AM216 Stochastic Differential Equations

Lecture 19

List of topics in this lecture

- Smoluchowski-Kramers approximation, an intuitive derivation based on ODE
- Time scale of inertia, time scale of thermal excitation
- Equipartition of energy, root-mean-square velocity of a particle
- Characters of molecular motors vs macroscopic motors
- Time scale of Smoluchowski-Kramers approximation

Smoluchowski-Kramers approximation

Consider the stochastic motion of a small particle in water

It is governed by the Langevin equation (Newton's second law)

$$dX = Y\,dt$$

$$m\,dY = -bY\,dt + F(X,t)\,dt + q\,dW \qquad \text{(S01)}$$

where

X: position

Y: velocity

$m = 4\pi/3\ a^3$: mass of the particle

a: radius of the particle

$b = 6\pi\,\eta\,a$: drag coefficient of the particle

$F(X, t)$: external force

$q = \sqrt{2k_B T\,b}$: the magnitude of thermal excitation

Claim:

As $a \to 0$, the stochastic motion is approximately governed by

$$dX = \frac{F(X,t)}{b}dt + \sqrt{2D}\,dW\,, \qquad D = \frac{k_B T}{b}$$

This equation is called the over-damped Langevin equation.

This process is called the Smoluchowski-Kramers approximation.

We are going to "derive" the Smoluchowski-Kramers approximation in several ways.

An intuitive derivation based on the result of a deterministic ODE

A model ODE

Consider a deterministic ODE

$$\begin{cases} y' = -\lambda\big(y - g(t)\big) \\ y(0) = y_0 \end{cases} \qquad \text{(D01)}$$

where λ is positive and large.

Theorem (on the model ODE)

The solution of (D01) satisfies

$$\lim_{\lambda\to+\infty} y(t;\lambda) = g(t) \qquad \text{for } t > 0$$

Proof:

We solve (D01) analytically. First, we rewrite it as

$$y' + \lambda y = \lambda g(t)$$

Multiplying by the integrating factor, we have

$$e^{\lambda t} y' + \lambda e^{\lambda t} y = \lambda g(t) e^{\lambda t}$$

$$\Longrightarrow \quad \left(e^{\lambda t} y\right)' = \lambda g(t) e^{\lambda t}$$

Integrating from 0 to t, we get

$$e^{\lambda t} y(t) - y_0 = \lambda \int_0^t g(s) e^{\lambda s}\, ds$$

$$\Longrightarrow \quad y(t) = e^{-\lambda t} y_0 + \lambda \int_0^t g(s) e^{\lambda(s-t)}\, ds$$

Applying change of variables $u = t - s$, we write $y(t)$ as

$$y(t) = e^{-\lambda t} y_0 + \lambda \int_0^t g(t-u) e^{-\lambda u}\, du$$

For λ positive and large, the dominant contribution of the integral comes from the region near $u = 0$. We expand function g near $u = 0$.

$$y(t)=e^{-\lambda t}y_0+\lambda\int_0^t\left[g(t)-g'(t)u+\frac{1}{2}g''(t)u^2+\cdots\right]e^{-\lambda u}\,du$$

Integration formula:

$$\int_0^t u^k e^{-\lambda u}\,du=\frac{1}{\lambda^{k+1}}\int_0^{(\lambda t)} w^k e^{-w}\,dw \qquad \text{change of variables } w=(\lambda u)$$

$$=\frac{1}{\lambda^{k+1}}\left(\int_0^\infty u^w e^{-w}\,dw+\text{T.S.T.}\right)=\frac{1}{\lambda^{k+1}}\left(k!+\text{T.S.T.}\right)$$

T.S.T. = Transcendentally small term <u>with respect to (λt)</u>

$$=o\left(\frac{1}{(\lambda t)^N}\right) \text{ for any } N$$

$k=0$: $\displaystyle\int_0^t e^{-\lambda u}\,du=\frac{1}{\lambda}\left(1+\text{T.S.T.}\right)$

$k=1$: $\displaystyle\int_0^t u e^{-\lambda u}\,du=\frac{1}{\lambda^2}\left(1+\text{T.S.T.}\right)$

