C.f. → Chandra

1.

Kinetics

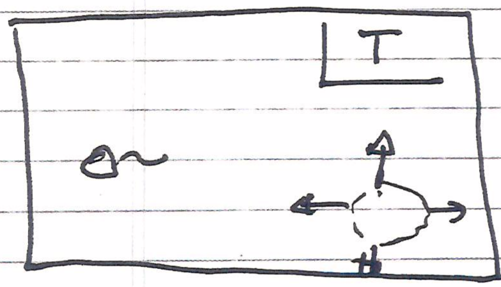
Fokker-Planck,

Lecture [redacted] II: 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

$P(\underline{x}, t)$

i.e. $\langle \delta v^2 \rangle = D_v t$

else ?

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

⇒ Basic aspects of Fokker-Planck Theory. → {Calculate $P(x,t)$, not moments $\langle x^n \rangle$.

⇒ Motivated by random walk, no memory

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

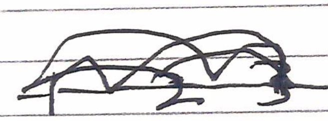
Consider system with no memory ↔ each step in τ independent prior history

so

$$P(x_3,t_3 \mid x_1,t_1) = \int dx_2 \; P(x_3,t_3 \mid x_2,t_2)\, P(x_2,t_2 \mid x_1,t_1)$$

Prob. of x_3 at t_3 starting from x_1 at t_1 — integrate over intermediate — $2 \to 3$ jump — $1 \to 2$ jump

$$\xrightarrow[3]{} \;=\; \sum$$



each step independent

→ multiplicative, as independent steps

→ sum over intermediate steps

⇒ Chapman – Kolmogorov Equation

Now, re-write as:

→ transition probability

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

at x

Δx in τ

$t_2 - t_1$ is jump time τ

T finite width

$x_2 - x_1$ is jump step Δx

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

and expand. lowest order, even/odd.

$$\frac{\partial P}{\partial t} = -\frac{\partial}{\partial x} \cdot \Big\{ \underbrace{\frac{\langle \Delta x \rangle}{\tau}}_{\text{drift}} P - \frac{\partial}{\partial x} \underbrace{\frac{\langle \Delta x \Delta x \rangle}{2\tau}}_{\text{diffn.}} \cdot P \Big\}$$

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

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)

$T \sim 1 / \left[1 + (\Delta x)^{\alpha} \right]$

$(\alpha > 3)$

③ → T non uniform.

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

Memory / correlations → LTCM.

Lowenstein, "When Genius Failed".

For Brownian Motion:

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

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

so, for pdf P:

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

expand:

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

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

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

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

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

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

$\equiv$

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

so finally, have Fokker-Planck Eqn.

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

$$= -\frac{\partial}{\partial \underline{v}}\cdot\underline{\Gamma}_P$$

conserves probability $\Leftrightarrow$ Liouville structure

$\Leftrightarrow$ derivative order matters! $\rightarrow$ stochastic

example: Brownian Motion

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

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

$$\frac{\langle \Delta v \Delta v \rangle}{2\Delta t} = \underbrace{D_v}_{\text{velocity diffusion coeff}} \begin{bmatrix} 1, & 0 \\ 0, & 1 \end{bmatrix}$$

Now, direct:

$$\langle \Delta v \Delta v \rangle = \int^{t} dt' \int^{t''} dt'' \, e^{-\beta(t-t')} e^{-\beta(t-t'')} * \underbrace{\langle \tilde{a}(t'') \tilde{a}(t') \rangle}_{|\tilde{a}_0|^2 \tau_{ac} \delta(t'-t'')}$$

etc.

easier here: (1D)

$$\partial_t P(v,t) = -\frac{\partial}{\partial v} \Big\{ -\beta v P + \underbrace{\frac{\partial}{\partial v} D_v P}_{\text{Gaussian}} \Big\}$$

cet 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 / equilib'm: $P \sim e^{-v^2/v_{Th}^2}$

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

$$\boxed{D_V = \theta V_{th}^2}$$

$$\boxed{P_{eq} \simeq \exp\left[-\theta V^2/2 D_V\right]}$$

[→ Gaussian formed by balance drag with diffusion]

w/o drag:

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

how, ?

