

Reading Notes – Langevin equation and dynamics

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03/27/20

Paper (A) The dynamic mean-field density functional method and its application to the mesoscopic dynamics of quenched block copolymer melts

1. Terminology

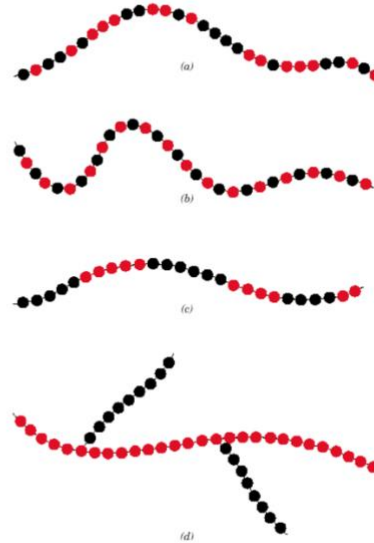
1.1 Copolymer (MSE250 Slides – Polymer I (3-25-20 PolymerStructure.pdf))

Two or more monomers polymerized together

Copolymer

MICHIGAN STATE
UNIVERSITY

- **random** – A and B randomly positioned along chain
- **alternating** – A and B alternate in polymer chain
- **block** – large blocks of A units alternate with large blocks of B units
- **graft** – chains of B units grafted onto A backbone



adapted from Callister Textbook Fig. 14.9

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1.2 “Quench”: wiki

“In materials science, *quenching* is the rapid cooling of a workpiece in water, oil or air to obtain certain material properties. A type of heat treating, *quenching* prevents undesired low-temperature processes, such as phase transformations, from occurring”.

1.3 “Stokes’ law”: wiki

“It describes “the frictional force (also called drag force) exerted on spherical objects with very small Reynolds numbers in a viscous fluid.

The force of viscosity on a small sphere moving through a viscous fluid is given by:

$$F_d = 6\pi\mu Rv$$

Where F_d is the frictional force – known as Stokes’ drag – acting on the interface between the fluid and the particle; μ is the viscosity (some authors use the symbol η); R is the radius of the spherical object; v is the flow velocity relative to the object. In SI units, F_d is given in newtons ($= \text{kg m s}^{-2}$), μ in $\text{Pa}\cdot\text{s}$ ($= \text{kg m}^{-1} \text{s}^{-1}$), R in meters, and v in m/s .”

1.4 “Einstein relation (kinetic theory)”: Wiki

([https://en.wikipedia.org/wiki/Einstein_relation_\(kinetic_theory\)](https://en.wikipedia.org/wiki/Einstein_relation_(kinetic_theory)))

“In physics, the Einstein relation is a connection related to *Brownian motion*. The general form of the equation is

$$D = \mu k_B T$$

Where D is the diffusion constant; μ is the "mobility", or the ratio of the particle's terminal drift velocity to an applied force, $\mu = v_d/F$.

Two frequently used important special forms of the relation are:

$$(1) D = \frac{\mu_q k_B T}{q} \text{ . (electrical mobility equation, for diffusion of charged particles)}$$

$$(2) D = \frac{k_B T}{6\pi\eta r} \text{ . (Stokes–Einstein equation, for diffusion of spherical particles through a liquid with low Reynolds number)}$$

Where q is the electrical charge of a particle; μ_q is the electrical mobility of the charged particle; η is the dynamic viscosity; r is the radius of the spherical particle."

1.5 "Langevin Equation"

(A) Wiki

"In physics, Langevin equation is a stochastic differential equation describing the time evolution of a subset of the degrees of freedom. These degrees of freedom typically are collective (macroscopic) variables changing only slowly in comparison to the other (microscopic) variables of the system. The fast (microscopic) variables are responsible for the stochastic nature of the Langevin equation."

Brownian motion as a prototype:

The original Langevin equation describes Brownian motion, the apparently random movement of a particle in a fluid due to collisions with the molecules of the fluid,

$$m \frac{d\mathbf{v}}{dt} = -\lambda \mathbf{v} + \boldsymbol{\eta}(t)$$

The degrees of freedom of interest here is the velocity \mathbf{v} of the particle, m denotes the particle's mass. The force acting on the particle is written as a sum of a viscous force proportional to the particle's velocity (Stokes' law), and a noise term $\boldsymbol{\eta}(t)$ (the name given in physical contexts to terms in stochastic differential equations which are **stochastic processes**) representing the effect of the collisions with the molecules of the fluid. The force $\boldsymbol{\eta}(t)$ has a Gaussian probability distribution with correlation function

$$\langle \eta_i(t) \eta_j(t') \rangle = 2\lambda k_B T \delta_{ij} \delta(t - t')$$

where k_B is Boltzmann's constant, T is the temperature and $\eta_i(t)$ is the i -th component of the vector $\boldsymbol{\eta}(t)$. The δ -function form of the correlations in time means that the **force at a time t is assumed to be completely uncorrelated with the force at any other time**. This is an approximation; the actual random force has a nonzero correlation time corresponding to the collision time of the molecules. However, the Langevin equation is used to describe the motion of a "macroscopic" particle at a much longer time scale, and in this limit the δ -correlation and the Langevin equation becomes virtually exact.

