The core idea of First passage problem: solve Smoluchowski equation

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For A quick procedure of the code, you can go directly to section 3: Implement numerical method of First passage calculation in Matlab

Introduction about Smoluchowski equation

The most original idea about Smoluchowski is to use probability density and probability flux function to describe the time evolution of some stochastics process. Some other equation systems like Nernst-Plank, diffusion convection, etc, essentially describe the same thing. The reason for calling First passage calculation is

The idea of probability density and probability density flux is have different meanings, but correlate to each other.

The probability $P(x,x',t)dx$ that a random walker with position x' in the pore at $t=0$ will be found between x and $x+dx$ after time t.

This probability fluxes function obeys the Smoluchowski equation.

$$\frac{\partial P(x',t)}{\partial t}=\frac{\partial}{\partial x'}\frac{F(x')}{\gamma}P(x',t)+\frac{\partial^2}{\partial x'^2}DP(x',t)$$

Specific boundary conditions are discussion in the later section.

The conception of probability flux seems used for a more specific reason: first passage time!

A first passage time in a stochastic system, is the time taken for a state variable to reach a certain value. For instance, in the one dimension random walker case, the first passage time distribution re given by the probability fluxes $f_0(x',t)$ and $f_L(x',t)$ out of each boundary ($x=0$ and $x=L$), with $f_{0,L}(x',t)=\pm D[\partial P/\partial x]_{x=0,L}$, where D is the diffusion constant.

This probability fluxes function obeys an equation adjoint to the Smoluchowski equation.

$$\frac{\partial f_{0,L}(x',t)}{\partial t}=\frac{F(x')}{\gamma}\frac{\partial f_{0,L}(x',t)}{\partial x'}+D\frac{\partial^2 f_{0,L}(x',t)}{\partial x'^2}$$

Specific boundary conditions are discussion in the later section. Integral of the probability flux over initial position can give the passage odd for the random walker to pass certain boundary. Integral of the probability flux with first passage time can give the average first passage time for the random walker to pass certain boundary.

Numerical solution for probability and probability flux

Adjoint Smoluchowski equation derivation

Therefore in the next we are going to discuss how to use PDE toolbox obtain the numerical result of probability function and probability flux function at different boundary condition.

As mentioned before, $P(x,x',t)dx$ predicts the probability to find a random walker with initial position x' in the pore at $t=0$ will be found between x and $x+dx$ after time t. The probability fluxes $f_0(x',t)$ and $f_L(x',t)$ out of each boundary ($x=0$ and $x=L$), with $f_{0,L}(x',t)=\pm D[\partial P/\partial x]_{x=0,L}$, where D is the diffusion constant. The probability flux function obeys an equation adjoint to the Smoluchowski equation.

$$\frac{\partial f_{0,L}(x',t)}{\partial t}=\frac{F(x')}{\gamma}\frac{\partial f_{0,L}(x',t)}{\partial x'}+D\frac{\partial^2 f_{0,L}(x',t)}{\partial x'^2}$$

Let’s try to solve the adjoint Smoluchowski equation first.

We set the boundary at $x=0$ is reflecting boundary; and boundary at $x=L$ is the absorbing boundary, which are the most typical boundary conditions in solving a stochastics problem.

Due to the reflecting at $x=0$, $\partial f_0(x',t)/\partial x'$ is constantly 0.

For the absorbing boundary at $x=L$, $f_L(0,t)=0$; $f_L(L,t)=\delta(t)$

And the initial value of probability flux is $f_L\left(x',0\right)=0\ \left(x'<L\right)$

Matlab PDE tool summarizes all PDE into four prototypes: Elliptic, Parabolic, Hyperbolic and Eigenmodes. We need to transfer the Adjoint Smoluchowski equation into Parabolic shape first: d*u'+div(c*grad(u))+a*u=f.

We need to transfer our equation into parabolic format equation.

$$\frac{\partial f_{0,L}\left(x',t\right)}{\partial t}=\frac{F\left(x'\right)}{\gamma}\frac{\partial f_{0,L}\left(x',t\right)}{\partial x'}+D\frac{\partial^2 f_{0,L}\left(x',t\right)}{\partial x'^2}$$

