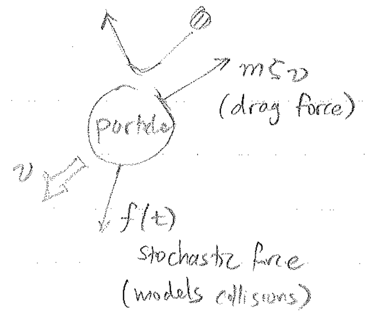
Langevin Equations

(The Free Langevin Equation) – Brownian Motion   — one dimension



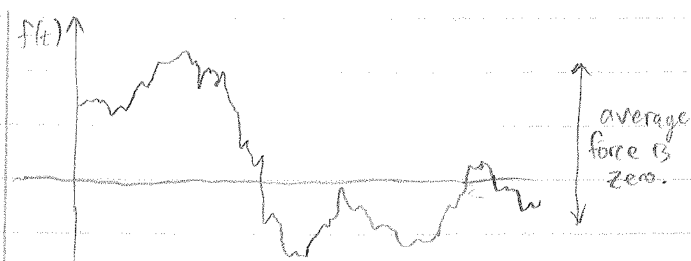
$$m\dot{v} = \underbrace{-m\overset{[\text{time}]^{-1}}{\zeta} v}_{\substack{\text{drag force} \\ \text{(Irreversibility)}}} + \underset{\text{stochastic}}{f(t)}$$

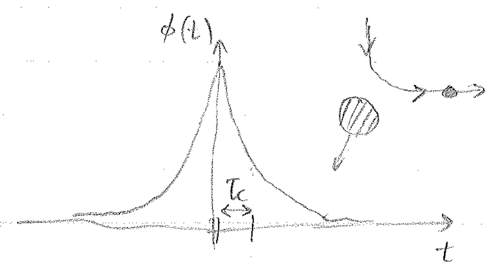
The precise form of $f(t)$ is not known – (see later for possible explicit form for $f(t)$)
But its average and auto-correlation are known:

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

def^{n}: of average $\langle \dots \rangle \hat{=} \underbrace{\lim_{T\to\infty} \frac{1}{T}\int_0^T dt\, f(t)}_{\text{Long time average}} = \underbrace{\frac{1}{\Omega(E)}\int d(PS)\, f(t)}_{\text{Ensemble Average}}$ (ergodic theorem)

$\langle f(t) f(t')\rangle = \phi(t-t')$





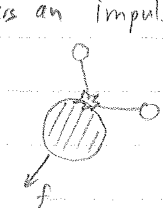
Force turns on somewhat before striking particle.
(think Scattering)

Since we are interested in the motion of the particle over times of order t, which are much longer than τ_c: $t \gg \tau_c$, ok to approximate
τ_c – collisional time.

$$\phi(\tau) = \lambda\, \delta(\tau)$$

$\delta(\tau)$: Instantaneous collisions, with a strength – delivers an impulse, like a Billiard's ball.

λ: whose mean-sq. dev. is $\lambda \doteq [\text{Force}^2][\text{time}]$



Now, since the particles that deliver the stochastic force, $f(t)$, to the Brownian particle are the very same particles that supply the drag force $\doteq -m\zeta v$, we should, at the very least, expect a relationship between λ and ζ.

λ: characterizes stochastic force

ζ: characterizes drag force $\doteq [\text{time}]^{-1}$

Solution to the Langevin equation

Define the retarded Green's function $G(t)$:

$$\left(\frac{d}{dt} + \zeta\right) G(t,t') = \delta(t-t') \Rightarrow G(t-t') = \overbrace{\underbrace{\theta(t-t')}_{\text{step function}} e^{-\zeta(t-t')}}^{\text{solution}}$$

Proof:

$$\left(\frac{d}{dt} + \zeta\right) \theta(t-t') e^{-\zeta(t-t')}$$

$$= \left(\underbrace{\delta(t-t')}_{\text{use this to set } t=t'.} e^{-\zeta(t-t')} \cancel{- \theta(t-t')\zeta e^{-\zeta(t-t')}}\right) \cancel{+ \zeta\theta(t-t')e^{-\zeta(t-t')}}$$

$$= \delta(t-t') \checkmark$$

So, bring $-m\zeta v$ term over to other side:

$$\left(m\frac{d}{dt} + m\zeta\right) v = f(t) \Rightarrow \boxed{\left(\frac{d}{dt} + \zeta\right) v = \frac{1}{m} f(t)}$$

Initial condition $v(t=0) = v_0$: So the solution is:

$$v(t) = v_0 e^{-\zeta t} + \int dt' \frac{1}{m} f(t') \underbrace{\theta(t-t') e^{-\zeta(t-t')}}_{G(t-t')}$$

$$\boxed{= v_0 e^{-\zeta t} + e^{-\zeta t} \int_t^{\infty} dt' e^{\zeta t'} \frac{f(t')}{m}}$$

Since we don't know the precise form of $f(t)$, (only its statistics), let us evaluate $\langle v^2 \rangle$:

$$\langle v(t)^2 \rangle = \langle (v_0 e^{-\zeta t})^2 \rangle + \left\langle e^{-2\zeta t} \int_0^t dt' \int_0^t dt'' e^{\zeta(t'+t'')} \frac{f(t') f(t'')}{m^2} \right\rangle$$

$$+ 2 \left\langle v_0 e^{-2\zeta t} \int_0^t dt' e^{\zeta t'} \frac{f(t')}{m} \right\rangle \leftarrow \text{vanishes because } \langle f(t') \rangle = 0.$$

$$= v_0^2 e^{-2\zeta t} + e^{-2\zeta t} \int_0^t dt' \int_0^t dt'' e^{\zeta(t'+t'')} \frac{\phi(t'-t'')}{m^2}$$