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

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

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

2's → symmetry

for short τ_{ac}

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

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

$$= 2 D_V \, t$$

$$D_V = |\tilde{q}_0|^2 \tilde{\tau}_{ac}$$

→ generic structure:

drag/drift term → $\frac{\langle \Delta V \rangle}{\Delta t} P \rightarrow \underset{\text{drift velocity}}{\underbrace{\bar{V}}} P$

diffusion term → $-\frac{\partial}{\partial \underline{V}} \cdot \frac{\langle \Delta \underline{V} \Delta \underline{V} \rangle}{2\Delta t} P$

$$= -\frac{\partial}{\partial \underline{V}} \cdot \underline{\underline{D}}_V P$$

diffusion term/tensor.

$$\frac{\partial}{\partial t} P + \nabla_V \cdot (\bar{V} P) = \underline{\nabla}_V \cdot \underline{\nabla}_V \cdot \underline{\underline{D}}_V P$$

$$\Gamma_V = -\bar{V} P - \underline{\nabla}_V \cdot \underline{\underline{D}}_V P$$

drift → deterministic element motion

→ diffusion – random noise relevant

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

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

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

$$\frac{dz}{dt} = \frac{\partial H}{\partial p}, \quad \frac{dp}{dt} = -\frac{\partial H}{\partial z} \qquad p', z' \Big|_{t} \rightarrow p, z \Big|_{t+dt}.$$

— For Hamiltonian system:

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

~ akin Liouville $\Rightarrow$ incompressibility phase space flow stochastic system.

so

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

(QL)

Now $\rightarrow$ bivariate evolution

$\rightarrow$ evolve V, X.

random

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

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

→ 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

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

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

determinisitic

$$\frac{d\underline{x}}{dt} = \frac{\underline{g}_{ext}}{\beta} + \frac{\tilde{\underline{g}}}{\beta}$$

random

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

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

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

Schmoluchowski Equation
n, not f.

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

and recall from FDT

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

$$= D_V$$

but

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

$$= \left(\beta V_{Th}^2 / \beta^2 \right) t = \left(V_{Th}^2 / \beta \right) t$$

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

$$D_x \sim V_{Th}^2 / \beta$$

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

$D_x \to$ spatial diffusion coefficient

Applications: $\to$ focus

* – sedimentation

– transport thru/over barrier

– reactions, etc.

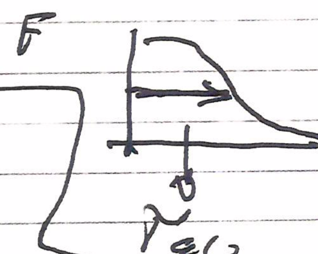
N.B.:

- Note:

$$\langle \Delta x \, \Delta x \rangle = \int^{t} dt_1 \int_0^{\infty} d\tau \, \frac{|\tilde{f}|^2}{m^2} \frac{\tau_{ac}}{\beta^2} \delta(\tau)$$

so, can induce general form of D:
generic

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

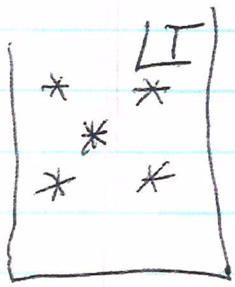


$$D = \int_0^{\infty} \langle \tilde{v}(0) \tilde{v}(\tau) \rangle \, d\tau$$

D as integral of Lagrangian correlation function.

→ sedimentation: Pg. 13

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



$\downarrow g$

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

What is spatial distribution? How evolve?

- particles random walk $\to T$
- " 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)

$$\frac{d\underline{x}}{dt} = -\frac{g}{\alpha}\hat{z} + \frac{\tilde{\underline{a}}}{\alpha}$$

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

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

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

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

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

↳ drift speed

$$D_z \sim \frac{\langle \tilde{v}^2 \Delta t^2 \rangle}{\Delta t} \sim \Big\langle \underbrace{\left(\frac{\tilde{a}}{\alpha}\right)}_{\text{fluctn. part}}{}^2 \Big\rangle \Delta t$$

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

but:

$$\underline{D_z} \sim \frac{\tilde{a}^2}{\alpha^3} \sim \frac{1}{m_p^2} \frac{\tilde{f}^2}{\beta^3} m_p^3 \sim \underbrace{T/\beta}_{\text{as usual}}$$

Now, $D = T/\beta$

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

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

$= \mu \underline{F}$

— $\underline{\text{mobility}}$, here $\underline{= 1/\beta}$

— generic to friction produced terminal free-fall.

