# DIFFUSION

## DIFFUSION UNDER POTENTIAL

*Vinay Vaibhav*

*The Institute of Mathematical Sciences*

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# OUTLINE

- Diffusion Under Time-Independent External Potential
  - SDE-FPE Correspondence
  - Linear Potential : Sedimentation
  - Parabolic Potential : Brownian Oscillator
- Diffusion Under Time-Dependent External Potential
  - Langevin Equation
  - Linear Response Theory

# Diffusion Under Time-Independent External Potential

- *Fluid remains in thermal equilibrium in the presence of such external potential*

*How the probability distributions of the velocity and position of the tagged particle are modified?*

- *Assumption: Heat bath is not affected significantly by the presence or absence of the external force*

  *- Fluctuation-dissipation relation still remains valid i.e.,* $\Gamma = 2m\gamma k_B T$

- *Langevin equation:*

$$\dot{x} = v$$

$$m\dot{v} + m\gamma v = -V'(x) + \eta(t)$$

*where* $\eta(t) = \sqrt{\Gamma}\zeta(t)$ *s.t.* $\zeta(t)$ *is delta correlated GWN with zero mean*

*- In general, the equation is nonlinear*

# General SDE-FPE Correspondence

- *Consider a general multi-component diffusion process represented by the following SDE:*

$$\dot{\mathbb{X}} = \mathbf{f}(\mathbb{X}) + \mathbf{g}(\mathbb{X})\boldsymbol{\xi}(\mathbf{t})$$ *Out of n equations, $\nu$ equations have noise*

$\mathbb{X}$ *: n x 1 vector* $\quad$ $\mathbf{f}(\mathbb{X})$ *: n x 1 vector (drift vector)*

$\mathbf{g}(\mathbb{X})$*: n x $\nu$ matrix* $\quad$ $\boldsymbol{\xi}(t)$ *: $\nu$ x 1 matrix (GWN)*

*What is the FPE satisfied by PDF corresponding to this SDE?*

$$\frac{\partial}{\partial t}\rho(\mathbb{X},t) = -\frac{\partial}{\partial x_i}[f_i\rho(\mathbb{X},t)] + \frac{\partial^2}{\partial x_i x_j}(\mathbb{D}_{ij}\rho(\mathbb{X},t))$$

*where* $\mathbb{D} = \frac{1}{2}(\mathbf{g}\mathbf{g}^{\mathbf{T}})$

- *For 1-D i.e. n=2 and $\nu$=1: Kramers equation*

$$\mathbf{f} = \begin{pmatrix} v \\ -\gamma v - V'(x)/m \end{pmatrix} \qquad \mathbf{g} = \begin{pmatrix} 0 \\ (2\gamma k_B T/m)^{1/2} \end{pmatrix} \qquad \mathbb{D} = \begin{pmatrix} 0 & 0 \\ 0 & \gamma k_B T/m \end{pmatrix}$$

$$\rho(x,v,t) : \frac{\partial\rho}{\partial t} = -v\frac{\partial\rho}{\partial x} + \frac{1}{m}V'(x)\frac{\partial\rho}{\partial v} + \gamma\frac{\partial}{\partial v}(v\rho) + \frac{\gamma k_B T}{m}\frac{\partial^2\rho}{\partial v^2}$$

- *Consider long-time regime or high friction approximation:*
  - *In the presence of $V(x)$, the long time limit is not guaranteed to be diffusive*
  - $t \gg \gamma^{-1}$ *(Smoluchowski time)*
  - *Long-time limit consideration also requires: Applied force doesn't vary significantly over distances of the order of characteristic length* $\langle v^2 \rangle_{eq}^{1/2} / \gamma$
  - *In such limit, velocity of tagged particle may be assumed to be thermalised*