$k=2$: $\displaystyle\int_0^t u^2 e^{-\lambda u}\,du=\frac{1}{\lambda^3}\left(2+\text{T.S.T.}\right)$

Using the integration formula, we obtain

$$y(t)=\underbrace{e^{-\lambda t}y_0}_{\text{T.S.T.}}+\lambda\left[g(t)\frac{1}{\lambda}-g'(t)\frac{1}{\lambda^2}+g''(t)\frac{1}{\lambda^3}+\cdots\right]+\text{T.S.T.}$$

Neglecting all terms that are transcendentally small, we arrive at

$$y(t)=g(t)-g'(t)\frac{1}{\lambda}+g''(t)\frac{1}{\lambda^2}+\cdots$$

For large λ, to the leading order, we have

$$\boxed{y(t)=g(t)}$$

Remarks:

- The T.S.T. is negligible when (λt) is moderately large.
- For large λ, when (λt) is moderately large (i.e. when t is not too small), we have $y(t)\approx g(t)$ and the influence of initial condition $y(0)$ disappears.
- For $(\lambda t)<1$, $y(t)\approx g(t)$ is invalid. In particular, for small (λt), $y(t)$ is highly affected by the initial condition. We expand $y(t)$ for large λ and small (λt).

$$y(t)=e^{-\lambda t}y_0+\lambda\int_0^t g(t-u)e^{-\lambda u}\,du \qquad \text{change of variable } w=\lambda u$$

$$=e^{-(\lambda t)}y_0+\int_0^{(\lambda t)} g\left(t-\frac{w}{\lambda}\right)e^{-w}\,dw=\left(1-(\lambda t)+\cdots\right)y_0+(\lambda t)\left(g(t)+\cdots\right)$$

$$=y_0+(\lambda t)\left(g(t)-y_0\right)+\cdots$$

Applying the theorem "formally" to the SDE

We ignore the fact that (S01) is a stochastic differential equation. We treat it "formally" as a deterministic ODE and write it in the form $y' = -\lambda\,[y-g(t)]$.

$$m\,dY=-bV\,dt+F(X,t)dt+q\,dW$$

$$\Longrightarrow \quad \frac{dY}{dt}=-\frac{b}{m}\left[Y-\left(\frac{F(X,t)}{b}+\frac{q}{b}\frac{dW}{dt}\right)\right] \qquad \text{(S01B)}$$

Compare it with the ODE

$$y'=-\lambda\left[y-g(t)\right], \qquad \lambda=\frac{b}{m}$$

As $a\to 0$, we have

$$b = O(a), \qquad m = O(a^3)$$

$$\Longrightarrow \quad \lambda=\frac{b}{m}=O(a^{-2})\to\infty \qquad \text{as } a\to 0$$

We "formally" apply the theorem above to (S01B) to obtain

$$Y(t)=\left(\frac{F(X,t)}{b}+\frac{q}{b}\frac{dW}{dt}\right)$$

Multiplying by dt and using $Ydt = dX$, we arrive at

$$dX=\frac{F(X,t)}{b}dt+\sqrt{2D}\,dW\,, \qquad D=\frac{k_B T}{b}$$

This is the over-damped Langevin equation.

A more rigorous derivation

What we learned in the ODE $y' = -\lambda\,[y-g(t)]$

- The time scale of the influence of initial condition is $O(1/\lambda)$.

- For $t \in \left[0,\ O(1/\lambda)\right]$, we don't have $y(t) = g(t)$.
- For $t >> O(1/\lambda)$, the influence of initial condition disappears and we have $y(t) \approx g(t)$.

