$$\dot{p} = -\gamma p - \frac{\partial \tilde{V}}{\partial x} + \xi$$

DRIFT

(i)

$$\langle \xi \xi \rangle = \frac{2M}{\beta} \gamma \delta(t-t')$$

$$\dot{p} = -\gamma p + F + \xi$$ Ornstein-Uhlenbeck with forcing term

$$p(t) = e^{-\gamma t} p(0) + \int_0^t dt' e^{-\gamma(t-t')} [\xi(t') + F]$$

$$\langle p(t) \rangle = e^{-\gamma t} \langle p(0) \rangle + F e^{-\gamma t} \frac{e^{\gamma t} - 1}{\gamma}$$

average over particles' initial condition can be ommitted

$$\langle p(t) \rangle \longrightarrow \frac{F}{\gamma}$$ Aristotele's law $\langle p \rangle \propto F$!

$F = eE$ along a given direction say x

$$M \langle v \rangle = \frac{eE}{\gamma}$$

for N particle the number current

$$J_x = n \langle v \rangle \qquad n = \frac{N}{V}$$ ← volume

the electrical current

$$J_x = e n \langle v \rangle$$

scattering time

$$J_x = e n \frac{eE}{M\gamma} = n \frac{e^2 \tau}{M} E \qquad \tau = \frac{1}{\gamma}$$ damping rate

Drude

see below

$\mu \Rightarrow \langle v \rangle = \mu E$ $\boxed{\mu = \frac{e}{M\gamma}}$

DIFFUSION

"free" particle: a particle under the sole action of the bath $F=0$

$$p(t) = e^{-\gamma t} p(0) + \int_0^t dt'\, e^{-\gamma(t-t')}\, \xi(t')$$

average over particle's initial conditions ~~can be omitted~~

$$\langle p(t)\rangle = e^{-\gamma}\langle p(0)\rangle \longrightarrow 0$$

what's about $\langle p^2(t)\rangle$?

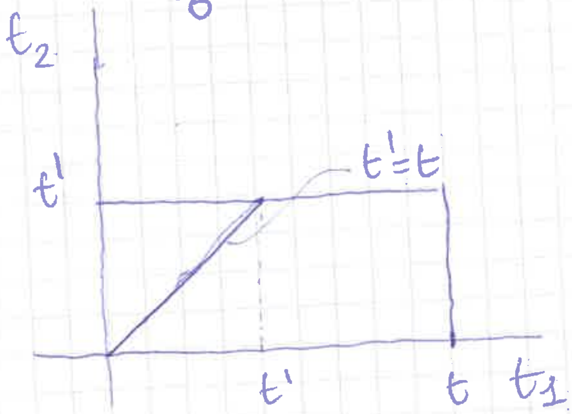
let us evaluate the correlation function

$$\langle p(t)\, p(t')\rangle = e^{-\gamma(t+t')}\langle p^2(0)\rangle +$$

$$+ \underbrace{\int_0^t dt_1 \int_0^{t'} dt_2\, e^{-\gamma(t+t'-t_1-t_2)} \underbrace{\langle \xi(t_1)\, \xi(t_2)\rangle}_{\frac{2M\gamma}{\beta}\delta(t_1-t_2)}}_{\int_0^{\mathrm{Min}(t,t')} dt_1^*\, e^{-\gamma(t+t'-2t_1)} \frac{2M\gamma}{\beta}}$$

~~assume~~ $t > t'$

$$\int_0^{\mathrm{Min}(t,t')} dt_1^*\, e^{-\gamma(t+t'-2t_1)}\, \frac{2M\gamma}{\beta}$$



$t > t'$

3

$$\langle p(t)p(t')\rangle = e^{-\gamma(t+t')}\langle p^2(0)\rangle +$$

$$+ \frac{\cancel{2}M\cancel{\gamma}}{\beta} e^{-\gamma(t+t')} \frac{e^{2\gamma \min(t,t')} - 1}{\cancel{2\gamma}}$$

