Recap: Damped Brownian motion in 1D

Dynamics described by stochastic differential equation (SDE)

$$M\frac{dV}{dt} = \underbrace{-M\gamma V(t)}_{\text{Drag force}} + \underbrace{F_L(t)}_{\text{stochastic force}}$$

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

and $\langle F_L(t) F_L(t')\rangle = \mathcal{K}(t-t')$

Solution to process constructed by solving EOMs for each microscopic realization

$t > t_0$: $$V(t) = V(t_0)\, e^{-\gamma(t-t_0)} + \int_{t_0}^{t} dt'\, F_L(t')$$

So $$\langle V(t)\rangle = \langle V(t_0)\rangle\, e^{-\gamma(t-t_0)} \xrightarrow[t-t_0 \gg \gamma]{} 0$$

while

$$\delta V(t) = V(t) - \langle V(t)\rangle$$

$$\sigma_V^2(t) = \langle \delta V(t)\, \delta V(t)\rangle = \langle \delta V^2(t_0)\rangle\, e^{-2\gamma(t-t_0)} + \frac{1}{M^2}\int_{t_0}^{t} dt' \int_{t_0}^{t} dt''\, \langle F_L(t') F_L(t'')\rangle\, e^{-\gamma(t-t')}\, e^{-\gamma(t-t'')}$$

Specifically for $\mathcal{K}(t-t') = 2DM^2\,\delta(t-t')$

$$= \langle \delta V^2(t_0)\rangle\, e^{-2\gamma(t-t_0)} + \frac{D}{\gamma}\left[1 - e^{-2\gamma(t-t_0)}\right]$$

By imposing the long time limit

$$\sigma_v^2(t \gg t_0) = \frac{D_v}{\gamma}$$

expect that in the limit

$$\left\langle E_{kin}^{(M)} \right\rangle = \left\langle \frac{1}{2} M v^2(t) \right\rangle \to \frac{k_B T}{2}$$

$\Rightarrow$ fluctuation dissipation relation

$$\boxed{D_v = \frac{k_B T}{M} \gamma}$$

Started to look at process in coordinate space, r

Solution takes a similar structure to our microscopic velocity

$$x(t) = x(t_0) + \frac{v(t_0)}{\gamma}\left(1 - e^{-\gamma(t-t_0)}\right) + \frac{1}{M}\int_{t_0}^{t} dt' \, \frac{1 - e^{-\gamma(t-t')}}{\gamma} \, F_L(t')$$

Such that on average

$$\langle x(t) \rangle = \langle x(t_0) \rangle + \frac{\langle v(t_0) \rangle}{\gamma}\left(1 - e^{-\gamma(t-t_0)}\right)$$

corresponding to ballistic motion at early times and a finite displacement in the limit $t - t_0 \gg \frac{1}{\gamma}$

Next we can consider also the fluctuations

$$\delta x(t) = x(t) - \langle x(t)\rangle = x(t_0) - \langle x(t_0)\rangle + \frac{v(t_0) - \langle v(t_0)\rangle}{\gamma}\left(1 - e^{-\gamma(t-t_0)}\right)$$

$$+ \frac{1}{M}\int_{t_0}^{t} dt' \, \frac{1 - e^{-\gamma(t-t')}}{\gamma} F_L(t')$$

So we get

$$\langle \delta x(t) \delta x(t)\rangle = \langle \delta^2 x(t_0)\rangle + \left\langle \delta x(t_0) \frac{\delta v(t_0)}{\gamma}\left(1 - e^{-\gamma(t-t_0)}\right)\right\rangle$$

$$+ \left\langle \frac{\delta v^2(t_0)}{\gamma^2}\right\rangle \left(1 - e^{-\gamma(t-t_0)}\right)^2$$

$$+ \frac{1}{M^2\gamma^2}\int_{t_0}^{t} dt' \int_{t_0}^{t} dt'' \left(1 - e^{-\gamma(t-t')}\right)\left(1 - e^{-\gamma(t-t'')}\right) \langle F_L(t') F_L(t'')\rangle$$

So within approximation of auto-correlation function the last term becomes

$$\frac{2D_v}{\gamma^2}\int_{t_0}^{t} dt' \left(1 - e^{-\gamma(t-t')}\right)^2$$

$$= \frac{2D_v}{\gamma^2}\left(t - t_0 - \frac{2}{\gamma}\left(1 - e^{-\gamma(t-t_0)}\right) + \frac{1}{2\gamma}\left(1 - e^{-2\gamma(t-t_0)}\right)\right)$$

