AM216 Stochastic Differential Equations

Lecture 14

List of topics in this lecture

- Kramers' theory of reaction kinetics, physical exit time, effects of energy barrier, diffusion coefficient, and potential width
- Memoryless property of exit time, exponential distribution, escape rate
- Application of Kramers' theory: a simple model of ignition
- Feynman-Kac formula, fatality/growth rate, path integral $u(x, t, T)$, interpretation of path integral as relative population, governing equation of $u(x, t, T)$

Recap

Escape of a Brownian particle from a potential well

Smoluchowski-Kramers approximation in the limit of small particle

$$\underbrace{mdY = -bY\,dt - V'(X)dt + \sqrt{2k_BTb}\,dW}_{\text{Langevin equation}} \quad ==> \quad \underbrace{dX = -\frac{D}{k_BT}V'(X)dt + \sqrt{2D}\,dW}_{\text{over-damped Langevin equation}}$$

Dimensionless SDE

$$dX = -V'(X)dt + \sqrt{2}\,dW$$

Exact integral solution of the average exit time

$$T(x) = \int_x^1 dy \exp(V(y)) \int_0^y ds \exp(-V(s))$$

Deep potential well

$V(x) = \Delta G\, \phi(x)$, $\min \phi(x) = \phi(x_1) = 0$, $\max \phi(x) = \phi(x_2) = 1$,

ΔG is moderately large.

Kramers' approximate solution of $T(x)$

$$T(x) \approx \exp(\Delta G) \cdot \frac{1}{\Delta G} \sqrt{\frac{(2\pi)^2}{\phi''(x_1)\cdot(-\phi''(x_2))}} \quad \text{independent of } x \text{ for } x < x_2$$

$T(x)$ is independent of the starting position x when x is inside the potential well.

Kramers' theory of reaction kinetics

Physical escape time in terms of physical quantities

Recall the non-dimensionalization.

$$t = \frac{D}{L^2} t_{\text{phy}}, \qquad T(x) = \frac{D}{L^2} T_{\text{phy}}(x_{\text{phy}}), \qquad \Delta G = \frac{1}{(k_B T)} \Delta G_{\text{phy}}$$

Substituting these into the expression of $T(x)$, we get

$$T(x) = \exp(\Delta G) \cdot \frac{1}{\Delta G} \sqrt{\frac{(2\pi)^2}{\phi''(x_1) \cdot (-\phi''(x_2))}}$$

$$\Longrightarrow \qquad \frac{D}{L^2} T_{phy}(x_{phy}) = \exp\left(\frac{\Delta G_{phy}}{k_B T} \right) \cdot \frac{k_B T}{\Delta G_{phy}} \sqrt{\frac{(2\pi)^2}{\phi''(x_1) \cdot (-\phi''(x_2))}}$$

Caution on the notation:

- T in $(k_B T)$ is the temperature.
- $T(x)$ is the average exit time.

The physical escape time has the expression

$$T_{phy}(x_{phy}) = \underbrace{\frac{L^2}{D}}_{\substack{\text{Effect of} \\ \text{mobility}}} \cdot \underbrace{\exp\left(\frac{\Delta G_{phy}}{k_B T} \right) \frac{k_B T}{\Delta G_{phy}}}_{\substack{\text{Effect of} \\ \text{energy barrier}}} \underbrace{\sqrt{\frac{(2\pi)^2}{\phi''(x_1) \cdot (-\phi''(x_2))}}}_{\substack{\text{Effect of} \\ \text{relative geometry}}}$$

We can see how the physical escape time scales with other physical quantities.

- When the width of potential L is doubled, T_{phy} is increased by a factor of 4.
  It is more difficulty to escape from a wide potential well.
- When the diffusion coefficient D is doubled, T_{phy} is halved.
  It is easier for a smaller particle to escape.
- T_{phy} increases exponentially with the energy barrier ΔG_{phy}. When ΔG_{phy} is increased by $2.3 k_B T$, T_{phy} is increased by a factor of 10.
  By far, the energy barrier ΔG_{phy} has the dominant influence on T_{phy}.

An example:

Consider the escape of a 1-nm (diameter) particle from a potential well of width 0.5nm.

