

Lecture 21: “Physical” Brownian Motion II

Scribe: Ken Kamrin

Department of Mathematics, MIT

May 3, 2005

Resources

An instructive applet illustrating physical Brownian motion can be found at:

<http://www.phy.ntnu.edu.tw/java/gas2D/gas2D.html>

For more information on this topic, see:

H. Risken, *The Fokker-Planck Equation* (Springer, 2nd ed., 1989).

Einstein’s Theory

Einstein’s theory of Brownian motion (i.e. “Mathematical” Brownian motion) treats the process as a random walk with iid steps. Specifically, the motion considers both diffusion and drift such that

$$\bar{v} = \text{drift velocity} = \mu F$$

$$\text{where } \mu = \frac{D}{kT}.$$

This description of Brownian motion was considered to a greater extent in past lectures.

Langevin's Theory

After Einstein's theory was developed, Langevin published another model of Brownian motion (i.e. "Physical" Brownian motion). Langevin's model emphasizes that a particle moving due to random collisions with, say, gas molecules, does not actually experience independent steps since its inertia tends to keep it moving in roughly the same direction as its previous step.

To account for inertia, the model is based on an expression of Newton's second law:

$$m\dot{v} = F_{tot} = F_{ext} - \alpha v + m\Gamma(t). \quad (1)$$

The αv term accounts for drag forces and the function $\Gamma(t)$ is a stochastic noise term which accounts for random collisions with gas molecules. The function $\Gamma(t)$ is truly a "white noise" in that

$$\langle \Gamma(t) \rangle = 0,$$

$$\langle \Gamma(t)\Gamma(t') \rangle = q \delta(t - t').$$

The above is like a continuous version of iid steps and the variable q is equivalent to $2D_v$. In equation 1, the noise term is not multiplied by v , so we can reduce the equation to the Weiner-Îto SDE when $F_{ext} = 0$:

$$\boxed{dv = -\gamma v dt + \sqrt{D_v} dz}$$

In the above, $\gamma = \frac{\alpha}{m} \equiv \tau^{-1}$ where τ can be thought of as the time needed for drag to kill acceleration. The Fokker-Planck equation for the resultant PDF is therefore

$$\boxed{\frac{\partial \rho}{\partial t} - \gamma \frac{\partial}{\partial v} (\rho v) = D_v \frac{\partial^2 \rho}{\partial v^2}}$$

At this point, it is worthwhile to discuss the behavior for a general stochastic process of the form

$$\dot{x} = a(x, t) + b(x, t)\Gamma(t)$$

with $\Gamma(t)$ a white noise. There are actually two different treatments of the problem each invoking different methods of numerical solution. In solving iteratively for x to various orders of accuracy, it becomes necessary to define how we evaluate integrals of the form

$$\int_0^\tau \Phi(w(t), t) d(w(t))$$

for a non-stochastic function Φ where $w(\tau) \equiv \int_t^{t+\tau} \Gamma(t') dt'$ for some fixed t .

1. **Îto** : Under Îto's definition, the integral is solved using

$$\int_{t_i}^{t_{i+1}} \Phi(w(t), t) d(w(t)) \Rightarrow \Phi(w(t_i), t_i)[w(t_{i+1}) - w(t_i)]$$

where i is the step index. Numerical solution via the Îto definition resembles the *forward Euler* method for solving PDE's in one time derivative. The resulting Fokker-Planck equation has drift coefficient $D_1 = a(x, t)$.

2. **Stratonovich**: Under this definition, we solve the SDE in a manner analagous to the *Crank-Nicholson* scheme, using

$$\int_{t_i}^{t_{i+1}} \Phi(w(t), t) d(w(t)) \Rightarrow \Phi\left(\frac{w(t_i) + w(t_{i+1})}{2}, \frac{t_i + t_{i+1}}{2}\right) [w(t_{i+1}) - w(t_i)].$$