We consider the case of $F(x, t) \equiv F_0$. We discuss

- Time scale of inertia
- Time scale of thermal excitation.
- Equipartition of energy, root-mean-square velocity of a particle
- Time scale of the Smoluchowski-Kramers approximation

Time scale of inertia

$$m dY = -bY\,dt + F_0 dt + q\,dW$$

$$\Longrightarrow \quad m\,d\left(Y - \frac{F_0}{b}\right) = -b\left(Y - \frac{F_0}{b}\right)dt + q\,dW$$

Let $V(t) = \left(Y(t) - \frac{F_0}{b}\right)$. We write it as an Ornstein-Uhlenbeck process.

$$m\,dV = -bV\,dt + q\,dW$$

Previously, for the OU process, we derived

$$V(t) = V(0)\exp\left(-\beta t\right) + N\left(0,\ \frac{\gamma^2}{2\beta}(1 - e^{-2\beta t})\right), \qquad \beta = \frac{b}{m}, \qquad \gamma = \frac{q}{m}$$

$$\Longrightarrow \quad Y(t) - \frac{F_0}{b} = \left(Y(0) - \frac{F_0}{b}\right)\exp\left(-\beta t\right) + N\left(0,\ \frac{\gamma^2}{2\beta}(1 - e^{-2\beta t})\right)$$

We write $Y(t)$ in terms of $t_0 \equiv m/b$.

$$Y(t) = Y(0)\exp\left(\frac{-t}{t_0}\right) + \frac{F_0}{b}\left(1 - \exp\left(\frac{-t}{t_0}\right)\right) + N\left(0,\ \frac{\gamma^2 t_0}{2}(1 - e^{-2t/t_0})\right), \qquad t_0 \equiv \frac{1}{\beta} = \frac{m}{b}$$

$t_0 = \frac{m}{b}$ has the dimension of time and is called the time scale of inertia.

Observation: the effect of inertia is a matter of time scale.

- The regime of $t << t_0$

$$Y(t) = Y(0) - \left(Y(0) - \frac{F_0}{b} \right)\left(1 - e^{-t/t_0}\right) + N\left(0,\ \frac{\gamma^2 t_0}{2}(1 - e^{-2t/t_0}) \right) \approx Y(0)$$

$$1 - e^{-t/t_0} = t / t_0 = o(1)$$

In this regime, the inertia is dominant. The velocity at time t is almost entirely determined by the initial velocity.

- The regime of $t = O(t_0)$

$$Y(t) = Y(0)e^{-t/t_0} + \frac{F_0}{b}\left(1 - e^{-t/t_0}\right) + N\left(0,\ \frac{\gamma^2 t_0}{2}(1 - e^{-2t/t_0}) \right)$$

$$e^{-t/t_0} = O(1), \qquad 1 - e^{-t/t_0} = O(1)$$

In this regime, the remaining effect of inertia is still significant while other terms are no longer negligible.

- The regime of $t >> t_0$

$$Y(t) = Y(0)e^{-t/t_0} + \frac{F_0}{b}\left(1 - e^{-t/t_0}\right) + N\left(0,\ \frac{\gamma^2 t_0}{2}(1 - e^{-2t/t_0}) \right) \approx \frac{F_0}{b} + N\left(0,\ \frac{\gamma^2 t_0}{2} \right)$$

In this regime, the effect of inertia is negligible. The distribution of velocity at time t is independent of the initial velocity.

<u>Example:</u>

The time scale of inertia for a bead of radius a in water.

$b = 6\pi\eta a$ (drag coefficient)

$m = \rho \frac{4\pi a^3}{3}$, $\rho = 1$ g (cm)$^{-3}$

==> $t_0 = \frac{m}{b} = \frac{2\rho a^2}{9\eta} \propto a^2$

For a bead of 1 μm diameter in water, we have

$a = 0.5$ μm $= 0.5 \times 10^{-4}$ cm (radius)

$\eta = 0.01$ poise $= 0.01$ g (cm)$^{-1}$ s^{-1} (viscosity of water)

==> $t_0 = \frac{2\rho a^2}{9\eta} \approx 5.6 \times 10^{-8} s = 56\,\text{ns}$ (ns $= 10^{-9}$ s)

For a bead of 10 nm diameter in water, we have

$$t_0 = \frac{2\rho a^2}{9\eta} \approx 5.6\times 10^{-12}\ \text{s} = 5.6\ \text{ps}$$

For molecular motors, we are concerned with reactions and motions in time scale of ms (ms = 10^{-3} s). So the effect of inertia can be neglected. If we want to know their detailed dynamics in time scale of ps, the inertia plays the dominant role.