$$\rho(x, v, t)|_{\gamma t \gg 1} \to p_{eq}(v) \times p(x, t)$$

*where* $p(x,t)$ *denotes the PDF of the position*

  - *Consider Langevin equation:*

$$m\ddot{x} + m\gamma\dot{x} = -V'(x) + \sqrt{2m\gamma k_B T}\zeta(t)$$

  - *In high friction limit, inertia term is neglected*

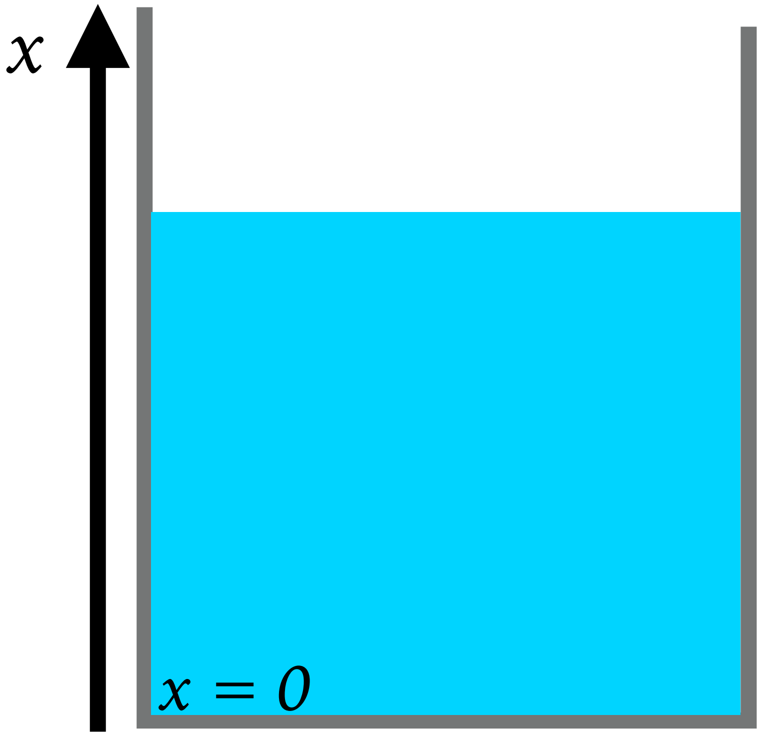
$$\dot{x} \simeq -\frac{1}{m\gamma}V'(x) + \sqrt{\frac{2k_B T}{m\gamma}}\zeta(t)$$

  - *The FPE correspondence to this SDE is called Smoluchowski equation*

$$\frac{\partial}{\partial t}p(x,t) = \frac{1}{m\gamma}\frac{\partial}{\partial x}[V'(x)p(x,t)] + \frac{k_B T}{m\gamma}\frac{\partial^2}{\partial x^2}p(x,t)$$

  - *Phase-space FPE is reduced to Smoluchowski equation in high friction limit*

# Sedimentation




- *Sedimentation: Diffusion in constant force field*
- *Sedimentation of particles in a fluid held in container, under the influence of gravity*
- *Potential* $V(x) = mgx \equiv Kx$ *with* $x \geq 0$
- *Assume* $x = 0$ *is perfectly reflecting boundary*

➤ *The Smoluchowski equation:*

$$\frac{\partial}{\partial t}p(x,t) = \frac{K}{m\gamma}\frac{\partial}{\partial x}p(x,t) + \frac{k_B T}{m\gamma}\frac{\partial^2}{\partial x^2}p(x,t)$$

- *Writing* $\frac{K}{m\gamma} \equiv c$ *and* $\frac{k_B T}{m\gamma} \equiv D$

$$\frac{\partial}{\partial t}p(x,t) = c\frac{\partial}{\partial x}p(x,t) + D\frac{\partial^2}{\partial x^2}p(x,t)$$

- *The two terms on RHS represent the effect of drift and diffusion respectively*
- *c/D: A natural or characteristic length scale*

*What is the p(x,t) with some given I.C. and B.C. ?*

- *Consider the following I.C. and B.C. :*
  - *I.C. :* $p(x,0) = \delta(x - x_o)$
  - *B.C. :* $lim_{x\to\infty} p(x,t) = 0$ *and at x= 0 the perfectly reflecting boundary implies the probability current through the boundary vanishes identically i.e.,* $\left[\frac{\partial}{\partial x} p(x,t) + \frac{c}{D} p(x,t)\right]_{x=0} = 0$
- *Equilibrium PDF :*
  - $p_{eq}(x) = \frac{c}{D}\exp(-\frac{cx}{D})$ *Barometric distribution*
  - $\langle x^2 \rangle_{eq} - \langle x \rangle_{eq}^2 = (D/c)^2$ *No long-range diffusion*
  - *In such limit, velocity of tagged particle may be assumed to be thermalised*
- *Time-dependent PDF :*
  - *Can be solved using Laplace transform*

# Brownian Oscillator

- *Consider harmonically bound Brownian particles in a heat bath with high-friction approximation:* $V(x) = \frac{1}{2} m\omega_o^2 x^2$
- *The Langevin equation:* $\dot{x} \simeq -\frac{\omega_o^2}{\gamma} x + \frac{1}{m\gamma}\eta(t)$
- *The corresponding Smoluchowski equation:*

$$\frac{\partial}{\partial t} p(x,t) = \frac{\omega_o^2}{\gamma}\frac{\partial}{\partial x}[xp(x,t)] + \frac{k_B T}{m\gamma}\frac{\partial^2}{\partial x^2} p(x,t)$$

