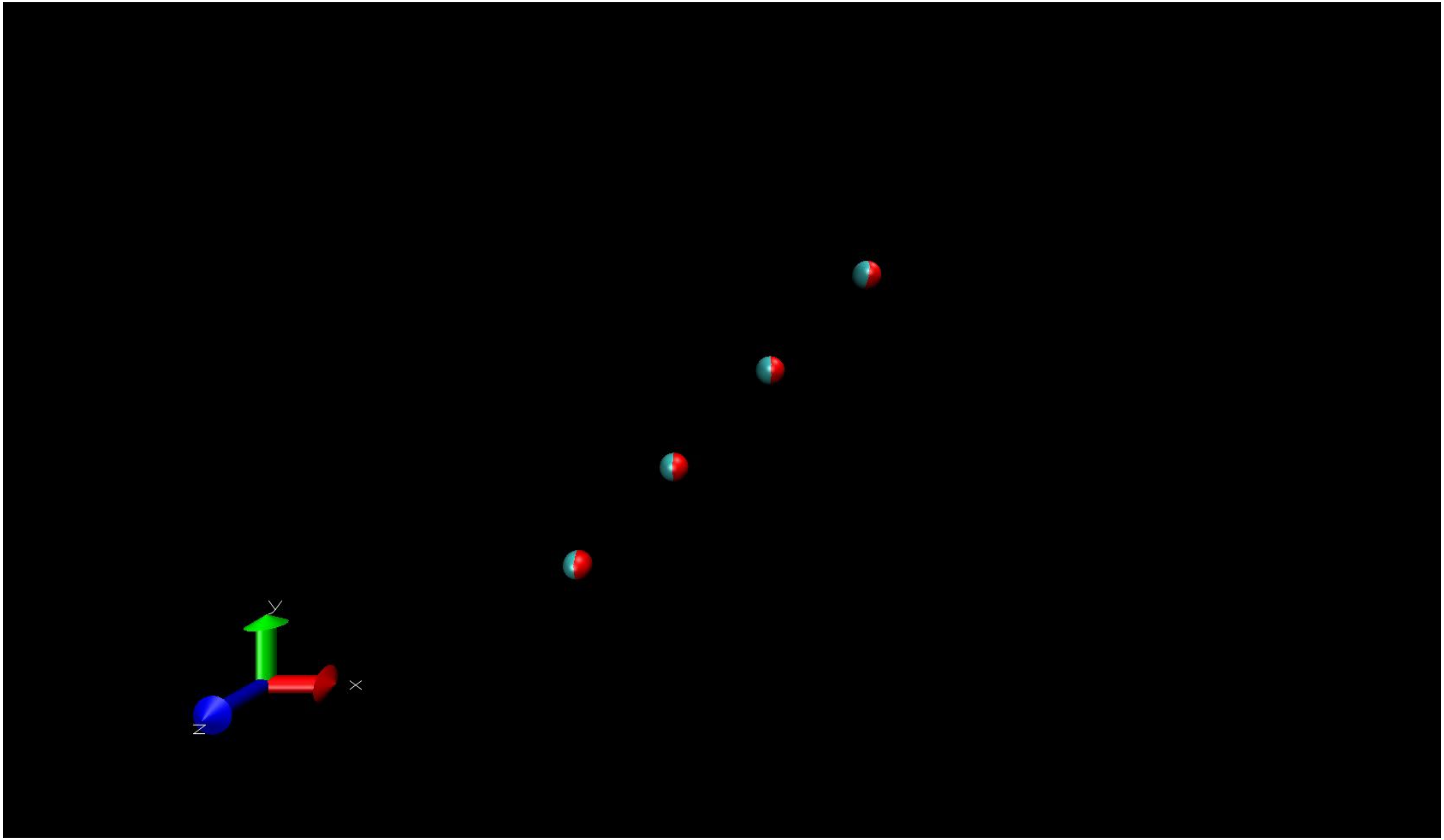
- 粒子边界thermostat
- 固定溶液平均温度

Self-diffusiophoretic Janus particle

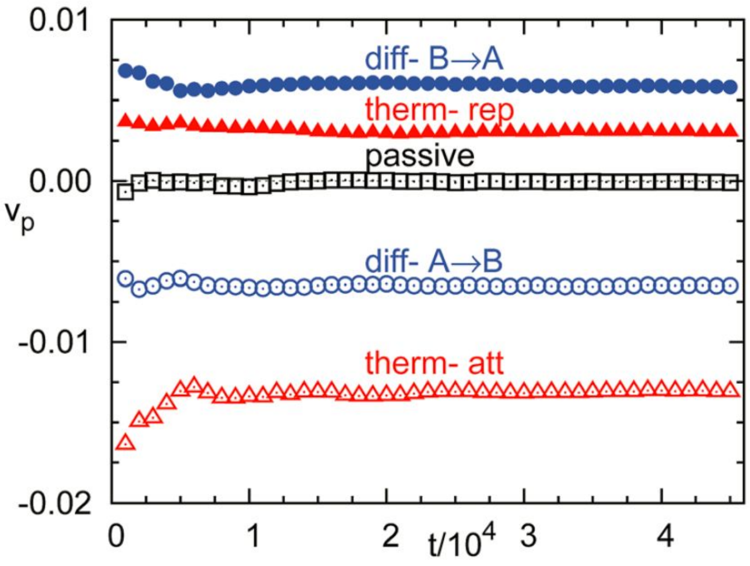


反应产物浓度分布

