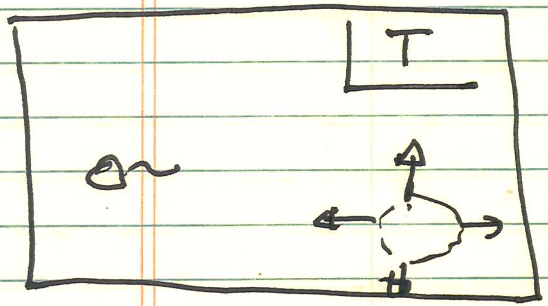
Lecture VI : Kinetics – A Crash Course II

This continues basic kinetics.

2.) Diffusion, Transport

Returning to Brownian Motion, in addition to FDT, can ask:



i.) how does pdf for ensemble of Brownian particles evolve?

i.e. $f(v, t)$

ii.) If [redacted] initialize cloud of particles, how does it spread out, evolve in time?

$$n(t=0) = n_0 \delta(\underline{r}-\underline{r}_0)$$

$n(\underline{r}, t)$?

both

⇒ Diffusion – random walk
– evolution mean square

i.e. $\langle \delta V^2 \rangle = D_V t$

else ?

$\langle \delta x^2 \rangle = D t$

⇒ Basic aspects of Fokker-Planck Theory.

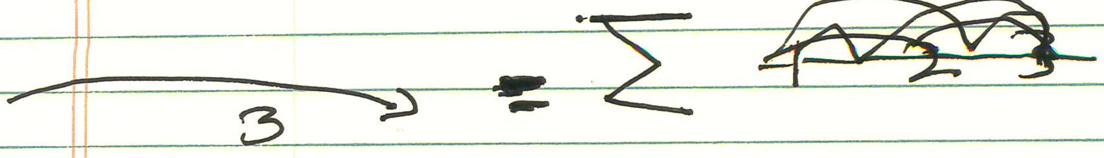
⇒ Motivated by random walk, no memory

→ Fokker-Planck Theory
- { An Introduction
  To be continued later

Consider system with no memory ↔ each step in T independent prior history

so

$$\underbrace{P(x_3,t_3 \mid x_1,t_1)}_{\text{Prob. of } x_3 \text{ at } t_3 \text{ starting from } x_1 \text{ at } t_1} = \underbrace{\int dx_2}_{\text{integrate over intermediate}} \underbrace{P(x_3,t_3 \mid x_2,t_2)}_{2\to 3 \text{ jump}} \underbrace{P(x_2,t_2 \mid x_1,t_1)}_{1\to 2 \text{ jump}}$$



→ multiplicative, as independent steps

→ sum over intermediate steps

⇒ Chapman – Kolmogorov Equation

Now, re-write as:

↳ transition probability at x, Δx in τ

$$P(x_2, t_2 | x_1, t_1) = T(x, \Delta x, \tau)$$

$t_2 - t_1$ is jump time τ

$x_2 - x_1$ is jump step Δx

$$P(x, t+\tau) = \int d(\Delta x)\, P(x - \underset{\text{small increment.}}{\underbrace{\Delta x}}, t)\, T(x, \Delta x, \tau)$$

and expand.

$$\frac{\partial P}{\partial t} = -\frac{\partial}{\partial x}\left\{ \frac{\langle \Delta x \rangle}{\tau} P - \frac{\partial}{\partial x} \frac{\langle \Delta x \Delta x \rangle}{2\tau} \cdot P \right\}.$$

→ "coarse grains" on $t < \tau$, $x < \Delta \cancel{x}$.

Buried bodies:

① → no long time/range correlations

② → $\langle \Delta x^2 \rangle = \int d\Delta x \, (\Delta x)^2 T$

exists ?!

i.e. only need T normalizable.

i.e. T → Gaussian, ~~[illegible]~~ exponential, ok ✓

→ Power law ? (self-similar)

$$T \sim 1/1+(\Delta x)^{\alpha}$$

$$(\alpha > 3)$$

③ → T non uniform.