$t > t'$

$$\langle p(t)p(0)\rangle = e^{-\gamma(t+t')}\langle p^2(0)\rangle +$$

$$+ \frac{M}{\beta}\left(\underline{e^{-\gamma(t-t')} - e^{-\gamma(t+t')}}\right)$$

now lets $t \to \infty$, $t' \to \infty$ $t - t' = \text{const}$

$$\boxed{\langle p(t)\, p(t')\rangle \simeq \frac{M}{\beta} e^{-\gamma(t-t')} \qquad t > t'}$$

fading of velocity correlation

$$\langle p^2(t)\rangle = \cancel{e^{-2\gamma t}\langle p^2(0)\rangle} + \frac{M}{\beta}(1 - \cancel{e^{-2\gamma t}}) = M k_B T$$

$$\frac{\langle p^2(t)\rangle}{2M} = \frac{1}{2} k_B T$$ equilibrium

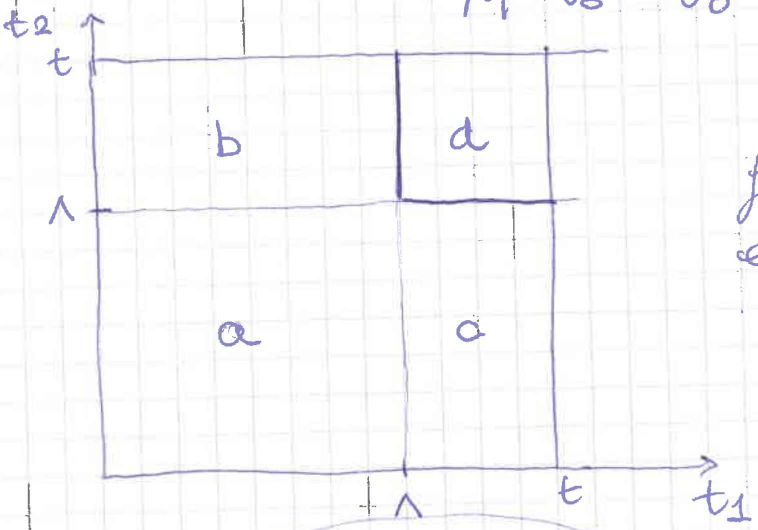
particle diffusion

MSD of a particle

$\langle |X(t)-X(0)|^2 \rangle$

$$X(t) = X(0) + \frac{1}{M}\int_0^t dt'\, p(t')$$

$$\langle |X(t)-X(0)|^2 \rangle = \frac{1}{M^2}\int_0^t dt_1 \int_0^t dt_2 \underbrace{\langle p(t_1)p(t_2)\rangle}_{C}$$



for $t \gtrsim \Lambda$ asymptotic expression of $\langle p(t)p(t')\rangle$ holds

$$MSD = \underbrace{\frac{1}{M^2}\int_0^\Lambda dt_1 \int_0^\Lambda dt_2\, C(t_1,t_2)}_{(a)} +$$

constant

$$\cancel{\frac{1}{M^2}\int_\Lambda^t dt_1 \int_0^\Lambda dt_2\, C(t_1,t_2)} \quad (c)$$

$t_1 \gg t_2$ $C \to 0$ expon

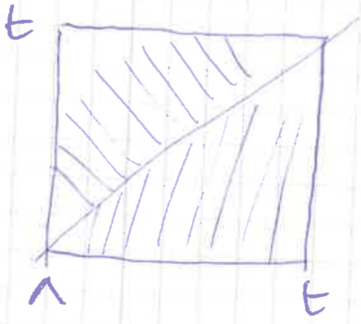
$$\cancel{\frac{1}{M^2}\int_0^\Lambda dt_1 \int_\Lambda^t dt_2\, C(t_1,t_2)} \quad (b)$$