Another prototypical feature of the Langevin equation is the occurrence of the damping coefficient λ in the correlation function of the random force, a fact also known as Einstein relation.

Mathematical aspects:

A strictly δ -correlated fluctuating force $\boldsymbol{\eta}(t)$ is not a function in the usual mathematical sense and even the derivative $\frac{d\mathbf{v}}{dt}$ is not defined in this limit. This problem disappears when the Langevin equation is written in integral form $m\mathbf{v} = \int_{t_0}^t (-\lambda \mathbf{v} + \boldsymbol{\eta}(t)) dt$ and a **Langevin equation always should be interpreted as an abbreviation for its time integral**. The general mathematical term for equations of this type is "stochastic differential equation".

Examples: Trajectories of free Brownian particles

Consider a free particle of mass m with equation of motion described by

$$m \frac{d\mathbf{v}}{dt} = -\frac{\mathbf{v}}{\mu} + \boldsymbol{\eta}(t),$$

where $\mathbf{v} = \frac{d\mathbf{r}}{dt}$ is the particle velocity, μ is the particle mobility, and $\boldsymbol{\eta}(t) = m\mathbf{a}(t)$ is a rapidly fluctuating force whose time-average vanishes over a characteristic timescale t_c of particle collisions, i.e. $\overline{\boldsymbol{\eta}(t)} = 0$. The general solution to the equation of motion is

$$\mathbf{v}(t) = \mathbf{v}(0)e^{-t/\tau} + \int_0^t \mathbf{a}(t')e^{-(t-t')/\tau} dt'$$

where $\tau = m\mu$ is the relaxation time of the Brownian motion. As expected from the random nature of Brownian motion, the average drift velocity $\langle \mathbf{v}(t) \rangle = \mathbf{v}(0)e^{-t/\tau}$ quickly decays to zero at $t \gg \tau$. It can also be shown that the autocorrelation function of the particle velocity \mathbf{v} is given by

$$\begin{aligned} R_{vv}(t_1, t_2) &\equiv \langle \mathbf{v}(t_1) \cdot \mathbf{v}(t_2) \rangle \\ &= v^2(0)e^{-(t_1+t_2)/\tau} + \int_0^{t_1} \int_0^{t_2} R_{aa}(t'_1, t'_2)e^{-(t_1+t_2-t'_1-t'_2)/\tau} dt'_1 dt'_2 \\ &\simeq v^2(0)e^{-|t_2-t_1|/\tau} + \left[\frac{3k_B T}{m} - v^2(0) \right] \left[e^{-|t_2-t_1|/\tau} - e^{-(t_1+t_2)/\tau} \right] \end{aligned}$$

(Note: “autocorrelation” (Google): correlation between the elements of a series and others from the same series separated from them by a given interval)

where we have used the property that the variables $\mathbf{a}(t'_1)$ and $\mathbf{a}(t'_2)$ become uncorrelated for time separations $t'_2 - t'_1 \gg t_c$. Besides, the value of $\lim_{t \rightarrow \infty} \langle v^2(t) \rangle = \lim_{t \rightarrow \infty} R_{vv}(t, t)$ is set to be equal to $3k_B T/m$ such that it obeys the equipartition theorem. Note that if the system is initially at thermal equilibrium already with $v^2(0) = 3k_B T/m$, then $\langle v^2(t) \rangle = 3k_B T/m$ for all t , meaning that the system remains at equilibrium at all times.

(Note: “Equipartition theorem” (Wiki) --- “In classical statistical mechanics, the equipartition theorem relates the temperature of a system to its average energies. The original idea of equipartition was that, in thermal equilibrium, energy is shared equally among all of its various forms; In other words, the total kinetic energy of a system is shared equally among all of its independent parts, on the average, once the system has reached thermal equilibrium.”.)