Because PDE toolbox defines the geometry in the domain and boundary dimensionless, we need transfer $\partial x'$ into $\partial x'/L$ first. Then the figure draw should be…

$$\exp\left(\frac{-\int_{x'}^{L}Fdx}{k_BT}\right)\frac{L^2}{D}\frac{\partial f_{0,L}\left(x',t\right)}{\partial t}=\exp\left(\frac{-\int_{x'}^{L}Fdx}{k_BT}\right)\frac{F\left(x'\right)}{k_BT}\frac{dx}{\partial x'/L}\frac{\partial f_{0,L}\left(x',t\right)}{\partial x'/L}+\exp\left(\frac{-\int_{x'}^{L}Fdx}{k_BT}\right)\frac{\partial^2 f_{0,L}\left(x',t\right)}{\partial x'/L^2}$$

Next is the Product rule in calculus

$$\exp\left(\frac{-\int_{x'}^{L}Fdx}{k_BT}\right)\frac{L^2}{D}\frac{\partial f_{0,L}\left(x',t\right)}{\partial t}=\frac{\partial}{\partial x'/L}\left(\exp\left(\frac{-\int_{x'}^{L}Fdx}{k_BT}\right)\frac{\partial f_{0,L}\left(x',t\right)}{\partial x'/L}\right)$$

Hence, compare to the original format of parabolic equation: d*u'+div(c*grad(u))+a*u=f

d= $\exp\left(\frac{-\int_{x'}^{L}Fdx}{k_BT}\right)\frac{L^2}{D}$, c= $\exp\left(\frac{-\int_{x'}^{L}Fdx}{k_BT}\right)$,

a=0, f=0. And u is the probability fluxes function.

According to my experience, diffusion constant had better to be simplify as constant. The force expression should be costumer design to describe the potential profile is the domain.

Next, the boundary condition and initial condition of first passage model can fit the request of parabolic equation:

In equations	In code
F_L(x=L,t)=delta(t),	`pdesetbd(2,'dir',1,'1','exp(-t*10e12)*10e12')`
d(F_L(x=0,t))/dx=0;	`pdesetbd(4,'neu',1,'0','0')`
Up boundary on the rectangular	`pdesetbd(1,'dir',1,'0','0')`
Down boundary on the rectangular	`pdesetbd(3,'dir',1,'0','0')`

F_L(x,t=0)=delta(x-L)	100000*exp((x-L)*100000)

Smoluchowski equation derivation

The probability function is obtained by solving Smoluchowski equation. To allow PDE toolbox solve the equation numerically, we need to transfer Smoluchowski equation into parabolic format equation.

$$\frac{\partial P(x',t)}{\partial t} = \frac{\partial}{\partial x'}\frac{F(x')}{\gamma}P(x',t) + \frac{\partial^2}{\partial x'^2}DP(x',t)$$

Still use the Product rule in calculus, equation can be written into:

$$\frac{\partial P(x',t)}{\partial t} = \left(\frac{\partial F/\gamma}{\partial x'} + \frac{\partial^2 D}{\partial x'^2}\right)P(x',t) + \left(\frac{F}{\gamma} + 2\frac{\partial D}{\partial x'}\right)\frac{\partial}{\partial x'}P(x',t) + D\frac{\partial^2}{\partial x'^2}P(x',t)$$

By using $A^*(x') = -\left(\gamma^{-1}\vec{F} + 2\frac{\partial D}{\partial x'}\right)$ and $B^*(x')/2 \to D$ and $C^*(x') = \frac{\partial F/\gamma}{\partial x'} + \frac{\partial^2 D}{\partial x'^2}$

$$\Phi(x) = \int_M^x \frac{-2A^*(y)}{B^*(y)}dy \text{ or } \Phi(x) = \int_x^L \frac{2A^*(y)}{B^*(y)}dy = \int_x^L -\frac{\left(\gamma^{-1}\vec{F} + 2\frac{\partial D}{\partial x'}\right)}{D}dx' = \int_x^L\left(-\frac{\vec{F}}{k_B T} - 2\frac{\partial \ln D}{\partial x'}\right)dx'$$

Can transform into that

$$\exp\Phi(x')\frac{2}{B}\frac{\partial P(x',t)}{\partial t} = C\exp\Phi(x')P(x',t) + \frac{\partial}{\partial x'}\exp\Phi(x')\frac{\partial P(x',t)}{\partial x'}$$

After normalizing the walk domain, it is

$$\exp\Phi(x')\frac{2}{B}\frac{\partial P(x',t)}{\partial t} = C\exp\Phi(x')P(x',t) + \frac{\partial}{\partial x'}\exp\Phi(x')\frac{\partial P(x',t)}{\partial x'}$$

d*u'+div(c*grad(u))+a*u=f

d= $\exp\Phi(x')\frac{1}{D}$, c= $\exp\Phi(x')$, a= $C\exp\Phi(x')$, f=0

u is the probability function.

The transformation into parabolic format work!