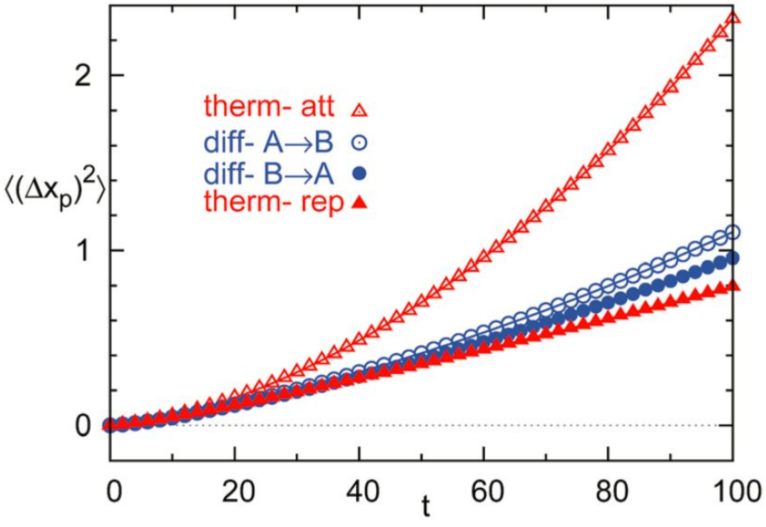



Y
X
Z

Self-propelled velocity



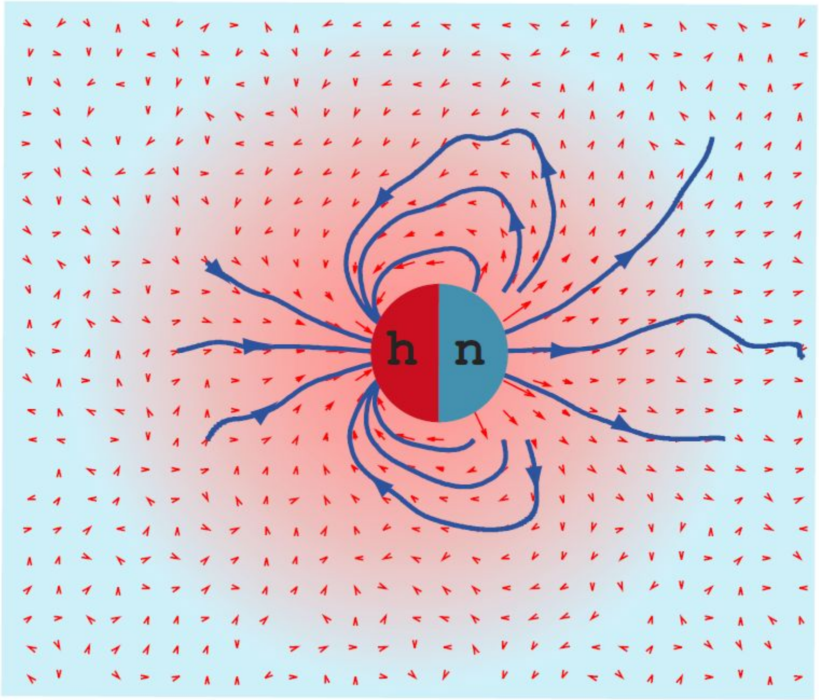
$$v_{\mathrm{p}} = \langle \mathbf{V} \cdot \mathbf{n} \rangle$$