The velocity $\mathbf{v}(t)$ of the Brownian particle can be integrated to yield its trajectory (assuming it is initially at the origin)

$$\mathbf{r}(t) = \mathbf{v}(0)\tau(1 - e^{-t/\tau}) + \tau \int_0^t \mathbf{a}(t') \left[1 - e^{-(t-t')/\tau} \right] dt'.$$

Hence, the resultant average displacement $\langle \mathbf{r}(t) \rangle = \mathbf{v}(0)\tau(1 - e^{-t/\tau})$ asymptotes to $\mathbf{v}(0)\tau$ as the system relaxes and randomness takes over. In addition, the [mean squared displacement](#) can be determined similarly to the preceding calculation to be

$$\langle r^2(t) \rangle = v^2(0)\tau^2(1 - e^{-t/\tau})^2 - \frac{3k_B T}{m}\tau^2(1 - e^{-t/\tau})(3 - e^{-t/\tau}) + \frac{6k_B T}{m}\tau t.$$

It can be seen that $\langle r^2(t \ll \tau) \rangle \simeq v^2(0)t^2$, indicating that the motion of Brownian particles at timescales much shorter than the relaxation time τ of the system is (approximately) [time-reversal](#) invariant. On the other hand,

$\langle r^2(t \gg \tau) \rangle \simeq 6k_B T\tau t/m = 6\mu k_B T t = 6Dt$, which suggests that the long-term random motion of Brownian particles is an [irreversible dissipative process](#). Here we have made use of the [Einstein–Smoluchowski relation](#) $D = \mu k_B T$, where D is the diffusion coefficient of the fluid.

”

(B) YouTube?

(C) 中文资料

(i) <https://www.zhihu.com/question/348483881> (抽样理论中有哪些令人印象深刻(有趣)的结论?)

郎之万动力学采样方法源自于布朗运动，同时也是一个变优化为采样的神奇方法。

抽样方法的目标就是抽样一个分布。

郎之万动力学采样法:

我们从布朗运动出发，通过郎之万动力学，架起来动力学和分布的桥梁。接下来就可以利用这个桥梁来采样了：

通过模拟动力学来采样分布，具体而言就是精确模拟粒子在势能以及热涨落中运动，捕捉粒子的位置，作为样本，就会得到想要的分布。

最后要给大家交代的的就是“势能”以及“热涨落”怎么来模拟：

热涨落力具有高斯分布，于是我们可以用高斯分布来模拟这个力：

$$\langle \eta_i(t) \eta_j(t') \rangle = 2\lambda k_B T \delta_{i,j} \delta(t - t'),$$

对于贝叶斯分布后验分布， $p(\theta|X) \propto p(\theta) \prod_{i=0}^N p(x_i|\theta)$ ，其中 θ 是参数。根据玻尔兹曼分布，其

势能就是 $U(\theta) = -\log p(\theta|X)$ 。于是势能力就可以通过对势能求梯度而获得。

于是当势能和热涨落都可以模拟的情况下，我们就可以通过模拟粒子运动来采样了：

$$\Delta\theta_t = \frac{\epsilon_t}{2} \left(\nabla \log p(\theta_t) + \frac{N}{n} \sum_{i=1}^n \nabla \log p(x_{ti}|\theta_t) \right) + \eta_t$$
$$\eta_t \sim N(0, \epsilon_t)$$

知乎 @45

这个公式来自于 Bayesian Learning via Stochastic Gradient Langevin Dynamics，具体细节大家可以参考这篇文章。

Notes: Bayes' theorem (贝叶斯定理) (<https://zh.wikipedia.org/zh-cn/%E8%B4%9D%E5%8F%B6%E6%96%AF%E5%AE%9A%E7%90%86>)

贝叶斯定理是概率论中的一个定理，描述在已知一些条件下，某事件的发生概率。比如，如果已知某癌症与寿命有关，使用贝叶斯定理则可以通过得知某人年龄，来更加准确地计算出他罹患癌症的概率。通常，事件 A 在事件 B 已发生的条件下发生的概率，与事件 B 在事件 A 已发生的条件下发生的概率是不一样的。然而，这两者是有确定的关系的，贝叶斯定理就是这种关系的陈述。贝叶斯公式的一个用途，即通过已知的三个概率而推出第四个概率。

贝叶斯定理是关于随机事件A和B的**条件概率**的一则定理。

$$P(A | B) = \frac{P(B | A)P(A)}{P(B)}$$

其中A以及B为**随机事件**，且 $P(B)$ 不为零。 $P(A|B)$ 是指在事件B发生的情况下事件A发生的概率。

在贝叶斯定理中，每个名词都有约定俗成的名称：

- $P(A|B)$ 是已知B发生后，A的**条件概率**。也由于得自B的取值而被称作A的**后验概率**。
- $P(A)$ 是A的**先验概率**（或**边缘概率**）。之所以称为"先验"是因为它不考虑任何B方面的因素。
- $P(B|A)$ 是已知A发生后，B的条件概率。也由于得自A的取值而被称作B的**后验概率**。
- $P(B)$ 是B的**先验概率**。

