Elementary Physics of Random Walks and Diffusion

Basic ideas:

- random walk → stochastic → evolution of mean square
- Markov Process → no memory, step-to-step
  Each step uncorrelated and unbiased,
  Each set by microscopic pdf.

Diffusion equation:

$$\frac{\partial n}{\partial t} + \underline{\nabla} \cdot \underline{\Gamma} = S_{i,o}$$

conserving flux

Fick's Law

$$\Gamma = - D \nabla n \quad \rightarrow \text{where from?}$$

Generally: seek macro-density evolution from micro-step probability

i.e.

$n(x,t)$ evolution from:

transition probability of step Δx in Δt

$$n(x, t+\Delta t) = \int d(\Delta x) \left[T(\Delta x, \Delta t)\, n(x-\Delta x, t) \right]$$

density up-dated to Δt ahead

$\boxed{\text{Chapman-Kolmogorov Eqn.}}$

density one step away

n evolves by small random kicks, so:

$$n(x,t) + \Delta t \frac{\partial n}{\partial t} = \int d(\Delta x)\, T(\Delta x, \Delta t) \left[n(x,t) - \Delta x \frac{\partial n}{\partial x} + \frac{(\Delta x)^2}{2} \frac{\partial^2 n}{\partial x^2} \right]$$

$\int d(\Delta x) T = 1$ (probability normalizable)

$\int d(\Delta x)\, \Delta x\, T = \langle \Delta x \rangle$ → mean step

$\int d(\Delta x) (\Delta x)^2 T = \langle \Delta x^2 \rangle$ → mean square step

$$n(x,t) + \Delta t \frac{\partial n}{\partial t} = n(x,t) - \langle \Delta x \rangle \frac{\partial n}{\partial x} + \frac{\langle \Delta x^2 \rangle}{2} \frac{\partial^2 n}{\partial x^2}$$

so

$$\frac{\partial n}{\partial t} = -\frac{\partial}{\partial x}\left[\frac{\langle \Delta x \rangle}{\Delta t} n - \frac{\langle \Delta x^2 \rangle}{2\Delta t}\frac{\partial n}{\partial x}\right]$$

Important to note:

$\left.\begin{array}{l}\Delta x \to \text{step size} \\ \Delta t \to \text{step time}\end{array}\right\}$

Every random walk characterized by these.

Now: $D = \frac{\langle (\Delta x)^2 \rangle}{2\Delta t} \to$ diffusion coefficient

$$V = \text{drift speed} = \frac{\langle \Delta x \rangle}{\Delta t}$$

(N.B. Obv. scheme not limited to space)

$\Rightarrow$

$$\boxed{\frac{\partial n}{\partial t} = -\frac{\partial}{\partial x}\left[V n - D\frac{\partial n}{\partial x}\right]} \to \text{Fokker-Planck Eqn.}$$

Important Points:

- $\langle (\Delta x)^2 \rangle^{1/2} < L$ assumed in expansion
  i.e. small kicks! (Boltzmann not so limited)

- n should be regarded as coarse grained, on small scale, i.e.
  $n \to \langle n \rangle$

- formulation of F.P.E, diffn requires
  $\int d(\Delta x)\,(\Delta x)^2\, T < \infty$.

  i.e. second moment of T must converge.

  e.g. $T \sim \exp\left[-(\Delta x)^2/\ell^2\right]$

  $\Rightarrow$ Gaussian works.

  $T \sim S/\left(\ell^2 + (\Delta x)^2\right)$ –

  $\Rightarrow$ Lorentzian fails

  $T \sim f(\Delta x)\,(\Delta x/\ell)^{-\alpha}$

  $\Rightarrow$ Power Law requires $\alpha > 3$.

Lesson: Tail of transition pdf can have big effect on validity of diffusive, random walk models

$\Rightarrow$ 'Fat Tail' problem.

