# Statistical mechanics for molecular simulations (2016)

2/11/2015.

## Lecture 6

Nonequilibrium systems I:
Stochastic dynamics for coarse-grained dynamics.

* Brownian dynamics.
* Dissipative particle dynamics.
* Kinetic Monte Carlo

So far we have focus on equilibrium ~~systems~~ dynamics/sampling and microscopic systems. In recent years, the subjects of "multiscale modeling" & "coarse-graining" have drawn much attention. In this lecture we will attempt to introduce several such "mesoscale" stochastic methods that are suitable for providing non-equilibrium properties of various systems.

Stochastic behavior emerges from coarse-graining, i.e. neglected degrees of freedom ~

simplest stochastic process.

* Brownian motion

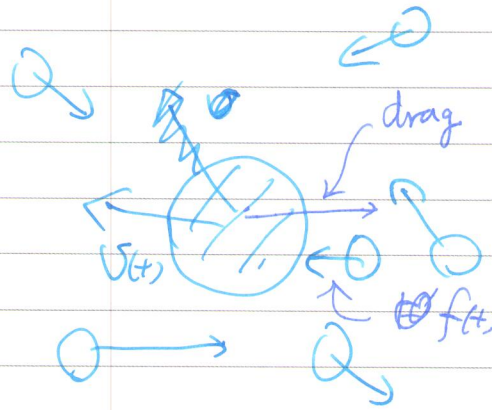
The phenomenon of Brownian motion was named after the botanist Robert Brown due to his discovery in 1827. You know the story already. What is less known is the importance of Einstein's theory of Brownian motion (1905) and later Perrin's experimental works that conclusively showed the atomic nature of matter.

traj. of a Brownian particle

Nobel prize in 1926 was awarded to Jean Baptiste Perrin "for his work on the discontinuous structure of matter, and especially for his discovery of sedimentation equilibrium"

Here, we will use the general framework developed by Langevin to develop a theoretical description of diffusion of a Brownian particle.

Let's consider a massive particle immerse in a homogeneous liquid:




Stokes law

$F_d = 6\pi\mu R \cdot v(t)$

for a spherical particle

$\mu$: dynamic viscosity

R: radius of the particle

The Newton's equation states. Stokes' law

↓ frictional force

$$F = ma \Rightarrow m \cdot \frac{dv(t)}{dt} = -\gamma \cdot v(t) + f(t)$$

mobility $\eta = \frac{v_d}{F} = \frac{1}{\gamma}$

↑ random timeless force

This is a first order stochastic differential equation that can be solved to yield useful information after averaged. Due to the nature of the random force, we will assume, quite reasonably:

$$\langle f(t) \rangle \xrightarrow{\text{ensemble averaged!!}} 0.$$

In terms of velocity, the equation reads.

Langevin equation.

$$\dot{v}(t) = -\frac{\gamma}{m} v(t) + \frac{1}{m} \cdot f(t). \quad \text{----} (1)$$

ensemble average eliminates the effects of random forces

Note that average of this gives a trivial "relaxation" of the velocity due to frictional force., notice that $\langle \dot{v}(t) \rangle = \frac{d}{dt} \langle v(t) \rangle$

$$\frac{d}{dt} \langle v(t) \rangle = -\frac{\gamma}{m} \langle v(t) \rangle + \frac{1}{m} \underbrace{\langle f(t) \rangle}_{=0}$$

$$\therefore \langle v(t) \rangle = v(0) \cdot e^{-\frac{\gamma}{m} t}$$

This is, of course, uninteresting.

Interesting physics occurs when we "average" after calculating the dynamics.