按这些术语，贝叶斯定理可表述为：

$$\text{后验概率} = (\text{似然性} * \text{先验概率}) / \text{标准化常量}$$

也就是说，后验概率与先验概率和相似度的乘积成正比。

另外，比例 $P(B|A)/P(B)$ 有时被称作标准似然度（standardised likelihood），贝叶斯定理可表述为：

$$\text{后验概率} = \text{标准似然度} * \text{先验概率}$$

(ii) <https://www.zhihu.com/question/268833647> (请问朗之万分子动力学和耗散粒子动力学有什么区别？)

这个学期上的Multi-scale Modeling里刚好涉及到郎之万动力学和耗散粒子动力学，来强答一发。没看过这方面的中文文献，所以不确定的地方还是用英文描述，望见谅。

两者都是在中尺度(meso-scale)上的动力学，对于原有的系统都做了coarse-graining，为了保留系统内布朗运动的特性，引入了耗散力和随机力

$$\begin{aligned}\dot{\mathbf{r}}_i &= \frac{\mathbf{p}_i}{m_i} \\ \dot{\mathbf{p}}_i &= \mathbf{F}_i + \mathbf{F}_i^D + \mathbf{F}_i^R\end{aligned}$$

在动量表达式中，第一项为守恒力（conservative），第二项为耗散力（dissipative force），第三项为随机力（random force）。

郎之万动力学的形式如下，

$$\mathbf{F} = -\nabla U - m\gamma\mathbf{v} + \sqrt{2m\gamma k_B T}\mathbf{R}(t)$$

它的耗散力通过摩擦系数（friction coefficient）引入，为了满足fluctuation-dissipation relation, 获得了随机力的系数，要求R(t)为平均值为0，方差为1的高斯分布随机函数。

耗散粒子动力学的形式如下（在此可忽略DPD对守恒力的简化为soft conservative interaction），

$$\begin{aligned}\vec{F}_{ij}^C &= -\nabla U(r_{ij}) \\ \vec{F}_{ij}^D &= -\gamma(r_{ij})(\vec{v}_{ij}\hat{r}_{ij})\hat{r}_{ij} \\ \vec{F}_{ij}^R &= \sigma(r_{ij})\eta_{ij}\hat{r}_{ij}\end{aligned}$$

耗散力都是成对出现的，依赖于相对速度，并引入了截断距离。同样为了满足friction-dissipation relation,

$$\sigma^2 = 2k_B T\gamma,$$

并要求随机函数

$$\begin{aligned}\langle \eta_{ij} \rangle &= 0 \\ \langle \eta_{ij}(t)\eta_{i'j'}(t') \rangle &= (\delta_{ii'}\delta_{jj'} + \delta_{ij'}\delta_{i'j})\delta(t-t')\end{aligned}$$

从结果上说，郎之万动力学会无法实现动量传递（momentum transport），因此无法用于计算扩散系数(diffusion coefficient)，而离散例子动力学则可以。

Notes: Dissipative Forces (耗散力)

https://en.wikiversity.org/wiki/Advanced_Classical_Mechanics/Dissipative_Forces

Dissipative forces are forces of such nature that energy is lost from a system when motion takes place. Of course, **energy is in general conserved but it is lost from the degrees of freedom of interest into heat (the random motion of internal degrees of freedom) or radiation (the motion of new particles created by the motion -- light usually).**

The force can often be represented by the following equation. Depending on the value of the index n we have different types of dissipative forces.

$$|\vec{F}| = a(\vec{r}, t) |\vec{v}|^n$$

Types of Dissipative Forces [\[edit \]](#)

Frictional Forces (Dry Friction) [\[edit \]](#)

The force of kinetic friction is supposed to be proportional to the normal force and independent of area of contact or speed. It is simply a property of the materials in contact. Specifically, we have $|\vec{F}| = \mu |F_{\text{normal}}|$ so $n = 0$.

The frictional force opposes the relative motion of two surfaces.

Viscous Forces [\[edit \]](#)

Here the frictional force increases as the first power of the relative speed between the surfaces and opposes the relative motion. Viscous friction is important for wet surfaces at small relative velocities.