- N.B. Existance of second moment of transition probability enables application of Central Limit Thm:

(Simply Put) CLT:

As long as $\langle (\Delta x)^2 \rangle$ finite, then after N steps:

$$P_N(R) = \frac{\exp\left[-x^2 / N\langle \Delta x^2 \rangle \right]}{\left(N\langle (\Delta x)^2 \rangle \right)^{1/2}}$$

(1D)

i.e. probability of location after N steps is Gaussian, with $\langle x^2 \rangle \sim N\langle (\Delta x)^2 \rangle$

- F.P.E. is conservative

i.e. 'particles' moved around, but not lost, up to boundary.

$$\partial n / \partial t = -\nabla \cdot \Gamma$$

$$\Gamma = -D \frac{\partial n}{\partial x} + Vn$$

$V = 0$, pure diffusion

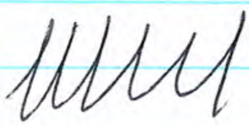
- fundamentally, mathematical structure of random walk paths is <u>rough</u>

$$dx^2 \sim D\,t \quad , \quad \Delta x \sim (\Delta t)^{1/2}$$

as compared to usual $\Delta x \sim \Delta t$

i.e. usual: $f(t+\Delta t) - f(t) \sim \Delta t$

diffn: $\begin{cases} f(t+\Delta t) - f(t) \sim (\Delta t)^{1/2} \\ f = \Delta x \end{cases}$ → non-differentiable

i.e. 

Ex: Brownian Motion

- classic example of diffusion arises in random walk of particle driven by thermal random kicks, and restricted by drag.

small particle:
$\ell \to$ scale
$\eta = \rho\nu = \rho\, v_{Th}\, \ell_{mfp}$
viscosity

→ Diffusion has an ⊙ H-Thm.

$$\frac{\partial n}{\partial t} = \frac{\partial}{\partial x} D \frac{\partial n}{\partial x}$$

closed system ($\Gamma \to 0$, on bndry)

$$\partial_t \int d^3x \; n^2 = -D \int d^3x \; (\nabla n)^2$$

so $\quad \partial_t \int d^3x \, n^2$ decreases unless

$\nabla n = 0$, everywhere.

→ $\quad$ "S" $= -\int d^3x \, n^2$

$$m_p \frac{d\underline{v}}{dt} = -\beta \underline{v} + \tilde{f}$$

m_p → particle mass.

β → Stokes drag $\sim 6\pi\eta \ell$ → dim.

$\tilde{f}$ → Brownian force, random (additive) → thermal flctns. → noise

n.b. Fluid exerts both drive (thermal fluctuations) and drag (β) on Brownian particle.

$\tilde{f}$ → Random Force / No Memory

$$\langle \tilde{f}(t_1)\, \tilde{f}(t_2) \rangle = \underbrace{\tilde{f}^2 \tau_{ac}}_{\text{strength}}\, \delta(t_2 - t_1)$$

τ_{ac} → required for dimensions
→ memory time of force, necessarily shortest time in problem.

$$\langle \tilde{f}^2 \rangle_\omega = \int e^{-i\omega(t_2 - t_1)} \langle \tilde{f}(1)\, \tilde{f}(2) \rangle\, d(t_2 - t_1)$$

$$= \tilde{f}^2 \tau_{ac} \rightarrow \text{const} \rightarrow \text{"white noise"}.$$

What is $\tilde{f}$?

$$m_p \frac{d\underline{v}}{dt} = -\beta \underline{v} + \underline{\tilde{f}}$$

steady state:

$$\underbrace{\beta \langle v^2 \rangle}_{\substack{\text{Power} \\ \text{dissipated} \\ \text{by drag}}} = \underbrace{\langle \underline{\tilde{f}} \cdot \underline{v} \rangle}_{\substack{\text{Power input} \\ \text{by Brownian force.}}} \qquad \text{at } T.$$

but $m_p \langle v^2 \rangle \sim T$ $\Rightarrow$ bath sets thermal reservoir, at T.

$\Rightarrow$

$$\langle v^2 \rangle \sim \frac{T}{M_p} \sim \frac{\langle \underline{\tilde{f}} \cdot \underline{v} \rangle}{\beta}$$

but $\underline{v} \sim \underline{\tilde{f}}/\beta$ (SS)

$$\langle v^2 \rangle \sim \frac{T}{m_p} \sim \frac{\langle \underline{\tilde{f}} \cdot \underline{v} \rangle}{\beta} \sim \frac{\langle \tilde{f}^2 \rangle}{\beta^2}$$

$\Rightarrow$ arrives at particularly simple form of <u>Fluctuation</u> - <u>Dissipation</u> <u>Theorem</u>!

ue,

→ drag-induced energy dissipation balances fluctuation work at steady state, to maintain temperature T.

