Langevin equations

Consider again the dynamics of a Brownian particle in a potential field $V(q)$:

$$m\ddot{q} = -\nabla V(q) - \underbrace{\gamma \dot{q}} + \sqrt{2D\alpha}\; W(t)$$

$\nabla V(q) \equiv F(q)$

Deterministic force $F(q)$

Frictional damping force (e.g. Stokes drag)

diffusion coefficient for random force

α = constant

TBD

For now, consider the case when $D\alpha$ is constant independent of q, so the interpretation does not matter, and we can just choose Ito.

Also, to determine α, for now set $V(q)=0$ to get the Ornstein-Uhlenbeck equation:

$$m\ddot{q} = -\gamma\dot{q} + \sqrt{2D\alpha}\,\mathcal{W}(t), \text{ set } m=1$$

$$\Longleftrightarrow \boxed{\dot{u} = -\gamma u + \sqrt{2D\alpha}\,\mathcal{W}(t)}, \quad u=\dot{q}$$

We know that at equilibrium, the velocity should follow the Maxwell-Boltzmann distribution

$$P(v) \sim e^{-\frac{mv^2}{2kT}}$$

so the variance of u is

$$\langle u^2 \rangle = \frac{kT}{m}$$

and $\langle u \rangle = 0$ in the absence of forcing

What α achieves this variance?

Recall $m = 1$ for now...

There are many ways to derive this. Let's start from a pedestrian but useful for numerical analysis avenue:

$$\begin{cases} u^{n+1} = u^n - \gamma \Delta t u^n + \sqrt{2D\alpha \Delta t}\, \widetilde{W}^n \\ u^n \simeq u(t = n\Delta t) \end{cases}$$

Assume that the equilibrium variance is $C_u = \langle u^2 \rangle$

For the multi-variable case, this is just the <u>covariance matrix</u>

$$C_u = \langle u u^* \rangle \leftarrow \text{generalization}$$

$$C_u^{n+1} = \langle (u^{n+1})^2 \rangle = \langle (1-\gamma\Delta t)^2 (u^n)^2 \rangle + 2D\alpha\,\Delta t \,\langle (\widetilde{W}^n)^2 \rangle$$

$$C_u^{n+1} = (1-\gamma\Delta t)^2\, C_u^n + 2D\alpha\,\Delta t$$

At the steady (equilibrium) state,

$$C_u^{n+1} = C_u^n = C_u \Rightarrow$$

$$\left[(1-\gamma\Delta t)^2 - 1\right] C_u = 2D\alpha\,\Delta t$$

$$\Rightarrow C_u = \frac{D\alpha}{\gamma} + O(\Delta t^2) = kT$$

Therefore, to obtain the right covariance for velocity in the limit $\Delta t \to 0$ we require:

$$D\alpha = \gamma k T$$

This is one particular instance of a <u>fluctuation-dissipation</u> relation between dissipation and random forcing.

Its physical origin is in the common microscopic degrees of freedom that cause both friction and fluctuations.

$\to$ see Mori-Zwanzig formalism later

With all the proper units, the Langevin equation thus becomes:

$$\boxed{m\dot{u} = -\gamma u + \sqrt{2\gamma kT}\, W(t)}$$

The formal solution to this equation is

$$u(t) = u_0 e^{-(\gamma/m)t} + \sqrt{\frac{2\gamma kT}{m^2}} \underbrace{\int_0^t e^{\frac{\gamma}{m}(s-t)} W(s)\, ds}_{\text{Stochastic integral}}$$

Let's consider the stochastic integral

$$I(t) = \int_0^t e^{a(s-t)} W(s)\, ds$$

This is a linear functional of the Gaussian process $W(t)$ (white noise), so it is itself Gaussian. All we need is its mean and variance.

$$\langle I(t) \rangle = 0$$

$$\langle I^2(t) \rangle = \int_0^t \int_0^t e^{a(s_1-t)+a(s_2-t)} (ds_1 ds_2) \langle W(s_1) W(s_2) \rangle$$

Recall $= \delta(s_1 - s_2)$

$$\Rightarrow \langle I^2(t) \rangle = \int_0^t e^{2a(s-t)}\, ds = \frac{1}{2a}\left(1-e^{-2at}\right)$$

So the velocity can be sampled as:

$$u(t) = u_0 e^{-\gamma/m\, t} + \mathcal{N}(0,1) \cdot \sqrt{\frac{2\gamma kT}{m^2}} \cdot \sqrt{\frac{m}{2\gamma}\left(1-e^{-2\gamma/m\, t}\right)}$$

$$u(t) = u_0 e^{-(\gamma/m)\,t} + \sqrt{\frac{kT}{m}\left[1-e^{-2(\gamma/m)\,t}\right]} \cdot \mathcal{N}(0,1)$$

<u>Exact</u> solution!

normal random number

In the equilibrium state, $t \to \infty$

$$u(t) \to \sqrt{\frac{kT}{m}} \cdot \mathcal{N}(0,1)$$

which is indeed a Gaussian variable with the correct variance.