Next, we set the initial condition and boundary condition. Here we still use simplified model. Assuming a random walker from initial position x_0 as the initial condition $P(x, x_0, 0) = \delta(x - x_0)$, the driving force pushes the walker to approach left boundary x=0, where is reflecting boundary condition $\frac{\partial}{\partial y} P(0, x_0, t) + \frac{\vec{F} P(0, x_0, t)}{k_B T} = 0$. And if the driving force is big enough, such walker should have low chance to approach right boundary, as $P(L_{domian}, x_0, t) = 0$.

The typical format of reflecting boundary can be written as: $J = AP - \frac{1}{2} \frac{\partial}{\partial y} BP = 0$.

$A(y) \to -\gamma^{-1} \vec{F}$ is the drift term,. The diffusion constant $B(y)/2 \to D$.

$$-\gamma^{-1} \vec{F} P - \frac{\partial}{\partial y} DP = 0$$

$$\frac{\partial}{\partial y} P + \frac{\vec{F} P}{k_B T} = 0$$

$$c \frac{\partial}{\partial y} P + c \frac{\vec{F} P}{k_B T} = 0$$

To implement the boundary condition and initial condition in the code:

In equations	In code
Left boundary c*grad(u)+qu=g;	`pdesetbd(4,'neu',1, q ,'0')%q need its own calculation`
Right boundary h*u=r	`pdesetbd(2,'dir',1,'1','0')`
Up boundary on the rectangular	`pdesetbd(1,'dir',1,'0','0')`
Down boundary on the rectangular	`pdesetbd(3,'dir',1,'0','0')`
F_L(x,t=0)=delta(x-L)	100000*exp((x-L)*100000)

Implement numerical method of First passage calculation in Matlab

Implement Adjoint Smoluchowski equation into matlab PDE Toolbox

The procedure to solve the adjoint Smoluchowski equation is shown as follows. The first passage time distribution/probability flux for an energy well escape model can be plot by following this procedure. The detail of this model is well described in my paper Biophysical Journal 2015 109(7) 1439–1445. And the user should be able to plot the typical exponential time distribution for energy-well-escape model.

1. Draw the PDE geometry and design boundary condition based on the "PDE tool",
   ```
   >>Ldomain=7; %walk domain; default value is 7
   >>drawgeom_ref(Ldomain).m
   ```
2. Output the boundary parameter from the PDE toolbox to get the parameter 'b' and 'g'.
   First, GUI→boundary→export decomposed geometry, boundary condition.
   Then,
   ```
   >>fid = wgeom(g, 'prob1g');
   ```
3. Build and solve the PDE
   ```
   >>Diff=6;%diffusion constant
   >>force=0.4; %build the energy well for escape; default is 0.4
   >>Tau=3e-3; %Duration to observe the escape process; default is 3e-3
   >>[u p tlist]=Rightpass(b,Diff,force,Ldomain,Tau);
   ```
   u is the probability flux function depend on the time(tlist) and initial position of random walker(p);
4. Plot the escape time distribution.
   ```
   >>xinit=1; %assume an initial position for the random walker
   >> yprob=probabilityflux_xa(p,u,tlist,Ldomain, xinit);
   >>plot(tlist,yprob); %escape time probability/first passage time probability;
   ```

Implement Smoluchowski equation into matlab PDE Toolbox

The procedure to solve the Smoluchowski equation is shown as follows. The time evolution of probability for a drift-diffusion model can be plot by following this procedure. The detail of this model is well described in my paper Biophysical Journal 2015 109(7) 1439–1445.

1. Draw the PDE geometry and design boundary condition based on the "PDE tool",
   ```
   >>Ldomain=7; %walk domain; default value is 7
   >>force=1.8; %build the potential profile for distribution evolution; default is 1.8
   >>drawgeomright1(Ldomain, qfun(force));
   ```
2. Output the boundary parameter from the PDE toolbox to get the parameter 'b' and 'g'.
   First, GUI→boundary→export decomposed geometry, boundary condition.
   Then,
   ```
   >>fid = wgeom(g, 'prob1g');
   ```
3. Build and solve the PDE
   ```
   >>Diff=6;%diffusion constant
   >> Tdomain=2e-8; %Duration to observe the evolution process; default is 2e-8
   >>[u p tlist]=Rightpass(b,Diff,force,Ldomain,Tdomain);
   ```
4. Plot the probability evolution curves:
   ```
   >>[y1b, xdomain]=Time_evolution(u,p,tlist,Tdomain);
   ```

With these code the user should be able to plot the time-evolution probability function as shown in the figure 4 of my paper Biophysical Journal 2015 109(7) 1439–1445

Analytic solution for conditional average first passage time

The interesting thing is probability density and probability density flux usually have no analytical solution, but total first passage odds and average first passage time do have analytical solutions. Even though they are variables describing a scholastics process on a very broad scope, but they are still very convenient to provide quick evaluation or estimation on statistical problem. Analytic calculation on average first passage odd and average first passage time is extracted from N. G. Van Kampen, Stochastic Processes in Physics and Chemistry.