If $f(t)$ is known, the Langevin equation can be integrated to yield:

$$v(t) = v_0 \cdot e^{-\frac{\gamma}{m}t} + \frac{1}{m}\int_0^t ds \cdot e^{-\frac{\gamma}{m}(t-s)} \cdot f(s)$$

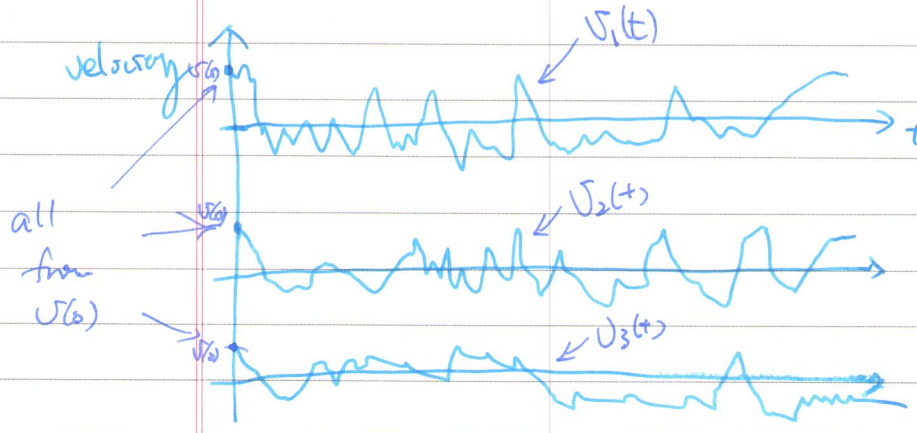
and

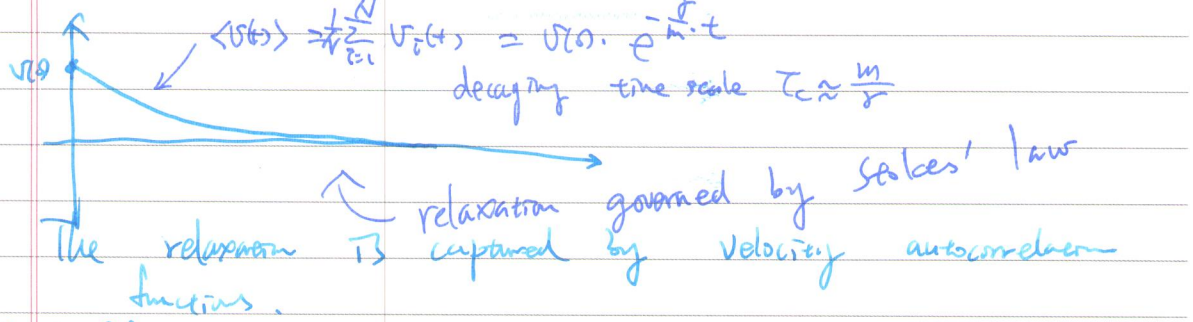
$$x(t) = x_0 + \frac{m}{\gamma}\left(1 - e^{-\frac{\gamma}{m}t}\right) + \frac{1}{\gamma}\int_0^t ds \left(1 - e^{-\frac{\gamma}{m}(t-s)}\right) \cdot f(s)$$

These two equalities are easy to verify by taking the derivatives with respect to $t$.

In the following we examine two properties of this equation to illustrate some important ideas in nonequilibrium stat. mech.

Illustration of ensemble average.




The relaxation is captured by velocity autocorrelation functions.

* Diffusion

the diffusive motion of a Brownian particle is measured by its mean-square-displacement.

Set $x_0 = 0$, so we want to calculate $\langle x^2 \rangle$, the mean-square displacement.

Notice that

$\frac{d}{dt}$ is linear! →

$$\frac{d}{dt}\langle x^2(t)\rangle = \left\langle \frac{d}{dt}(x^2)\right\rangle = 2\cdot\langle x(t)\dot{x}(t)\rangle$$

from the Langevin eq.

$$\ddot{x}(t) = -\frac{\gamma}{m}\dot{x}(t) + \frac{1}{m}f(t)$$

multiply both sides by $x(t)$ and take average:

$$\text{LHS}: \langle x(t)\ddot{x}(t)\rangle = \left\langle\left[\frac{d}{dt}(x(t)\dot{x}(t)) - \dot{x}(t)^2\right]\right\rangle$$

$$= \frac{d}{dt}\underbrace{\langle x(t)\dot{x}(t)\rangle}_{G(t)=\langle x(t)\dot{x}(t)\rangle} - \langle \dot{x}^2(t)\rangle \qquad \frac{1}{2}m\langle v^2\rangle = \frac{1}{2}k_B T$$

here we used the equilibrium property of the system (or thermal bath!!) ↑ assume 1-D system!!