$t_2 \gg t_1$ $C \to 0$ expon

$$\frac{1}{M^2}\int_\Lambda^t dt_1 \int_\Lambda^t dt_2 \underbrace{C(t_1,t_2)}_{\text{asympt}}$$

$$\int_\Lambda^{t} dt_1 \int_\Lambda^{t} dt_2 \, \frac{M}{\beta} e^{-\gamma|t_1-t_2|} =$$

$$= 2\int_\Lambda^{t} dt_1 \int_\Lambda^{t_1} dt_2 \, \frac{M}{\beta} e^{-\gamma(t_1-t_2)} =$$



$$\int_\square = 2\int_\Delta$$

$$= 2\int_\Lambda^{t} dt_1 \, e^{-\gamma t_1} \frac{M}{\beta} \frac{1}{\gamma}\left(e^{\gamma t_1} - e^{\gamma\Lambda}\right) =$$

$$= 2\int_\Lambda^{t} dt_1 \, \frac{M}{\beta\gamma} + \dots$$

$$= \frac{2M}{\beta\gamma}(t-\Lambda)$$

increase with time

$$\boxed{\langle |X(t)-X(0)|^2 \rangle \longrightarrow \frac{2}{\beta M \gamma} t}$$

$$\sqrt{\langle |X(t)-X(0)|^2} \propto \sqrt{t}$$

definition

$$\lim_{t\to\infty} \langle |X(t)-X(0)|^2 \rangle = 2dDt \Rightarrow \boxed{D = \frac{k_B T}{M\gamma}}$$

Dimension $d=1$

Relation Drift - Diffusion

(6)

$$\mu = \frac{e}{M\gamma}$$

in the presence of external electric field

$$D = \frac{K_B T}{M\gamma}$$

in absence of external field

$$\mu = \frac{e D}{K_B T}$$

Einstein's relation

Drude AC conductivity

$$\langle p(t)\rangle = e^{-\gamma t}\langle p(0)\rangle + \int_0^t dt'\, e^{-\gamma(t-t')}\, e E(t')$$

$$E(t) = E_0 \cos\omega t$$

$$\int_0^t dt'\, e^{-\gamma(t-t')} e^{\pm i\omega t'} = e^{-\gamma t}\int_0^t dt'\, e^{(\gamma \pm i\omega)t'} = e^{-\gamma t}\,\frac{e^{(\gamma(\pm i\omega)t} - 1}{\gamma \pm i\omega}$$

$$\langle p(t)\rangle = e^{-\gamma t}\langle p(0)\rangle + \frac{eE_0}{2}\left(\frac{e^{i\omega t} - e^{-\gamma t}}{\gamma + i\omega} + \frac{e^{-i\omega t} - e^{-\gamma t}}{\gamma - i\omega}\right)$$

$t \to \infty$

$$\langle p(t)\rangle \simeq \frac{eE_0}{2}\;\frac{e^{i\omega t}(\gamma - i\omega) + e^{-i\omega t}(\gamma + i\omega)}{\gamma^2 + \omega^2}$$

$$= eE_0 \frac{\gamma}{\gamma^2+\omega^2}\cos\omega t$$

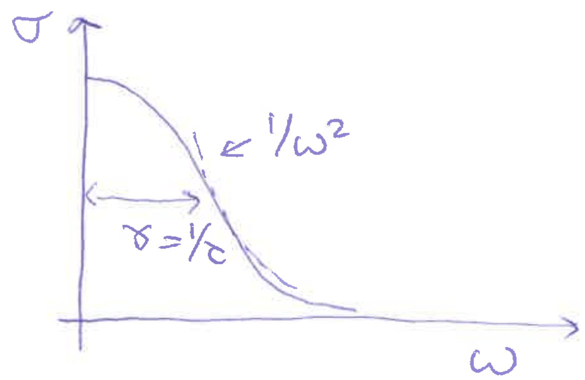
$$\langle J\rangle = ne\frac{\langle p(t)\rangle}{M} = \frac{ne^2}{M}\,\frac{\gamma}{\gamma^2+\omega^2}\,E(t)$$

$$\sigma(\omega) = \sigma(0)\,\frac{\gamma^2}{\gamma^2+\omega^2}$$

Drude Peak

Drude AC response

$$\sigma(0) = \frac{ne^2}{M\gamma} = \frac{ne^2\tau}{M}$$ Drude DC conductivity



Overdamped limit & Brownian Motion

The diffusive behaviour obtained at large times from the Langevin equation in absence of external drift

$$\langle |X(t)-X(0)|^2\rangle \longrightarrow 2Dt \qquad (t\to\infty)$$

$$D=\frac{k_BT}{M\gamma}$$

is usually associated to Brownian motion. However the Ornstein-Uhlenbeck process which describes the evolution of momenta

$$\dot{p}=-\gamma p+\xi(t)$$

does not give Brownian motion at all times.

