Diffusion coefficient and velocity autocorrelation function

Mean-squared displacement

Let $x(t)$ be the stochastic trajectory of a particle. We assume that the trajectory is probabilistically equivalent under time shift. Then, we define the mean-squared displacement (MSD), denoted $\overline{\Delta x^2}(\tau)$, of the particle with lag time τ:

$$\overline{\Delta x^2}(\tau) = \left\langle (x(\tau) - x(0))^2 \right\rangle .$$

The average is taken with respect to possible instances of the stochastic trajectories. MSD represents how "fast" the particle can diffuse, but it encodes far deeper information as we see below.

Diffusion coefficient

Consider the scaled slope of MSD:

$$D(\tau) = \frac{1}{2} \frac{d\overline{\Delta x^2}(\tau)}{d\tau}.$$

$D(\tau)$ is called the (time-dependent) diffusion coefficient of the particle. For the simplest Brownian particle of mass m and mobility μ at temperature T, the diffusion coefficient is known to be

$$D(\tau) = \mu k_{\mathrm{B}} T \left(1 - \exp\left(-\frac{t}{m\mu}\right)\right).$$

Velocity autocorrelation function

Another characteristic function of the stochastic dynamics is the velocity autocorrelation function (VACF):

$$C(\tau) = \langle v(\tau) v(0) \rangle$$

where $v(t)$ is the velocity of the particle, i.e., $v(t) = dx(t)/dt$. It represents how long the particle *remembers* the memory of its own trajectory.

Interestingly, VACF is related to diffusion coefficient in the following way:

$$D(\tau) = \int_0^\tau C(t)\, dt;$$

or, equivalently, $C(\tau) = dD(\tau)/d\tau$. This relation is relatively easy to show. Firstly, note:

$$x(\tau) - x(0) = \int_0^\tau v(t)\, dt.$$

Injecting this into the definition of MSD gives

$$\begin{aligned}
D(\tau) &= \frac{1}{2}\frac{d}{d\tau}\left\langle (x(\tau)-x(0))^2 \right\rangle \\
&= \frac{1}{2}\frac{d}{d\tau}\left\langle \left(\int_0^\tau v(t)\,dt\right)^2 \right\rangle \\
&= \frac{1}{2}\left\langle \frac{d}{d\tau}\left(\int_0^\tau v(t)\,dt\right)^2 \right\rangle \\
&= \left\langle v(\tau)\int_0^\tau v(t)\,dt \right\rangle \\
&= \int_0^\tau \langle v(\tau)v(t)\rangle\,dt.
\end{aligned}$$

Now, by time shift invariance, we may shift time uniformly by $-t$ in the bracket. So, we get

$$\begin{aligned}
D(\tau) &= \int_0^\tau \langle v(\tau-t)v(0)\rangle\,dt \\
&= \int_0^\tau \langle v(t)v(0)\rangle\,dt \\
&= \int_0^\tau C(t)\,dt.
\end{aligned}$$

So, the second derivative of MSD is VACF!

$$\frac{d^2}{d\tau^2}\left\langle (x(\tau)-x(0))^2 \right\rangle = C(\tau).$$

Potential hessian

The asymptotic behavior of short-time VACF ($\tau \to 0$) gives mechanistic insight into the system. With Taylor expansion,

$$\begin{aligned}
C(\tau) &= \langle v(0)v(\tau)\rangle \\
&= \langle v(-\tau/2)v(\tau/2)\rangle \\
&\simeq \left\langle \left(v(0)-\frac{\tau}{2}v'(0)\right)\left(v(0)+\frac{\tau}{2}v'(0)\right)\right\rangle \\
&= \left\langle v(0)^2 \right\rangle - \frac{\tau^2}{4}\left\langle v'(0)^2 \right\rangle.
\end{aligned}$$

If the population is the canonical ensemble, we have

$$\left\langle v(0)^2 \right\rangle = \frac{k_{\mathrm{B}}T}{2}.$$

And, if the particle obey the Langevin dynamics

$$v'(0) = -\frac{1}{m}\nabla V - \gamma v(0) + \sigma\frac{dW}{dt},$$

...? Then?