Now recognize $\langle \dot{x}^2(t)\rangle = \langle v^2\rangle = \frac{k_B T}{m}$ from the equipartition theorem ⇒ $\text{LHS} = \frac{d}{dt}G(t) - \frac{k_B T}{m}$

$$\text{RHS}: -\frac{\gamma}{m}\langle x(t)\dot{x}(t)\rangle + \frac{1}{m}\langle x(t)f(t)\rangle$$

$\langle x(t)\rangle\langle f(t)\rangle = 0$ random force does not have spatial dependence

$$= -\frac{\gamma}{m}G(t)$$

We obtain

$$\frac{d}{dt}G(t) - \frac{k_B T}{m} = -\frac{\gamma}{m}G(t)$$

So $\dot{G}(t) + \frac{\gamma}{m} G(t) - \frac{k_B T}{m} = 0$.

This simple differential equation is solved to yield

$$G(t) = C \cdot e^{-\frac{\gamma}{m}t} + \frac{k_B T}{\gamma}$$

the integration constant $C$ is determined by $X(0) = 0$.

$\therefore G(0) = 0 \Rightarrow C = -\frac{k_B T}{\gamma}$

Therefore $G(t) = \langle X(t)\dot{X}(t)\rangle = \frac{k_B T}{\gamma} \cdot (1 - e^{-\frac{\gamma}{m}t})$

Now recognize that

$$\frac{d}{dt}\langle X^2(t)\rangle = 2 \cdot \langle X(t)\dot{X}(t)\rangle = \frac{2k_B T}{\gamma}(1 - e^{-\frac{\gamma}{m}t})$$

$$\therefore \langle X^2(t)\rangle = \frac{2k_B T}{\gamma}\left[t - \frac{m}{\gamma}(1 - e^{-\frac{\gamma}{m}t})\right]$$

here we also used $\langle X^2(0)\rangle = 0$. because $X(0) = 0$.

This result is time-dependent as expected.

① short time $t \ll \left(\frac{m}{\gamma}\right)$ ← this is a characteristic relaxation d time scale. (inertial motion)

In this case

$$e^{-\frac{\gamma}{m}t} \approx 1 - \frac{\gamma}{m}t + \frac{1}{2}\cdot\frac{\gamma^2}{m^2}\cdot t^2 + \cdots$$

$$\therefore \langle x^2(t)\rangle \approx \frac{2k_BT}{\gamma}\cdot\left[t - \frac{m}{\gamma}\cdot\left(1 - 1 + \frac{\gamma}{m}t - \frac{1}{2}\frac{\gamma^2}{m^2}\cdot t^2\right)\right]$$

$$= \frac{2k_BT}{\gamma}\cdot\frac{m}{\gamma}\cdot\frac{1}{2}\cdot\frac{\gamma^2}{m^2}\cdot t^2$$

$$= \frac{k_BT}{m}\cdot t^2$$

So the mean-square displacement (for the Brownian particle) is quad. in time.

This is just like a free particle with a mean velocity of $\sqrt{\frac{k_BT}{m}}$.

Note $\frac{1}{2}m\langle v\rangle^2 = \frac{1}{2}k_BT \Rightarrow \sqrt{\langle v^2\rangle} = \sqrt{\frac{k_BT}{m}}$ !!

No time to feel $\gamma$ !!

In this time scale the Brownian particle is free, not hitting by the solvent, so the motion is inertial. The system does not reach equilibrium yet.