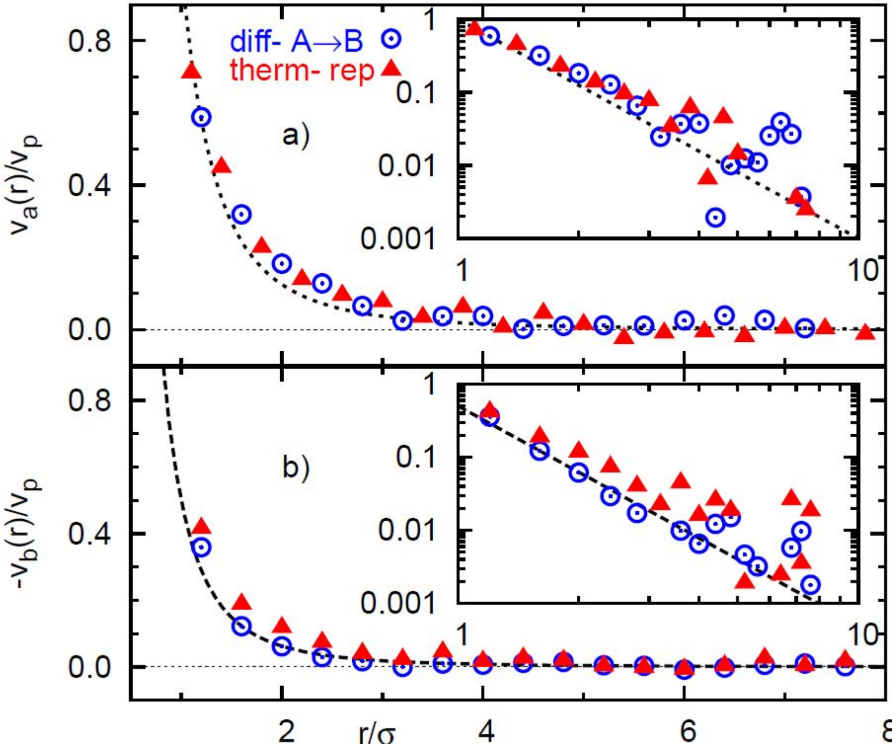


$$\langle (\Delta x_{\mathrm{p}})^2 \rangle = 2D_{\mathrm{p}}t + {v_{\mathrm{p}}}^2 t^2$$

	Therm-att	Therm-rep	Diff-A → B	Diff-B → A
v_{p} (direct)	−0.0131	0.0030	−0.0065	0.0059
v_{p} (indirect)	−0.0133	0.0035	−0.0070	0.0059
D_{p} (indirect)	0.0029	0.0035	0.0032	0.0032
v_{p} (dimer)	−0.0068	0.0047		
D_{p} (dimer)	0.0028	0.0034		