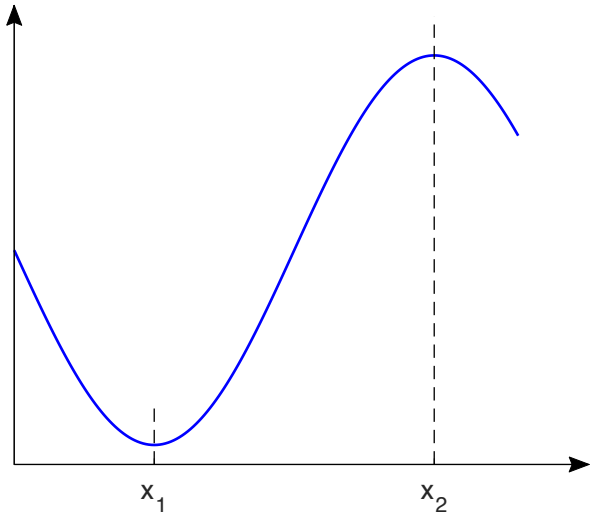
Particle radius: a = 0.5nm; viscosity of water: η = 0.01 g(cm)$^{-1}$s^{-1}.

Diffusion coefficient: $D = \frac{k_B T}{6\pi\eta a} = 4.350 \times 10^8 \,\text{nm}^2\text{s}^{-1}$.

Potential: $V(x) = \Delta G\, \phi(x)$, $\quad \phi(x) = \frac{1}{2} + \frac{1}{2}\sin\left(\pi(1.8x - 1.0)\right)$.

$$x_1 = \arg\min \phi(x) = \frac{5}{18}, \qquad x_2 = \arg\max \phi(x) = \frac{15}{18}$$

$$\phi''(x_1) = \frac{1}{2}(1.8\pi)^2, \qquad \phi''(x_2) = \frac{-1}{2}(1.8\pi)^2$$



Substituting these quantities into the expression of T_{phy}, we obtain

$$T_{phy}(x_{phy}) = \exp\left(\frac{\Delta G_{phy}}{k_B T}\right)\frac{k_B T}{\Delta G_{phy}}\left(2.258\times 10^{-10}\,\text{s}\right)$$

- $\Delta G_{\text{phy}} = 10\ k_B T$ ==> $T_{\text{phy}} = 4.974\times10^{-7}$ s = 0.497 μs
- $\Delta G_{\text{phy}} = 20\ k_B T$ ==> $T_{\text{phy}} = 5.478\times10^{-3}$ s = 5.48 ms
- $\Delta G_{\text{phy}} = 40\ k_B T$ ==> $T_{\text{phy}} = 1.329\times10^{+6}$ s = 15.38 days

Distribution of the random exit time

Let $Y(\omega)$ denote the random exit time. In the above, we studied

$T(x) \equiv E(Y(\omega)|X(0) = x)$

Question: What can we say about the distribution of $Y(\omega)$?

Answer: For a deep potential well, the escape process is memoryless.

Specifically, the solution of $T(x)$ tells us

$$T(x) \approx \exp(\Delta G)\cdot\frac{1}{\Delta G}\sqrt{\frac{(2\pi)^2}{\phi''(x_1)\cdot(-\phi''(x_2))}} \quad \text{independent of } x$$

That is, the average exit time is memoryless. Mathematically it gives us

$$E(Y-t_0 \,|\, Y>t_0) = E(Y) \quad \text{independent of } t_0 \qquad \text{(E01)}$$

Let $\rho(t)$ be the probability density of Y.

Previously (in Lecture 2) we derived $\rho(t)$ based on the memoryless property of Y. It turns out that the memoryless property of $E(Y)$ is sufficient for deriving $\rho(t)$.

We write (E01) in terms of $\rho(t)$.

$$\frac{1}{\int_{t_0}^{\infty} \rho(t)dt} \int_{t_0}^{\infty} (t-t_0)\rho(t)dt = E(Y) \quad \text{independent of } t_0 \qquad \text{(E01B)}$$

Let $G(t) \equiv \int_t^{\infty} \rho(s)ds$. We have $\rho(t) = -G'(t)$.