② long time $t \gg \frac{m}{\gamma}$ (diffusive motion).

on the other hand, as $t \gg \frac{m}{\gamma}$

$$\lim_{t\to\infty} \langle x^2(t)\rangle = \frac{2k_B T}{\gamma} \cdot t$$

the mean-square displacement depends linearly on time! this is the diffusive regime!!

by definition, the diffusion coefficient is defined as

$$\langle x^2\rangle(t) = 2 \cdot D \cdot t$$ ← for 1-D; for 3-D: $6Dt$

$r^2(t) = x^2(t) + y^2(t) + z^2(t)$
$= 3 \cdot x^2(t)$.

Therefore $D = \frac{k_B T}{\gamma}$ ← independant of the mass of the particle!!

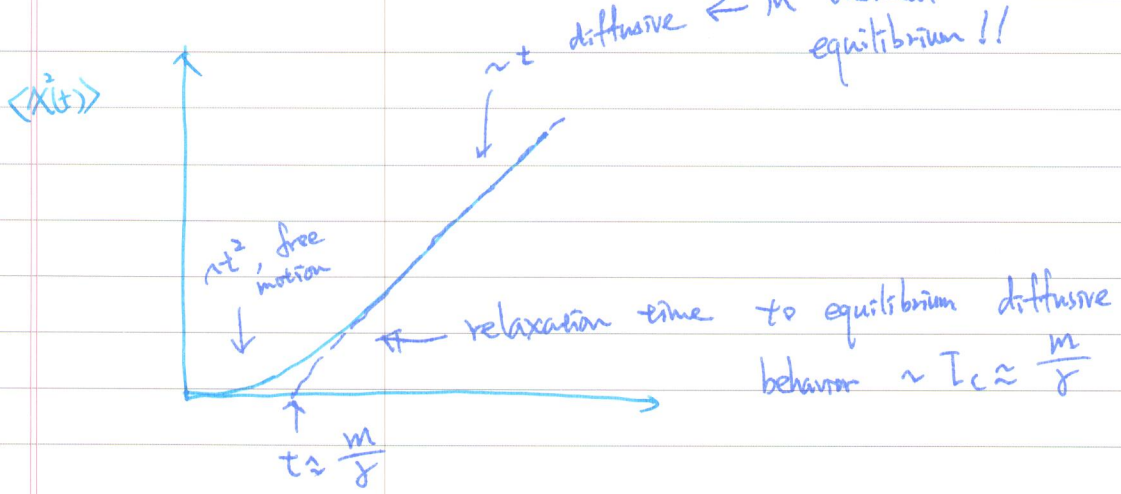
Einstein relation.

we can further apply Stokes' law for a spherical particle $\gamma = 6\pi\mu R$ (μ: dynamic viscosity; R: radius of the particle.)

so $$D = \frac{k_B T}{6\pi\mu R}$$

This is the Einstein-Stokes relation.

In summary, the mean-square displacement goes like:




## ✳ Fluctuation - dissipation theorem.

The Einstein relation is a remarkable result since it relates a dissipative coefficient with the equilibrium property.

Recall that $\tau_c = \frac{m}{\gamma}$ defines the time scale for velocity relaxation (energy relaxation) in the system.

So $\gamma = \frac{k_B T}{D}$ ← thermal equilibrium quantities.

↑ relaxation, dissipation

In fact, in general the diffusion coefficient can be related to the autocorrelation function of the random force. With some more mathematics one can derive:

macroscopic!! ↙ ↘ microscopic!!

$$\gamma = \frac{1}{k_B T} \int_0^\infty \underbrace{\langle f(0) f(t) \rangle}_{\text{force-force auto-correlation function.}} dt.$$

This is a quite general relation. In fact, it turns out that in the linear response regime (i.e. small perturbation) the dissipative force is always connected to the fluctuating random force in equilibrium. This is captured generally by the regression hypothesis by Lars Onsager, which will be discussed later.

So far we have focused on the analytical solution to the Langevin equation

$$\dot{v}(t) = \frac{-\gamma}{m} v(t) + \frac{1}{m} f(t).$$

Actually this equation can be solved numerically, for general cases with potential terms, to simulate behavior of systems in the mesoscopic scale.

This is the so called Langevin dynamics.