The overdamped limit of the Langevin eq. does

$$p(t)=e^{-\gamma t}p(0)+\int_0^t dt'\,\frac{1}{\gamma}\underbrace{\boxed{\gamma e^{-\gamma(t-t')}}}_{\gamma\to\infty\ \delta(t-t')}\xi(t') \simeq \xi(t)/\gamma$$

$$\dot{X}=\frac{1}{M\gamma}\xi(t) = \frac{1}{M\gamma}\sqrt{\frac{2M\gamma}{\beta}}\,\eta(t) \qquad \langle\eta(t)\rangle=0 \quad \langle\eta(t)\eta(t')\rangle=\delta(t-t')$$

the solution is the Wiener process

$$X(t)=X(0)+\sqrt{\epsilon}\int_0^t dt'\,\eta(t') \qquad \epsilon=\sqrt{\frac{2k_BT}{M\gamma}}$$

therefore

$$\langle |X(t)-X(0)|^2\rangle = \epsilon\int_0^t dt'\int_0^t dt''\,\langle\eta(t')\eta(t'')\rangle = \overbrace{\epsilon t}^{\text{diffusive}} = \frac{2k_BT}{M\gamma}t$$

$$\boxed{D=\frac{k_BT}{M\gamma}}$$ diffusion constant

General form of Langevin equation

deterministic DRIFT term

$$\dot{x} = + \overbrace{F(x(t))} + \underbrace{\sqrt{\varepsilon}\,\eta(t)}$$

stochastic term

$$\langle \eta(t)\,\eta(t') \rangle = \delta(t-t')$$ dimensions of $\eta = \frac{1}{\text{time}}$

ε is the variance of the noise

— e.g. the momentum equation in absence of force —

$$\dot{p} = -\gamma p + \xi(t)$$

drift

noise $\longrightarrow \sqrt{\frac{2M\gamma}{\beta}}\,\eta(t)$

— the position equation in the overdamped limit —

$\gamma \gg \gamma_{pot}$ $\quad \gamma t \gg 1$

$$\cancel{M\ddot{x}} = -M\gamma\dot{x} - \frac{\partial \tilde{V}}{\partial x} + \xi$$

$\sqrt{\frac{2M\gamma}{\beta}}\,\eta(t)$

$$\dot{x} = -\frac{1}{M\gamma}\frac{\partial \tilde{V}}{\partial x} + \sqrt{\frac{2}{\beta M\gamma}}\,\eta(t)$$

in absence of potential it can be integrated to give

$$x(t) - x(0) = \sqrt{\frac{2}{\beta M\gamma}} \int_0^t dt'\,\eta(t')$$

$$\langle |x(t)-x(0)|^2 \rangle = \frac{2}{\beta M\gamma} \int_0^t dt' \int_0^t dt'' \underbrace{\langle \eta(t)\,\eta(t') \rangle}_{\delta(t-t')} = \frac{2}{\beta M\gamma}\,t$$

the long-time limit of the MSD $\quad D = \frac{k_B T}{M\gamma}$

Discretization of Langevin eq.
(how to simulate it ...)

$$\dot{x}(t) = F(x) + \sqrt{\epsilon}\,\eta(t)$$

$$\langle \eta(t)\eta(t') \rangle = \delta(t-t')$$

infinite variance

$$x(t_{k+1}) - x(t_k) = \int_{t_k}^{t_k+\Delta t} dt'\, F(x(t')) + \sqrt{\epsilon}\underbrace{\int_{t_k}^{t_k+\Delta t} dt'\,\eta(t')}_{\Delta W(t_k)}$$

$$\langle \Delta W(t_k)\Delta W(t_e) \rangle = \int_{t_k}^{t_k+\Delta t} dt_1 \int_{t_e}^{t_e+\Delta t} dt_2\, \langle \eta(t_1)\eta(t_2) \rangle =$$