→ given any 2 of T, drag, fluctuations (force), can deduce third.

For diffusion of Brownian Particle:

$$D \sim \frac{\langle \Delta x^2 \rangle}{\Delta t} \sim \frac{V_{Th}^2 (\Delta t)^2}{\Delta t} \sim V_{Th}^2 \, \Delta t$$

now $$m_p \frac{d\underline{v}}{dt} = -\beta \underline{V} + \underline{f}$$

$$\frac{d\underline{v}}{dt} = \frac{-\beta}{m_p} \underline{v} + \underline{a}$$

velocity ~~[illegible]~~ acts over time scale $\Delta t \sim m_p/\beta$ (~ akin colln time)

$$D \sim \langle V^2 \rangle \Delta t \sim \frac{T}{m_p} \frac{m_p}{\beta} \sim \frac{T}{\beta}$$

so, $\boxed{D \sim \dfrac{T}{6\pi \eta \ell}}$

→ diffusivity, in space, of Brownian particle.

→ alternatively:

$$m_p \frac{d\underline{v}}{dt} = -\beta \underline{v} + \underline{\tilde{f}}$$

$d\underline{v}/dt = 0 \Rightarrow$ terminal velocity

$$\frac{d\underline{x}}{dt} = \frac{\tilde{f}}{\beta} \qquad \delta x \sim \int \frac{\tilde{f}}{\beta}\, dt$$

$$\langle \delta x^2 \rangle \sim \frac{\tilde{f}^2}{\beta^2} (\Delta t)\, t \qquad \langle \delta x^2 \rangle \sim \iint \frac{\tilde{f}^2}{\beta^2}\, dt\, dt' \sim \frac{\tilde{f}^2}{\beta^2} \Delta t\, t$$

F-D T: $\langle \tilde{f}^2 \rangle = \beta^2 T / m_p$

$$\Delta t = m_p / \beta$$

$$\langle \delta x^2 \rangle \sim \frac{\tilde{f}^2}{\beta^2} \Delta t\, \cancel{t} \sim \left(\frac{\cancel{\beta^2} T}{\cancel{m_p}} \frac{\cancel{m_p}}{\beta\, \cancel{\beta^2}} \right) t$$

$$\sim \beta^{-1} T\, t$$

$$\sim (T/\beta)\, t \; ✓.$$

⇒ As usual, back to Basic Scales in Random Walk / Diffusion of Brownian Particle

τ_{ac} → self-correlation time of Brownian Force
~ effectively → 0
White Noise ⟷ band width → ∞

τ_c → step time, velocity correlation time
Δt

i.e. $\tilde{v}\,\Delta t \sim \tilde{v}\,\tau_c \sim V_{th}\,\tau_c \sim \Delta r$

$\tau_c^{-1} \sim \beta/m_p$.

spatial step

τ_d → macro-diffusion time

$1/\tau_d \sim D/L^2 \sim T/\beta L^2$

$$\tau_c/\tau_d \sim \frac{T}{\beta L^2}\,\frac{m_p}{\beta} \sim \frac{V_{th}^2}{L^2}\left(\frac{m_p}{\beta}\right)^2$$

$$\sim \frac{\Delta r^2}{L^2} \quad !$$

So – analogy:

Boltzmannia	Fokker–Planckology
$\tau_{int} = \ell/v_{th}$ collisional interaction	τ_{ac}
$\tau_{col} = \dfrac{\ell_{mfp}}{v_{th}}$	τ_c
$\tau_{relax} \sim \tau_{col} \dfrac{L^2}{\ell_{mfp}^2}$	$\tau_{macro} \sim \tau_c \dfrac{L^2}{(\Delta x)^2}$.