②, ③ → $\left\{ \begin{array}{l} \text{fractional function} \\ \text{CTRW.} \end{array} \right.$

For Brownian Motion:

$$m \frac{dv}{dt} = -@v + \tilde{f}$$

$$\langle \tilde{f}(t)\, \tilde{f}(t') \rangle = |\tilde{f}|^2 \tau_{ac}\, \delta(t'-t)$$

so, for pdf ρ!

$$\rho(\underline{v}, t+\Delta t) = \int d(\Delta \underline{v})\, \underbrace{\rho(\underline{v}-\Delta\underline{v}, t)}_{\text{state at } t}\, \underbrace{T(\Delta\underline{v}, \Delta t)}_{\text{transition probability}}$$

expand!

$$\rho(\underline{v},t) + \Delta t \frac{\partial \rho}{\partial t} = \int d(\Delta\underline{v}) \Big\{ \rho(\underline{v},t)\, \underbrace{T(\Delta\underline{v}, \Delta t)}_{T \text{ normalizable}}$$

$$- \frac{\partial}{\partial \underline{v}} \cdot \left(\Delta\underline{v}\, T(\Delta\underline{v}, \Delta t)\, \rho(\underline{v},t) \right)$$

$$+ \frac{1}{2} \frac{\partial^2}{\partial \underline{v}^2} \left(\Delta\underline{v}\, \Delta\underline{v}\, T(\Delta\underline{v}, \Delta t)\, \rho(\underline{v},t) \right) \Big\}$$

$$\int d(\Delta\underline{v})\, T(\Delta\underline{v}, \Delta t) = 1$$

$$\int d(\Delta\underline{v})\, T(\Delta\underline{v}, \Delta t)\, \Delta\underline{v} = \langle \Delta\underline{v} \rangle$$

$$\int d(\Delta \underline{v})\, \Delta \underline{v}\, \Delta \underline{v}\, T(\Delta \underline{v}, \Delta t) = \langle \Delta \underline{v}\, \Delta \underline{v} \rangle$$

so

$=$

$$P(\underline{v},t) + (\Delta t)\frac{\partial P}{\partial t} = P(\underline{v},t) - \frac{\partial}{\partial \underline{v}} \cdot \left(\langle \Delta \underline{v} \rangle P(\underline{v},t)\right)$$

$$+ \frac{1}{2}\frac{\partial}{\partial \underline{v}} \cdot \left[\frac{\partial}{\partial \underline{v}} \cdot \left(\langle \Delta \underline{v}\, \Delta \underline{v} \rangle P(\underline{v},t)\right)\right]$$

so finally, have Fokker-Planck Eqn.

$$\frac{\partial P(\underline{v},t)}{\partial t} = -\frac{\partial}{\partial \underline{v}} \cdot \left\{ \overset{\text{drift}}{\frac{\langle \Delta \underline{v} \rangle}{\Delta t} P(\underline{v},t)} - \overset{\text{Diffusion}}{\frac{\partial}{\partial \underline{v}} \cdot \frac{\langle \Delta \underline{v}\, \Delta \underline{v} \rangle}{2\Delta t} P(\underline{v},t)} \right\}$$

$$= -\frac{\partial}{\partial \underline{v}} \cdot \Gamma_P$$

↓

conserves probability ⟺ Liouville structure

⟺ derivative order matters! → stochastics

example: Brownian Motion

$$\frac{\partial \underline{v}}{\partial t} = -\beta \underline{v} + \tilde{a}(t) \qquad \beta = \gamma/m$$

$$\frac{\langle \Delta \underline{v} \rangle}{\Delta t} = -\beta \underline{v} + \cancel{\langle \tilde{a} \rangle}$$

$$\frac{\langle \Delta v \, \Delta v \rangle}{2 \Delta t} = \underset{\downarrow}{D_v} \begin{bmatrix} 1, & 0 \\ 0, & 1 \end{bmatrix}$$

velocity
diffusion
coeff

Now, direct:

$$\langle \Delta v \, \Delta v \rangle = \int^{t} dt' \int^{t''} dt'' \, e^{-\beta(t-t')} \, e^{-\beta(t-t'')} \, *$$

