Langevin equations

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

\[ m \dddot{q} = - \nabla V(q) - \gamma \dot{q} + \sqrt{2D \alpha} \, W(t) \]

- Deterministic force $F(q)$
- Frictional damping force (e.g. Stokes drag)
- Diffusion coefficient for random force
  \[ \alpha = \text{constant} \]
  \[ \text{TBD} \]
For now, consider the case when \( D \) is constant independent of \( q \), so the interpretation does not matter, and we can just choose \( \bar{d} \).

Also, to determine \( \alpha \), for now set \( \sqrt{\alpha} = 0 \) to get the Ornstein–Uhlenbeck equation:

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

\[
\iff \dot{u} = -\bar{\gamma} \, u + \sqrt{2D \alpha} \, W(t), \, u = \dot{q}
\]
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 \( v \) is

\[ \langle v^2 \rangle = \frac{kT}{m} \]

and \( \langle v \rangle = 0 \) in the absence of forcing.

What \( k \) 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:

\[
\begin{align*}
\mathbf{u}^{n+1} &= \mathbf{u}^n - \gamma \Delta t \mathbf{u}^n + \sqrt{2D \Delta t} \mathbf{W}^n \\
\mathbf{u}^n &\sim \mathbf{u}(t = n \Delta t)
\end{align*}
\]

Assume that the equilibrium variance is

\[
C_n = \langle u^2 \rangle
\]

For the multi-variable case, this is just the covariance matrix

\[
C_u = \langle uu^* \rangle \rightarrow \text{generalization}
\]
\[ C_{n+1} = \langle (u_{n+1})^2 \rangle = \langle (1 - \delta \chi \Delta t) u_n^2 \rangle + 2D \Delta x \Delta t \langle (\tilde{w}_n)^2 \rangle \]

\[ C_{n+1} = (1 - \delta \chi \Delta t)^2 C_n + 2D \Delta x \Delta t \]

At the steady (equilibrium) state,

\[ C_{n+1} = C_n = C_n \Rightarrow \]

\[ \left( (1 - \delta \chi \Delta t)^2 - 1 \right) C_n = 2D \Delta x \Delta t \]

\[ \Rightarrow C_n = \frac{D \Delta x}{\delta \chi} + O(\Delta t^2) = kT \]
Therefore, to obtain the right covariance for velocity in the limit $\Delta t \to 0$ we require:

$$D\mathbf{x} = \mathbf{F} \, h \mathbf{T}$$

This is one particular instance of a fluctuation-dissipation 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:

\[
\dot{\mathbf{u}} = -\mathbf{f} \mathbf{u} + \sqrt{2 g k T} \mathbf{W}(t)
\]

The formal solution to this equation is

\[
\mathbf{u}(t) = \mathbf{u}_0 e^{-\xi(t)/m} \left( t \right)
\]

\[
+ \sqrt{\frac{2 g k T}{m^2}} \int_0^t e^{\frac{\xi(s-t)}{m}} W(s) \, ds
\]

\underline{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.

\[ \langle I(t) \rangle = 0 \]

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

Recall \( \delta(s_1-s_2) \)
So the velocity can be sampled as:

\[ v(t) = u_0 e^{-\frac{g}{m} t} + \sqrt{\frac{2 \gamma k T}{m}} \cdot \sqrt{\frac{m}{2g}} \left( 1 - e^{-2\frac{g}{m} t} \right) \cdot N(0,1) \]

\[ v(t) = u_0 e^{-\frac{g}{m} t} + \sqrt{\frac{\hbar T}{m}} \left[ 1 - e^{-2\frac{g}{m} t} \right] \cdot N(0,1) \]

Exact solution!
In the equilibrium state, \( t \to \infty \)

\[
U(t) \to \sqrt{\frac{\hbar T}{m}} \cdot N(0,1)
\]

which is indeed a Gaussian variable with the correct variance.

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

\[
\begin{cases}
\text{Now let's go back to adding} \\
\text{a non-trivial potential } U(q)
\end{cases}
\]
\[ \begin{aligned}
q &= \dot{u} \\
\dot{u} &= -\frac{\partial V}{\partial q} - \gamma u + \sqrt{2\gamma kT} \, W(t)
\end{aligned} \]

\[ \text{Let} \quad p = m \dot{u} \quad \text{and} \quad z = (q, p) \]

The Fokker-Planck equation is

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

\[ \text{FPE} \quad + \frac{\gamma^2}{2} \left( g kT \cdot \mathbf{p} \right) \]

\[ \text{Note: No problem with } \gamma = \gamma(q) \text{ not constant!} \]
We want $P = \mathbb{E}^{-1} e^{-H/kT}$ to be the stationary (equilibrium) distribution, with Hamiltonian

$$H(x) = V(q) + \frac{P^2}{2m}$$

$$\mathbb{E}^t \left[ e^{-H/kT} \right] = e^{-H/kT} \cdot$$

$$\mathbb{E}^t \left[ \left( -\frac{P}{m} \frac{\partial V}{\partial q} + \frac{2P}{2m} \frac{\partial V}{\partial q} \right) / kT \right]$$

$$= \frac{\partial}{\partial P} \left( \frac{1}{kT} \left( \frac{\partial}{\partial P} \left( \frac{\partial H}{\partial P} \right) \right) \right)$$

$$= 0$$
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 $q \cdot \frac{d^2 q}{dt^2} = \frac{1}{2} \frac{d^2 (q^2)}{dt^2} - (\frac{dq}{dt})^2$

which uses classical calculus because $\lambda = \dot{q}(t)$ is a continuous process (no noise in $q$ equation)
\[ \langle q^2 \frac{d^2q}{dt^2} \rangle = \langle q \dot{u} \rangle = \langle -\frac{q}{m} \frac{d}{dt} \dot{q} \dot{q} \rangle \]

\[ = -\frac{g}{2m} \frac{d}{dt} (q^2) \]

\[ \Rightarrow \text{combined with previous identity} \]

\[ \frac{d^2 \langle q^2 \rangle}{dt^2} + \frac{g}{m} \frac{d}{dt} \langle q^2 \rangle = 2 \langle \dot{q}^2 \rangle \]

\[ = 2 \frac{\hbar \Omega}{m} \]

which can be solved with ICS:

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

\[ \Rightarrow q(t) = 2 \frac{\hbar \Omega}{g} \left[ t - \frac{m}{g} \left( 1 - e^{-g/mt} \right) \right] \]
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For large $t$, we get diffusive behavior

\[ q(t) \to 2 \frac{ht}{\gamma} t \]

\[ D = \frac{ht}{\gamma} \text{ Einstein relation} \]

diffusion coefficient

It seems that at long times compared to the scale $\frac{m}{\gamma}$ the motion of the particle looks diffusive. Next time we will explicitly consider the overdamped or Brownian or diffusive limit $\frac{m}{\gamma} \to 0$
In higher dimensions, the friction tensor is a matrix or linear operator that relates forces to velocities (inverse mobility), and the mass is a matrix or linear operator as well.

The generalization is "trivial":

\[
\begin{align*}
\frac{d \mathbf{q}}{dt} &= \mathbf{u} \\
\frac{m}{\mathbf{u}} \frac{d \mathbf{u}}{dt} &= - \left[ D_q V(q) - \mathbf{g} \cdot \mathbf{u} + N \cdot W(t) \right]
\end{align*}
\]

where \( \left\langle W W^* \right\rangle = \text{Identity} \)