- *Valid for only overdamped oscillator:* $\gamma^{-1} < (2\omega_o)^{-1}$
- *The Langevin equation for $x(t)$ in this case is same in form as the Langevin equation for velocity $v(t)$ of a free tagged particle*
- *I.C.* $p(x,0) = \delta(x - x_o)$ *and free B.C., the PDF $p(x,t)$ is same as OU density*
- *Using above Smoluchowski equation:*

$$\overline{x(t)} = e^{-\omega_o^2 t/\gamma} x_o \qquad \overline{x^2(t)} = e^{-2\omega_o^2 t/\gamma} x_o^2 + \frac{k_B T}{m\omega_o^2}(1 - e^{-2\omega_o^2 t/\gamma})$$

$$\overline{x^2(t)} - (\overline{x(t)})^2 = \frac{k_B T}{m\omega_o^2}(1 - e^{-2\omega_o^2 t/\gamma})$$

- *The variance saturates to some equilibrium value in long time limit*
- *With given mean and variance of $x(t)$, $p(x,t|x_o)$ can be easily written*

# Kramers' Escape Rate Formula

# Diffusion Under Time-dependent External Potential

# Langevin Equation

- *Langevin equation in the presence of some external force:*

$$\dot{v} + \gamma v = \frac{1}{m}\eta(t) + \frac{1}{m}F_{ext}(t)$$

  - *System is out of equilibrium*
  - *We are interested in knowing the response of the system in terms of velocity*
  - *Conditional average of velocity*

$$\begin{aligned}\overline{v(t)} &= v_o e^{-\gamma t} + \frac{1}{m}\int_0^t dt' e^{-\gamma(t-t')}\overline{\eta(t')} \\ &\quad + \frac{1}{m}\int_0^t dt' e^{-\gamma(t-t')}F_{ext}(t') \\ &= v_o e^{-\gamma t} + \frac{1}{m}\int_0^t dt' e^{-\gamma(t-t')}F_{ext}(t')\end{aligned}$$

- *If* $F_{ext}(t) = F_o (= constant)$

$$\overline{v(t)} = v_o e^{-\gamma t} + \frac{F_o}{m\gamma}(1 - e^{-\gamma t})$$

  - *Here transient is also included in response*
  - *Steady state response :* $\overline{v(t)} \xrightarrow{t\to\infty} \frac{F_o}{m\gamma}$ *As per expectation*
  - *Under continuous const. force: Particles reach terminal velocity, don't accelerate*

- *Mobility :* $\lim_{t\to\infty} \frac{\overline{v(t)}}{F_o} = \frac{1}{m\gamma} \equiv \mu$
  - *Steady state average velocity per unit external force*
  - *Diffusion constant* $D = \frac{k_B T}{m\gamma} = \mu k_B T$
  - *In general, if forces are time-dependent:* $D = \mu(t) k_B T$ $\mu(t)$ *: Dynamic mobility*
- *If* $F_{ext}(t) = F_o e^{-i\omega t}$ *(for given* $\omega$*)*

$$\overline{v(t)} = v_o e^{-\gamma t} + \frac{F_o}{m} e^{-\gamma t} \int_0^t dt' e^{(\gamma - i\omega)t'}$$

$$= v_o e^{-\gamma t} + \frac{F_o}{m} \frac{(e^{-i\omega t} - e^{-\gamma t})}{\gamma - i\omega} \quad \xrightarrow{t\to\infty} \quad \frac{F_o e^{-i\omega t}}{m(\gamma - i\omega)}$$

  - *A general time-dependent applied force may be written as a Fourier integral over all frequencies (in general, the force is non-periodic)*
  - *Dynamic mobility:* $\mu(\omega) = \frac{1}{m(\gamma - i\omega)}$

# Linear Response Theory

- *Linear response theory:*
  - *Provides the link b/w correlation functions and response to weak perturbations*
  - *Basic philosophy: A disturbance created in a system by a weak external perturbation decays in the same way as a spontaneous fluctuation in equilibrium*
  - *The response of a system property* $\mathbf{B}$ *due to a perturbation field* $\mathbf{F(t)}$ *which couples to the system property* $\mathbf{A}$ *s.t. the equilibrium hamiltonian* $\mathcal{H}_o$ *is changed to* $\mathcal{H}(t) = \mathcal{H}_o + \mathcal{H}'(t) = \mathcal{H}_o - AF(t)$ *, is given to linear order in* $\mathbf{F(t)}$ *as*

$$\langle \Delta B(t) \rangle = \int_{-\infty}^{t} dt' \; F(t') \Phi_{AB}(t-t')$$

*where* $\Phi_{AB}$ *which connects the response to stimulus, is called response function*

$$\Phi_{AB}(t-t') = \beta \langle \dot{A}(0) B(t-t') \rangle_{eq}, \qquad (t \geq t')$$

  - *Here we have assumed :*
    1. $\mathbf{F(t)}$ *has been switched on at* $t = -\infty$
    2. *response is causal and retarded*