$$\langle \tilde{a}(t'') \, \tilde{a}(t') \rangle$$

$$\downarrow$$

$$|\tilde{a}_0|^2 \tau_{ac} \, \delta(t'-t'')$$

etc,
easier here: (1D)

$$\partial_t P(v,t) = -\frac{\partial}{\partial v} \left\{ -\beta v P + \frac{\partial}{\partial v} D_v P \right\}$$

at stationary state:

$$\partial_t P = 0 \quad \Rightarrow \quad -\beta v P + \frac{\partial}{\partial v} D_v P = 0$$

$$P \sim ( ) \, e^{-\beta v^2 / D_v}$$

but F-D-T / eqbrm: $P \sim e^{-v^2/v_{Th}^2}$

$$\Rightarrow \boxed{D_v / \beta = v_{Th}^2}$$

● $$\boxed{D_V = \beta V_{th}^2}$$

$$\boxed{P_{eq} \cong \exp\left[-\beta V^2/2 \cdot D_V\right]}$$

→ Gaussian formed by balance <u>drag</u> with diffusion

w/o drag:

$$P(V,t) = \frac{1}{\sqrt{\pi D_V t}} \exp\left[-V^2/2D_V t\right]$$

now, β

$$\langle \Delta V \Delta V \rangle = 2\int_0^t dt' \int_0^t dt'' \, \cancelto{1}{e^{-\beta(t-t')}} \, \cancelto{1}{e^{-\beta(t-t'')}} \langle \tilde{a}(t') \tilde{a}(t'') \rangle$$

$$\langle \tilde{a}(t') \tilde{a}(t') \rangle = |\tilde{a}_0|^2 \tau_{ac} \, \delta(t'-t'')$$

$$\int dt' \int dt'' = \int d(t'+t'') \int d(t'-t'')$$

2's → symmetry

for short τ_{ac}

$$\langle \Delta v \Delta v \rangle = 2 \int^{t} d\tau \, |\tilde{a}_0|^2 \tilde{\tau}_{ac}$$

$$= 2 |\tilde{a}_0|^2 \tilde{\tau}_{ac} \, t$$

$$= 2 D_v t$$

$$D_v = |\tilde{a}_0|^2 \tilde{\tau}_{ac}.$$

→ generic structure:

drag/drift term → $\dfrac{\langle \Delta v \rangle}{\Delta t} P \rightarrow \underset{\substack{\downarrow \\ \text{drift velocity}}}{V} P$

diffusion term → $-\dfrac{\partial}{\partial \underline{v}} \cdot \dfrac{\langle \underline{\Delta v} \, \underline{\Delta v} \rangle}{2 \Delta t} P$

$$= -\frac{\partial}{\partial \underline{v}} \cdot \underset{\substack{\downarrow \\ \text{diffusion term/tensor}}}{\underline{\underline{D}}_v} P$$

$$\frac{\partial}{\partial t} P + \nabla_v \cdot (V P) = \underline{\nabla}_v \cdot \underline{\nabla}_v \cdot \underline{\underline{D}}_v P$$

$$\Gamma_v = -\underset{\substack{\downarrow \\ \text{drift} \rightarrow \\ \text{deterministic} \\ \text{element motion}}}{\underline{V}} P - \underline{\nabla}_v \cdot \underline{\underline{D}}_v P$$

↳ diffusion — random, noise relevant

— need $\langle \Delta V \rangle < \infty$

$\langle \Delta V \Delta V \rangle < \infty$

— Fokker-Planck equation ⟺ Markov process or chain which is gradual unfolding of transition probability just as conservative dynamical system is unfolding of contact transformation

— For Hamiltonian system:

$$\left[\frac{1}{2} \left[\frac{\partial}{\partial v} \cdot \langle \underline{\Delta v}\, \underline{\Delta V} \rangle \right] = \langle \underline{\Delta V} \rangle \right]$$

~akin Liouville ⇒ incompressibility phase space flow, stochastic system.

so

$$\frac{\partial P(v,t)}{\partial t} = \frac{\partial}{\partial \underline{v}} \cdot \underline{\underline{D}}_v \cdot \frac{\partial P}{\partial \underline{v}} \qquad (\text{order } \delta v)$$

