Kinetics

Langevin,

Lecture [redacted] I: Kinetics – A Crash Course, I

Here, concerned with:

1) Thermal equilibrium fluctuations and Fluctuation – Dissipation Theorem

2) Pdf evolution, transport, diffusion.

1.) Thermal Equilibrium Fluctuations

– simplest possible dynamics question

$\Rightarrow$ What is spectrum of thermal equilibrium fluctuations in plasma?

– result:

(Spectrum) ~ (Dissipn) T

$\Rightarrow$ Fluctuation – Dissipation Theorem!

– follows from emission – absorption balance.

consider Brownian Motion (simplest)

$$m\frac{d\underline{v}}{dt} = -\gamma\underline{v} + \underline{f}$$

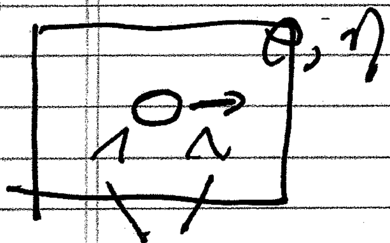
Langevin Eqn.

here: $\tilde{F}$ → rndm forcing due thermal flctns

$$\gamma = 6\pi\eta\ell$$

→ stokes law

I



$\tilde{f}$ → thermal flucts

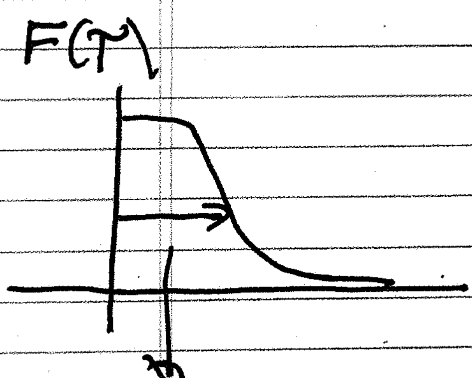
as $\tilde{F}$ random →

$$\langle \tilde{F}(t_1)\,\tilde{F}(t_2)\rangle = f_0^2\, F(t_2 - t_1)$$

f_0^2 ↓ strength

$(t_2 - t_1)$ → τ

F ↑ stationary series



↓

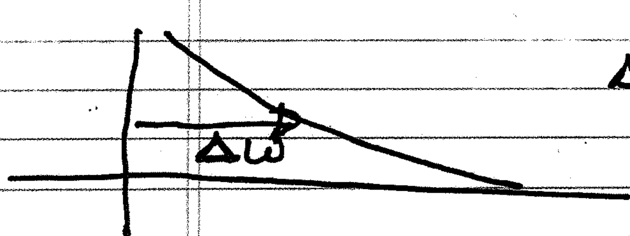
τ_{ac} ≡ self-correlation / coherence time

↓

spectral autocorrelation time

$$\int e^{+i\omega\tau} F(\tau) = F(\omega)$$

$\downarrow$ forcing spectrum (in frequency)



$\Delta\omega \equiv$ bandwidth

$$\Delta\omega \, \tau_{ac} \sim 1 \Rightarrow \tau_{ac} \sim 1/\Delta\omega$$

so for white noise: $\Delta\omega \to \infty$, $\tau_{ac} \to$ small

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

time order. $\leftarrow$; $\downarrow$ dims ; $\downarrow$ delta - correlated

Now, to solve for motion:

$$\frac{d\tilde{v}}{dt} + \frac{\gamma}{m}\tilde{v} = \frac{\tilde{f}}{m}$$

$$\tilde{v}(t) = e^{-\frac{\gamma t}{m}}\tilde{v}(0) + \int_0^t dt'\, e^{-\frac{\gamma}{m}(t-t')} \frac{\tilde{f}(t')}{m}$$

so

$$|\tilde{v}|^2 = e^{-2\frac{\gamma}{m}t}|\tilde{v}(0)|^2 + \text{cross terms}$$

$$\downarrow$$
$$T \qquad + \int^t dt' \, e^{-\frac{\gamma}{m}(t-t')}\frac{\tilde{f}(t')}{m} \int^t dt'' e^{-\frac{\gamma}{m}(t-t'')}\frac{\tilde{f}(t'')}{m}$$

so

$$\langle|\tilde{v}|^2\rangle = e^{-\cancel{2}\frac{\gamma}{m}t}|\tilde{v}(0)|^2$$
$$+ \int_0^t dt' \int_0^t dt'' \, e^{-\frac{\gamma}{m}(t-t'')} e^{-\frac{\gamma}{m}(t-t')} * \langle \tilde{f}(t')\,\tilde{f}(t'')\rangle / m^2$$