While the Brownian dynamics is an effective means, it assumes overly damped dynamics & lacks several key effects:

① no action-reaction, does not conserve momentum $\Rightarrow$ third law.

② totally independent in space & in time $\Rightarrow$ does not reproduce hydrodynamics.

We neglect the practical issues in Langevin/Brownian dynamics simulations. See the literature if you are interested.

## hydrodynamics ?

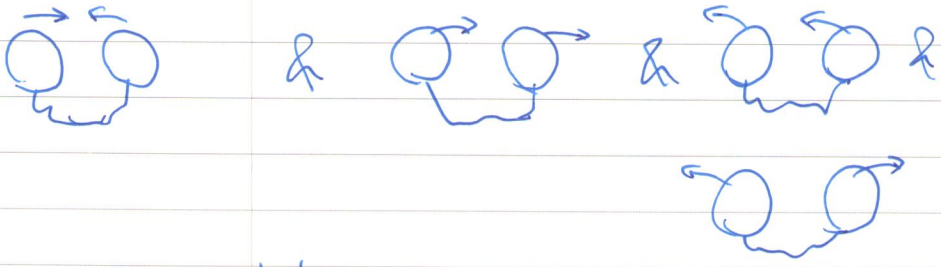
imagine motions of two domains.

fluctuation simulated by

the Brownian dynamics,
friction is considered —.

But : motions are not correlated.

So.



equally likely ⇒ but not true if

consider solvent "hydrodynamics"

≠ current induce by one particle should affect another particle

⇒ to avoide this, we need dissipative particle dynamics !!

timeless !

* dissipative particle dynamics.

DPD & Kawakatsu, see slides

The problem about the Brownian dynamics approach can be largely eliminated by considering a slightly different form of force:

$$f_i = \sum_{j \neq i} \left( F_{ij}^{C} + F_{ij}^{D} + F_{ij}^{R} \right)$$

($f_i$: force acting on the $i$-th particle; $F_{ij}^{C}$: conservative force; $F_{ij}^{D}$: dissipative force, ie. friction; $F_{ij}^{R}$: random force.)

Where the dissipative force & random force are defined as

$$F_{ij}^{D}(\vec{r}_{ij}, \vec{v}_{ij}) = -\gamma \cdot w^{D}(|r_{ij}|) \times (\vec{v}_{ij} \cdot \hat{r}_{ij}) \cdot \hat{r}_{ij}$$

($\gamma$: strength of friction; $w^{D}(|r_{ij}|)$: distance dependent correlation factor.)

$\vec{r}_{ij} = \vec{r}_i - \vec{r}_j$

$\vec{v}_{ij} = \vec{v}_i - \vec{v}_j$

Note that this force simulates hydrodynamics & spatial correlation of the dynamics.

and random force.

standard normal random variable

$$F^R_{ij}(\vec{r}_{ij}) = \sigma \cdot w^R(|\vec{r}_{ij}|) \cdot \xi_{ij} \cdot \hat{r}_{ij} \qquad \xi_{ij} = \xi_{ji}$$

and

↑ magnitude of random pair force.

Note that the forces are all pairwise & satisfy action-reaction ⇒

$$F^D_{ij} = -F^D_{ji} \quad \& \quad F^R_{ij} = -F^R_{ji}.$$

⇒ always momentum conserved.

correlation due to "hydrodynamics" of the ~~dissipative~~ solvent

Now, ~~just like~~ $w^D(|\vec{r}_{ij}|)$ & $w^R(|\vec{r}_{ij}|)$ are "spatial correlations" & cannot be chosen independently, must enforce

$$w^D(r_{ij}) = [w^R(r_{ij})]^2.$$

also the fluctuation-dissipation.

$$\sigma^2 = 2k_B T \cdot \gamma \qquad \text{(for 1-D)}.$$

↑ std. dev. for fluctuation.

This form of DPD can recover "hydrodynamic" behavior on sufficiently large length & time scales.