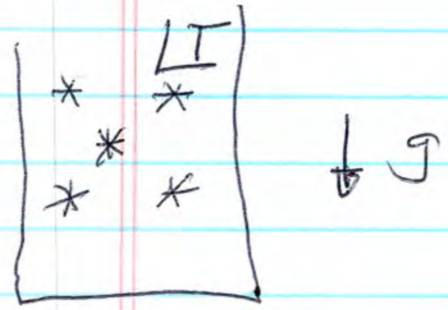
N.B. ① Analogy, only!

② Note:

– Boltzmannia allows arbitrary collision

– F.P. E $\Rightarrow$ weak glancing collision, so $|\Delta p| \ll |p|$

- interesting application: <u>sedimentation</u>



Brownian particles of size l, in fluid of T, ρ.

What is spatial distribution?

- particles random walk $\Rightarrow T$
- " drift, due gravity

Profile: at st state $\Rightarrow$

$$n(z) = e^{-mgz/T}$$

Now, $$m_p \frac{d\underline{v}}{dt} = -\beta \underline{v} - m_p g \hat{z} + \tilde{f}$$

or, in 1D:

$$\frac{dv}{dt} = -\alpha v - g + \tilde{a}$$

Now, at terminal velocity, drag and forces balance so:
(neglects transient)

$$\frac{dx}{dt} = -\frac{g}{\alpha}\hat{z} + \frac{\tilde{a}}{\alpha}$$

Consider $\hat{z}$ direction, only, so:

$$\frac{dz}{dt} = -\frac{g}{\alpha} + \frac{\tilde{a}}{\alpha}$$

Now, F.P. E. $\Rightarrow$

$$\frac{\partial n}{\partial t} = -\frac{\partial}{\partial z}\left\{ \frac{\langle \Delta z \rangle}{\Delta t} n - D_z \frac{\partial n}{\partial z} \right\}$$

$$\frac{\langle \Delta z \rangle}{\Delta t} = \left\langle \frac{dz}{dt} \right\rangle = -\frac{g}{\alpha} = V$$

$\hookrightarrow$ drift speed

$$D_z \sim \frac{\langle \tilde{v}^2 \Delta t^2 \rangle}{\Delta t} \sim \left(\frac{\tilde{a}}{\alpha}\right)^2 \Delta t$$

fluctn. part

$$\sim \frac{\tilde{a}^2}{\alpha^2} \underbrace{\Delta t}_{\alpha^{-1}} \sim \frac{\tilde{a}^2}{\alpha^3}$$

but:

$$D_z \sim \frac{\tilde{a}^2}{\alpha^3} \sim \frac{1}{m_p^2} \frac{\tilde{f}^2}{\beta^3} m_p^3 \sim T/\beta$$

as usual

Now, $D = T/\beta$

$$V = -\frac{g M_p}{\beta}$$

Observe: $\underline{V} = \frac{1}{\beta} \underbrace{\underline{F}}_{\text{force}}$ $\qquad \underline{F} = -g M_p \vec{z}$

$= \mu \underline{F}$

— mobility, here $= 1/\beta$

— generic to friction produced terminal free-fall.

$D = T/\beta = \mu T$ ✓

example of Einstein Relation

$$\boxed{D = \mu T}$$

relates D to mobility.
Mobility easy to calculate

generic to Brownian Motion type EOM:
and FDT

$$M_p \frac{dV}{dt} = -\beta \underline{V} + \underline{\tilde{f}} .$$

⇒ For steady state:

$$\frac{\partial n}{\partial t} = -\frac{\partial}{\partial z}\left\{ -\frac{mg}{\beta}\, n - \frac{T}{\beta}\frac{\partial n}{\partial z}\right\}$$

$$0 = -\frac{mg}{\beta}\, n - \frac{T}{\beta}\frac{\partial n}{\partial z}$$

balance is:
- vertical drift
<u>vs.</u>
- upper diffusion

$$\Rightarrow \quad n = \exp\left[-\frac{mgz}{T}\right] \quad \checkmark$$

of course can obtain time relaxation to equilibrium, as well.

⇒ 

full evolution:
→ vertical sedimentation
→ radial diffusion at D_n.

Key PT: - drift, diffusion relation

- stationarity from zero flux condition.