$D = T/\beta = \mu T$ ✓ $\qquad$ get mobility from Drift.

example of Einstein Relation

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

relates D to mobility
(*) Mobility easy to calculate

generic to Brownian Motion type EOM!
and FDT

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

→ For steady state:

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

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

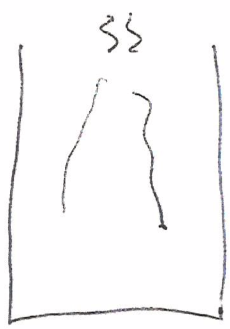
Balance is:
- vertical drift

vs.

- 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_1.

Key PT: - drift, diffusion relation

- stationarity from zero flux condition

Text ↑ Reality ↑

→ Noise: Additive and Multiplicative

Langevin Equation

$$m\frac{dv}{dt} = -\gamma \underline{v} + \tilde{f}(t)$$

Noise ↔ Brownian Force

here additive ↔ standard textbook problems

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

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

$$\frac{dN}{dt} = N(k - N)$$ population

competition – saturation → N^2

→ exponential growth + nonlinear saturation

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

Now, introduce variability in k,

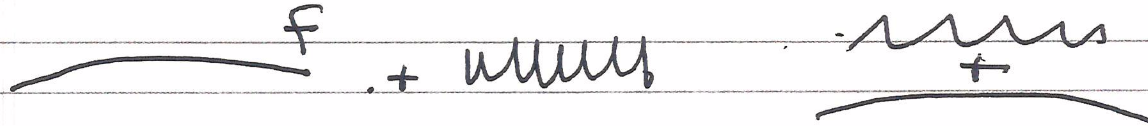
$$\frac{dN}{dt} = N(k_0 + \tilde{\gamma}(t) - N] = (k_0 + \tilde{\gamma}(t))N - N^2$$

mult. noise

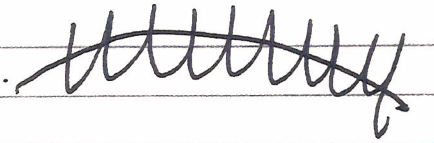
multiplicative noise (γ stochastic)

i.e. environmental variability

i.e. additive:



Multiplicative



f – TBD
rapid variation

obviously multiplicative noise presents several problems.

How treat:

- here: $\langle \tilde{\gamma}(t)\, \tilde{\gamma}(t') \rangle = |\tilde{\gamma}|^2 \tau_{c_0}\, \delta(t-t')$,
  for simplicity   easy
- Fokker–Planck Eqn.

$\Rightarrow$

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

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

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

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

$\downarrow$

nonlinearity in D (trademark of multiplicative noise)

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

so stationary $f(N) \Rightarrow$

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

N.B. could have additive noise, too, to resolve $N \to 0$

i.e.

$$\frac{dN}{dt} = N(k_0 + \tilde{\gamma}(t) - N) + \tilde{\alpha}(t)$$

$\Rightarrow$ for $\sigma^2 = |\gamma_0|^2 \tilde{\tau}_{ac}$

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

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

need $\underset{n\to 0}{f} > 1/n$ to avoid log. singularity

Perhaps more simply:

$$\frac{dN}{dt} = N(k_0 + \underset{\substack{\text{pert.} \\ \downarrow}}{\tilde{\gamma}} - N)$$

$$N = k_0 + n$$

$$\frac{dn}{dt} = (k_0 + n)(\cancel{k_0} + \tilde{\gamma} - \cancel{k_0} - n)$$

$$= k_0\tilde{\gamma} - k_0 n + O(n^2)$$

linearize abt. fixed pt. k_0
$\Rightarrow$ validity?

$$\partial_t f(n) = -\frac{\partial}{\partial n}\left[-k_0 n f(n) - \frac{\partial}{\partial n} k_0^2 \frac{|\gamma_0|^2 \tilde{\tau}_{ac}}{2} f(n)\right]$$

$$= -\frac{\partial}{\partial n}\left[-k_0 n f(n) - \frac{k_0^2 \sigma^2}{2}\frac{\partial f(n)}{\partial n}\right]$$

$$f(n) = C e^{-n^2/\tau^2 k_0}$$

Lon. vertical

Valid for $\langle (n/k_0)^2 \rangle < 1$ i.e. $\langle (n/N_0)^2 \rangle < 1$

$$\langle n^2 \rangle = \frac{\tau^2 k_0}{2}$$

$$\langle (n/k_0)^2 \rangle < 1 \Rightarrow \frac{\tau^2}{2 k_0} < 1$$

$$\Rightarrow \text{again } \boxed{\tau^2 < 2 k_0} \checkmark$$

Kinetics Lecture III : Central Limit Theorem, etc. 1.