So in particular if these are initially in thermal $\delta x(t_0) = 0$ $\delta v(t_0) = 0$ respectively, i.e. position and velocity of particle are known with certainty

$$\langle \delta x^2(t) \rangle = \frac{2D_v}{\gamma^2}\left(t - t_0 - \frac{2}{\gamma}\left(1 - e^{-\gamma(t-t_0)}\right) + \frac{1}{2\gamma}\left(1 - e^{-2\gamma(t-t_0)}\right)\right)$$

So for $t - t_0 \ll \frac{1}{\gamma}$ linear and quadratic terms cancel

$$\langle \delta x^2(t) \rangle \simeq \frac{2D_v}{3} t^3$$

in the long time limit $t - t_0 \gg \frac{1}{\gamma}$

$$\langle \delta x^2(t) \rangle \simeq \frac{2D_v}{\gamma^2}(t - t_0)$$

linear growth as in ordinary diffusion process

We conclude that the coordinate space diffusion constant is given by

$$D = \frac{D_v}{\gamma^2}$$

using fluctuation dissipation relation $\gamma = \frac{M D_v}{k_B T}$

we conclude that $D = \frac{(k_B T)^2}{M^2 D_v}$ is inversely proportional to velocity diffusion constant

Spectral analysis

Consider the process in the frequency domain rather than in time domain

Will focus on stationary stochastic processes ie processes where statistical properties of noise same for time translation invariant

e.g. $\langle F_L(t) F_L(t') \rangle = \Gamma\delta(t-t')$

Define

$$\tilde{F}_L(\omega) = \int_{-\infty}^{\infty} dt \; F_L(t) \, e^{+i\omega t}$$

$$\tilde{V}(\omega) = \int_{-\infty}^{\infty} dt \; V(t) \, e^{+i\omega t} \qquad V(t) = \int_{-\infty}^{\infty} \frac{d\omega}{(2\pi)} \tilde{V}(\omega) e^{-i\omega t}$$

How the EOM reads in ω-space

$$M \frac{dV}{dt} = - M\gamma V(t) + F_L(t)$$

$$-i\omega \tilde{V}(\omega) = - M\gamma \tilde{V}(\omega) + \tilde{F}_L(\omega)$$

So we have

$$\tilde{V}(\omega) = \frac{1}{M} \frac{1}{\gamma - i\omega} \tilde{F}_L(\omega)$$

We can thus look at the auto-correlation function.

$$\langle F_L(t)\, F_L(t') \rangle = \mathcal{K}(t-t')$$

$$\langle \tilde{F}_L(\omega)\, \tilde{F}_L^*(\omega') \rangle = \int_{-\infty}^{\infty} dt \int_{-\infty}^{\infty} dt' \, \langle F_L(t)\, F(t') \rangle \, e^{i\omega t} e^{-i\omega' t'}$$

So for stationary process

$$\Delta t = t - t' \qquad T = \frac{t+t'}{2}$$

$$= \int_{-\infty}^{\infty} d\Delta t \int_{-\infty}^{\infty} dT \; \mathcal{K}(\Delta t)\, e^{i\omega\left(T + \frac{\Delta t}{2}\right)} e^{-i\omega'\left(T - \frac{\Delta t}{2}\right)}$$

$$= \int_{-\infty}^{\infty} d\Delta t \; \mathcal{K}(\Delta t)\, e^{i\omega \Delta t} (2\pi)\, \delta(\omega - \omega')$$

$$= 2\pi\, \delta(\omega - \omega')\, \tilde{\mathcal{K}}(\omega)$$

Specifically for white-noise approximation of noise we have

$$\mathcal{K}(\Delta t) = 2 D_v M^2\, \delta(\Delta t)$$

$$\Rightarrow \tilde{\mathcal{K}}(\omega) = 2 D_v M^2 \quad \text{(independent of } \omega)$$

noise is spectrally white, i.e. all frequency components are equally represented

So we get for the auto-correlation function of the velocity (for stationary stochastic process)

$$\langle \tilde{V}(\omega)\, \tilde{V}^*(\omega') \rangle = \frac{1}{M^2} \frac{1}{\gamma^2+\omega^2} \tilde{\xi}(\omega)\, (2\pi)\, \delta(\omega-\omega')$$