$$= \delta_{ke}\,\Delta t$$

$$\langle \Delta W(t_k) \rangle = 0$$

$\Delta W(t_k)$ gaussian number of variance Δt

$$x(t_{k+1}) - x(t_k) = F(x(t_k))\Delta t + \sqrt{\epsilon}\sqrt{\Delta t}\, g_k$$ (ITÔ sense)

gaussian of variance 1

this is Euler's method

In W. Rümelin SIAM J. Numer. Anal. 19, 604 (1982)
has been demonstrated that for a 1-d process
the step error cannot be smaller than $O(\Delta t^3)$
for an n dimensional case the highest precision is
that of a simple Euler's method

The Fokker-Planck equation

given Langevin eq

$$\dot{x} = F(x) + \sqrt{\varepsilon}\,\eta(t)$$

the distribution of x $P(x,t)$ satisfies

$$\frac{\partial P}{\partial t} = \underbrace{-\frac{\partial}{\partial x}(FP)}_{\text{DRIFT}} + \underbrace{\frac{\varepsilon}{2}\frac{\partial^2 P}{\partial x^2}}_{\text{DIFFUSION}}$$

for a particle in a potential

a) $P(p, t\to\infty) \propto e^{-\beta \frac{p^2}{2M}}$

b) $P(x, t\to\infty) \propto e^{-\beta \tilde{V}(x)}$

$\beta = \frac{1}{K_B T}$ Bath Temp.

To proof let's start with the fundamental probability formula

$$P(x) = \int dy\, P_c(x|y)\, P(y)$$

prob of x

CONDITIONAL probability of X GIVEN y

prob of y

let $x = X(t+\Delta t)$

$y = X(t)$

What is the conditional probability of $X(t+\Delta t)$ given $X(t)$?

We can write

$$P_c(\overbrace{X(t+\Delta t)}^{x}|\overbrace{X(t)}^{y}) = \langle \delta(\underbrace{X(t+\Delta t)-X(t)-F(X(t))\Delta t-\sqrt{\varepsilon}\Delta W(t)}_{\text{Constraint}})\rangle$$

Euler's scheme

$$X(t+\Delta t)-X(t) = F(X(t))\Delta t+\sqrt{\varepsilon}\Delta W(t)$$

$\langle(\ldots)\rangle$ = average over the random variables ΔW which are gaussian zero mean and variance Δt

$$P_c(x|y) = \int_{-\infty}^{+\infty} \frac{d\Delta W}{\sqrt{2\pi\Delta t}} e^{-\frac{(\Delta W)^2}{2\Delta t}} \delta(x-y-F(y)\Delta t-\sqrt{\varepsilon}\Delta W)$$

$$= \frac{1}{\sqrt{2\pi\varepsilon\Delta t}} e^{-\frac{1}{2\varepsilon\Delta t}[x-y-F(y)\Delta t]^2}$$

$$z = \frac{x-y}{\sqrt{\varepsilon\Delta t}} \qquad y = x-\sqrt{\varepsilon\Delta t}\,z$$

$$P(x,t+\Delta t) = \int_{-\infty}^{+\infty} \frac{dz}{\sqrt{2\pi}} e^{-\frac{1}{2}\left[z-\frac{F(x-\sqrt{\varepsilon\Delta t}z)}{\sqrt{\varepsilon}}\sqrt{\Delta t}\right]^2} P(x-\sqrt{\varepsilon\Delta t}\,z)$$

Carefully develop the exponential and the P in Δt to get a differential equation for P

$$P(x,t+\Delta t)=\int_{-\infty}^{+\infty}\frac{dz}{\sqrt{2\pi}}e^{-z^2/2}\left[P(x,t)+U(z)\sqrt{\Delta t}+W(z)\Delta t\right]$$

13

$$\boxed{U(z)=-z\frac{\partial P}{\partial x}\sqrt{\epsilon}+z\frac{F(x)}{\sqrt{\epsilon}}P}$$

$$\boxed{W(z)=-z^2F\frac{\partial P}{\partial x}+\left(\frac{z^2}{2\varepsilon}F^2-\frac{F^2}{2\varepsilon}-z^2\frac{\partial F}{\partial x}\right)P+\frac{1}{2}\varepsilon\frac{\partial^2 P}{\partial x^2}z^2}$$

