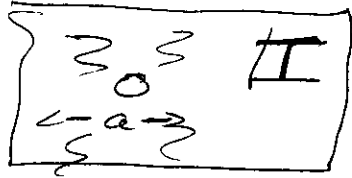


→ What's the Physics



- small particle immersed in thermally conducting fluid at T , which exhibits thermal fluctuations
- thermal fluctuations "kick" particle \Rightarrow random, noise force acts on particle: \tilde{F}
- scales: $(\Delta x)_{th} \ll a \ll L$
 - Δx_{th} : typical scale of fluctuation mode
 - a : particle size
 - L : system size
- \Rightarrow noise is spatially homogeneous.
- dissipative system \Rightarrow drag of fluid on particle is important.

80

$$M \frac{dv}{dt} = F_{\text{friction}} + f_{\text{thermal noise}}$$

$$= -\gamma_s (v - v_{\text{fluid}}(x,t)) + f_{\text{thermal noise}}$$

$\underbrace{\gamma_s}_{\text{Stokes drag}} \quad \underbrace{\quad}_{\text{frictional slippage force}}$

for $M\omega \ll \gamma_s \Leftrightarrow$ dissipation dominated limit (equivalent to inertialess particle)

\Rightarrow

$$\frac{d\underline{v}}{dt} = -\gamma \underline{v} + \tilde{Q}_{\text{thermal}}$$

Langevin Equation

$\gamma = \gamma_s / M$

$\gamma_s = 6\pi\eta a \rightarrow$ Stokes Drag

η fluid viscosity (mass dependent)
 a particle size

main problem:

$\frac{d\underline{v}}{dt} = -\gamma \underline{v} + \tilde{Q}_{\text{thermal}}$

\downarrow dissipation
 \downarrow noise \rightarrow "Random" [additive noise]

typical questions:

- \rightarrow what is $\langle \underline{v}(t) \underline{v}(t') \rangle$? [correlation function]
- \rightarrow determine $\langle \underline{v}^2 \rangle$, $\langle \underline{v}^2 \rangle_\omega$ - spectrum [level]
- relate $\langle \underline{v}^2 \rangle_\omega$, $\langle \underline{a}^2 \rangle_\omega$ & γ
 (Fluctuation - Dissipation)

→ Basic Time Scales

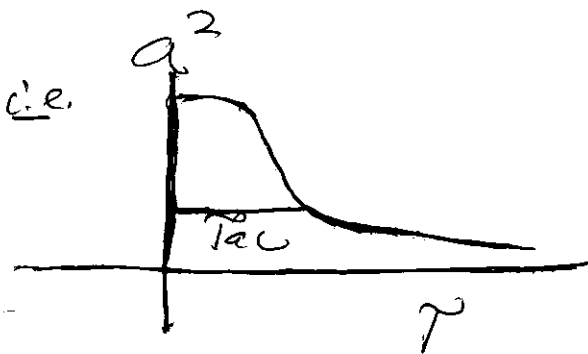
- $\tau_{ac} = \tau_{\text{autocorrelation}} \rightarrow$ self-correlation time of random force
- $\gamma^{-1} \rightarrow$ velocity relaxation time (i.e. damping time)
- $\tau_{\text{macro}} \rightarrow$ any macroscopic time scale
i.e. time to drift across box.

and order: $\tau_{ac} \ll \gamma^{-1} \ll \tau_{\text{macro}} \rightarrow$ key ordering

→ Meaning of "Random" and " τ_{ac} "

- τ_{ac} is self-correlation time of \tilde{q} , i.e.

$$\begin{aligned} \langle \tilde{q}(t) \tilde{q}(t+\tau) \rangle &= \text{(auto) correlation function of } \tilde{q} \\ &= \langle \tilde{q}^2(t) \rangle \text{ for stationary process} \\ &\text{(no bias forward/back in temporal evolution)} \end{aligned}$$



τ_{ac} is decay time of self-correlation function

$\rightarrow \tau_{\text{co}}$ measures duration time of φ
 "random kick"

(*)