Specifically for white noise

$$= \frac{2D_v}{\gamma^2+\omega^2} (2\pi)\, \delta(\omega-\omega')$$

⇒ while all frequencies are excited equally by the noise term the system responds differently to different frequency excitations

Can use this result to reconstruct auto-correlation function in time domain

<u>Inverse FT</u>

$$V(t) = \int_{-\infty}^{\infty} \frac{d\omega}{(2\pi)} \tilde{V}(\omega)\, e^{-i\omega t} = \int \frac{d\omega}{(2\pi)} \tilde{V}^*(\omega)\, e^{+i\omega t}$$

complex conjugation

$$\langle V(t)\, V(t+\Delta t) \rangle = \int_{-\infty}^{\infty} \frac{d\omega}{(2\pi)} \int_{-\infty}^{\infty} \frac{d\omega'}{(2\pi)} \langle V(\omega)\, V^*(\omega') \rangle e^{-i\omega t} e^{+i\omega'(t+\Delta t)}$$

stationary process

$$= \int_{-\infty} \frac{d\omega}{(2\pi)} \frac{\tilde{\xi}(\omega)}{M^2} \frac{1}{\gamma^2+\omega^2} e^{i\omega \Delta t}$$

Note that result holds more generally as it is basically a property of FT for stationary stochastic process

Namely

$$\langle \tilde{V}(\omega)\, \tilde{V}^*(\omega') \rangle = \underbrace{(2\pi)\,\delta(\omega-\omega')}_{\text{stationarity}} \; \underbrace{S_V(\omega)}_{\text{spectral density}}$$

$$\langle \tilde{F}_L(\omega)\, \tilde{F}_L^*(\omega') \rangle = (2\pi)\,\delta(\omega-\omega') \; S_{F_L}(\omega)$$

the EOM tells → relations between spectral densities

$$S_V(\omega) = \frac{1}{M^2} \frac{1}{|\gamma - i\omega|^2} S_{F_L}(\omega)$$

the non-trivial result here is that the auto-correlation function

$$\langle V(t)\, V(t+\Delta t) \rangle = \int_{-\infty}^{+\infty} \frac{d\omega}{(2\pi)} S_V(\omega)\, e^{i\omega\Delta t}$$

<u>Wiener Khinchin theorem</u>

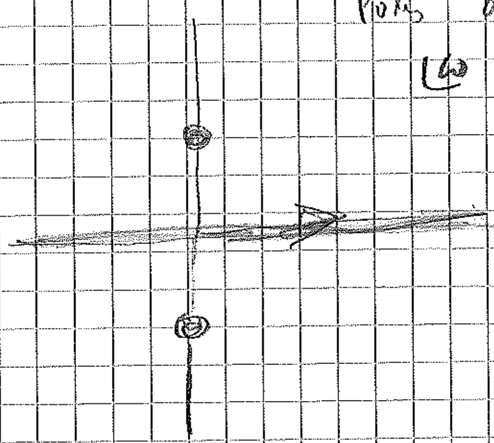
⇒ relation between auto correlation & spectral density for stationary stochastic process

$$S_V(\omega) = \int_{-\infty}^{\infty} d\Delta t \, \langle V(t)\, V(t+\Delta t) \rangle \, e^{-i\omega\Delta t}$$

So lets verify that we get the same for white noise

$$\langle v(t)\, v(t+\Delta t)\rangle = \int_{-\infty}^{\infty} \frac{d\omega}{(2\pi)} \frac{2D_v}{\gamma^2+\omega^2} e^{i\omega\Delta t}$$

Poles at $\omega = \pm i\gamma$



Can use contour integration technique

So for $\Delta t > 0$ can close contour

such that on A $\mathrm{Im}(\omega) > 0$

$\mathrm{Re}(i\omega\Delta t) < 0$

Contour A does not give contribution

$\Rightarrow$ integral is then given by the residue at the pole of integrand

$$\frac{1}{\gamma^2+\omega^2} = \frac{1}{(\omega-i\gamma)}\frac{1}{(\omega+i\gamma)}$$