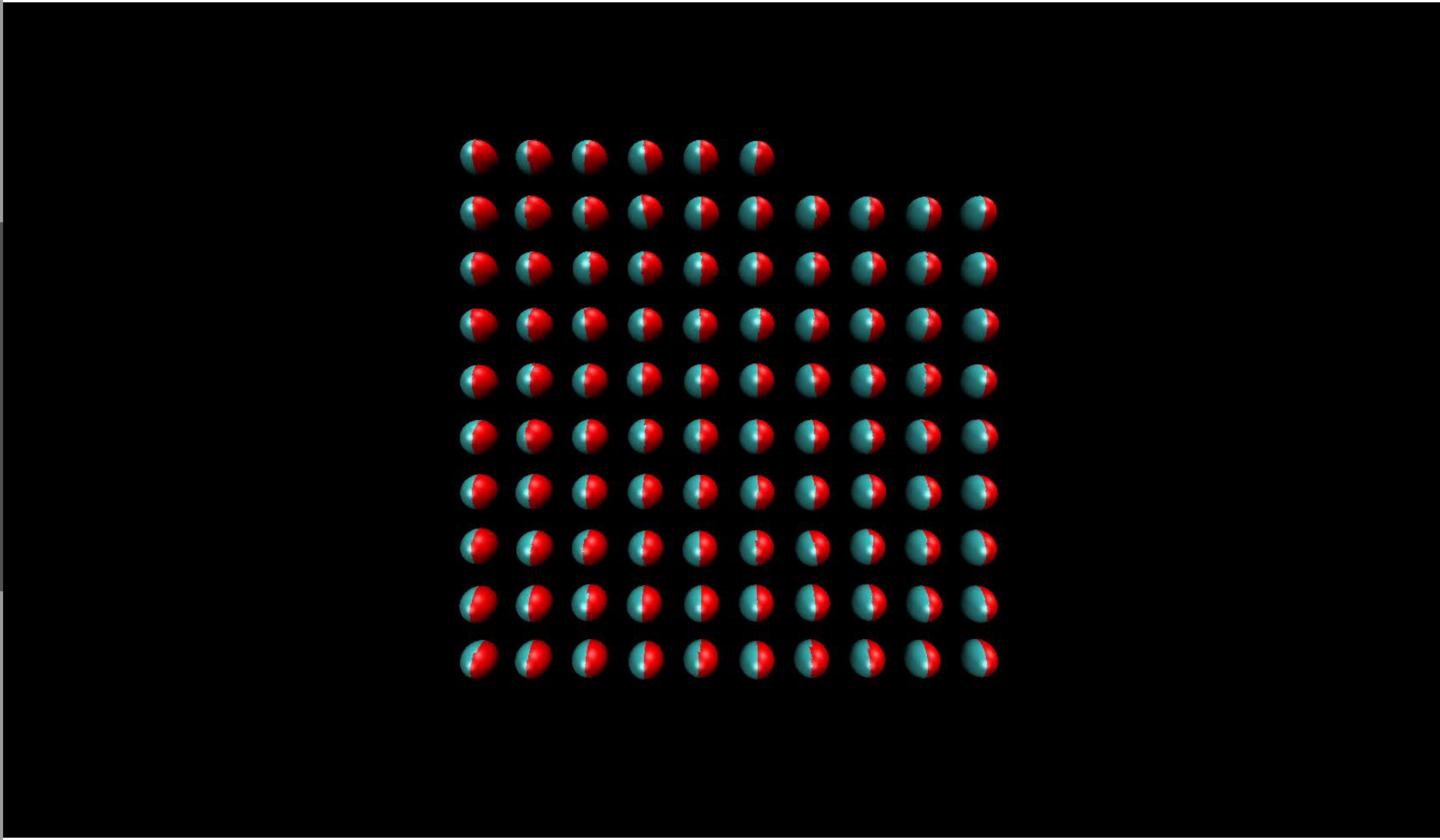
Flow field





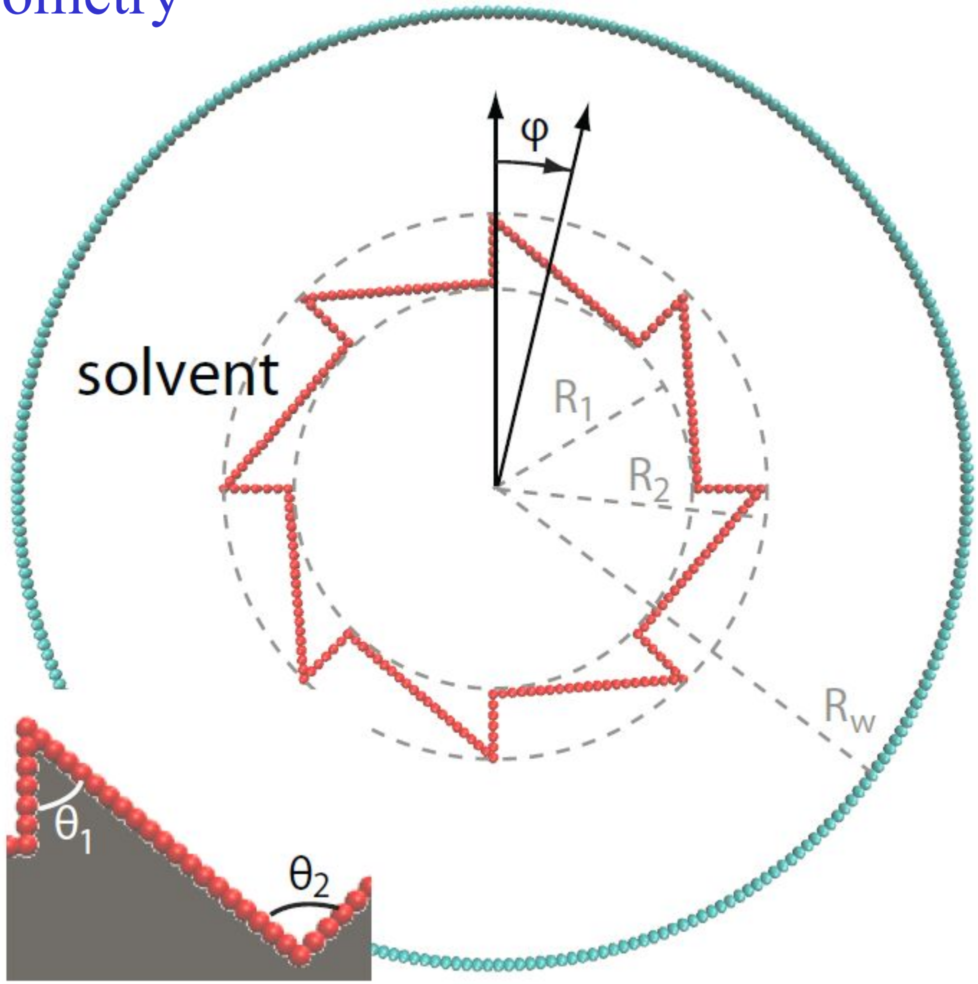
$$\mathbf{v}(\mathbf{r}) = \frac{\sigma^3}{2r^3}\left(3\frac{\mathbf{r}\mathbf{r}}{r^2} - \mathbf{I}\right)\cdot\mathbf{v}_\mathrm{p}$$