The proof of the above expressions is out of the scope of this class & can be found in

Espanol & Warren, Europhys. Lett. 30, 191 (1995).

Groot & Warren, J. Chem. Phys, 107, 4423 (1997).

* either $W^R$ or $W^D$ can be chosen arbitrary, but not both

* A commonly used $W^R$ & $W^D$ is a simple cut-off.

(correlation in space decays quadratically)

$$W^D(r) = [W^R(r)]^2 = \begin{cases} (r_c - r)^2 & \text{if } r < r_c \\ 0 & \text{if } r \geq r_c \end{cases}$$

* ~~A simple Euler method~~ a modified velocity-Verlet algorithm should be used (see discussions in Groot & Warren).

* how again, the random force amplitude depends on $\delta t$ ← time step, as we have discussed in last lecture for DPD.

pick from normal distribution. ← standard

$$\therefore \vec{F}^R_{ij} = \sigma \cdot w^R(|\vec{r}_{ij}|) - \xi_{ij} \cdot \frac{1}{\sqrt{\delta t}} \times \hat{r}_{ij}$$

The procedure allows dynamics without solvent while keeping hydrodynamics & momentum conservation.

⇒ key is "long range correlations" induced by hydrodynamics.

⇒ critical for modeling collective behaviors induced by thermodynamics ⇒ block copolymer, membranes, proteins ... very important !!

⇒ will give examples using slides later.

Finally, we reach our last topic,

## Dynamical Monte Carlo.

In many cases, in a mesoscopic / bulk simulation one likes to consider transitions between states according to pre-defined "transition rates" (from microscopic simulations, phenomenological models, experimental measurements ...). The rate can be constant or not and this kind of process (very important in physics) can very generally been cast into a "stochastic mold", i.e. stochastic processes representing dynamical events.

General mathematical methods for such stochastic processes include stochastic integral methods (Ito formulism), Markov / generalized Markov chain model, random walk

A general simulation technique is the DMC method, here, we consider DMC for kinetic processes, i.e. well defined transition rates. If the system can exist in $k$ states, then such process is generally described by a "Master equation:

$P_k(t)$: probability that a system in state $k$

$$\frac{\partial P_k(t)}{\partial t} = \sum_{k'} W_{k' \to k} \cdot P_{k'}(t) - \sum_{k'} W_{k \to k'} \cdot P_k(t)$$

$W_{k' \to k}$: rate from $k' \to k$.

according to detailed balance, $W_{k' \to k} \cdot e^{-\beta E_{k'}} = W_{k \to k'} e^{-\beta E_k}$

$$\therefore \frac{W_{k' \to k}}{W_{k \to k'}} = \frac{e^{-\beta E_k}}{e^{-\beta E_{k'}}} = e^{-\beta (E_k - E_{k'})}$$

We want to simulate this dynamical process using the Monte Carlo procedure, i.e. treat the dynamical stochastically, but MC is intrinsically without time, can we recover the same info?

The answer is yes, but we need to consider a few words about stochastic process, to be specific, we wanna to consider Poisson process.

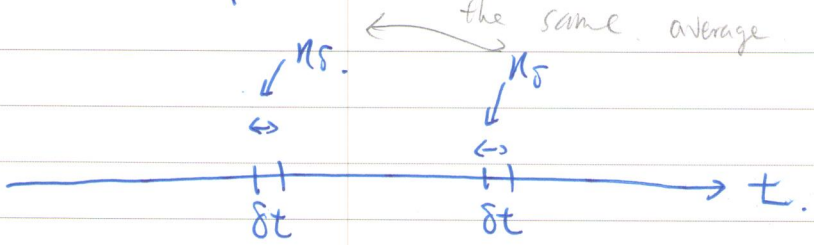
## Poisson process

Consider $A \xrightarrow{W} B$ rate $W$.

event: A became B, in a discrete transition (jump).

rate means probability of making this jump is uniform in time. $\Leftarrow$ Poisson $\sim$.

Consider many "A particles", all can make the jump




$n_{\delta t}$ is the number of particles making the jump in the interval $\delta t$. ; note that.