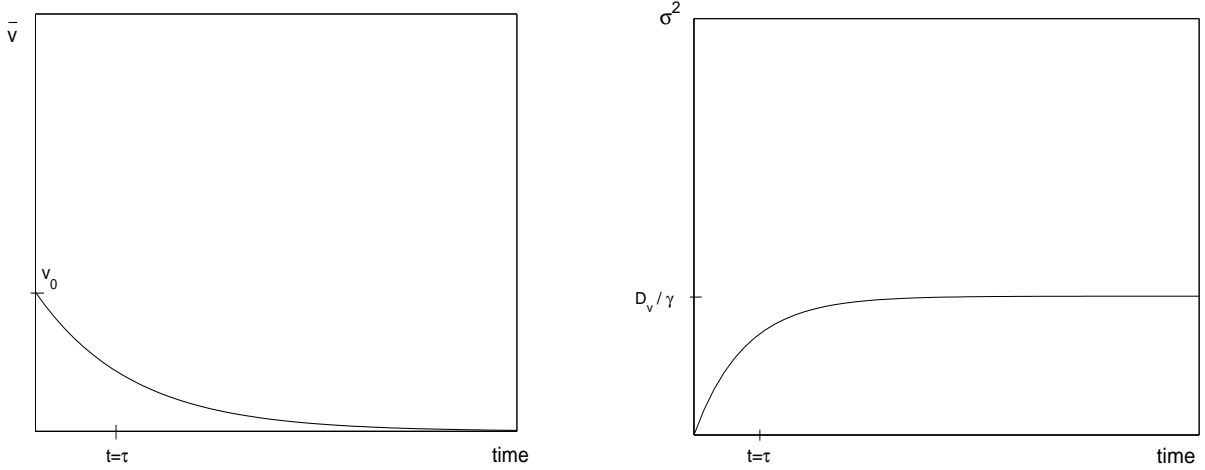
The resulting Fokker-Planck equation has drift coefficient $D_1 = a(x, t) + b_x(x, t)b(x, t)$. The additional term is called the *noise induced drift*.

The diffusion coefficient D_2 is, however, the same under both definitions. For clarity, if the Îto definition is intended, the SDE will be displayed in terms of increments (e.g. $dx = a dt + b dz$), and if the Stratonovich definition is intended, the SDE will be written in terms of stochastic derivatives (e.g. $\dot{x} = a + b \Gamma(t)$).

We now return to the physical Brownian motion SDE, $dv = -\gamma v dt + \sqrt{D_v} dz$. Either of the previous definitions suffices here since $b(x, t) = \text{constant}$. Our SDE is actually the Ornstein-Uhlenbeck process for velocity. Its solution is

$$\rho(v, t) = \frac{\exp\left(-\frac{(v-\bar{v}(t))^2}{2\sigma_v(t)^2}\right)}{\sqrt{2\pi\sigma_v(t)^2}}$$

where $\bar{v}(t) = v_0 \exp(-\gamma t)$ and $\sigma_v(t)^2 = D_v(1 - \exp(-2\gamma t))/\gamma$.



The figures above illustrates the ballistic to diffusive transition which occurs near $t = \gamma^{-1} = \tau$.

In a steady state, we have $\bar{v} = 0$, $\sigma_v^2 = D_v/\gamma$. This yields:

$$\rho(v, \infty) = \frac{\exp\left(-\frac{\gamma v^2}{2D_v}\right)}{\sqrt{2\pi D_v/\gamma}} \propto \exp(-E/kT) = \exp(-mv^2/2kT) \leftarrow \text{Maxwell's Distribution.}$$

Thus we may deduce:

$$\frac{\gamma v^2}{2D_v} = \frac{mv^2}{2kT} \implies \boxed{D_v = \gamma kT/m = \gamma v_{thermal}^2}$$

At this point we may now draw an interesting connection to mathematical Brownian motion. In steady state, the force balance becomes

$$0 = F_{tot} = F_{ext} - \alpha v + m\Gamma(t).$$

When $F_{ext} = 0$ the Green-Kubo expression for D_x yields

$$\begin{aligned} D_x &= \int_0^\infty \langle v(0)v(t) \rangle dt = \gamma^{-2} \int_0^\infty \langle \Gamma(0)\Gamma(t) \rangle dt \\ &= 2D_v\gamma^{-2} \int_0^\infty \delta(t) dt = \gamma^{-2}D_v = \frac{kT}{\gamma m}. \end{aligned}$$

Recall that in Einstein's theory,

$$\mu = \frac{v_{drift}}{F_{ext}} = \frac{D_x}{kT}.$$

The force expression above indicates that in steady state, $\frac{v_{drift}}{F_{ext}} = \alpha^{-1} = (\gamma m)^{-1}$. Thus we have deduced

$$(\gamma m)^{-1} = \frac{D_x}{kT} \implies D_x = \frac{kT}{\gamma m}.$$

This was our precise result from analyzing the Langevin Equation.

Kramer's Theory

Kramer's solution to physical Brownian motion deals with phase space coordinates (x, v) .