Time scale of thermal excitation

$$Y(t) = \frac{F_0}{b} + \left(Y(0) - \frac{F_0}{b} \right) e^{-t/t_0} + N\left(0,\ \frac{\gamma^2 t_0}{2}(1-e^{-2t/t_0}) \right)$$

==> $$\text{var}\left(Y(t)\middle| Y(0)\right) = \frac{\gamma^2 t_0}{2}(1-e^{-2t/t_0})$$

Observation: the time scale of thermal excitation is also t_0.

- For $t << t_0$

$$\text{var}\left(Y(t)\middle| Y(0)\right) = \frac{\gamma^2 t_0}{2}(1-e^{-2t/t_0}) \approx \gamma^2 t_0 \cdot \frac{t}{t_0}$$ grows linearly with t.

- For $t \gg t_0$

$$\text{var}\left(Y(t)\middle| Y(0)\right) = \frac{\gamma^2 t_0}{2}(1-e^{-2t/t_0}) \approx \frac{\gamma^2 t_0}{2}$$ reaches its saturation level.

Equipartition of energy

In the case of $F_0 = 0$ (i.e., in the absence of an external driving force), for $t \gg t_0$ (i.e., after reaching equilibrium), we have

$$E\left(Y(t)\right) = 0$$

$$E\left(Y(t)^2\right) = \frac{\gamma^2 t_0}{2} = \frac{\gamma^2}{2\beta} = \frac{q^2}{m^2}\cdot\frac{m}{2b} = \frac{2k_B T b}{2mb} = \frac{k_B T}{m}$$

==> $$\frac{1}{2} m E\left(Y(t)^2\right) = \frac{1}{2} k_B T$$

This is called equipartition of energy, which says

At equilibrium, the thermal energy associated with each degree of freedom is $k_B T/2$, independent of particle size and independent of mass and density."

Root-mean-square velocity of a particle

The root-mean-square (RMS) velocity gives us the typical magnitude of the particle velocity (which is stochastic).

$$\sqrt{E(Y^2)} = \sqrt{\frac{k_B T}{m}} = \sqrt{\frac{3k_B T}{4\pi\rho a^3}} \propto a^{-3/2}$$

Example:

RMS velocity of a 1 μm bead (diameter) in water:

$k_B T = 4.1$ pN·nm

$\rho = 1$ g (cm)$^{-3}$

$a = 0.5$ μm $= 0.5 \times 10^{-4}$ cm

$$\sqrt{E(Y^2)} = \sqrt{\frac{k_B T}{m}} = \sqrt{\frac{3k_B T}{4\pi\rho a^3}}$$

$= 0.28$ cm/s $= 2.8\times 10^3$ μ m/s = 2800 body-size/s

which is fairly large relative to its size.

Time scale of inertia: $t_0 = 56$ ns $= 5.6\times 10^{-8}$ s.

RMS velocity of a 10 nm bead (diameter) in water:

$\sqrt{E(Y^2)} = 280\,\text{cm}/s = 2.8m/s$ $= 2.8\times 10^8$ body-size/s.

which is huge relative to its size.

Time scale of inertia: $t_0 = 5.6$ ps $= 5.6\times 10^{-12}$ s.

RMS velocity of water molecules (approximately 0.3 nm in diameter):

$\sqrt{E(Y^2)} > 50000\,\text{cm}/s = 500m/s$.

which is truly enormous!

It is even larger than the sound speed (343m/s)!

Time scale of inertia: $t_0 = 5.0$ fs $= 5.0\times 10^{-15}$ s.

1 femtosecond (fs) $= 10^{-15}$ second.

Example:

Magnitude of thermal excitaiton.

Suppose hypothetically all molecules in a bottle of 1-Litter water move in the same direction with the same velocity and with no relative motion with respect to each other. The velocity would be > 500 m/s.

With a velocity > 500m/s, the object (the bottle of water) is lethal.