$n_{\delta t}$ is a random variable but $\langle n_{\delta t} \rangle = W \times \delta t$.

actually, the definition of rate is take the long time average.

$$w = \lim_{\delta t \to 0,\, K \to \infty} \frac{\sum_{i=1}^{K} n_\delta^{(i)}}{K \cdot \delta t}$$

Taking a very small $\delta t$ such that each interval at most one event, now the probability of containing an event in the interval is $w \cdot \delta t$, containing no event is $1 - w \cdot \delta t$.

for very small $\delta t$, in each interval

prob. has one event $\Rightarrow w \cdot \delta t$.

" has no event $\Rightarrow 1 - w \cdot \delta t$.

So, the probability of having $n_e$ events in total time $t$ is ($K = t/\delta t$ : total # of intervals):

$$P(n_e) = \binom{K}{n_e} \cdot (w \cdot \delta t)^{n_e} \times (1 - w \cdot \delta t)^{K - n_e}$$

($P(n_e)$: just $n_e$; $\binom{K}{n_e}$: fill $n_e$ in $K$ intervals; $(w \cdot \delta t)^{n_e}$: with one event; $(1 - w \cdot \delta t)^{K-n_e}$: without an event)

In the limit $\delta t \to 0$ ($\Leftrightarrow K \to \infty$), the distribution becomes

binomial

$$P(n_e, wt) = \lim_{K\to\infty} \frac{K!}{n_e!\,(K-n_e)!} \times \left(\frac{wt}{K}\right)^{n_e} \times \left(1-\frac{wt}{K}\right)^{K-n_e} \to e^{-wt}$$

$$= \lim_{K\to\infty} \underbrace{\frac{K!}{K^{n_e} \times (K-n_e)!}}_{\to 1} \times \left(\frac{(wt)^{n_e}}{n_e!}\right) \times \underbrace{\left(1-\frac{wt}{K}\right)^{K}}_{\to e^{-wt}} \times \underbrace{\left(1-\frac{wt}{K}\right)^{-n_e}}_{\to 1}$$

Poisson

$$= \frac{\lambda^{n_e}}{n_e!} \times e^{-\lambda}$$

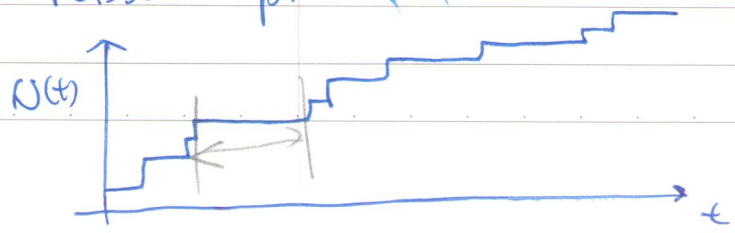
defined $\lambda = wt \Leftarrow$ averaged # of events.

This yields the distribution for $n_e$ events,

~~We are interesting in $n_e$!~~

~~$f(t) = P(n_e = 1) =$~~

typical Poisson process?



To simulate the dynamics, we are interested in the distribution of "waiting time" between two jump events, i.e. distribution of time for $n_e = 0$

waiting time distribution:

$$\bar{f}_0(t) = P(n_e = 0) = e^{-wt}$$

the normalized form is $f(t) = w \cdot e^{-wt}$.

the average waiting time is the $\langle t \rangle = \frac{1}{w}$ ✱

This provides us a receipt to correctly simulate time:

0. $t_n$,
1. choose a process, make a jump
2. make $t_{n+1} = t_n + t_w$ using a $t_w$ picks from the waiting time distribution.

⇒ exponential: generate $U \in [0,1]$

exponential!! ⟶ $t_w = -\frac{1}{w} \times \ln U$

The process can easily be generate to multiple pchannels
algorithm for N particles & the transitions, see.

Eichthorn & Weinberg

Theoretical foundations of dynamical Monte Carlo simulations.

J. Chem. Phys. 95, 1090 (1991).

* The End.

Watch Slides