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

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

$\boxed{\text{Claim:}}$

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

Consider a deterministic ODE

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

where λ is positive and large.

Theorem

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 $u = 0$.

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

An integration formula:

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

T.S.T. = Transcendentally small term with respect to (λt)

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

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

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

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 the TST, we arrive at

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

$$\boxed{y(t) = g(t) + O(1/\lambda)}$$

Remarks:

- When (λt) is moderately large, the influence of initial condition $y(0)$ is TST.
- When λ is LARGE λ and t is not too small, (λt) is moderately large and we have $y(t) \approx g(t)$.
- When $(\lambda t) < 1$, $y(t)$ is highly affected by $y(0)$ and $y(t) \approx g(t)$ is invalid.
  In particular, for $(\lambda t) \ll 1$, solution $y(t)$ has the expansion

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

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 $y' = -\lambda\,[y - g(t)]$.

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

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

It has the form $y' = -\lambda\,[y-g(t)]$ where

$$\lambda\equiv\frac{b}{m}, \qquad g(t)\equiv\left(\frac{F(X,t)}{b}+\frac{q}{b}\frac{dW}{dt}\right)$$

As $a\to 0$, we have

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

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

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

$$Y(t)=\left(\frac{F(X,t)}{b}+\frac{q}{b}\frac{dW}{dt}\right), \qquad q=\sqrt{2k_B Tb}\,, \qquad \frac{q}{b}=\sqrt{\frac{2k_B T}{b}}=\sqrt{2D}$$

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

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

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 $y(0)$ is $O(1/\lambda)$.
- For $t\in[0, O(1/\lambda)]$, we don't have $y(t) = g(t)$.
- For LARGE λ and $t \gg O(1/\lambda)$, the influence of $y(0)$ 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

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

==> $$m\,d\left(Y - F_0/b\right) = -b\left(Y - F_0/b\right)dt + q\,dW$$

Let $V(t) \equiv \left(Y(t) - F_0/b\right)$.

$$m\,dV = -bV\,dt + q\,dW \qquad \text{an Ornstein-Uhlenbeck process}$$

Previously, for an OU process, we derived

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

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

We write $Y(t)$ in terms of $t_0 \equiv 1/\beta = m/b$.

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

$t_0 \equiv m/b$ has the dimension of time and is called the <u>time scale of inertia.</u>

<u>Observation:</u> the effect of inertia is a matter of time scale.

- The regime of $t << t_0$

  $$Y(t) = Y(0) + O(t/t_0) + N\left(0,\ O(t/t_0)\right) \approx Y(0)$$

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

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

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

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

- The regime of $t >> t_0$

  $$Y(t) = \frac{F_0}{b} + N\left(0,\ \frac{\gamma^2 t_0}{2}\right) + \text{T.S.T.}$$

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

<u>Examples</u> (time scale of inertia)

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

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

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

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

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

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

  $\rho = 1$ g (cm)$^{-3}$ (density of bead material)

  $\eta = 0.01$ 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.

<u>Time scale of thermal excitation</u>

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

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

Given $Y(0)$, the variance var($Y(t)|Y(0)$) comes from thermal excitation.

<u>Observation:</u> the time scale of thermal excitation is also t_0.

- For $t << t_0$

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

- For $t \gg t_0$

  $$\text{var}\Big(Y(t)\Big|Y(0)\Big) = \frac{\gamma^2 t_0}{2}(1-e^{-2t/t_0}) \approx \frac{\gamma^2 t_0}{2}$$ which has reached its saturation level.

Equipartition of energy

In the absence of an external driving force ($F_0 = 0$), after reaching equilibrium ($t \gg t_0$),

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

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

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

This is called equipartition of energy:

> 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 stochastic instantaneous velocity.

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

Examples (RMS velocity)

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

  $k_B T$ = 4.1 pN·nm = 4.1×10^{-14} g (cm)^2 s^{-2}

  ρ = 1 g (cm)$^{-3}$

  a = 0.5 μm = 0.5×10^{-4} cm

  $$\sqrt{E(Y^2)} = \sqrt{\frac{3k_B T}{4\pi\rho a^3}}$$ = 0.28 cm/s = 2.8×10^3 μ m/s = 2800 body-size/s

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

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

Example (magnitude of thermal excitation)

Consider a bottle of water. Suppose the thermal energy is used to drive all water molecules to move in the same direction with the same velocity and with no relative motion with respect to each other. This uniform velocity would be > 500 m/s.

With a velocity > 500m/s, a bottle of water is lethal.

Characters of molecular motors

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

Characters of macroscopic motors (e.g., vehicles)

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

Time scale of Smoluchowski-Kramers approximation

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

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

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

We write the particle position in terms of $t_0 \equiv 1/\beta$.