$\tau_{\text{co}} < \gamma^{-1} < \tau_{\text{macro}} \Rightarrow$ many kicks in
 motion damping time

$\rightarrow \tau_{\text{co}} \leftrightarrow$ bandwidth of forcing spectrum...

i.e. Wiener-Khinchine Theorem:

$$\langle \tilde{f}(t) \tilde{f}(t+\tau) \rangle = \int e^{-i\omega\tau} |f(\omega)|^2 d\omega / 2\pi$$

\downarrow auto-correlation function \downarrow spectral density

true
 for
stationary

process

Proof: Stationarity $\Rightarrow \langle \tilde{f}_\omega \tilde{f}_{\omega'} \rangle = |f(\omega)|^2 \delta(\omega + \omega')$
 $\equiv \langle \tilde{f}^2 \rangle_\omega \delta(\omega + \omega')$

i.e. $\langle \tilde{f}^2 \rangle_\omega$ is F.T. (in τ) of
 correlation function

of course: $\int d\omega \langle \tilde{f}^2 \rangle_\omega = \int d\omega |f(\omega)|^2$

strength parameter

usually:

$$\langle \tilde{F}^2 \rangle_\omega = \frac{\tilde{f}_0^2 \Delta\omega}{(\omega - \omega_0)^2 + \Delta\omega^2}$$

\downarrow
 centroid frequency \downarrow
 bandwidth linewidth

a.) $\langle \tilde{F}(t) \tilde{F}(t+\tau) \rangle \sim \tilde{f}_0^2 e^{-i\omega_0 \tau} e^{-|\Delta\omega| \tau}$

\downarrow
 oscillation \downarrow
 decay of correlation

so

$$\tau_{\text{cor}} = 1/\Delta\omega$$

\downarrow
bandwidth

b.) $\Delta\omega \rightarrow 0, |f(\omega)|^2 \rightarrow \delta(\omega - \omega_0)$

coherency \rightarrow
narrow bandwidth
case

c.) $\Delta\omega \rightarrow \infty \Rightarrow |f(\omega)|^2 = \tilde{f}_0^2 / \Delta\omega$

$$\langle \tilde{F}(t) \tilde{F}(t+\tau) \rangle = \frac{\tilde{f}_0^2}{\Delta\omega} \delta(\tau)$$

"delta correlated" limit.

→ re: What does "Random" Mean?

Consider what response to noise appears...

$$\frac{dv}{dt} + \gamma v = \tilde{q}(t)$$

$$(-i\omega + \gamma)V_\omega = \tilde{q}_\omega$$

$$\therefore |\tilde{v}(\omega)|^2 = |\tilde{q}(\omega)|^2 / [\omega^2 + \gamma^2]$$

$$= |R(\omega)|^2 |\tilde{q}(\omega)|^2$$

\int
response
function.

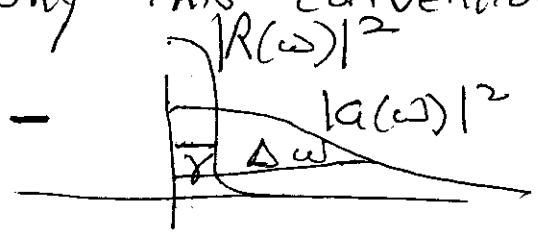
↳ forcing spectrum
(i.e. Lorentzian, as
before)

Effectively, "Random" \Leftrightarrow

- \tilde{q} distributed statistically (i.e. quasi-Gaussian, etc.)

- $\Delta\omega \gg \gamma$ a.e. bandwidth exceeds response rate.

Why this convention?



\Rightarrow can take $|a(\omega)|^2 \sim \text{flat}$

o.o

- can take noise spectrum as effectively "white" \Leftrightarrow constant in ω .

N.B. "Of course, can speak of "colored noise"
 "Colored noise" \rightarrow statistically distributed \vec{a}
 \rightarrow non-flat spectrum
 i.e. $\langle \vec{a}^2 \rangle_{\omega} \sim \omega^{-p}$

"Colored noise" \Leftrightarrow { effective memory
range of time scales

\rightarrow can become tricky

- "white noise" is classic example \Rightarrow only time scale is system response.