So for $\Delta t > 0$ we pick up pole at $\omega = i\gamma$

we got for $\Delta t > 0$

$\underline{\Delta t > 0}$ $$\langle v(t)\, v(t+\Delta t)\rangle = (2\pi i) \frac{2D_v}{\omega + i\gamma} e^{i\omega\Delta t}\Big|_{\omega = i\gamma}$$

residue theorem

$$= \frac{D_v}{\gamma} e^{-\gamma\Delta t}$$

we need for $\Delta t < 0$ need to close contour in the other direction

$\underline{\Delta t < 0}$: $$\langle v(t)\, v(t+\Delta t)\rangle = -(2\pi i) \frac{2D_v}{\omega - i\gamma} e^{i\omega\Delta t}\Big|_{\omega = -i\gamma}$$

residue theorem with contour going in opposite way

$$= \frac{D_v}{\gamma} e^{+\gamma\Delta t}$$

So in summary

$$\langle v(t)\, v(t+\Delta t)\rangle = \frac{D_v}{\gamma} e^{-\gamma|\Delta t|}$$

which gives the long time limit of our previous result

Note that in order to perform full Fourier transform we had to send $t_0 \to -\infty$, .

In this limit the initial condition is in the remote past and the system is in equilibrium at any finite time

Beyond giving us a different way to calculate what we already know, spectral analysis is particularly useful in characterizing response to external perturbations

$$M \frac{dv(t)}{dt} = -M\gamma v(t) + F_L(t) + F_{ext}(t)$$

transforms into algebraic equation in frequency space

$$-i\omega M \tilde{v}(\omega) = -M\gamma \tilde{v}(\omega) + \tilde{F}_L(\omega) + \tilde{F}_{ext}(\omega)$$

so in particular $\langle \tilde{F}_L(\omega) \rangle = 0$

$$\langle \tilde{v}(\omega) \rangle = \underbrace{\frac{1}{M} \frac{1}{\gamma - i\omega}} \tilde{F}_{ext}(\omega)$$

So we obtain a linear response relation

$$\langle \tilde{v}(\omega) \rangle = Y(\omega) \tilde{F}_{ext}(\omega)$$

where $Y(\omega) = \frac{1}{M} \frac{1}{\gamma - i\omega}$ is a

complex response coefficient called the admittance

Now in principle the external force is not that different from the Langevin force, so information related to how system responds to external perturbations should already be contained in equilibrium correlation functions.

Namely if we ask how the velocity responds to fluctuating Langevin force:

$$\left\langle \tilde{V}(\omega) \tilde{F}_L^*(\omega') \right\rangle = \frac{1}{M} \frac{1}{\gamma - i\omega} \left\langle \tilde{F}_L(\omega) \tilde{F}_L^*(\omega') \right\rangle$$

$$= Y(\omega) \, (2\pi) \delta(\omega - \omega') \, S_{F_L}(\omega)$$

Since the physical effect of the Langevin force is to drive velocity fluctuations, it is therefore not surprising that the admittance can be inferred from equilibrium velocity correlation functions.

$$Y(\omega) = \frac{1}{k_B T} \int_0^\infty dt \left\langle v(t) v(t + \Delta t) \right\rangle e^{i\omega \Delta t}$$

How to do this?

Start from

$$\frac{dv}{dt}(t) = -\gamma\, v(t) + F_L(t)$$

and look at EOM for $v(t)\, v(t^*)$ with $t > t^*$

$$\frac{d}{dt} v(t)\, v(t_*) = -\gamma\, v(t)\, v(t_*) + F_L(t)\, v(t_*)$$

but now $\langle F_L(t)\, v(t_*)\rangle = 0$ for $t > t_*$

so

$$\frac{d}{dt}\langle v(t)\, v(t_*)\rangle = -\gamma \langle v(t)\, v(t_*)\rangle$$

Can then look at one sided Fourier transform

$$\int_{t^*}^{\infty} dt\; e^{i\omega(t-t^*)} \frac{d}{dt}\langle v(t)\, v(t_*)\rangle$$

integrate by parts

$$= -i\omega \int_{t^*} dt\, e^{i\omega(t-t^*)} \langle v(t)\, v(t_*)\rangle - \langle v(t_*)\, v(t_*)\rangle$$

on the RHS we have the same object

$$= -\gamma \int_{t^*}^{\infty} dt\; e^{i\omega(t-t^*)} \langle v(t)\, v(t^*)\rangle$$

Smith Mod

$$\int_{t^*}^{\infty} dt\; e^{i\omega(t-t^*)} \langle v(t) v(t^*) \rangle = \langle v(t_*) v(t_*) \rangle \frac{1}{\gamma - i\omega}$$

now

$$= \langle M v(t_*)^2 \rangle \frac{1}{M} \frac{1}{\gamma - i\omega}$$

$$= k_B T \quad Y(i\omega)$$