$\downarrow$ ensemble, statistical average

but $\langle \tilde{f}(t_1)\,\tilde{f}(t_2)\rangle = 2|\tilde{f}_0|^2 \tilde{\tau}_{ac}\,\delta(t_2-t_1)$

$$\langle|\tilde{v}|^2\rangle = e^{-2\frac{\gamma}{m}t}\langle|\tilde{v}(0)|^2\rangle$$
$$+ \int_0^t dt' \int_0^t dt'' \left[e^{-\frac{\gamma}{m}(t-t'')} e^{-\gamma(t-t')} * \frac{2|\tilde{f}_0|^2 \tilde{\tau}_{ac}}{m^2}\,\delta(t'-t'') \right]$$

integrating:

$$= e^{-2\frac{\gamma}{m}t}\langle|\tilde{v}(0)|^2\rangle$$
$$+ e^{-2\frac{\gamma}{m}t}\,\frac{2|\tilde{f}_0|^2\tilde{\tau}_{ac}}{m^2}\,\frac{1}{2\frac{\gamma}{m}}\left(e^{2\frac{\gamma}{m}t}-1\right)$$

$$\langle|\tilde{v}|^2\rangle = e^{-\frac{2\gamma}{m}t}\langle|\tilde{v}(0)|^2\rangle + \frac{\cancel{2}|\tilde{f}_0|^2\tilde{\tau}_{ac}}{\cancel{2}\gamma M}\left(1 - e^{-\frac{2\gamma}{m}t}\right)$$

so, for long time: $\gamma t \gg 1$

$$\langle|\tilde{v}|^2\rangle \cong \frac{|\tilde{f}_0|^2\tilde{\tau}_{ac}}{\gamma M}$$

but, as particle in thermal bath (fluid) at T:

$$\frac{m\langle|\tilde{v}|^2\rangle}{2} = T$$

$$T \cong \frac{|\tilde{f}_0|^2\tilde{\tau}_{ac}}{2\gamma}$$

$$\Rightarrow \boxed{\gamma T = \frac{|\tilde{f}_0|^2\tilde{\tau}_{ac}}{2}}$$

simple version: Fluctuation-Dissipation Theorem.

i.e.

(Noise) ~ (Damping) T

- clearly,

  Noise $\sim |\tilde{f}_0|^2 \tilde{\tau}_{ac}$

  Damping $\sim \gamma$

- given 2 of 3, deduce the third.

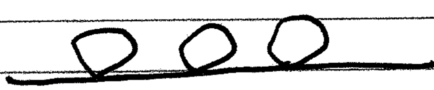
- equilibrium: → emission by noise

  → absorption by damping

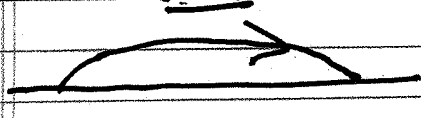
  ∴ balance matches T.

N.B.: Additional assumption: Linear system

→ emission and absorption at same scale

i.e. 

not



Alternatively:

① $$\partial_t \tilde{v} + \frac{\gamma}{m}\tilde{v} = \frac{\tilde{f}}{m}$$

$$\partial_t \cancel{\left\langle \frac{\tilde{v}^2}{2} \right\rangle}_{0} + \frac{\gamma}{m}\langle \tilde{v}^2 \rangle = \frac{\langle \tilde{f}\tilde{v} \rangle}{m}$$

stationary:

$$\gamma \langle \tilde{v}^2 \rangle = \langle \tilde{f}\tilde{v} \rangle$$

but $$\tilde{v}(t) = e^{-\gamma/m\, t}\,\tilde{v}(0) + \int_0^t e^{-\frac{\gamma}{m}(t-t')}\,\frac{\tilde{f}(t')}{m}\,dt'$$

$$\Rightarrow$$

$$\langle \tilde{v}^2 \rangle = \frac{2T}{m} = \frac{\cancel{m}}{\gamma}\left\langle \tilde{f}\int_0^t dt'\, e^{-\frac{\gamma}{m}(t-t')}\,\frac{\tilde{f}(t')}{m} \right\rangle$$