High-Velocity Friction [\[edit \]](#)

At higher velocities, the force of friction increases as a higher power of the relative velocity. For example, $n = 2$ gives a good approximation to the dissipative force experienced by objects travelling through fluids at high Reynolds number $Re = (vL)/\nu$ where ν is the viscosity of the fluid.

(iii) <https://www.zhihu.com/question/27566698> (以现有的超算的算力，能否在原子的级别上，模拟一杯水的物理状态？)

2 Determining the Generalized Force

2.1 Partial derivatives

2.1.1 Damped Pendulum

2.2 Power function

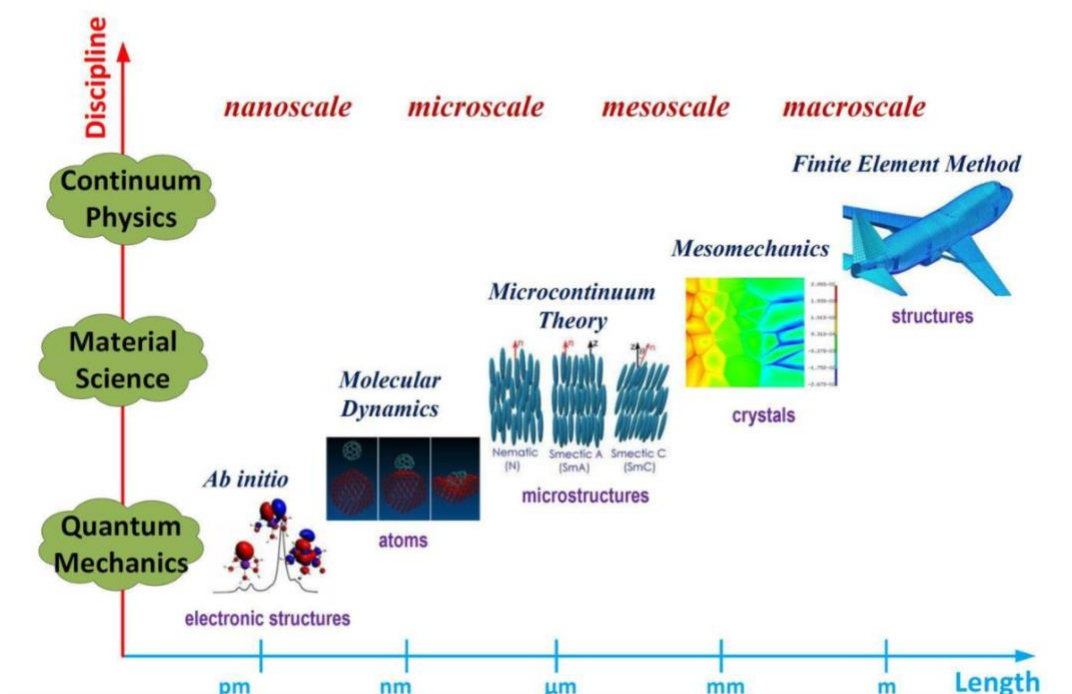
2.2.1 Damped Pendulum

2.2.2 More Generally

3 A Useful Example with Dry Friction

计算物理/计算化学中每处理一个体系之前，我们都要问我们想算什么，然后根据我们需要计算的性质来选择合适的工具，这样才能保证用有限的计算资源获得我们想知道的性质。

现在一个比较热门的词叫做“多尺度模拟” (multiscale modeling)，套用这张图（图片出处：xqwang.engr.uga.edu）



对于不同的尺度的体系的处理方法，从原子级别一直到宏观级别，所采用的处理方法一般是量子力学（从头计算法, ab initio）- 统计力学（分子动力学模拟, MD）- 流体力学或连续介质力学（有限元, Finite element），等等。不同尺度下所采用不同的方法，所关心的性质都不一样，拿水作为例子来讲：

- 原子尺度下更关心水分子的波函数，化学键，电子密度，光谱等等，这时就要用量子力学来处理。
- 纳米尺度下已经是成千上万个水分子了，这时更关心的就是水分子的热力学性质了，这时就要用统计力学处理。为了计算统计力学中的各种均值，我们需要对系统进行采样，所以要用到分子动力学（MD）或者蒙特卡洛（MC）。
- 微米尺度或更高尺度下，水分子的大小跟系统的尺度大小相比可以忽略不计，所以可以把体系视为连续介质，这时就可以用流体力学来处理，流体力学可以研究的性质也是非常多，比如水溶液中物质的运输，水中的湍流，等等。