Which brings us to

→ the answer: velocity correlation function

In $\Delta\omega \rightarrow \infty$, (white noise) limit:

$$\langle v(t)v(t+\tau) \rangle = \int \frac{e^{-i\omega\tau}}{2\pi} \frac{|g_0|^2 d\omega}{\Delta\omega (\omega^2 + \gamma^2)}$$

$$\sim \frac{|g_0|^2}{\Delta\omega} \frac{e^{-\gamma|\tau|}}{\gamma}$$

and

$$\langle v(t)v(t) \rangle = \langle v(0)^2 \rangle = |g_0|^2 / \Delta\omega\gamma$$

→ but particle is in thermal fluid, at thermal equilibrium, at temperature T ,

$$\frac{M \langle v^2 \rangle}{2} = \frac{k_B T}{2}$$

but

$$\frac{M \langle v^2 \rangle}{2} = \frac{M |g_0|^2}{2 \Delta\omega\gamma}$$

∞

$$q_0^2 / \Delta\omega \gamma = k_B T$$

$$\Rightarrow \left\{ \frac{q_0^2}{\Delta\omega} = \gamma k_B T \right.$$

noise intensity
damping
temperature

\Rightarrow primitive form of "Fluctuation-Dissipation Theorem".

i.e. more rigorous form: (will prove)

$$X(\omega) = \alpha(\omega) f(\omega)$$

displacement
forcing

response function

i.e. susceptibility $\leftrightarrow \epsilon(k, \omega)$, etc.

$$\alpha = \alpha_{\text{real}} + i \alpha_{\text{IM}}$$

when $F=D$, T. relation is:

fluctuating intensity
↕
↪ temp.

$$\langle X^2 \rangle_\omega = \frac{2T}{\omega} \frac{\text{Im } \alpha(\omega)}{\omega}$$

↪ damping

$$\hbar\omega \ll k_B T$$

or in QM case:

$$\langle X^2 \rangle_\omega = \hbar \text{Im } \alpha(\omega) \coth \frac{\hbar\omega}{2T}$$

↕
operator expectation

$$\hbar\omega / k_B T \text{ finite}$$

→ basically same content as simple case ...
Will demonstrate general case next week via consideration of generalized susceptibility.

→ Essence of F-D. Thm:

- temperature, dissipation rate (Im α) and fluctuation intensity "locked" together at thermal equilibrium, via.

$$(\text{Intensity}) \sim (\text{Damping Rate}) T$$

- pick 2 + equilibrium ⇒ 3rd.

- at equal T, more damping ⇒ stronger intensity fluctuations.

→ Related: Random Processes and Diffusion - A Review

→ Fundamental: Central Limit Theorem

Meaning: IF:

- observation 'error' X is accumulation of large number of small errors ($N \rightarrow \infty$)
- moments of small error pdf exist

Then Total Error X follows Gaussian or "Normal" Distribution.

Precise Statement:

→ Consider a sum of $N \gg 1$ independent random variables (increments)

$$\Delta X_1, \Delta X_2, \dots, \Delta X_N.$$

take:
$$X_N = \sum_{i=1}^N \Delta X_i$$
 (accumulated increment)

$$\sigma_N^2 = \sum_{i=1}^N \sigma_i^2$$

where: $\langle \Delta x_i \rangle = 0$

$\langle \Delta x_i^2 \rangle = \sigma_i^2 \rightarrow$ key provided:
2nd moment exists.

then gives 'appropriate conditions' on
 Δx_i ,

\Rightarrow Pdf of $y_n = X_n/S_n \rightarrow$ Gaussian Distribution
as $N \rightarrow \infty$

so $\lim_{N \rightarrow \infty} \text{Pdf}(X_n/S_n) \rightarrow \frac{1}{\sqrt{2\pi}} \exp(-y^2/2)$

"Appropriate Conditions":

second
- moment of each random step/variable
pdf exists

\rightarrow THIS IS CRUCIAL ----

- N random variables Δx_i "all alike" i.e.
no special few 'bias' or 'dominate'
the others ----

Example: IMPORTANT

- net displacement of Brownian particle is sum of many, successive small displacements

$$\text{i.e. } \tau_{\text{micro}} < \delta t < \tau_{\text{macro}}$$

∴

- expect distribution of net displacement

$$\Delta X_N = \sum_{i=1}^N \Delta X_i$$

to be Gaussian (as $N \rightarrow \infty$) even if

a random walk description is not valid

for short intervals of time.