This turns the problem into solving two coupled SDE's:

$$\text{(It\^o)} \quad dx = v dt, \quad dv = \left(-\gamma v + \frac{F_{ext}}{m}\right) dt + \sqrt{D_v} dz$$

or

$$\text{(Stratonovich)} \quad \dot{x} = v, \quad \dot{v} = -\gamma v + \frac{F_{ext}}{m} + \sqrt{D_v} \Gamma(t).$$

We proceed by writing the multi-dimensional Fokker-Planck equation for $\rho(x, v, t)$:

$$\frac{\partial \rho}{\partial t} + \vec{\nabla} \cdot (\vec{D}_1 \rho) = (\vec{\nabla} \vec{\nabla}) : (\underline{D}_2 \rho)$$

where \vec{D}_1 is the drift vector (first moment vector) and \underline{D}_2 is the diffusion matrix (second moment matrix). They are defined naturally by

$$\begin{aligned} \vec{D}_1 &= -\underline{\gamma} \begin{pmatrix} x \\ v \end{pmatrix} \quad \text{for} \quad \underline{\gamma} = \begin{pmatrix} 0 & 1 \\ 0 & -\gamma \end{pmatrix}, \quad \text{and} \\ \underline{D}_2 &= \begin{pmatrix} 0 & 0 \\ 0 & D_v \end{pmatrix}. \end{aligned}$$

Applying the Fokker-Planck equation in phase space yields Kramer's equation for the time evolution of the PDF:

$$\frac{\partial \rho}{\partial t} + \frac{\partial}{\partial x}(v\rho) - \gamma \frac{\partial}{\partial v}(v\rho) = -\frac{1}{m} \frac{\partial}{\partial v}(F(x)\rho) + D_v \frac{\partial^2 \rho}{\partial v^2}.$$

This is typically solved using characteristics. When $F_{ext} = -k_s x$, the Kramer's equation can be solved exactly using principles from vector Ornstein-Uhlenbeck processes. Letting $k_s \rightarrow 0$ yields

$$\rho(x, v, t|x_0, v_0, t_0 = 0) = \frac{\exp\left(-\frac{1}{2}\vec{z} \cdot \underline{A}\vec{z}\right)}{\sqrt{2\pi|\underline{A}|}}$$

where

$$A = \text{variance matrix}, \quad \vec{z} = \begin{pmatrix} x \\ v \end{pmatrix} - \begin{pmatrix} \bar{x} \\ \bar{v} \end{pmatrix},$$

$$\bar{x}(t) = x_0 + \frac{v_0}{\gamma}(1 - \exp(-\gamma t)), \quad \bar{v}(t) = v_0 \exp(-\gamma t).$$

The components of the variance matrix are

$$A_{xx} = \frac{kT}{m\gamma^2}(2\gamma t - 3 + 4\exp(-\gamma t) - \exp(-2\gamma t))$$

$$A_{vv} = \frac{kT}{m}(1 - \exp(-2\gamma t))$$

$$A_{xv} = A_{vx} = \frac{kT}{m}(1 - \exp(-\gamma t))^2.$$

We can construct a PDF for position, $c(x, t|x_0, t_0 = 0)$, based on this extended PDF $\rho(x, v, t|x_0, v_0, t_0 = 0)$. We remove dependence on the initial velocity v_0 by averaging it out over a Maxwell distribution of possible starting velocities. We then remove dependence on the final velocity v by integrating this result over all possible final velocities. Thus,

$$\begin{aligned} c(x, t) &= \int_{v=-\infty}^{\infty} \left(\int_{v_0=-\infty}^{\infty} \rho(x, v, t|x_0, v_0, t_0 = 0) \underbrace{\frac{\exp\left(-\frac{mv_0^2}{2kT}\right)}{\sqrt{2\pi kT/m}}}_{\text{Maxwell Distribution}} dv_0 \right) dv \\ &= \frac{\exp\left(-\frac{x^2}{2\sigma_x(t)^2}\right)}{\sqrt{2\pi\sigma_x(t)^2}} \end{aligned}$$

where $\sigma_x(t)^2 = \frac{2v_{thermal}^2}{\gamma^2}(\gamma t - 1 + \exp(-\gamma t))$. Note that:

$$\sigma_x(t)^2 \sim \begin{cases} v_{thermal}^2 t^2 & \text{for } \gamma t \ll 1 \\ 2D_x t & \text{for } \gamma t \gg 1. \end{cases}$$

This indicates the ballistic \rightarrow diffusive transition akin to the result from Telegrapher's Equation in solving for persistent random walks.