回到你一开始的问题：“模拟一杯水中每一个原子的行为”。这个目标本身就很含糊，是要在量子力学下描述每个原子的行为，还是要在把每个原子近似成经典力学下的粒子来描述？如果是量子力学下的粒子，那么根据不确定性原理，你无法同时得到原子在某个时刻的精确位置和动量，而只能得到一个位置和动量的概率分布函数。量子力学的计算量非常大，几千个原子的高精度计算就足以占满一台大型计算机了。

如果是把原子视为经典力学下的粒子进行分子动力学模拟，如前面所提到的现在的超级计算机也只能处理百万个原子，这连一滴水的零头都不到。而且，又如 @周杨超 前面所提到的，这是一个多体问题，而经典力学下的多体问题是没有解析解的，是混沌的。分子动力学模拟本身算法是存在误差的，这样随着模拟的不断进行，模拟得到的轨迹是会随时间偏离粒子的真实轨迹越来越远。

那么既然无法算准每个原子在每个时刻的位置和动量，那是否极大影响我们获得水的物理性质呢？答案是否定的。对于分子动力学模拟和流体力学计算，我们根本就不关心某个原子在某个时刻的位置，也不关心某个原子在某一段时间内走过的轨迹，We don't give a shit about that. 分子动力学只关心是否所有的原子在指定的相空间区域里能够历经各态(ergodic)，然后对所有原子求平均就可以得到我们想要的热力学性质。流体力学就更不care这些了，它所做的不过是在解各种复杂初始和边界条件的Navier-Stokes方程（在我们化学狗看来）。

补充一句，如果只是想算水的热力学性质，不需要对一杯水进行分子动力学模拟，现在上万个水分子的分子动力学模拟已经能够比较好的给出水的热力学性质了。

郎之万方程：此方程描述了布朗运动由于流体的分子碰撞，粒子在流体中做的无规则运动 (<https://zhuanlan.zhihu.com/p/24391461>)

(iv) Notes: <https://www.zhihu.com/question/58150754>

作者：知乎用户 链接：<https://www.zhihu.com/question/58150754/answer/184974070> 来源：知乎 著作权归作者所有。商业转载请联系作者获得授权，非商业转载请注明出处。

目前 DFT 作为计算材料学中比较准确的方法，越来越多的人关注到这个领域，DFT 的优势是算的比较准，同时得到的结果与实验值符合的很好。我认为 **DFT 的好处是扩展性相对较强**，上可做 Beyond DFT (PAW, GGA) 下可为 MD 拟合新的势函数，同时 VASP 之类的量子计算软件稳定性好，报错信息详细，不需要大量写代码，当然写代码进行数据预处理和后处理还是需要的，同时在 Github 上有很多组开发的 Python 自动化库，基本上来说 DFT 计算已经半自动化了，所以整体比较成熟。虽然目前 DFT 算的体系仍然比较小 (Max~500 atoms)，但是随着半导体技术的发展和 CUDA 等显卡辅助计算的出现，我相信算的体系会越来越大的。回到 MD，答主是做 MD 的，个人觉得做 **MD 需要你的势能够准确描述你的体系，势能很大程度上决定最后结果的好坏**，我现在就比较惨，我还没有找到一个能够较好描述我研究的那个二元体系的势函数，所以只能等组里面的另一个博士拟合针对这个体系的新势函数，显然，大大拖慢了这个项目的进度。而且 LAMMPS 报错信息做的很差，一不小心就会丢原子，而且还不知道哪里写错了，如果我能够重新选择的话肯定选 DFT 了。另外，题主可以关注一下量子蒙特卡洛和机器学习在材料中的应用，这两个最近在学术界很火

(v)

<https://thuxxs.github.io/2016/12/16/%E9%83%8E%E4%B9%8B%E4%B8%87%E6%96%B9%E7%A8%8B/> (郎之万方程)

郎之万方程

📅 Dec 16, 2016 | 📄 Hits



介绍郎之万运动及其数值模拟

理论分析

布朗粒子在液体中会受到液体分子的随机碰撞而产生随机运动，以一维粒子为例

$$\begin{aligned} m \frac{dv}{dt} &= K(t) \\ &= -\gamma_0 v + F_0(t) \end{aligned}$$

其中 $-\gamma_0 v$ 是与速度相关的摩擦力， $F_0(t)$ 是粒子收到碰撞的随机力，其作用时间非常短，我们可以假设为一 δ 函数形式，冲击力对所有冲击取平均值应该为零，而不同时间点的冲击力相乘应该是无关的，所以 $F_0(t)$ 应该满足如下形式

$$\overline{F_0(t)} = 0, \overline{F_0(t)F_0(t')} = c\delta(t - t')$$

那么我们把布朗运动简化为郎之万方程

$$\begin{aligned} \frac{dv}{dt} &= -\gamma v + F(t) \\ \overline{F(t)} &= 0 \\ \overline{F(t)F(t')} &= Q\delta(t - t') \end{aligned}$$