<u>Characters of molecular motors</u>

- Time scale of inertia is short ~ ns
- Average velocity is ~ 1 μm, small in the absolute scale, large relative to the size of molecular motors.
- Root-mean-square velocity ≫ average velocity

$$\sqrt{E(Y^2)} >> E(Y)$$

$$==> \quad \text{std}(Y) >> E(Y)$$

- Velocity fluctuations ≫ average velocity.

<u>Characters of macroscopic motors</u> (e.g., vehicles)

- Time scale of inertia is long ~ s (or longer)
- Average velocity is ~ 10m/s (20 miles/h).
- Velocity fluctuations ≪ average velocity.

<u>Time scale of Smoluchowski-Kramers approximation</u>

Recall that $V(t) \equiv \left(Y(t) - F_0/b\right)$ is an Ornstein-Uhlenbeck process

Previously, for an Ornstein-Uhlenbeck process, we derived

$$\int_0^t V(s)ds = \frac{(1-e^{-\beta t})}{\beta}V(0) + \underbrace{N\left(0,\ \left(\frac{\gamma}{\beta}\right)^2\left(t - \frac{2(1-e^{-\beta t})}{\beta} + \frac{(1-e^{-2\beta t})}{2\beta}\right)\right)}_{\text{containing } dW\text{'s in } [0,t]}$$

Using $t_0 \equiv 1/\beta$, we write the particle position as

$$X(t) - X(0) = \int_0^t Y(s)ds = \frac{F_0}{b}t + \int_0^t V(s)ds$$

$$= \frac{F_0}{b}t + (1-e^{-t/t_0})t_0\left(Y(0) - \frac{F_0}{b}\right) + N\left(0,\ (\gamma t_0)^2 t_0\left(\frac{t}{t_0} - 2(1-e^{-t/t_0}) + \frac{(1-e^{-2t/t_0})}{2}\right)\right)$$

We examine the magnitudes of various terms as particle radius $a \to 0$.

$$m = \rho\frac{4\pi a^3}{3} = O(a^3)$$

$b = 6\pi\, \eta\, a = O(a)$

$$q = \sqrt{2k_B T\, b} = O(a^{1/2})$$

$$\beta = \frac{b}{m} = O(a^{-2}), \qquad t_0 = \frac{1}{\beta} = O(a^2)$$

$$\gamma = \frac{q}{m} = O(a^{-5/2})$$

$$\gamma^2 t_0 = O(a^{-3})$$

$$Y(0) - \frac{F_0}{b} = N\left(0,\ \frac{\gamma^2 t_0}{2}\right) = O(\sqrt{\gamma^2 t_0}) = O(a^{-3/2}) \qquad \text{from equilibrium of } V(0)$$

$$t_0\left(Y(0) - \frac{F_0}{b}\right) = O(a^{1/2})$$

$$(\gamma t_0)^2 = O(a^{-1}), \qquad (\gamma t_0)^2 t_0 = O(a)$$

For $t/t_0 \gg 1$, we have

$$X(t) - X(0) = \frac{F_0}{b}t + \underbrace{t_0\left(Y(0) - \frac{F_0}{b}\right)}_{\text{Term I}} + \underbrace{N\left(0,\ (\gamma t_0)^2 t_0 \left(\frac{t}{t_0}\right)\right)}_{\text{Term II}}$$

We compare Term I and Term II.

$$\text{Term I} = O(a^{1/2})$$

$$\text{Term II} = \sqrt{(\gamma t_0)^2 t_0} \cdot \sqrt{\frac{t}{t_0}} = O(a^{1/2}) \cdot \sqrt{\frac{t}{t_0}} >> O(a^{1/2})$$

For $t/t_0 \gg 1$, we neglect Term I and obtain

$$X(t) - X(0) = \frac{F_0}{b}t + N\left(0,\ 2Dt\right)$$

Here we used $(\gamma t_0)^2 = \left(\frac{\gamma}{\beta}\right)^2 = \left(\frac{q}{b}\right)^2 = \left(\sqrt{\frac{2k_B T}{b}}\right)^2 = 2D = O(a^{-1})$

Thus, for $dt/t_0 \gg 1$ (i.e., on a "coarse" grid), $X(t)$ satisfies

$$dX = \frac{F_0}{b}dt + \sqrt{2D}\, dW$$

which is the Smoluchowski-Kramers approximation.