Along the way we obtained an exponential integrator for the velocity Langevin equation.

Now let's go back to adding a non-trivial potential $U(q)$

$$\begin{cases} \dot{q} = u \\ m\dot{u} = -\dfrac{\partial V}{\partial q}(q) - \gamma u + \sqrt{2\gamma kT}\,\mathcal{W}(t) \end{cases}$$

← Hamiltonian dynamics + noise (fluctuations)

Let $p = mu$, $z = (q, p)$

The Fokker-Planck equation is

$$\partial_t P(z,t) = -\frac{\partial}{\partial q}\left(\frac{p P}{m}\right) + \frac{\partial}{\partial p}\left[\left(\frac{\partial V}{\partial q} + \frac{\gamma p}{m}\right) P\right]$$

FPE →

$$+ \frac{\partial^2}{\partial p^2}\left(\gamma kT \cdot P\right)$$

NOTE: NO PROBLEM with $\gamma \equiv \gamma(q)$ not constant!

A. DONEV

We want $P = Z^{-1} e^{-H/kT}$ to be the stationary (equilibrium) distribution, with Hamiltonian

$$H(z) = V(q) + \frac{p^2}{2m}$$

$$\partial_t \left[Z^{-1} e^{-H/kT} \right] = Z^{-1} e^{-H/kT} \cdot$$

cancel

$$\left\{ -\left(-\frac{p}{m} \frac{\partial V}{\partial q} + \frac{2p}{2m} \frac{\partial V}{\partial q} \right) / kT \right.$$

cancel   cancel

$$\frac{\gamma}{m} - \frac{\gamma p}{m} \cdot \frac{1}{kT} \cdot \left(\frac{\partial H}{\partial p} \right)$$

$$\left. + (\gamma kT) \left[-\frac{1}{kT} \left(\frac{\partial^2 H}{\partial p^2} \right) + \frac{1}{(kT)^2} \left(\frac{\partial H}{\partial p} \right)^2 \right] \right\} = 0$$

A. Donev

How about the time evolution of the position of a free Brownian walker $V(q)=0$?

It is a Gaussian variable also, so look at the variance:

Use $$q\cdot\frac{d^2q}{dt^2}=\frac{1}{2}\frac{d^2(q^2)}{dt^2}-\left(\frac{dq}{dt}\right)^2$$

which uses classical calculus because $v=\dot{q}(t)$ is a continuous process (no noise in q equation)

$$\langle q \frac{d^2 q}{dt^2} \rangle = \langle q \dot{u} \rangle = \langle -\frac{\gamma}{m} q \dot{q} \rangle$$
$$= -\frac{\gamma}{2m} \frac{d}{dt} (q^2)$$

$\Rightarrow$ combined with previous identity

$$\frac{d^2 \langle q^2 \rangle}{dt^2} + \frac{\gamma}{m} \frac{d}{dt} \langle q^2 \rangle = 2 \langle v^2 \rangle$$
$$= 2 \frac{kT}{m}$$

which can be solved with ICs:

$$\langle q^2 \rangle (0) = 0 \quad \text{and} \quad \frac{d \langle q^2 \rangle (0)}{dt} = 0$$

$$\Rightarrow q(t) = \frac{2kT}{\gamma} \left[t - \frac{m}{\gamma} \left(1 - e^{-\gamma/m \, t}\right) \right]$$

For large t, we get <u>diffusive</u> behavior

$$\boxed{q(t) \rightarrow 2\frac{kT}{\gamma}t}$$

$$\Rightarrow \boxed{D = \frac{kT}{\gamma} \quad \text{Einstein relation}}$$

diffusion coefficient

It seems that at long times compared to the scale $\boxed{\tau = \frac{m}{\gamma}}$ the motion of the particle looks diffusive. Next time we will explicitly consider the <u>overdamped</u> or <u>Brownian</u> or <u>diffusive</u> limit $\frac{m}{\gamma} \rightarrow 0$

In <u>higher dimensions</u>, the friction tensor is a matrix or linear operator that relates forces to velocities (inverse <u>mobility</u>), and the mass is a matrix or linear operator as well.

The generalization is "trivial":

FLUCTUATION-DISSIPATION BALANCE:

$$\boxed{\langle N N^* \rangle = 2kT \overleftrightarrow{\gamma}}$$

$$\begin{cases} \dfrac{d\vec{q}}{dt} = \vec{u} \\ \overleftrightarrow{m}\,\dfrac{d\vec{u}}{dt} = -\left[\nabla_q V(q)\right] - \overleftrightarrow{\gamma}\cdot\vec{u} + \overleftrightarrow{N}\cdot\vec{W}(t) \end{cases}$$

where $\langle \vec{W}\vec{W}^* \rangle = \text{Identity}$