方程的形式解为

$$v(t) = \int_0^t \exp[-\gamma(t - \tau)] F(\tau) d\tau + v(0) \exp[-\gamma t]$$

考虑足够长的时间，则上式最后一项实际上为零，所以后面我们都只考虑上式右边的第一项，也即考虑足够长的时间

由于碰撞时随机的，显然速度的平均值应当为零， $\overline{v(t)} = 0$ ，但这并不会给我们提供什么有用的信息，所以我们要考虑速度大小的平均值，我们计算

$$\overline{v(t)v(t')}$$

显然考虑极端情况，当 t 和 t' 相隔很远的时候，他们俩的速度之间没有任何关联，所以

$$\overline{v(t)v(t')} = \overline{v(t)}\overline{v(t')} = 0$$

但在一半情况下呢？我们计算

$$\begin{aligned}
 \overline{v(t)v(t')} &= \overline{\int_0^t \int_0^{t'} \exp[-\gamma(t-\tau)]F(\tau)d\tau \exp[-\gamma(t'-\tau')]F(\tau')d\tau'} \\
 &= \int_0^t \int_0^{t'} \exp[-\gamma(t-\tau)] \exp[-\gamma(t'-\tau')] \overline{F(\tau)F(\tau')} d\tau d\tau' \\
 &= Q \int_0^t \exp[-\gamma(t+t') + 2\gamma\tau] d\tau \\
 &= \frac{Q}{2\gamma} \{ \exp[\gamma(t-t')] - \exp[-\gamma(t+t')] \}
 \end{aligned}$$

任然考虑足够长时间，所以有不同时刻的关联度为

$$\overline{v(t)v(t')} = \frac{Q}{2\gamma} \exp[\gamma(t-t')]$$

只与所考虑的时间差有关，且与时间差呈指数下降趋势。

数值模拟

首先我们要进行计算的方程为

$$\begin{aligned}
 \frac{dv}{dt} &= -\gamma v + F(t) \\
 &= -\gamma v + \sqrt{Q}N(0,1)
 \end{aligned}$$

我们这里设随机力为强度为 \sqrt{Q} 的0 1正态分布，显然满足平均值为零，对于关联度我们有

$$\begin{aligned}
 \overline{F(t)F(t')} &= Q \overline{N_t(0,1)N_{t'}(0,1)} \\
 &= Q \overline{N^2(0,1)\delta(t-t')} \\
 &= Q\delta(t-t')
 \end{aligned}$$

我们可以解释为，当 $t \neq t'$ 时，两个正态分布无关，那么乘积的平均等于平均的乘积即为零，当 $t = t'$ 时，我们计算的是正态分布平方的平均值，肯定不为零。求解这个随机微分方程(SDE)我们需要用到[欧拉-丸山法](#)，具体来讲是要讲方程变形为

$$\begin{aligned}
 \frac{dv}{dt} &= -\gamma v + F(t) \\
 &= -\gamma v + \sqrt{Q} \frac{dW(t)}{dt} \\
 dv &= -\gamma v dt + \sqrt{Q} dW(t)
 \end{aligned}$$

而对于 dt 时间段内, $dW(t)$ 是一个维纳过程, 满足 $dW = W_j - W_i$ 服从 $N(0, j - i)$ 的正态分布, 即平均值为零, 方差为 $j - i$

“ 注意, 在 `python` 科学计算包中, 正态分布函数 `numpy.random.normal(loc, scale)` 中, `loc` 为平均值, `scale` 为标准差

所以在我们数值计算的 dt 过程中, dW 满足的是平均数为0, 方差为 dt (标准差为 \sqrt{dt})的正态分布。所以我们利用差分的方法可以计算得到

$$v_{i+1} = -\gamma v_i dt + \sqrt{Q} N(0, dt) + v_i$$

有了这个递推公式, 代码就很简单了

欧拉-丸山法

维基百科, 自由的百科全书

欧拉-丸山法是用数值求解随机微分方程 (SDE) 的方法, 是欧拉法求解常微分方程 (ODE) 在随机微分方程上的推广。此方法以欧拉和日本数学家丸山仪四郎命名。

考虑如下随机微分方程 (见伊藤积分)

$$dX_t = a(X_t) dt + b(X_t) dW_t,$$

以及给定的初始条件 $X_0 = x_0$, 其中 W_t 代表维纳过程, 假定我们要求解在时间区间 $[0, T]$ 上的此方程, 则使用此方法会得到 X 的解 Y , 是马可夫链, 其定义如下:

- 将区间 $[0, T]$ 划分为 N 个相等子区间 $\Delta t > 0$:

$$0 = \tau_0 < \tau_1 < \dots < \tau_N = T \text{ and } \Delta t = T/N;$$

- 令 $Y_0 = x_0$;
- 写成迭代的形式

$$Y_{n+1} = Y_n + a(Y_n)\Delta t + b(Y_n)\Delta W_n,$$

其中

$$\Delta W_n = W_{\tau_{n+1}} - W_{\tau_n}.$$

1.6 “Langevin dynamics”:

(A) Wiki

“In physics, Langevin dynamics is an approach to the mathematical modeling of the dynamics of molecular systems. The approach is characterized by the use of simplified models while accounting for omitted degrees of freedom by the use of stochastic differential equations.

Overview [edit]

A molecular system in the real world is unlikely to be present in vacuum. Jostling of solvent or air molecules causes friction, and the occasional high velocity collision will perturb the system. Langevin dynamics attempts to extend molecular dynamics to allow for these effects. Also, Langevin dynamics allows temperature to be controlled like with a thermostat, thus approximating the canonical ensemble.

Langevin dynamics mimics the viscous aspect of a solvent. It does not fully model an implicit solvent; specifically, the model does not account for the electrostatic screening and also not for the hydrophobic effect. For denser solvents, hydrodynamic interactions are not captured via Langevin dynamics.

For a system of N particles with masses M , with coordinates $X = X(t)$ that constitute a time-dependent random variable, the resulting Langevin equation is^[1]

$$M\ddot{X} = -\nabla U(X) - \gamma\dot{X} + \sqrt{2\gamma k_B T}R(t),$$

where $U(X)$ is the particle interaction potential; ∇ is the gradient operator such that $-\nabla U(X)$ is the force calculated from the particle interaction potentials; the dot is a time derivative such that \dot{X} is the velocity and \ddot{X} is the acceleration; γ is the viscosity; T is the temperature, k_B is Boltzmann's constant; and $R(t)$ is a delta-correlated stationary Gaussian process with zero-mean, satisfying

$$\begin{aligned}\langle R(t) \rangle &= 0 \\ \langle R(t)R(t') \rangle &= \delta(t - t')\end{aligned}$$

Here, δ is the Dirac delta.

If the main objective is to control temperature, care should be exercised to use a small damping constant γ . As γ grows, it spans from the inertial all the way to the diffusive (Brownian) regime. The Langevin dynamics limit of non-inertia is commonly described as Brownian dynamics. Brownian dynamics can be considered as overdamped Langevin dynamics, i.e. Langevin dynamics where no average acceleration takes place.

The Langevin equation can be reformulated as a Fokker-Planck equation that governs the probability distribution of the random variable X .

1.7 "Implicit solvent vs. Explicit solvent": Wiki

https://en.wikipedia.org/wiki/Implicit_solvation

"Implicit solvation (also called "continuum solvation") is a method to represent solvent as a continuous medium instead of individual "explicit" solvent molecules, most often used in molecular dynamics simulations and in other applications of molecular mechanics. The method is often applied to estimate free energy of solute-solvent interactions in structural and chemical processes, such as folding or conformational transitions of proteins, DNA, etc."

(B) 中文资料

(i) 百度（朗之万动力学）<https://baike.baidu.com/item/朗之万动力学>

朗之万动力学 (Langevin Dynamics) 是控制模拟系统能量的一种常用算法，在多种分子模拟软件中都可以看到。分子模拟在一定的系综下进行，所以要保持系统状态不变，比如控制系统温度，压强等。由于计算机不是百分百精准，微小的误差在长时间的模拟过程中可能被不停积累和放大，于是需要不同的方法对系统进行不停调整。这些调整的方法有很多，比如 Berendsen, Nose-hoover, Langevin。

模拟系统中的原子受到其周围原子相互作用力，依据所受作用力根据牛顿第二定律运动。朗之万动力学的实现方法是给原子添加两个额外的作用力，即摩擦力和随机力。该摩擦力大小为原子速度乘以其质量再乘以一个摩擦因子 (γ)，其方向与原子速度相反。而随机力可以理解为来自溶液分子的随机相互作用等。这两个力一起调节系统中各个原子的运动，以达到对整个系统能量的调控，即调控系统温度，压强等。