Many Janus particles



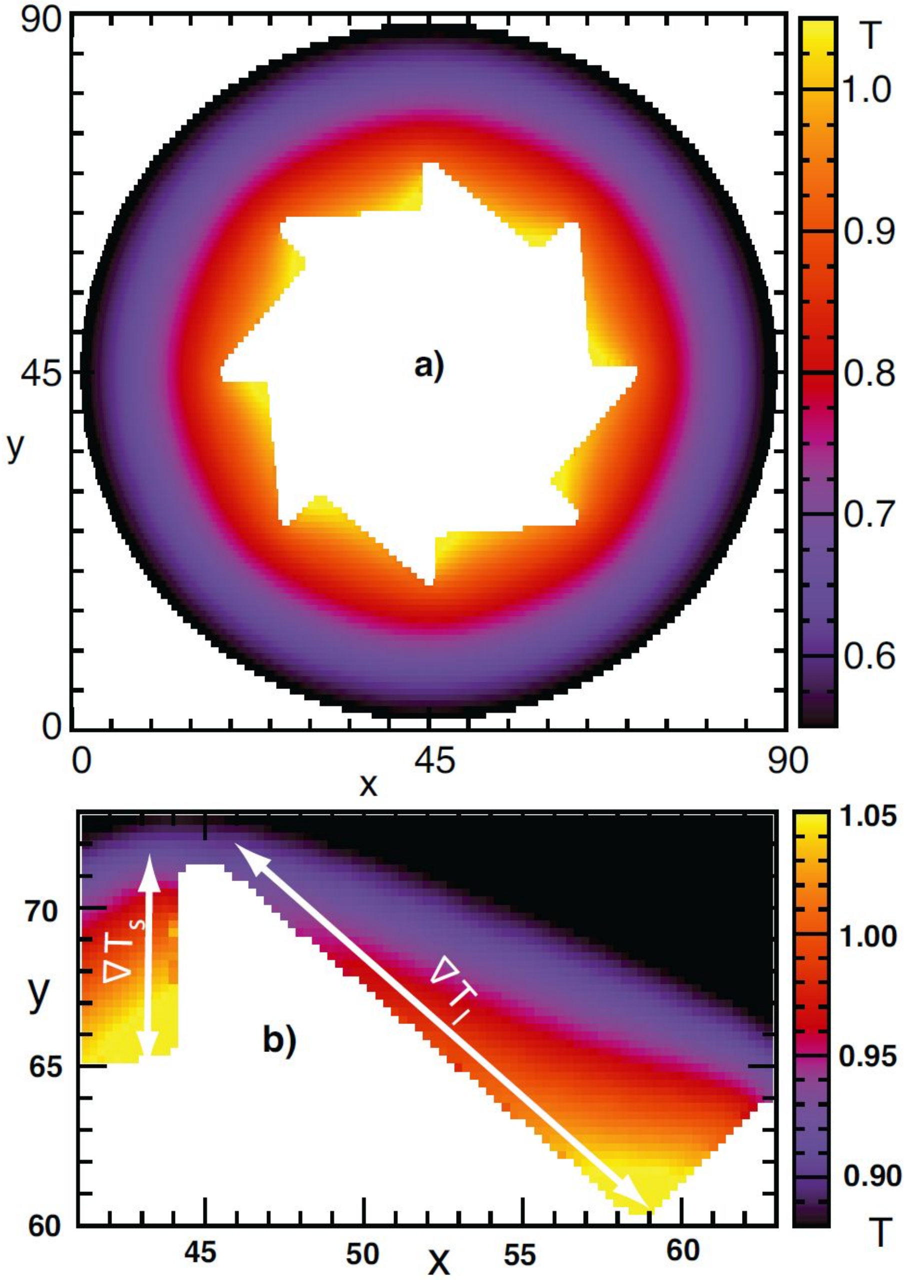
（4）Self-thermophoretic microgear

- homogeneous material
- asymmetric geometry

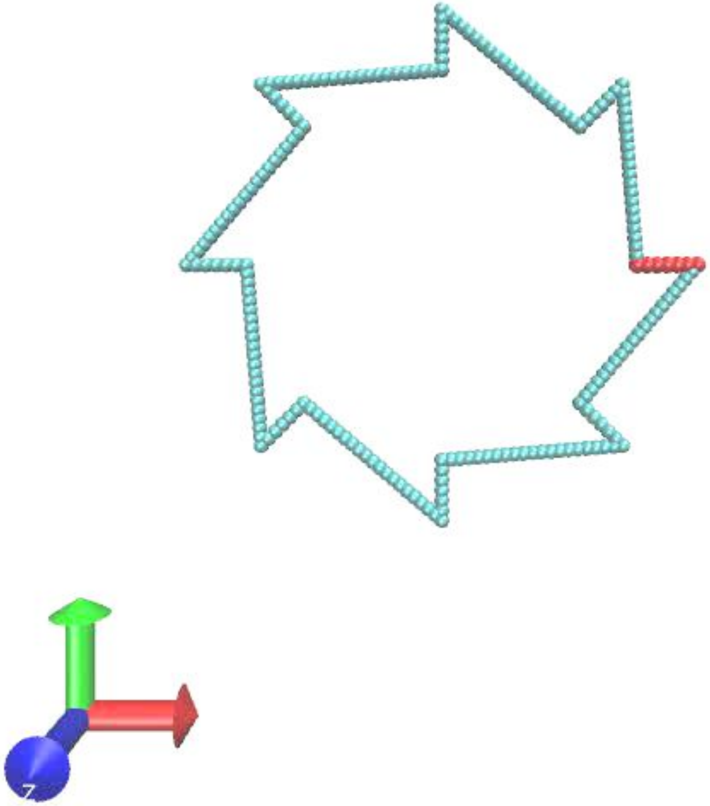


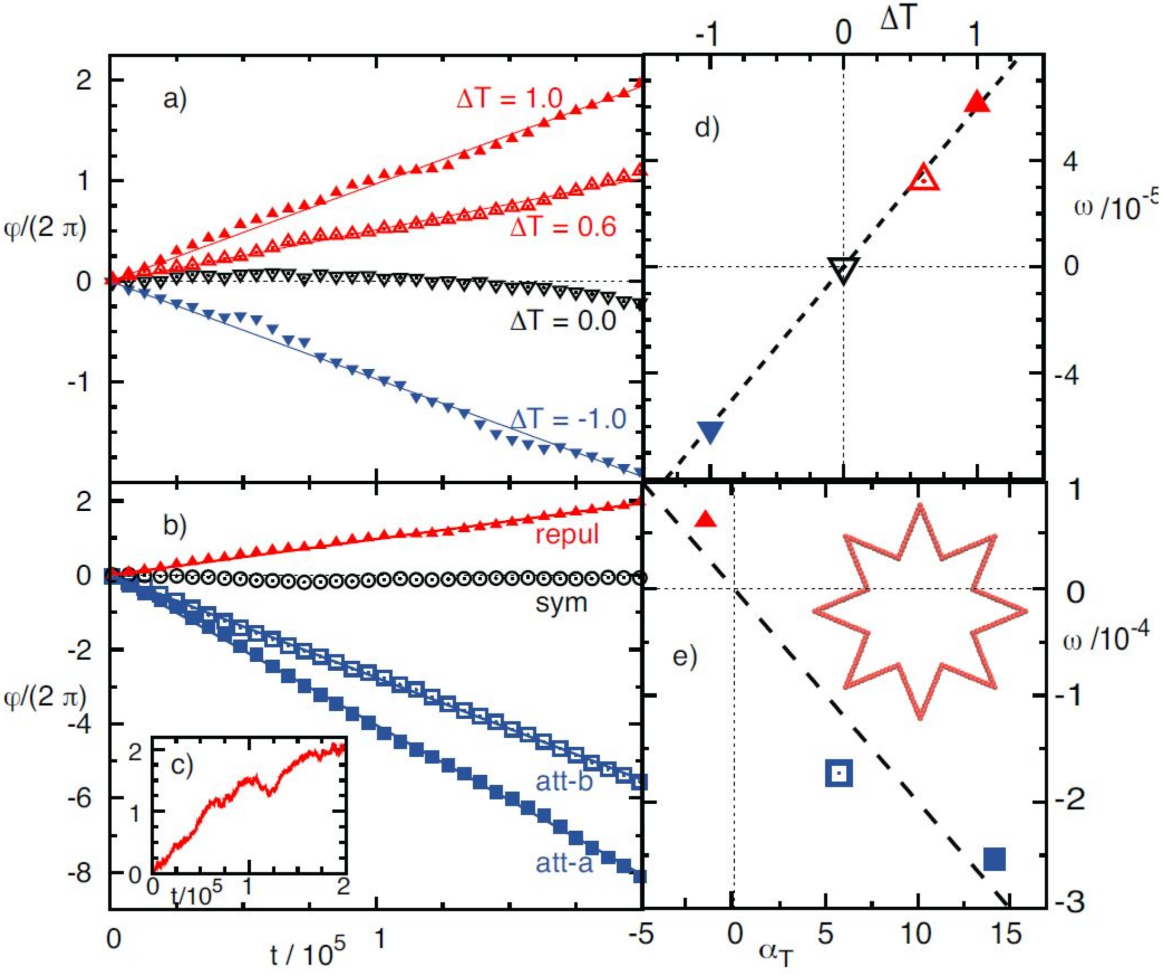