Carrying out integration by parts in the numerator and identify the denominator as $G(t_0)$, we write (E01B) as

$$\int_{t_0}^{\infty} G(t)dt = E(Y)G(t_0) \qquad \text{(E01C)}$$

Differentiating with respect to t_0, we arrive at

$$\frac{-1}{E(Y)} G(t_0) = G'(t_0) \quad \text{(the same ODE as we obtained previously.)}$$

We conclude that $Y(\omega)$ has the exponential distribution:

$$\rho(t) = r\exp(-rt), \qquad r \equiv \frac{1}{E(Y)} = \frac{1}{T(x)}$$

The escape rate, r, describes the conditional probability of escaping per time:

$$r = \frac{1}{\Delta t} \Pr\left(\text{escaping in } (t_0, t_0+\Delta t) \,\middle|\, \text{having not escaped by } t_0 \right)$$

The physical escape rate

$$r_{phy} = \frac{1}{T_{phy}(x_{phy})} = \underbrace{\frac{D}{L^2}}_{\substack{\text{Effect of} \\ \text{mobility}}} \cdot \underbrace{\exp\left(\frac{-\Delta G_{phy}}{k_B T} \right) \frac{\Delta G_{phy}}{k_B T}}_{\substack{\text{Effect of} \\ \text{energy barrier}}} \underbrace{\sqrt{\frac{\phi''(x_1)\cdot(-\phi''(x_2))}{(2\pi)^2}}}_{\substack{\text{Effect of} \\ \text{relative geometry}}}$$

This is the Kramers' theory of reaction kinetics (named after Hans Kramers).

Remarks:

- The chemical reaction between molecules A and B requires activation, which means crossing over an energy barrier. The energy barrier represents the situation where molecule A has to fluctuate to an energetically unfavorable configuration before reacting with molecule B.
- Crossing over an energy barrier is mathematically an escape process.

- When the energy barrier is large, the escape process is memoryless and is described by a reaction rate, which has a strong dependence on the temperature.

$$r_{phy} \sim \exp\left(\frac{-\Delta G_{phy}}{k_B T}\right)$$

- Another aspect of the chemical reaction is the probability of encounter between molecules A and B, which is affected by their concentrations.

A simple model of ignition

Let T_0 = the ambient temperature.

$T(t)$ = the spot temperature at time t at an interface of gasoline and air

(where locally there is a mix of gasoline and air)

Governing equation for $T(x)$

$T(t)$ is governed by Newton's law of cooling

$$\frac{dT(t)}{dt} = \underbrace{-\mu(T(t)-T_0)}_{\text{cooling}} + \underbrace{\alpha \exp\left(\frac{-\Delta G}{T(t)}\right)}_{\substack{\text{heat generated} \\ \text{by reaction}}}$$

Note: For simplicity, the Boltzmann coefficient k_B has been absorbed into ΔG.

Let $y(t) \equiv (T(t)-T_0)/T_0$, the normalized temperature increase.

We expand the non-linear term in the ODE for small y.

$T(t) = T_0(1+y(t))$

$$\frac{-\Delta G}{T(t)} = \frac{-\Delta G}{T_0(1+y(t))} = \frac{-\Delta G}{T_0}(1-y(t)+\cdots) = \frac{-\Delta G}{T_0} + \frac{\Delta G}{T_0} y(t) + \cdots$$

$$\exp\left(\frac{-\Delta G}{T(t)}\right) = \exp\left(\frac{-\Delta G}{T_0}\right)\exp\left(\frac{\Delta G}{T_0} y(t)+\cdots\right) = \exp\left(\frac{-\Delta G}{T_0}\right)\left(1+\frac{\Delta G}{T_0} y(t)+\cdots\right)$$

Substituting the expansion in the ODE yields

$$T_0 \frac{dy}{dt} = \underbrace{-\mu T_0 y}_{\text{cooling}} + \underbrace{\alpha \exp\left(\frac{-\Delta G}{T_0}\right)\left(1+\frac{\Delta G}{T_0} y+\cdots\right)}_{\substack{\text{heat generated} \\ \text{by reaction}}}$$

Dividing by T_0 and neglecting higher order terms, we obtain

Linearized ODE for $y(t)$

$$\frac{dy}{dt} = \underbrace{\left(\frac{\alpha\Delta G}{T_0^2}\exp\left(\frac{-\Delta G}{T_0}\right)-\mu\right)}_{\equiv\lambda(T_0)} y + \underbrace{\frac{\alpha}{T_0}\exp\left(\frac{-\Delta G}{T_0}\right)}_{\equiv q} \equiv \lambda(T_0)y+q$$

We study the behavior of IVP for $\lambda > 0$ and for $\lambda < 0$.

$$\begin{cases} y' = \lambda y + q \\ y(0) = 0 \end{cases}$$

Exact solution of $y(t)$:

$$y(t) = \left(e^{\lambda t}-1\right)\frac{q}{\lambda}$$

$\lambda < 0$: $\quad y(t) \to q/(-\lambda)$ as $t \to +\infty$

The temperature stabilizes at a finite value. No combustion.