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:

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

$\downarrow$

conserving flux

Fick's Law

$$\Gamma = -D \nabla n$$ → 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

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

②

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

Important to note:

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

Every random walk characterized by these.

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

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

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

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

- Important Points:

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

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

  $\Rightarrow$ 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

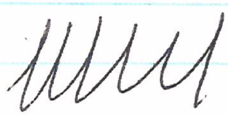
- fundamentally, mathematical structure of random walk paths is rough

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

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:
$\ell \rightarrow$ 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 $\partial_t \int d^3x \; n^2$ decreases unless

$\nabla n = 0$, everywhere.

→ "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, noise, random → thermal flctns. (additive)

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

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

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

$\tilde{f}^2 \tau_{ac}$ → strength

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

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

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

What is $\tilde{f}$?:

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

steady state:

$$\beta \langle v^2 \rangle = \langle \underline{\tilde{f}} \cdot \underline{v} \rangle \qquad \text{at} \quad T.$$

$\beta \langle v^2 \rangle$ ↓ Power dissipated by drag

$\langle \underline{\tilde{f}} \cdot \underline{v} \rangle$ ↓ Power input by Brownian force.

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

⇒

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

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

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

⇒ arrives at particularly simple form of <u>Fluctuation</u> <u>-Dissipation</u> <u>Theorem!</u>

i.e.

→ 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,

$$\boxed{D \sim \frac{T}{6\pi\eta\ell}}$$

→ diffusivity, in space, of Brownian particle.

→ alternatively:

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

$d\underline{v}/dt = 0$ ⇒ 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: $\langle \tilde{f}^2 \rangle = \beta^2 T / m_p$

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

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

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

$$\sim (T/\beta)\, t \checkmark.$$

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

τ_{ac} ⇒ self-correlation time of Brownian Force

$\sim$ effectively $\to 0$.

White Noise ⟺ band width $\to \infty$

τ_c ⇒ step time, velocity correlation time
Δt

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

Δr ⇓ spatial step

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

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
$\tau_{int} = d/v_{Th}$ collisional interaction	τ_{ac}
$\tau_{col} = \dfrac{l_{mfp}}{v_{Th}}$	τ_c
$\tau_{relax} \sim \tau_{col} \cdot \dfrac{L^2}{l_{mfp}^2}$	$\tau_{macro} \sim \tau_c \dfrac{L^2}{(\Delta x)^2}$.

N.B. ① Analogy, only !

② Note :

– Boltzmannia allows arbitrary collision

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

→ Multiplicative Noise

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

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

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

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

i.e.

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

- (rndm variable) n → unusual behavior

Logistic System

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

γn → Malthusian growth

αn^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 distribution of populations

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

can immediately write

$$\frac{dn}{dt} = (\gamma_0 + \tilde{\gamma})n - \alpha n^2$$

random

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

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

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

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

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

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

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

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

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

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

$$\sim 1/T \quad \checkmark$$

but now D nonlinear!! $\Rightarrow$ consequence of multiplicative character

$\Rightarrow$

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

$\Rightarrow$ Fokker-Planck Eqn. for f.

stationary state $\Rightarrow$

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

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

$\Rightarrow$

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

Now,

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

$$\cong -\frac{n}{\sigma^2} + \frac{\gamma_0}{\sigma^2} \ln(n)$$

$\Rightarrow$

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

PDF

and need:

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

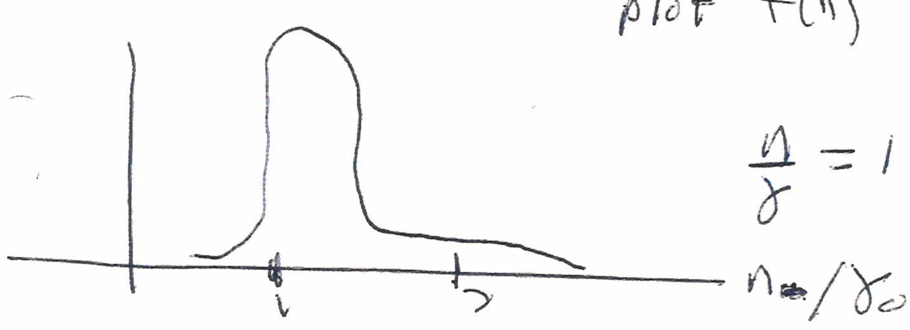
$\Rightarrow$

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

fluctuations in growth cannot be too large.

Meaning:

plot $f(n)$



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