Yang, Ripoll (2014) Soft Matter

温度分布



$$|\mathscr{T}| \simeq 8R_1 \; |f_{\mathrm{T,l}}|$$

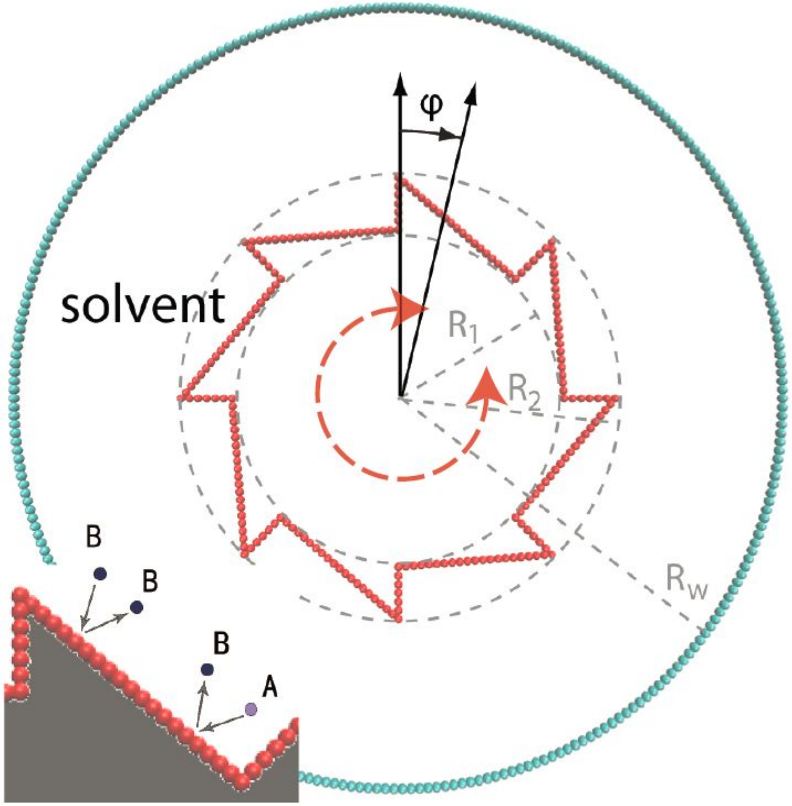

z



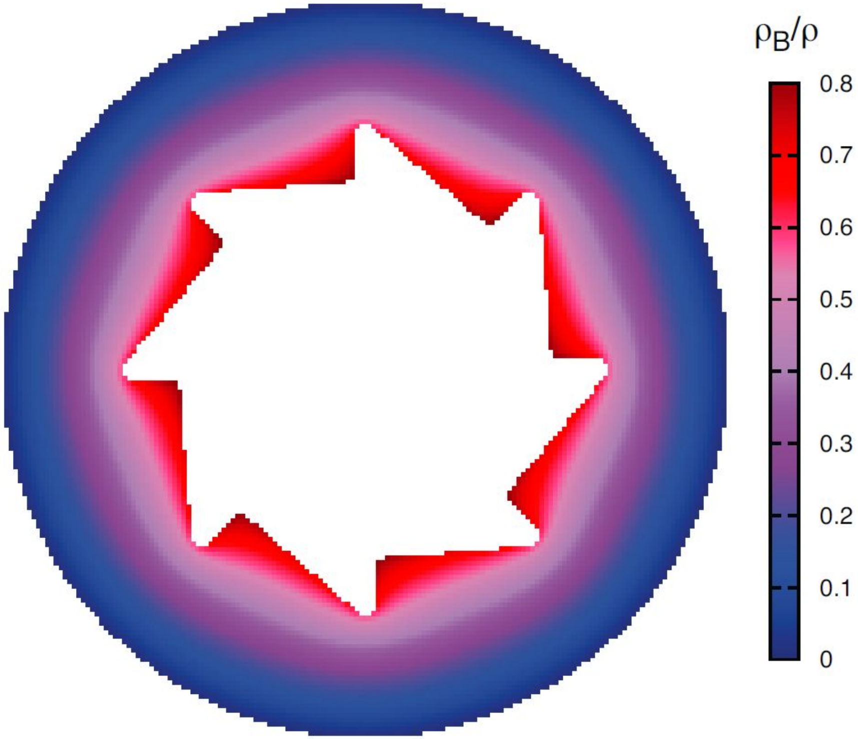
rotational angle angular velocity

$$\omega = -\frac{2\lambda_1\lambda_2 N_1 