$\lambda > 0$: $\quad y(t) \to +\infty$ as $t \to +\infty$

The temperature increases unbounded. Combustion.

The ignition temperature T_0^* is the solution of $\lambda(T_0^*) = 0$.

$\lambda(T_0)$ is an increasing function of T_0 for $\Delta G/T_0 > 2$.

$$\lambda(T_0) \equiv \frac{\alpha\Delta G}{T_0^2}\exp\left(\frac{-\Delta G}{T_0}\right)-\mu$$

$$\Longrightarrow \quad \frac{d\lambda}{dT_0} = \frac{\alpha\Delta G}{T_0^3}\exp\left(\frac{-\Delta G}{T_0}\right)\left(\frac{\Delta G}{T_0}-2\right) > 0$$

Remark: The case of $\Delta G/T_0 < 2$ is irrelevant since Kramers' theory of reaction kinetics is valid only for large $\Delta G/T_0$.

Feynman-Kac formula for the backward equation

We are back to the time-dependent (non-autonomous) SDE

$$dX = b(X,t)dt + \sqrt{a(X,t)}\,dW \qquad \text{(Ito interpretation)}$$

The moments of $(dX \mid X(t) = x)$ are

$$E(dX \mid X(t) = x) = b(x,t)dt + o(dt)$$

$$E((dX)^2 \mid X(t) = x) = a(x,t)dt + o(dt)$$

$$E((dX)^n \mid X(t) = x) = o(dt) \quad \text{for } n \geq 3$$

Definition of $u(x, t, T)$

$$u(x,t,T) \equiv E\left(\exp\left(-\int_t^T \psi(X(s),s)ds \right) \middle| X(t) = x \right)$$

Meaning of $u(x, t, T)$

Case1: $\psi(z, s)>0$:

We view $\psi(z, s)$ as the fatality rate of a "cell" at time s with $X(s) = z$.

Pr(fatality in $[s, s+\Delta s]$ | having survived to s with $X(s) = z$)

$= \psi(z, s) \times \Delta s$

Let us follow one particular path $x(s)$ from t to T.

We discretize the path on a time grid

$$\Delta s = \frac{T-t}{N}, \quad s_j = t + j\Delta s, \quad s_0 = t, \quad s_N = T$$

Along the given path $x(s)$, the probability of surviving from s_j to s_{j+1} is

Pr(surviving to s_{j+1} | having survived to s_j)

= 1 – Pr(fatality in $[s_j, s_{j+1}]$ | having survived to s_j)

$$= 1 - \psi(x(s_j), s_j)\Delta s \approx \exp\left(-\psi(x(s_j), s_j)\Delta s\right)$$

Along the given path $x(s)$, the probability of surviving from t to T is

Pr(surviving to T | having survived to t)

$$= \prod_{j=0}^{N-1} \exp\left(-\psi(x(s_j), s_j)\Delta s\right) = \exp\left(-\sum_{j=0}^{N-1} \psi(x(s_j), s_j)\Delta s \right)$$

$$\longrightarrow \exp\left(-\int_t^T \psi(x(s), s)ds \right) \quad \text{as } N \to \infty$$

We average the surviving probability over all paths starting at $X(t) = x$.

$$u(x,t,T) \equiv E\left(\exp\left(-\int_t^T \psi(X(s),s)ds \right) \middle| X(t) = x \right)$$

= probability of surviving from t to T | $X(t) = x$

Case2: $\psi(z, s)<0$:

We interpret $[-\psi(z, s)]>0$ as the growth rate of a cell at time s with $X(s) = z$.

Pr(split into two in $[s, s+\Delta s]$ | having survived to s with $X(s) = z$)

$= (-\psi(z, s)) \times \Delta s$

$u(x, t, T)$ = expected population at time T relative to that at time t | $X(t) = x$.