The total first passage odds $\pi_L(x)$ and $\pi_R(x)$ give the total odds of a random walker, given a starting position x, escapes from each boundary (L and R). They obey the equation

$$A(x)\frac{d\pi}{dx}+\frac{1}{2}B(x)\frac{d^2\pi}{dx^2}=0$$

For absorbing boundary on both sides

$$\begin{aligned} &\pi_L(L)=1 \quad \pi_L(R)=0 \\ &\pi_R(L)=0 \quad \pi_R(R)=1 \end{aligned}.$$

This equation has the formal solution

$$\pi_L(x)=\int_x^R e^{\Phi(y)}dy \bigg/ \int_L^R e^{\Phi(y)}dy, \quad \pi_R(x)=\int_L^x e^{\Phi(y)}dy \bigg/ \int_L^R e^{\Phi(y)}dy$$

with

$$\Phi(x)=\int_M^x \frac{-2A(y)}{B(y)}dy\ .$$

Here M is an arbitrary point between L and R. Corresponding to the drift-diffusion equation, $A(y)\to-\gamma^{-1}\vec{F}$ is the drift term, $B(y)/2\to D$ is the diffusion constant.

And there are mean first passage time $\tau_L(x)$ and $\tau_R(x)$ for a walker starting at position x to arrive either R or L boundary. Mean first passage time can be obtained by the product quantity dividing total passage odds.

If there are both absorbing boundary at L and R. The product quantity $\vartheta_R(x)=\pi_R(x)\tau_R(x)$ can be expressed as:

$$A(x)\frac{d\vartheta_R}{dx}+\frac{1}{2}B(x)\frac{d^2\vartheta_R}{dx^2}=-\pi_R(x)$$

With boundary condition $\vartheta_R(R)=0$ and $\vartheta_R(L)=0$;

From above equation we can obtain that:

$$\vartheta_R(x)=-\int_L^x e^{\Phi(y)}dy\int_L^y e^{-\Phi(y')}\frac{2\pi_R(y')dy'}{B(y')}+C\int_L^x e^{\Phi(y)}dy$$
$$C=\left[\int_L^R e^{\Phi(z)}dz\right]^{-1}\left[\int_L^R e^{\Phi(y)}dy\int_L^y e^{-\Phi(y')}\frac{2\pi_R(y')dy'}{B(y')}\right]$$

And so on:

$$\vartheta_L(x)=-\int_x^R e^{\Phi(y)}dy\int_y^R e^{-\Phi(y')}\frac{2\pi_R(y')dy'}{B(y')}+C\int_x^R e^{\Phi(y)}dy$$
$$C=\left[\int_L^R e^{\Phi(z)}dz\right]^{-1}\left[\int_L^R e^{\Phi(y)}dy\int_y^R e^{-\Phi(y')}\frac{2\pi_R(y')dy'}{B(y')}\right]$$

In the end, we could obtain mean first-passage time:

$$\tau_R(x)=\vartheta_R(x)/\pi_R(x)$$
$$\tau_L(x)=\vartheta_L(x)/\pi_L(x)$$

For one reflecting boundary and one absorbing boundary condition, the total odds to passage the reflecting boundary is $\pi_L(x)=0$; And the total odds to passage the absorbing boundary is $\pi_R(x)=1$. The mean first passage time $\tau_R(x)$ obey the equation:

$$A(x)\frac{d\tau_R}{dx}+\frac{1}{2}B(x)\frac{d^2\tau_R}{dx^2}=-1$$

With the reflecting boundary condition at L: $\tau_R(R)=0$;

And the absorbing boundary at R: $\frac{\partial\tau_R(L)}{\partial x}=0$

And there are conditional mean first passage time $\tau_R(x)$ for a walker starting at position x to arrive either R or L boundary.

$$\tau_R(x) = \int_x^R e^{\Phi(y)} dy \int_L^y e^{-\Phi(y')} \frac{2dy'}{B(y')}$$

The detail mathematical derivation of this equation and solution can been found in the book C. W. Gardiner Handbook of Stochastic Methods for Physics, Chemistry and Natural Sciences.