Smoluchowski Equation from Overdamped Langevin equation

Recall Langevin eqn in Force field:

$$m\ddot{x} = \underbrace{-m\zeta\dot{x}}_{\text{Friction}} + \underbrace{F(x)}_{\text{External force}} + \underbrace{f(t)}_{\text{stochastic force.}}$$

With strong damping $m\zeta\dot{x} \gg m\ddot{x}$, L. equation becomes,

$$0 = -m\zeta\dot{x} + F(x) + f(t)$$

$$\dot{x} = \frac{F(x)}{m\zeta} + \frac{f(t)}{m\zeta}$$

$$= -\frac{1}{m\zeta}\frac{\partial V}{\partial x} + \frac{f(t)}{m\zeta} \qquad \underline{\text{Solution}}: \Delta x(t) = \frac{1}{m\zeta}\int_0^t dt' \left(\frac{\partial V}{\partial x} + f(t)\right)$$

Given an initial coordinate distribution, $P(x, t_0)$, the distribution evolves through time due to Brownian motion:

$$\text{Define } P(x,t) = \langle \delta(x - \underbrace{x(t)}_{\substack{\text{Stochastic variable} \\ \text{(one function } x(t) \text{ for one} \\ \text{system in an ensemble) — a single realization.}}}) \rangle \qquad \text{(Ensemble average)}$$

Derive an equation of motion for $P(x,t)$. (How does P evolve?)

$$\frac{\partial}{\partial t}P(x,t) = \frac{\partial}{\partial t}\langle \delta(x - x(t))\rangle \qquad \text{use } \frac{\partial}{\partial t} = \frac{\partial x}{\partial t}\frac{\partial}{\partial x} = \frac{\partial x}{\partial t}\frac{-\partial}{\partial x}$$

$$= -\frac{\partial}{\partial x}\left\langle \delta(x - x(t))\frac{\partial x}{\partial t}\right\rangle \qquad \text{Langevin: } \frac{\partial x}{\partial t} = -\frac{1}{m\zeta}\frac{\partial V}{\partial x} + \frac{f(t)}{m\zeta}$$

$$= -\frac{\partial}{\partial x}\left\langle \delta(x - x(t))\left(\frac{-1}{m\zeta}\frac{\partial V}{\partial x} + \frac{f(t)}{m\zeta}\right)\right\rangle$$

$$= -\frac{\partial}{\partial x}\left\langle \delta(x - x(t))\frac{\partial V}{\partial x}\right\rangle \times \frac{-1}{m\zeta} - \frac{\partial}{\partial x}\left\langle \delta(x - x(t))\frac{f(t)}{m\zeta}\right\rangle$$

$$= \frac{1}{m\zeta}\frac{\partial}{\partial x}\left[\underbrace{\langle \delta(x - x(t))\rangle}_{P(x,t)}\frac{\partial V}{\partial x}\right] - \frac{1}{m\zeta}\frac{\partial}{\partial x}\underbrace{\langle \delta(x - x(t))\,f(t)\rangle}_{\text{simplify}}$$

Just like in deriving the Fokker-Planck Equation,

Use $P[f(t)] = e^{-\int_{t_i}^{t_f} dt\, \frac{1}{2} \frac{1}{2m\zeta k_B T} f^2(t)}$

Define: $Z[j(t)] = \int \mathcal{D}f(t)\, e^{-\int_{t_i}^{t_f} dt \left(\frac{1}{2} f(t) \frac{1}{2m\zeta k_B T} f(t) + j(t) f(t)\right)}$

$$= e^{-\int_{t_i}^{t_f} dt\, dt'\, \frac{1}{2} j(t)\, 2m\zeta k_B T\, \delta(t-t')\, j(t')}$$

So, we need

$$-\frac{1}{m\zeta} \langle \delta(x - x(t))\, f(t) \rangle = \frac{-1}{m\zeta} \int \mathcal{D}f(t')\, \delta(x - x(t))\, f(t)\, e^{-\int_{t_i}^{t_f} dt' \frac{1}{2} f(t') \frac{1}{2m\zeta k T} f(t')}$$

$$= \frac{+1}{\cancel{m\zeta}} (+\cancel{2m\zeta} kT) \int \mathcal{D}f(t')\, \delta(x - x(t)) \frac{\delta}{\delta f(t)} e^{-\int_{t_i}^{t_f} dt' \frac{1}{2} f(t') \frac{1}{2m\zeta k T} f(t')}$$

Now perform a functional integration by parts.

$$= -2k_B T \int \mathcal{D}f(t') \frac{\delta}{\delta f(t)} \delta(x - x(t))\, e^{-\int_{t_i}^{t_f} \cdots}$$

$$= -2k_B T \left\langle \frac{\delta}{\delta f(t)} \delta(x - x(t)) \right\rangle \qquad \frac{\delta}{\delta f(t)} = \frac{\delta x(t)}{\delta f(t)} \frac{\partial}{\partial x} = \frac{\delta x}{\delta f(t)} \frac{-\partial}{\partial x}$$

$$= +2k_B T \frac{\partial}{\partial x} \left\langle \frac{\delta x(t)}{\delta f(t)} \delta(x - x(t)) \right\rangle$$

$\uparrow$

Use solution

$$x(t) = \frac{1}{m\zeta} \int_0^t dt' \left(\frac{\partial V}{\partial x} + f(t')\right)$$

Then $\frac{\delta x(t)}{\delta f(t)} = \frac{1}{m\zeta} \int_0^t dt'\, \delta(t - t') = \frac{1}{2m\zeta}$ (half delta)

$$= \frac{2k_B T}{2m\zeta} \frac{\partial}{\partial x} \langle \delta(x - x(t)) \rangle = \frac{k_B T}{m\zeta} \frac{\partial P(x,t)}{\partial x}$$

So,

$$\boxed{\frac{\partial P(x,t)}{\partial t} = \frac{1}{m\zeta} \frac{\partial}{\partial x}\left[P(x,t) \frac{\partial V}{\partial x}\right] + \frac{k_B T}{m\zeta} \frac{\partial^2}{\partial x^2} P(x,t)}$$

Smoluchowski equation

The Smoluchowski equation can be cast as a continuity equation:

$$\frac{\partial P}{\partial t} + \frac{\partial}{\partial x} J(x,t) = 0,$$

where $J(x,t) = -\frac{1}{m\zeta}\Big(\underbrace{P(x,t)\frac{\partial V}{\partial x}}_{\substack{\text{drift term}\\ \text{-V-dependent}}} + \underbrace{k_B T \frac{\partial}{\partial x} P(x,t)}_{\substack{\text{diffusion term,}\\ \text{-temperature dep.}}}\Big)$

Solution $P(x,t) \propto e^{-V/k_BT}$ is a stationary solution.
In this case $J(x,t)=0$:

$$J = -\frac{1}{m\zeta}\left(e^{-V/k_BT}\frac{\partial V}{\partial x} + k_BT\frac{\partial}{\partial x}e^{-V/k_BT}\right)$$

$$= -\frac{1}{m\zeta}\left(e^{-V/k_BT}\frac{\partial V}{\partial x} + \frac{\cancel{k_BT}}{\cancel{k_BT}}\frac{-\partial V}{\partial x}e^{-V/k_BT}\right)$$

$$= \frac{-1}{m\zeta}(0) = 0 \quad ✓$$

Normalization:

$$\int P(x,t)\,dx = 1 \Rightarrow$$

$$P(x,t) = \frac{1}{\int dx\, e^{-V(x)/k_BT}} e^{-V(x)/k_BT}$$