The general case

We interpret $\psi(z, s)$ as the fatality/growth rate of a cell at time s with $X(s) = z$.

(Outcome in $[s, s+\Delta s]$ | having survived to s with $X(s) = z$)

$$= \begin{cases} \text{fatality with prob } = \psi(z,s)\Delta s & \text{if } \psi(z,s) > 0 \\ \text{split into two with prob } = \big(-\psi(z,s)\big)\Delta s & \text{if } \psi(z,s) < 0 \end{cases}$$

After splitting into two, both new cells are associated with the same $X(s)$ path. In this way, the evolution of $X(s)$ is solely governed by the SDE, not affected by $\psi(z, s)$.

Some sample path of $X(s)$ may have no cell; some may have many cells.

$u(x, t, T)$ = expected population at time T relative to that at time t | $X(t) = x$.

Examples:

1. $X(s)$ = temperature of a site at time s

   $u(x, t, T)$ = expected bacteria population at T relative to that at t | $X(t) = x$.
2. $X(s)$ = collective population of all predators in a region at time s

   $u(x, t, T)$ = expected population of a prey at T relative to that at t | $X(t) = x$.
3. $X(s)$ = oil price at time s.

   $u(x, t, T)$ = expected stock price of an oil company at T relative to that at t | $X(t) = x$.

Governing equation for $u(x, t, T)$

We apply the backward view on

$$u(x,t,T) = E\left(\exp\left(-\int_t^T \psi(X(s),s)ds \right) \middle| X(t) = x \right)$$

$[\, t \to T \,]$ is divided into $[t \to t+\Delta t\,]$ and $[\, t+\Delta t \to T\,]$.

$$\exp\left(-\int_t^T \psi(X(s),s)ds \right) = \exp\left(-\int_t^{t+dt} \psi(X(s),s)ds \right) \exp\left(-\int_{t+dt}^T \psi(X(s),s)ds \right)$$

$$= \underbrace{(1-\psi(x,t)dt)}_{\text{independent of path}} \exp\left(-\int_{t+dt}^T \psi(X(s),s)ds \right) + o(dt)$$

Averaging over all paths starting at $X(t) = x$, we get

$$u(x,t,T) = (1-\psi(x,t)dt) E\left(\exp\left(-\int_{t+dt}^T \psi(X(s),s)ds \right) \middle| X(t) = x \right) + o(dt) \qquad \text{(E02)}$$

On the RHS, the average is over $\{X(s),\ t \le s \le T\}$. We use the law of total expectation to rewrite is as averaging over $\{X(s) \mid X(t+\Delta t),\ t+\Delta t \le s \le T\}$ and then over $dX(t)$.

For any quantity Q, we have

$$E_{\{X(s),t\le s\le T\}}(Q\,|\,X(t)=x)=E_{dX}\left(E_{\{X(s),t+dt\le s\le T\}}(Q\,|\,X(t+dt)=x+dX)\right)$$

Apply this result to the expectation in (E02)

$$E\left(\exp\left(-\int_{t+dt}^{T}\psi(X(s),s)ds\right)\,\middle|\,X(t)=x\right)$$

$$=E_{dX}\left(E_{\{X(s),t+dt\le s\le T\}}\left(\exp\left(-\int_{t+dt}^{T}\psi(X(s),s)ds\right)\,\middle|\,X(t+dt)=x+dX\right)\right)$$

Definition of $u(x, t, T)$

$$=E_{dX}\left(u(x+dX,t+dt,T)\right)$$

Taylor expansion

$$=E_{dX}\left(u(x,t,T)+u_t dt+u_x dX+\tfrac{1}{2}u_{xx}(dX)^2\right)+o(dt)$$

Using moments of dX

$$=u(x,t,T)+u_t dt+u_x b(x,t)dt+\tfrac{1}{2}u_{xx}a(x,t)dt+o(dt)$$

Substituting this result into the RHS of (E02), we write (E02) as

$$u(x,t,T)=(1-\psi(x,t)dt)\left(u(x,t,T)+u_t dt+u_x b(x,t)dt+\tfrac{1}{2}u_{xx}a(x,t)dt\right)+o(dt)$$

$$=u(x,t,T)+u_t dt+u_x b(x,t)dt+\tfrac{1}{2}u_{xx}a(x,t)dt-\psi(x,t)u\,dt+o(dt)$$

Dividing by dt and taking the limit at $dt \to 0$, we obtain the governing equation

$$0=u_t+b(x,t)u_x+\frac{1}{2}a(x,t)u_{xx}-\psi(x,t)u$$

It is the backward equation with a fatality/growth term.