Appendix

<u>Several issues:</u>

- $t_0 = m/b$ is the smallest time scale on the "coarse" grid for the S-K approximation.

  The S-K approximation is valid only for $t \gg t_0$. For a small particle, t_0 is small

- RMS of inertia displacement is small.

  Inertia displacement refers to the displacement caused by the initial velocity:

  $$(1-e^{-t/t_0})t_0 Y(0) \quad \longrightarrow \quad t_0 Y(0) \quad \text{for } t >> t_0$$

  Based on $Y(0) \sim N\left(0, \frac{k_B T}{m}\right)$, the RMS of inertia displacement is

  $$\text{RMS of inertia displacement } = t_0\sqrt{E\left(Y(0)^2\right)} = \frac{m}{b}\sqrt{\frac{k_B T}{m}} = \frac{\sqrt{m k_B T}}{b}$$

  $$= \frac{\sqrt{\rho \frac{4}{3}\pi a^3 k_B T}}{6\pi\eta a} = \sqrt{a}\cdot\sqrt{\frac{\rho k_B T}{27\pi\eta^2}} = \sqrt{\frac{a}{[\text{nm}]}}\times 7\times 10^{-3}\ [\text{nm}]$$

  The inertia displacement is very small

  RMS = 0.16 nm for a 1μm bead

  RMS = 0.016 nm for a 10nm bead

  <u>Remark:</u>

  Although the RMS of inertia displacement decreases slowly with particle radius a, it is already very small for a fairly large particle.

- Over $[0, t_0]$, the RMS of diffusion displacement is comparable to the RMS of inertia displacement.

  $$\text{RMS of diffusion displacement } = \sqrt{2D t_0} = \sqrt{2\frac{k_B T}{b}\cdot\frac{m}{b}}$$

  $$= \sqrt{2}\frac{\sqrt{m k_B T}}{b} = \sqrt{2}\times(\text{RMS of inertia displacement})$$

  <u>Remark:</u>

  For $t \gg t_0$, the diffusion displacement dominates over the inertia displacement. Consequently, the S-K approximation is valid for $t \gg t_0$.

- Over $[0, t_0]$, the forced displacement is much smaller than the diffusion displacement unless F_0 is extraordinarily large.

We calculate how large the external force needs to be, in order to make the forced displacement comparable to the diffusion displacement over [0, t_0].

$$\frac{F_0}{b}t_0 = \sqrt{2D\,t_0} \qquad ==> \qquad F_0 = \sqrt{\frac{2D\,b^2}{t_0}}$$

It is sensible to examine the <u>force needed per mass</u>.

$$\frac{F_0}{m} = \sqrt{\frac{2D\,b^2}{m^2 t_0}} = \sqrt{\frac{2k_B T\,b^2}{m^3}} = \sqrt{\frac{2k_B T\,(6\pi\eta a)^2}{\left(\rho\pi a^3 4/3\right)^3}}$$

$$= \sqrt{\frac{2k_B T\,(6\pi\eta[\text{nm}])^2}{\left(\rho\pi[\text{nm}]^3 4/3\right)^3}} \cdot \left(\frac{a}{[\text{nm}]}\right)^{\frac{-7}{2}} = 2\times 10^{14}\,\frac{\text{Newton}}{\text{Kg}}\left(\frac{a}{[\text{nm}]}\right)^{\frac{-7}{2}}$$

The external force needed per mass for matching the diffusion displacement over time internal [0, t_0] is huge.

$$\frac{F_0}{m} = \begin{cases} = 7.2\times 10^{10}\,\dfrac{\text{Gravity}}{\text{Mass}} & \text{for a 10nm bead} \\ = 7.2\times 10^{3}\,\dfrac{\text{Gravity}}{\text{Mass}} & \text{for a 1}\mu\text{m bead} \end{cases}$$

In real applications, over [0, t_0], the forced displacement is much smaller than the diffusion displacement. But the effect of F_0 increases linearly with time. In contrast, the effect of diffusion increases with the square root of time. Over a long period, eventually, the effect of F_0 will catch up.