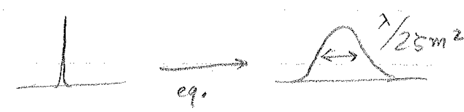
$$= v_0^2 e^{-2\zeta t} + e^{-2\zeta t} \int_0^t dt' \int_0^t dt'' e^{\zeta(t'+t'')} \frac{\lambda}{m^2} \delta(t'-t'')$$

Integrate over t'', fixing $t'' \to t'$

$$= v_0^2 e^{-2\zeta t} + e^{-2\zeta t} \int_0^t dt' e^{2\zeta t'} \frac{\lambda}{m^2}$$

$$= v_0^2 e^{-2\zeta t} + \frac{\lambda}{m^2} e^{-2\zeta t} \frac{1}{2\zeta} (e^{2\zeta t} - 1)$$

$$= v_0^2 e^{-2\zeta t} + \frac{\lambda}{2\zeta m^2} (1 - e^{-2\zeta t})$$



Now in the limit of large times (to equilibrium) $t \gg \zeta^{-1}$

$$\langle v^2 \rangle \longrightarrow \frac{\lambda}{2\zeta m^2}$$ (memory of initial value, v_0, lost).

We require that particles attain thermal equilibrium after long times, that is the average value of the kinetic energy obey the equipartition theorem,

$$\frac{1}{2} m \langle v(t)^2 \rangle = \frac{1}{2} k_B T$$

$$\Rightarrow \frac{1}{2} m \left(\frac{\lambda}{2\zeta m^2} \right) = \frac{1}{2} k_B T$$

or $\lambda = 2\zeta m k_B T$ coefficient of friction $\propto$ mean sq. dev of stochastic force.

Einstein Relation

The Langevin Equation in a Force Field
(Brownian motion in a force field)

External force field: $F(x) = -\frac{\partial V}{\partial x}$

Langevin eqn: $m\ddot{x} = \underbrace{-m\zeta\dot{x}}_{\substack{\text{Friction} \\ \text{(T-irreversibility)}}} + \underbrace{F(x)}_{\substack{\text{External} \\ \text{force}}} + \underbrace{f(t)}_{\substack{\text{Stochastic} \\ \text{force}}}$

Assumption made: collisions & frictional force remain unaffected by presence of external force.

Recall, stochastic force obeys:

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

$\langle f(t) f(t') \rangle = \phi(t-t') \approx \lambda \delta(t-t')$

Still, the Einstein relation holds: $\lambda = 2\zeta m k_B T$

Special case: strong damping $m\zeta\dot{x} \gg m\ddot{x}$

(for example periodic motion at low freq.)

Then Langevin equation becomes:

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

solve for $\dot{x}$

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

$$= -\frac{1}{m\zeta}\frac{\partial V}{\partial x} + \frac{f(t)}{m\zeta}$$ (Overdamped Langevin Equation)

Define normalized stochastic force: $\frac{f(t)}{m\zeta} = r(t)$ UNNECESSARY

Recall how we characterized $f(t)$:

$\langle r(t) \rangle = 0$ $\boxed{\text{Need to convert back to } f}$

$$\langle r(t) r(t') \rangle = \left(\frac{1}{m\zeta}\right)^2 \langle f(t) f(t') \rangle = \left(\frac{1}{m\zeta}\right)^2 \lambda \delta(t-t')$$

$$= \left(\frac{1}{m\zeta}\right)^{\cancel{2}} 2\cancel{\zeta m} k_B T \, \delta(t-t')$$

$$= \frac{2k_BT}{m\zeta} \delta(t-t')$$

aside:

To characterize higher moments, eg. $\langle r(t)\, r(t')\, r(t'') \rangle$, it is useful to write down a form for the probability distribution of $r(t)$.

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

(normalization moved into integration measure)

Given a functional form for $r(t)$

you get a number representing the probability density for $r(t)$.

Obviously, we must have $\int \mathcal{D}r(t)\; P[r(t)] = 1$

$$\int \mathcal{D}r(t) = \sqrt{\frac{m\zeta\epsilon}{4k_BT\pi}}\, dr(t_i) \sqrt{\frac{m\zeta\epsilon}{4k_BT\pi}}\, dr(t_i+\epsilon) \ldots \sqrt{\frac{m\zeta\epsilon}{4k_BT\pi}}\, dr(t_f)$$

lim $\epsilon \to 0$ implicit.

To extract higher moments, write as a generating functional:

$$Z[j(t)] \equiv \int \mathcal{D}r(t)\; e^{-\int_{t_i}^{t_f} dt \left(\frac{1}{2} \frac{m\zeta}{2k_BT} r^2(t) + j(t) r(t) \right)}$$

$$= \left(\frac{m\zeta\epsilon}{4k_BT\pi} \right)^{N/2} (2\pi)^N \left(\frac{1}{\mathrm{Det}\left[\frac{m\zeta}{2k_BT}\right]} \right)^{1/2} e^{-\int_{t_i}^{t_f} dt\, j(t) \frac{2k_BT}{m\zeta} j(t)}$$

$$= \cancel{\left(\frac{m\zeta\epsilon}{4k_BT\pi} \right)^{N/2} \left(\frac{2\pi}{\frac{m\zeta\epsilon}{2k_BT}} \right)^{N/2}} e^{-\int_{t_i}^{t_f} dt\, j(t) \frac{2k_BT}{m\zeta} j(t)}$$

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

So, $$\langle r(t_1) r(t_2) \rangle = \frac{\delta}{\delta(-j(t_1))} \frac{\delta}{\delta(-j(t_2))} Z[j(t)] \Big|_{j=0}$$

$$= \frac{2k_BT}{m\zeta} \delta(t_1 - t_2) \quad \checkmark$$