(QL)

Now → bivariate evolution

→ evolve V, X.

$$\frac{d\underline{v}}{dt} = -\beta\underline{v} + \underline{g}_{ext} + \overset{\text{random}}{\overset{\downarrow}{\tilde{\underline{g}}}}$$

$$\frac{d\underline{x}}{dt} = \underline{v}$$

→ Particle random walks in $\underline{x}, \underline{v}$

If interested in spatial distribution only;

$$\int d\underline{v}\; P(\underline{x}, \underline{v}, t) \rightarrow n(\underline{x}, t)$$

For times $t \gg \beta^{-1}$

i.e. particles reach terminal velocity

$$\cancel{\frac{d\underline{v}}{dt}} = -\beta\underline{v} + \underline{g}_{ext} + \tilde{g}$$

$$\frac{d\underline{x}}{dt} = \underline{v}$$

$$\frac{d\underline{x}}{dt} = \overset{\text{deterministi}}{\overset{\downarrow}{\frac{g_{ext}}{\beta}}} + \underset{\text{random}}{\underset{\uparrow}{\frac{\tilde{g}}{\beta}}}$$

So, can immediately F.P. for $n(\underline{x},t)$

$\Rightarrow$

$$\frac{\partial}{\partial t} n(\underline{x},t) = -\frac{\partial}{\partial \underline{x}} \cdot \left\{ \left\langle \frac{d\underline{x}}{dt} \right\rangle n(\underline{x},t) - \frac{\partial}{\partial \underline{x}} \left(\frac{\langle \Delta x \Delta x \rangle}{2\Delta t} n(\underline{x},t) \right) \right\}$$

$$= -\frac{\partial}{\partial \underline{x}} \cdot \left\{ \frac{\underline{a}_{ext}}{\beta} n(\underline{x},t) - \frac{\partial}{\partial \underline{x}} \cdot \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} D_x \, n(\underline{x},t) \right\}$$

Schmoluchowski Equation

For D_x: (1D)

$$\langle \Delta x \Delta x \rangle = \int_0^t dt' \int_0^t dt'' \frac{\langle \tilde{a}(t') \tilde{a}(t'') \rangle}{\beta^2}$$

but: $\langle \tilde{a}(t') \tilde{a}(t'') \rangle = \frac{[\underline{\tilde{f}}]^2 \tau_{ac}}{m^2} \delta(t'-t'')$

and recall from FDT

$$\frac{|\tilde{f}|^2 \tau_{ac}}{m^2} = \gamma \frac{T}{m^2} = \beta v_{th}^2$$

$$= D_v$$

but

$$\langle \Delta x \Delta x \rangle = \int^{t} dt_+ \int^{\infty} dt_- \frac{|\tilde{f}|^2 \tau_{ac}}{m^2 \beta^2} \delta(t_-)$$

$$= \left(\beta v_{th}^2 / \beta^2\right) t = \left(v_{th}^2 / \beta\right) t$$

$$\boxed{\begin{array}{l} (\Delta x)^2 \sim D_x t \\ D_x \sim T/\gamma \end{array}}$$

$$D_x \sim v_{th}^2/\beta$$

$$D_x \sim D_v/\beta^2$$

D_x → spatial diffusion coefficient

Applications:

- sedimentation
- transport thru/over barrier
- reactions, etc.

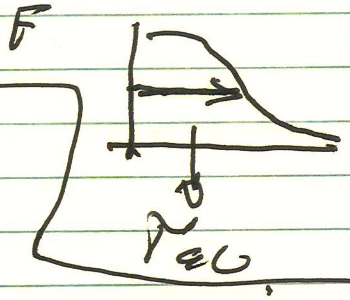
N.B.:

- Note:

$$\langle \Delta x \, \Delta x \rangle = \int^{t} dt_+ \int_0^{\infty} d\tau \, \frac{|\tilde{f}|^2}{m^2} \, \frac{\tilde{\tau}_{ac}}{\beta^2} \, \delta(\tau)$$

so, can induce general form of D:
generic

$$D_x = \int_0^{\infty} |\tilde{v}|^2 \, F(\tau/\tau_{ac}) \, d\tau$$



$$\boxed{D = \int_0^{\infty} \langle \tilde{v}(0) \tilde{v}(\tau) \rangle \, d\tau}$$

D as integral of Lagrangian correlation function.