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

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

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

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

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

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

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

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

$\gamma^2 t_0 = O(a^{-3})$ we need this quantity in the equilibrium of V.

$Y(0) - \frac{F_0}{b} = N\left(0, \frac{\gamma^2 t_0}{2}\right) = O(\sqrt{\gamma^2 t_0}) = O(a^{-3/2})$ based on 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

$$X(t) - X(0) = \underbrace{\frac{F_0}{b}t}_{\text{Term III}} + \underbrace{t_0\left(Y(0) - \frac{F_0}{b}\right)}_{\text{Term I}} + \underbrace{N\left(0, (\gamma t_0)^2 t_0\left(\frac{t}{t_0}\right)\right)}_{\text{Term II}} + \text{T.S.T.} \qquad \text{(SK0)}$$

We compare Term I and Term II.

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

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

For $t/t_0 \gg 1$, we neglect Term I, and keep Term II and Term III.

$$X(t) - X(0) = \frac{F_0}{b}t + N\left(0, (\gamma t_0)^2 t\right), \qquad (\gamma t_0)^2 = \left(\frac{q}{m}\cdot\frac{m}{b}\right)^2 = \frac{2k_B T}{b} = 2D$$

For $dt/t_0 \gg 1$ (i.e., on a “coarse” grid), $X(t)$ is governed by

$$dX = \frac{F_0}{b}dt + \sqrt{2D}\,dW \qquad \text{(SK1)}$$

This is the Smoluchowski-Kramers approximation (S-K approximation).

Several remarks on the S-K approximation

The S-K approximation

= neglecting Term I and keeping Term II and Term III.

Term I

Term I is the displacement attributed to the initial velocity.

$$(1-e^{-t/t_0})t_0\left(Y(0)-F_0/b\right) \longrightarrow t_0 V(0) \qquad \text{for } t>>t_0$$

Here we study $(Y(0)–F_0/b)$, the deviation from the constant driving/drifting.

Based on $V(0) \sim N(0, k_B T/m)$, the RMS displacement due to inertia is

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

$$= \frac{\sqrt{\rho\frac{4}{3}\pi a^3 k_B T}}{6\pi\eta a} = \sqrt{a}\cdot\sqrt{\frac{\rho k_B T}{27\pi\eta^2}} = \sqrt{\frac{a}{[\text{nm}]}}\times 7\times 10^{-3}\,[\text{nm}] \propto a^{1/2}$$

Examples:

RMS inertia displacement = 0.16 nm for a 1μm bead

RMS inertia displacement = 0.016 nm for a 10nm bead

Term II vs Term I

Term II is the displacement due to diffusion.

For $t = O(t_0)$, the RMS displacement due to diffusion (Term II) is comparable to the RMS displacement due to inertia (Term I).

$$\text{RMS diffusion displacement} = \sqrt{2Dt_0} = \sqrt{2\frac{k_B T}{b}\cdot\frac{m}{b}}$$

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

Time scale of the coarse grid in the S-K approximation

For $t \gg t_0$, Term II dominates Term I. Neglecting Term I is valid on a coarse grid of time scale $t \gg t_0$. Neglecting Term I is not valid on any fine grid of time scale $t \leq t_0$.

The assumption of $F(x, t) \equiv F_0$

This assumption is valid when

$$\frac{\Delta F}{F} \equiv \frac{F\left(x+\Delta x, t+\Delta t\right)-F(x,t)}{F(x,t)} \approx \frac{\partial F}{\partial x}\cdot\frac{\Delta x}{F} + \frac{\partial F}{\partial t}\cdot\frac{\Delta t}{F} << 1 \qquad \text{for } t_{\text{scale}} >> \Delta t >> t_0$$

where $\Delta x \equiv x(t+\Delta t) - x(t)$, Δt is the time scale of the coarse grid in the S-K approximation, and t_{scale} is the time scale of physical evolution.

Term III vs Term II

Term III is the displacement due to external force.

For $t = O(t_0)$, Term III is much smaller than Term II (diffusion displacement) unless F_0 is extraordinarily large. We calculate how large F_0 needs to be, in order to make Term III comparable to Term II for $t = O(t_0)$.

$$\frac{F_0}{b} t_0 = \sqrt{2D t_0} \qquad \Longrightarrow \qquad F_0 = \sqrt{\frac{2D b^2}{t_0}} = \sqrt{\frac{2k_B T b}{t_0}}$$

It is sensible to examine the force per mass.

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

For a small particle, this quantity is huge.

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

Why do we neglect Term I but not Term III?

In real applications, Term III is much smaller than Term II for $t = O(t_0)$. However, Term III is proportional to the time while Term II is proportional to the square root of time. For $t \gg t_0$, eventually, Term III will catch up with Term II.

For $t \gg t_0$, Term I does not grow; it converges to a constant $O(a^{1/2})$ that is negligible in comparison with Term II.