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

$$\langle \tilde{v}^2 \rangle = \frac{\cancel{2}T}{\cancel{m}} = \left(\frac{\cancel{2}}{\gamma}\right)\frac{|\tilde{f}_0|^2 \tau_{ac}}{\cancel{m}}$$

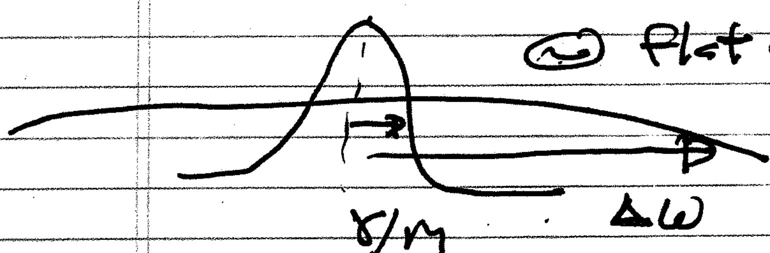
$\gamma T = 2|\tilde{f}_\omega|^2 \tau_{ac}$ (ignoring #)

(2) Transform in time:

$$(-i\omega + \gamma/M)\tilde{v}_\omega = \tilde{f}_\omega/M$$

$$|\tilde{v}_\omega|^2 = |\tilde{f}_\omega|^2 \Big/ M^2\left(\omega^2 + (\gamma/M)^2\right)$$

for white noise:



$\Delta\omega \gg \gamma/M$

$$\int d\omega\, |\tilde{v}_\omega|^2 = \int \frac{d\omega\, |\tilde{f}_\omega|^2}{M^2\left(\omega^2 + (\gamma/M)^2\right)}$$

$$\cong \frac{|\tilde{f}_\omega|^2}{M^2} \text{ [redacted] } \int d\omega \Big/ \left(\omega^2 + \left(\frac{\gamma}{M}\right)^2\right)$$

$$\cong \frac{|\tilde{f}_\omega|^2}{M^2} \frac{M}{\gamma} \; (\#)$$

Now, integrating:

$$\int d\omega \, |\tilde{V}_\omega|^2 = |\tilde{V}|^2 \cong T/m$$

$$\int d\omega \, |\tilde{f}_\omega|^2 d\omega \sim \Delta\omega |\tilde{f}_\omega|^2$$
$$\sim |\tilde{f}_0|^2 \qquad \Delta\omega \, T_{ac} \sim 1$$

$$|\tilde{f}_\omega|^2 \sim T_{ac} |\tilde{f}_0|^2$$

$\int d\tau \langle \tilde{F}^2(\tau) \rangle$

$\int d\tau \langle F(0) F(\tau) \rangle$

$= \int d\omega \langle \tilde{F}^2(\omega) \rangle$

$\langle \tilde{F}^2 \rangle_\omega = \int e^{-\omega\tau} \langle \tilde{F}(\tau) \rangle$

so

$$\frac{T}{\cancel{m}} \sim \frac{|f_0|^2}{\cancel{m^2}} T_{ac} \frac{\cancel{m}}{\gamma}$$

$$\boxed{|\tilde{f}_0|^2 T_{ac} \sim \gamma T}$$

Generally: $|\tilde{V}_\omega|^2 = \dfrac{|\tilde{f}_\omega|^2 / m^2}{|r(\omega)|^2}$

response function
(damping $\Leftrightarrow$ width)

$$\frac{I}{m} = \int d\omega \; \frac{|\overset{\text{acceleration}}{\tilde{a}(\omega)}|^2}{\underset{\text{response}}{|r(\omega)|^2}}$$

if now harmonically bound particle:

$$\ddot{x} + \gamma\dot{x} + \omega_0^2 x = \tilde{f}/m$$

$$|\tilde{x}_\omega|^2 = \frac{|\tilde{f}_\omega|^2/m^2}{(\omega_0^2-\omega^2)^2+(\gamma\omega)^2}$$