- the term in U is linear in z and vanishes once integrated
- the term in W contains only z^2 terms that gives 1 after average

$$P(x,t+\Delta t)=P(x,t)+\Delta t\int_{-\infty}^{+\infty}\frac{dz}{\sqrt{2\pi}}e^{-z^2/2}W(z)=$$

$$=P(x,t)+$$

$$+\Delta t\left[-F\frac{\partial P}{\partial x}+\left(\cancel{\frac{F^2}{2\varepsilon}}-\cancel{\frac{F^2}{2\varepsilon}}-\frac{\partial F}{\partial x}\right)P+\frac{1}{2}\varepsilon\frac{\partial^2 P}{\partial x^2}\right]$$

$$-\frac{\partial}{\partial x}(FP)$$

$$\boxed{\frac{\partial P}{\partial t}=-\frac{\partial}{\partial x}(FP)+\frac{\varepsilon}{2}\frac{\partial^2}{\partial x^2}P}$$

Fokker-Planck equation for additive state independent noise → Gardiner

Equilibrium distribution of the ~~velocity~~ position from F-P equation

(13)

overdamped equation for the position
(Meets diffusion at long times)

$$\dot{x} = -\frac{1}{M\gamma}\frac{\partial \tilde{V}}{\partial x} + \sqrt{\frac{2}{\beta M\gamma}}\,\eta(t)$$

$$\langle \eta(t)\,\eta(t')\rangle = \delta(t-t') \qquad \varepsilon = \frac{2}{\beta M\gamma}$$

Stationary solution of F-P Eq

$$\cancel{\frac{\partial P}{\partial t}} = -\frac{\partial}{\partial x}(FP) + \frac{\varepsilon}{2}\frac{\partial^2 P}{\partial x^2}$$

$$F = -\frac{\partial V}{\partial x}$$

$$-\frac{\partial}{\partial x}(FP) = \frac{\partial}{\partial x}\left(\frac{\partial V}{\partial x}P\right) = V''P + V'P'$$

$$V''P + V'P' + \frac{\varepsilon}{2}P'' = 0$$

$$P(x) = f(V(x))$$

$$P' = \frac{\partial f}{\partial V}V'$$

$$P'' = \frac{\partial^2 f}{\partial V^2}(V')^2 + \frac{\partial f}{\partial V}V''$$

$$\frac{\varepsilon}{2}\left(\frac{\partial^2 f}{\partial V^2}(V')^2 + \frac{\partial f}{\partial V}V''\right) + (V')^2\frac{\partial f}{\partial V} + V''f = 0$$

- $\frac{\varepsilon}{2}\frac{\partial^2 f}{\partial V^2} = -\frac{\partial f}{\partial V}$
- $\frac{\varepsilon}{2}\frac{\partial f}{\partial V} = -f$ not independent

$$\boxed{f(V) = e^{-\frac{2}{\varepsilon}V}\mathcal{N}}$$

stationary solution of FP Equation

normalisation constant

$V = \frac{\tilde{V}}{M\gamma}$ $\varepsilon = \frac{2}{\beta M\gamma}$

$\frac{2}{\varepsilon}V = \beta \cancel{M\gamma}\frac{\tilde{V}}{\cancel{M\gamma}}$ $P(x, t\to\infty) \propto e^{-\beta\tilde{V}(x)}$

Stationary distribution of the velocities

$$\dot{p} = -\gamma p + \sqrt{\frac{2M}{\beta}}\gamma\,\eta(t)$$

$$\varepsilon = \frac{2M}{\beta}\gamma$$

$$F(p) = -\gamma p$$

$$V(p) = \frac{\gamma p^2}{2}$$

$\frac{2}{\varepsilon}$ V

$$P(p) \propto e^{-\frac{2\beta}{2M\gamma}\frac{\gamma}{2}p^2} = e^{-\beta\frac{p^2}{2M}}$$

Maxwell's distribution