→ Noise: Additive and Multiplicative

Langevin Equation

$$m\frac{d\underline{v}}{dt} = -\gamma\,\underline{v} + \underset{\substack{\downarrow \\ \text{Noise} \leftrightarrow \text{Brownian Force}}}{\tilde{f}(t)}$$

here additive ↔ standard textbook problems

Reality: noise can be multiplicative
⇒ introduces complexity in F-P Eqn.

i.e consider Logistic Eqn. – Population.
↳ Malthusian growth

$$\frac{dN}{dt} = N(K - \underset{\substack{\downarrow \\ \text{competition -- saturation}}}{N}) \qquad \text{population}$$

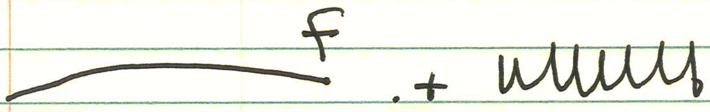
→ exponential growth + nonlinear saturation

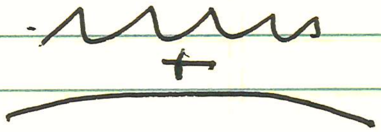
→ Fixed Pts. $N = 0$ (unstable)
$N = K$ (stable)

Now, introduce variability in K,

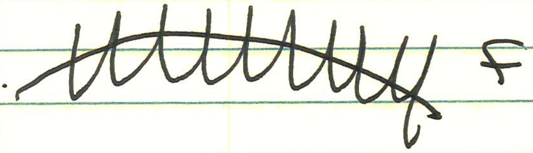
$$\frac{dN}{dt} = N(K_0 + \underset{\substack{\downarrow \\ \text{multiplicative} \\ \text{noise } (\gamma \text{ stochastic})}}{\tilde{\gamma}(t)} - N]$$

i.e. additive:





multiplicative



f - TBD

obviously multiplicative noise presents several problems.

How treat:

- here: $\langle \tilde{\gamma}(t) \tilde{\gamma}(t') \rangle = |\tilde{\gamma}|^2 \tau_{ac} \delta(t-t')$,

  for simplicity

- Fokker-Planck Eqn.

⇒

$$\frac{\partial}{\partial t} f(N) = -\frac{\partial}{\partial N}\left[(k_0 N - N^2) f(N) - \frac{\partial}{\partial N}\left(D_0 f(M) \right) \right]$$

$$\langle \Delta N \Delta N \rangle = \int^{t} dt' \int^{t} dt'' \langle \tilde{\gamma}(t') \tilde{\gamma}(t'') \rangle N^2$$

$$= |\gamma_0|^2 \tau_{ac} N^2 t$$

$$D = |\gamma_0|^2 \tau_{ac} \underset{\substack{\uparrow \\ \underline{\text{nonlinearity}}}}{N^2}$$

$$\partial_t f(N) = -\frac{\partial}{\partial N} \Big[(k_0 N - N^2) f(N) - \frac{\partial}{\partial N} \Big(\frac{|\gamma_0|^2}{2} \tau_{ac} N^2 f(N) \Big) \Big]$$

so stationary $f(N) \Rightarrow$

$$N (k_0 - N) f(N) = \frac{\partial}{\partial N} \Big(\frac{|\gamma_0|^2}{2} \tau_{ac} N^2 f(N) \Big)$$

$\Rightarrow$ for $\sigma^2 = |\tilde{\gamma}_0|^2 \tilde{\tau}_{ac}$

$$f(N) = \underset{\substack{\downarrow \\ \text{norm.}}}{C}\; n^{[2(k_0/\sigma^2)-2]}\, e^{-2N/\sigma^2}$$

need $k_0 > \sigma^2/2$.