R_1}{\pi\eta {R_{\mathrm{H}}}^2}\,\alpha_{\mathrm{T}} k_{\mathrm{B}} \Delta T \hat{z}$$

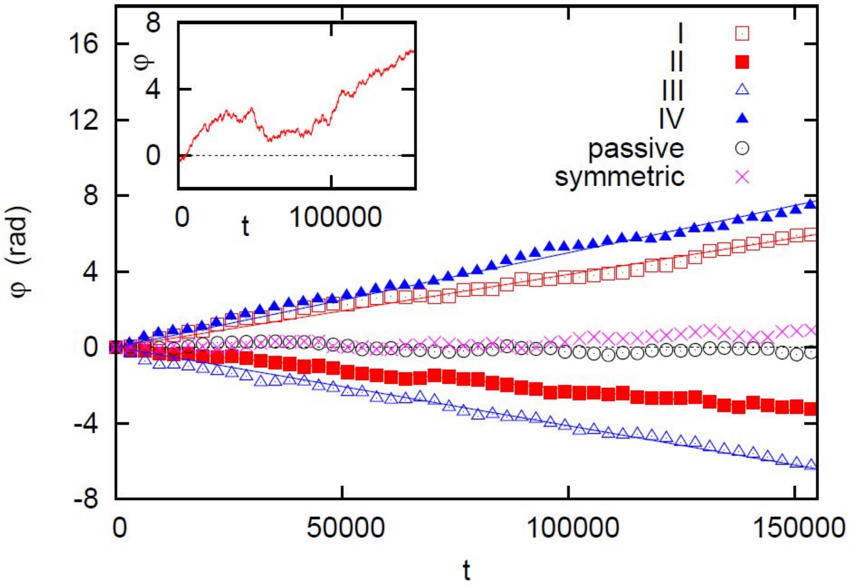
（5）Self-diffusiophoretic microgear



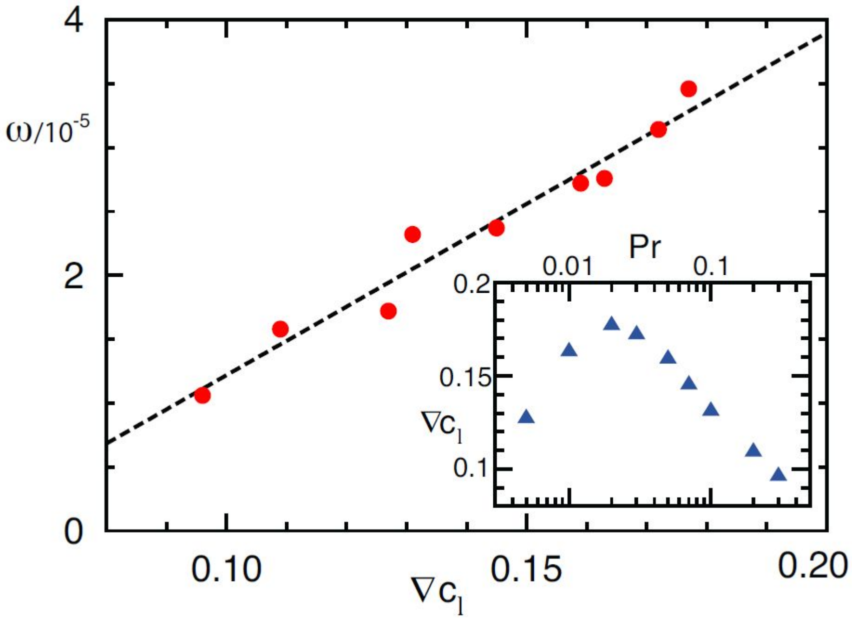
gear catalyze chemical reation



concentration distribution



rotation angular



angular velocity vs reaction probability

$$\omega = N\mu_r \mathbf{R}_l \times \mathbf{f}_{c,l}$$

小结

- 活性非平衡软物质系统

- 布朗动力学模拟

- 多粒子碰撞动力学模拟

- 介观流体模拟的例子
  - 热泳胶体溶液
  - 自泳微观游泳者
  - 自泳微观马达

谢谢大家！