$$|\tilde{x}_\omega|^2 = \frac{|\tilde{f}_\omega|^2/m^2}{|r_{real}(\omega)|^2+|r_{Im}(\omega)|^2}$$

and/

$$\int |\tilde{x}_\omega|^2 = \langle \tilde{x}^2 \rangle$$

$$2\left(\frac{1}{2} k \langle \tilde{x}^2 \rangle\right) = 2\left(\frac{m\omega_0^2}{2} \langle \tilde{x}^2 \rangle\right) = T$$

so

$$T = m\omega_0^2 \langle \tilde{x}^2 \rangle = m\omega_0^2 \int d\omega \frac{|\tilde{a}_\omega|^2}{|r_r(\omega)|^2 + |r_{Im}(\omega)|^2}$$

$$\frac{1}{|r|^2} = \frac{1}{(\omega-\omega_0)^2 \left(\frac{\partial r}{\partial \omega}\right)^2 + |r_{Im}(\omega_0)|^2}$$

→ "pole approx"

→ expansion abt resonance $\left\{ \begin{array}{l} \text{resonance} \\ \text{damping} \end{array} \right.$

for flat $|\tilde{a}_\omega|^2$

$$T = m\omega_0^2 |\tilde{a}_{\omega_0}|^2 \int \frac{d\omega}{(\omega-\omega_0)^2 |r'|^2 + |r_{Im}(\omega_0)|^2}$$

$$= m\omega_0^2 \frac{|\tilde{f}_\omega|^2}{m^2} \Big/ |r_{Im}(\omega_0)| \left|\frac{\partial r_r}{\partial \omega}\right|_{\omega_0}$$

so key to FDT relation:

→ collective modes

→ mode damping

So, for Plasma's

Collective Modes
Damping

→ Vlasov Eqn.
Warm Plasma Wave ✓
~ Landau damping

Langevin Eqn for Plasma case?

$$m \frac{dv}{dt} = qE$$

$$\frac{dv}{dt} = \frac{q}{m} \tilde{E}(x,t) \quad , \quad \frac{dx}{dt} = v$$

↑ stochastic (field from "other" particles)

Damping? → <u>Collective</u>

→ Particles emit (damped) waves

⇒ Maintains steady state.

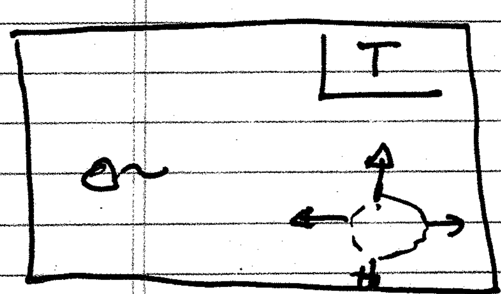
Kinetics — Fokker-Planck,

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

$\Rightarrow$ Diffusion – random walk
– evolution mean, square

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

else ?

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

$\Rightarrow$ Basic aspects of Fokker-Planck Theory.

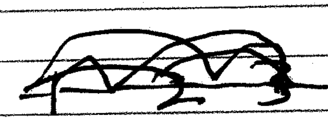
$\Rightarrow$ motivated by random walk, no memory

$\rightarrow$ Fokker-Planck Theory
$-\begin{cases}\text{An Introduction} \\ \text{To be continued later}\end{cases}$

Consider system with no memory $\leftrightarrow$ each step in τ independent prior history

so

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

$\xrightarrow{\quad 3 \quad} = \sum$ 

→ multiplicative as independent steps

→ sum over intermediate steps

⇒ Chapman - Kolmogorov Equation

Now, re-write as:

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

→ transition probability at x Δx in τ

$t_2 - t_1$ is jump time τ

$x_2 - x_1$ is jump step Δx

$$P(x, t+\tau) = \int d(\Delta x)\, P(x-\Delta x, t)\, T(x, \Delta x, \tau)$$

↓ small increment.

and expand.

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

→ "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)

$$T \sim 1/1 + (\Delta X)^\alpha$$

$(\alpha > 3)$

③ → T non uniform.