N.B.: Explains why macro/long time dynamics of many systems are Gaussian, even if micro dynamics are not Gaussian,

Why Gaussian random processes are ubiquitous?

→ Machinery for Gaussian Processes.

- If random variable X has pdf $f(x)$
s/f

$$\langle X^n \rangle = \int_{-\infty}^{+\infty} dx x^n f(x)$$

then can define characteristic function

$$\Phi(\varepsilon) = \langle e^{i\varepsilon X} \rangle = \int_{-\infty}^{+\infty} dx f(x) e^{i\varepsilon X}$$

$\Phi(\varepsilon) \Leftrightarrow$ Fourier transform of pdf; obviously of great interest!

- can relate to moments:

$$\langle X^n \rangle = i^{-n} \left[\left(\frac{d}{d\varepsilon} \right)^n \Phi(\varepsilon) \right]_{\varepsilon \rightarrow 0}$$

so equivalent to:

$$\Phi(\varepsilon) = \sum_{n=0}^{\infty} \frac{(i\varepsilon)^n}{n!} \langle X^n \rangle$$

ie. sum of moments defines $\bar{\Phi}(\epsilon)$ and thus pdf.

\Leftrightarrow knowledge of all moments equivalent to knowledge of pdf via characteristic function.

For Gaussian/Normal distribution:

$$f(x) = \frac{1}{\sqrt{2\pi}\sigma} \exp\left(-\frac{(x-\mu)^2}{2\sigma^2}\right)$$

\Rightarrow

$$\bar{\Phi}(\epsilon) = \exp\left[i\mu\epsilon - \frac{\sigma^2\epsilon^2}{2}\right]$$

Can define cumulant:

$$\bar{\Phi}(\epsilon) = e^{\psi(\epsilon)}$$

\downarrow
 cumulant function

$$\psi(\epsilon) = \ln \bar{\Phi}(\epsilon)$$

Now:

$$- \psi(\epsilon) = \sum_{n=1}^{\infty} \frac{(\epsilon)^n}{n!} \langle x^n \rangle_c$$

↓
nth cumulant

- i.e. $\langle x \rangle_c = \langle x \rangle$

$$\langle x^2 \rangle_c = \langle x^2 \rangle - \langle x \rangle^2$$

$$\langle x^3 \rangle_c = \langle x^3 \rangle - 3\langle x \rangle \langle x^2 \rangle + \langle x \rangle^3$$

etc.

- note analogy:

characteristic
function

$$\phi(\epsilon) = \langle e^{i\epsilon x} \rangle$$

Eq. brn Stat Mech
Partition
Function Z

Cumulant
function

$$\psi(\epsilon) = \ln \phi \leftrightarrow \text{Free Energy } F$$

→ Fluctuation Theory II

a.) Revisiting the Fluctuation-Dissipation Theorem
(Ref: Landau, Lifshitz, Stat. Physics)

To generalize the Fluctuation-Dissipation Theorem, need:

- generalized susceptibility
- Kramers-Kronig Relations
- F.D. Thm.