<u>The final condition</u>: $u(x, t, T)|_{t=T} = 1$

<u>The final value problem (FVP)</u>

$$\begin{cases} 0=u_t+b(x,t)u_x+\dfrac{1}{2}a(x,t)u_{xx}-\psi(x,t)u \\ u(x,t,T)\big|_{t=T}=1 \end{cases}$$

The solution of the FVP is given by

$$u(x,t,T)=E\left(\exp\left(-\int_{t}^{T}\psi(X(s),s)ds\right)\,\middle|\,X(t)=x\right)$$

This is called the Feynman-Kac path integral formula for the backward equation (named after Richard Feynman and Mark Kac).

A more general case of Feynman-Kac formula

Definition of $u(x, t, T)$

$$u(x,t,T) \equiv E\left(\exp\left(-\int_t^T \psi(X(s),s)ds \right) f(X(T)) \middle| X(t) = x \right)$$

Meaning of $u(x, t, T)$

$\psi(z, s)$ is the fatality/growth rate of a cell at time s with $X(s) = z$.

$f(z)$ is the reward for a cell surviving to time T with $X(T) = z$.

$u(x, t, T)$ = expected reward at final time T per unit population at time t | $X(t) = x$.

Each cell of the population gets its own reward. The growth increases the population size and increases the reward for the population.

Governing equation for $u(x, t, T)$

The governing equation is not affected by function $f(z)$.

$$0 = u_t + b(x,t)u_x + \frac{1}{2}a(x,t)u_{xx} - \psi(x,t)u$$

The final condition: $u(x, t, T)|_{t=T} = f(x)$

Note: the effect of $f(z)$ is contained in the final condition.

The final value problem (FVP)

$$\begin{cases} 0 = u_t + b(x,t)u_x + \frac{1}{2}a(x,t)u_{xx} - \psi(x,t)u \\ u(x,t,T)\big|_{t=T} = f(x) \end{cases}$$

The solution of the FVP is given by the Feynman-Kac path integral formula

$$u(x,t,T) = E\left(\exp\left(-\int_t^T \psi(X(s),s)ds \right) f(X(T)) \middle| X(t) = x \right)$$

Feynman-Kac formula for the forward equation

Definition of $u(x, t)$

$$u(x,t) \equiv E\left(\delta\big(X(t) - x\big) \exp\left(-\int_0^t \psi(X(s),s)ds \right) \right)$$

where $\psi(x, t)$ is the fatality/growth rate of a cell at time t with $X(t) = x$.

Items of the discussion:

1) We need to explain the δ function in the average.
2) We need to derive the governing equation for $u(x, t)$.
3) We need to explain the meaning of $u(x, t)$ and discuss the distribution of $X(0)$.

Item #1: We first explain the δ function in the average.

View #1: Approximate δ( ) using a boxcar function.

Let $I_{[x,x+\Delta x]}(z)$ be the indicator function defined as

$$I_{[x,x+\Delta x]}(z)=\begin{cases} 1, & x\le z\le x+\Delta x \\ 0, & \text{otherwise} \end{cases}$$

$u(x, t)$ can be viewed as

$$u(x,t)=\lim_{\Delta x\to 0}\frac{1}{\Delta x}E\left(I_{[x,x+\Delta x]}(X(t))\exp\left(-\int_0^t \psi(X(s),s)ds \right)\right)$$

View #2: Use the method of test function

We integrate the product $h(x)u(x, t)$.

$$\int h(x)u(x,t)dx = E\left(\left(\int h(x)\delta(X(t)-x)dx \right)\exp\left(-\int_0^t \psi(X(s),s)ds \right)\right)$$

which leads to

$$\boxed{\int h(x)u(x,t)dx = E\left(h(X(t))\exp\left(-\int_0^t \psi(X(s),s)ds \right)\right)}$$

Here $h(x)$ is any smooth function that decays to zero rapidly as $|x| \to \infty$.

The two views are equivalent to each other. We are going to use view #2 in the derivation of the governing equation for $u(x, t)$.