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

For Brownian Motion:

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

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

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:

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

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

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

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

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

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

$\stackrel{\text{so}}{\equiv}$

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

so finally, have Fokker-Planck Eqn.

drift Diffusion

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

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

$\Downarrow$

conserves probability $\Leftrightarrow$ Liouville structure

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

example : Brownian Motion

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

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

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

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)

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

at stationary state:

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

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

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

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

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

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

→ Gaussian formed by balance drag with diffusion

w/o drag:

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

how, ?

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

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

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

2's → symmetry

for short τ_{ac}

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

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

$$= 2 D_v t$$

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

→ generic structure:

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

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

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

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

$$\Gamma_v = -\underline{V} P - \underline{\nabla_v} \cdot \underline{\underline{D}}_v P$$

$\underline{V} P$: drift → deterministic element motion

$\underline{\nabla_v} \cdot \underline{\underline{D}}_v P$: ↳ diffusion — random noise relevant

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

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

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

— For Hamiltonian system:

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

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

so

$$\frac{\partial f(V,t)}{\partial t} = \frac{\partial}{\partial \underline{V}} \cdot \underline{\underline{D}}_V \cdot \frac{\partial f}{\partial \underline{V}} \qquad \left(\text{order } \frac{\partial}{\partial V} \right)$$

(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

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

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

deterministic

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

random

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

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

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

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

and recall from FDT

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

but

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

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

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

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

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

$D_x \rightarrow$ spatial diffusion coefficient

Applications:

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

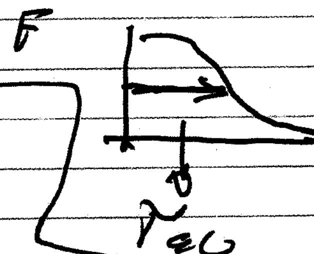
N.B.:

– Note:

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

so, can induce general form of D:
generic

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



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

D as integral of Lagrangian correlation function.

→ Noise: Additive and Multiplicative

Langevin Equation

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

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

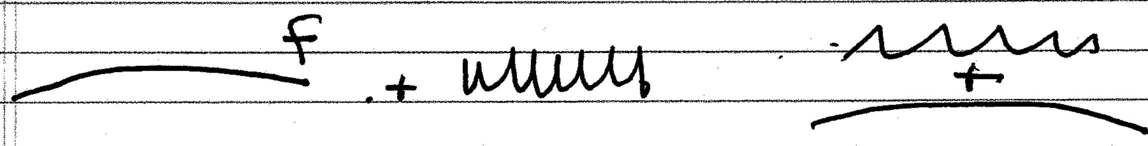
→ exponential growth + nonlinear saturation

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

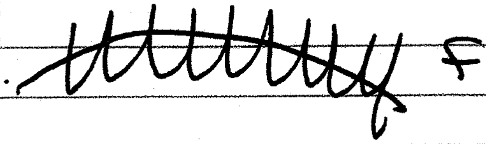
Now, introduce variability in k,

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

multiplicative noise (γ stochastic) i.e. additive:



multiplicative



f - TBD

obviously multiplicative noise presents several problems.

How treat:

- here: $\langle \tilde{\gamma}(t)\, \tilde{\gamma}(t') \rangle = |\tilde{\gamma}|^2 \tau_{c0}\, \delta(t-t')$, for simplicity
- Fokker-Planck Eqn.

$\Rightarrow$

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

[redacted]

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

$$= |\gamma_0|^2 \tilde{\tau}_{ac} N^2 \, t$$

$$D = |\gamma_0|^2 \tau_{ac} \underbrace{N^2}_{\text{nonlinearity}}$$

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

so stationary $f(N) \Rightarrow$

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

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

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

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

Kinetics Lecture III: Central Limit Theorem, etc.

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:

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

Γ ↓ # 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

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

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:

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

Every random walk characterized by these.