→ Multiplicative Noise

Additive: $\frac{dV}{dt} = -\alpha V + \tilde{a}(t)$

Multiplicative: $\frac{dn}{dt} = \gamma n - \alpha n^2$

$\gamma = \gamma_0 + \tilde{\gamma}$

$\langle \tilde{\gamma}(t_1)\tilde{\gamma}(t_2)\rangle = \tilde{\gamma}^2 \tau_{ac}\, \delta(t_1 - t_2)$

i.e.

- logistic population equation
- noise enters as multiplier on growth rate.

- (random variable) n → unusual behavior

Logistic System

$$\frac{dn}{dt} = \underbrace{\gamma n}_{\text{Malthusian growth}} - \alpha n^2$$

$-\alpha n^2$ → {saturation by competition

2 equilibria: $n = 0$ unstable
$n = \gamma/\alpha$ stable

Now, $\gamma = \gamma_0 + \tilde{\gamma}(t)$ → i.e. variability in conditions, food supply etc.
$\alpha = 1$

so, need <u>distribution</u> of populations

$\Rightarrow$ Fokker-Planck Eqn. for $f(n,t)$!

can immediately write

$$\frac{dn}{dt} = (\gamma_0 + \underset{\substack{\uparrow \\ \text{random}}}{\tilde{\gamma}})n - \alpha n^2$$

$$\frac{\partial f}{\partial t} = -\frac{\partial}{\partial n}\left\{ \left\langle \frac{dn}{dt} \right\rangle f - \frac{\partial}{\partial n} D f \right\}$$

$$D = \frac{\langle \delta n^2 \rangle}{2\Delta t}$$

Now, $\langle dn/dt \rangle = \gamma_0 n - \alpha n^2$

$$\frac{d}{dt}\delta n = \tilde{\gamma} n$$

$$\langle \tilde{\gamma}(t_1)\,\tilde{\gamma}(t_2) \rangle = \tilde{\gamma}^2 \tau_{ac}\, \delta(t_2 - t_1)$$

$$\Rightarrow \quad D = \frac{\langle \delta n \delta n \rangle}{2\Delta t}$$

$$= \int dt_1 \int dt_2 \; \frac{\tilde{\gamma}^2}{2} \tau_{ac}(t_2 - t_1)\, n^2 / \Delta t$$

$$\cong n^2 \sigma^2$$

$$\tilde{T}^2 \equiv \int \langle \tilde{\gamma}(t_1)\,\tilde{\gamma}(t_2)\rangle\, dt$$

$$\sim \tilde{\gamma}^2 \tau_{ac}$$

$$\sim 1/T$$

but now D nonlinear!! ⇒ consequence of multiplicative character

⇒

$$\boxed{\frac{\partial f}{\partial t} = -\frac{\partial}{\partial n}\left\{ (\gamma_0 n - n^2) f - \frac{\partial}{\partial n}\left(n^2 \tilde{T}^2 f\right) \right\}}$$

⇒ Fokker-Planck Eqn. for f.

stationary state ⇒

$$(\gamma_0 n - n^2) f - \frac{\partial}{\partial n}\left(n^2 \tilde{T}^2 f\right) = 0$$

$$A(n) f - \frac{\partial}{\partial n}(B f) = 0$$

⇒

$$f \sim \frac{1}{B(n)} \exp\left[\int dn' \frac{A(n')}{B(n')}\right]$$

Now,

$$\int dn' \left[\frac{\gamma_0 n' - n'^2}{\sigma^2 n'^2} \right] = \int dn' \left[\frac{\gamma_0}{\sigma^2 n'} - \frac{1}{\sigma^2} \right]$$

$$\stackrel{\circ}{=} -\frac{n}{\sigma^2} + \frac{\gamma_0}{\sigma^2} \ln(n)$$

$\Rightarrow$

$$\boxed{f = \frac{1}{\sigma^2 n^2} n^{\gamma_0/\sigma^2} \exp\left[-n/\sigma^2 \right]}$$

PDF

and need:

$$\frac{\gamma_0}{\sigma^2} - 2 > -1$$

to assure integrability

$\Rightarrow$

$$\boxed{\gamma_0/\sigma^2 > 1}$$

fluctuations in growth cannot be too large.

Meaning:

plot $f(n)$

$\frac{n}{\gamma} = 1$ is determ. eqbrm.