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

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

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

$\Rightarrow$

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

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. Existence 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

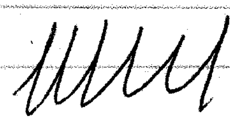
- fundamentally mathematical structure of random walk paths is rough

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

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

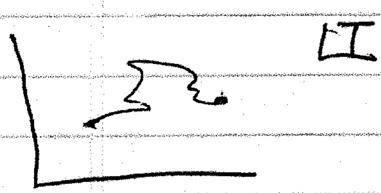
i.e. usual: $f(t+\Delta t) - f(t) \sim \Delta t$

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 $\partial_t \int d^3x \; n^2$ 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.

$-\beta \underline{v}$ → 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.

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

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

What is $\tilde{f}$?

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

steady state:

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

Power dissipated by drag — Power input by Brownian force.

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 $\underline{v} \sim \tilde{f}/\beta$ (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 Fluctuation-Dissipation Theorem!

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

→ 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

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

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

$$\sim \frac{\tilde{f}^2}{\beta^2} \Delta t\, t$$

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 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:

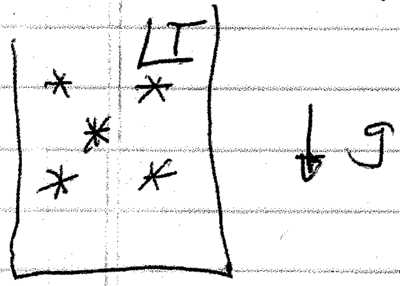
Boltzmannia	Fokker-Planckology
$\tau_{int} = d/v_{Th}$ collisional interaction	τ_{ac}
$\tau_{col} = \frac{l_{mfp}}{v_{Th}}$	τ_c
$\tau_{relax} \sim \tau_{col} \cdot \frac{L^2}{l_{mfp}^2}$	$\tau_{macro} \sim \tau_c \frac{L^2}{(\Delta x)^2}$

N.B. ① Analogy only!

② Note:

- Boltzmannia allows arbitrary collision
- F.P. I $\Rightarrow$ 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:
(neglect 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. ⇒

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

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

↳ drift speed

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

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

$$= \mu \underline{F}$$

— 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

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

→ for steady state:

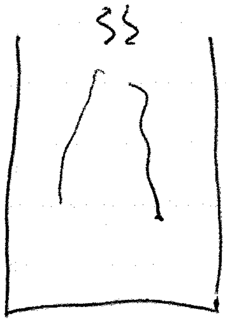
$$\frac{\partial n}{\partial t} = -\frac{\partial}{\partial z}\left\{-\frac{mg}{\beta} n - \frac{T}{\beta}\frac{\partial n}{\partial z}\right\}$$

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

balance is:
- vertical drift
vs.
- upper diffusion

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

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.

Multiplicative Noise

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

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

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

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

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

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

$$\langle \tilde{\gamma}(t_1)\, \tilde{\gamma}(t_2) \rangle = \tilde{\gamma}^{02}\, \tau_{ac}\, \delta(t_2 - t_1)$$

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

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

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

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

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

$$\sim 1/T$$

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

$\Rightarrow$

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

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

Stationary state $\Rightarrow$

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

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

$\Rightarrow$

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

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:

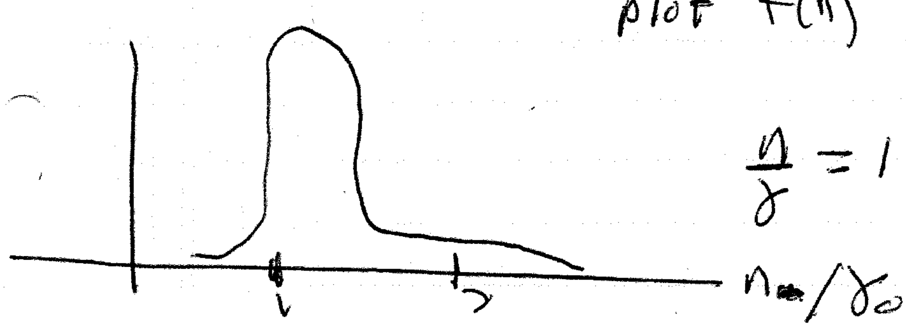
$\frac{\gamma_0}{\sigma^2} - 2 > -1$ to assure integrability

$\Rightarrow$

$\boxed{\gamma_0/\sigma^2 > 1}$ fluctuations in growth cannot be too large.

Meaning:

plot $f(n)$



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