1.) Generalized Susceptibility (extends to QM systems)

Each physical quantity associated with a thermal fluctuation in a system can be associated with a perturbation in the Hamiltonian, i.e.

$$H = H_0 + \hat{V}$$

where $\hat{V} = -\hat{X} f(t)$

\hat{X} → operator associated with physical quantity
 $f(t)$ → generalized force (fctn. of time)

Now, $\bar{X} \equiv$ mean, in quantum sense, of state of system → i.e. expected response

Then,

$$\bar{X}(t) = \bar{\chi} F = \int_{-\infty}^{\infty} \chi(\tau) f(t-\tau) d\tau$$

\downarrow system response to perturbation \downarrow forcing
generalized susceptibility (linear)
 \rightarrow determined by system

In ω space;

$$\bar{X}(\omega) = \chi(\omega) f(\omega)$$

\downarrow response \downarrow susceptibility \rightarrow forcing

d.e.

$$\underline{D}(\omega) = \epsilon(\omega) \underline{E}(\omega)$$

\downarrow displacement field \downarrow dielectric function \rightarrow electric field

or

$$X(\omega) = \alpha(\omega) f(\omega)$$

\downarrow oscillator displacement \downarrow linear response \rightarrow forcing

$$\begin{cases} m \frac{d^2 x}{dt^2} + 2m\gamma \frac{dx}{dt} + kx = fA \\ \alpha(\omega) = f/m / (\omega_0^2 - \omega^2 + 2i\gamma\omega) \end{cases}$$

General Properties of Susceptibility:

- $\chi(\omega)$ complex $\chi(\omega) = \chi_r(\omega) + i\chi_{IM}(\omega)$
 $= \chi'(\omega) + i\chi''(\omega)$
- $\chi(-\omega) = \chi(\omega)^*$

$$\text{from } \chi(\omega) = \int_0^{\infty} \chi(t) e^{i\omega t} dt$$

$$\infty \begin{cases} \chi_r(-\omega) = \chi_r(\omega) \\ \chi_{IM}(-\omega) = -\chi_{IM}(\omega) \end{cases}$$

$$- \chi(-\omega^*) = \chi^*(\omega)$$

- Meaning of $\chi_{IM} \leftrightarrow$ Dissipation!

$$\text{Now, } \frac{dE}{dt} = \overline{\partial H / \partial t} \rightarrow \text{rate of energy absorption}$$

↓
energy evolution

so mean rate of work done by external force is:
 \rightarrow rate of change of external force.

$$\frac{dE}{dt} = + \overline{\partial H} = - \overline{x} \frac{df(t)}{dt}$$

$$\text{Now, } \frac{dE}{dt} = \left\langle \frac{-1}{2} \left[\chi(\omega) f_0 e^{-i\omega t} + \chi(-\omega) f_0^* e^{i\omega t} \right] \left[\frac{1}{2} \left[c\omega f_0 e^{-i\omega t} + c\omega f_0^* e^{i\omega t} \right] \right] \right\rangle$$

(single ω)

dissipation rate



$$\therefore \frac{dE}{dt} = Q = -\frac{|f_0|^2}{4} \left\{ \alpha(-\omega)(-i\omega) + i\omega \alpha(\omega) \right\}$$

$$= \frac{|f_0|^2}{4} 2\omega \alpha_{IM}(\omega)$$

$$Q = \frac{|f_0|^2}{2} \omega \alpha_{IM}(\omega)$$

→ imaginary part $\alpha \leftrightarrow$ dissipation

→ as dissipation is absolutely necessary can conclude

$$\text{Im } \alpha(\omega) > 0, \text{ for } \underline{\underline{\text{all } \omega}}$$

[Can one formulate F-D. Thm for unstable system?]
 (i.e. system with growing modes)

- $\alpha(\omega)$ is single valued, regular function everywhere in UHP.

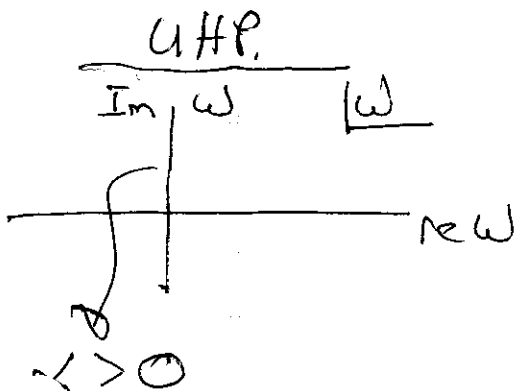
$$\text{i.e. } \alpha(\omega) = \int_0^{\infty} e^{i\omega t} \alpha(t) dt$$

finiteness, causality

Now, can prove the following theorem:

[see L&L Stat. Phys. pgs 380-381 for proof]

Thm: The function $\chi(\omega)$ does not take real values at any finite point in the UHP except on the imaginary axis, where it decreases monotonically from $\chi_0 > 0$ at $\omega = i0$ to $\chi = 0$ at $\omega \rightarrow i\infty$. Thus, $\chi(\omega)$ has no zeroes in



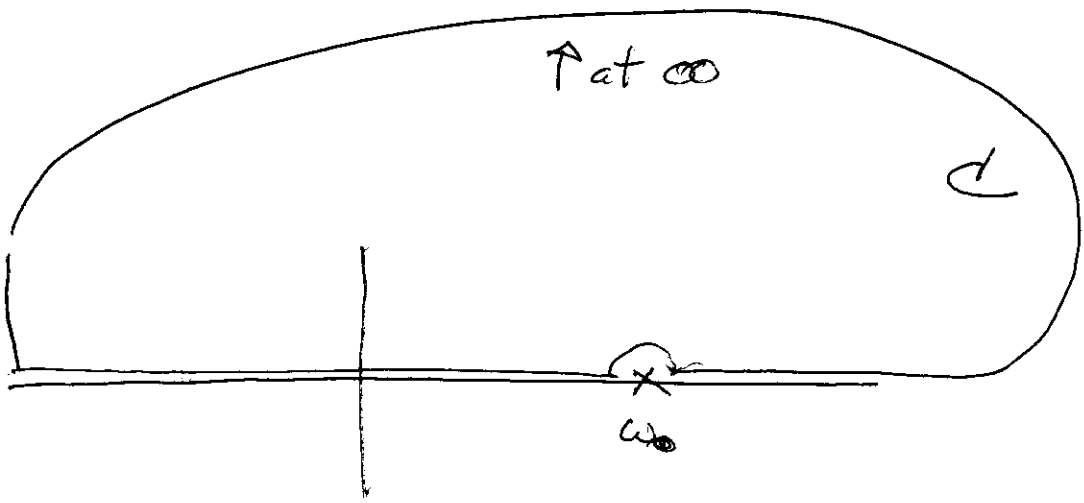
Point: $\chi(\omega)$ has no zeroes for $\text{Im } \omega > 0$.
i.e. zero is "real" value!

As a consequence of the theorem, can prove the Kramers-Kronig Relations.

b.) Kramers-Kronig Relations

Define:
$$I = \int_C \frac{\chi(\omega)}{\omega - \omega_0} d\omega$$

where contour C specified by:



Now $I = \int dw \frac{\alpha(w)}{w-w_0}$

and
 $\rightarrow w \rightarrow \infty \Rightarrow \alpha \rightarrow 0$
 $\rightarrow \alpha/w-w_0 \rightarrow 0$ more rapidly than $1/w$

$\therefore I$ converges

\rightarrow Since the point w_0 is excluded and Thm \Rightarrow
 $\alpha(w)$ is regular in UHP

$\Rightarrow I = 0!$

but $1/w-w_0 = \frac{P}{w-w_0} = i\pi \delta(w-w_0)$

so $I = \int_{-\infty}^{+\infty} dw \frac{\alpha(w)}{w-w_0} = \int_{-\infty}^{+\infty} dw \alpha(w) - i\pi \alpha(w_0)$

as semicircle-at-infinity contribution vanishes.

So

Have $i\pi\alpha(\omega) = P \int_{-\infty}^{+\infty} \frac{\alpha(\omega')}{\omega - \omega'} d\omega'$

Now, simply equate real and imaginary parts of above, noting: $\alpha(\omega) = \alpha_{\text{r}}(\omega) + i\alpha_{\text{IM}}(\omega)$

$$\alpha_{\text{r}}(\omega) = \frac{1}{\pi} P \int_{-\infty}^{+\infty} \frac{\alpha_{\text{IM}}(y)}{y - \omega} dy$$

$$\alpha_{\text{IM}}(\omega) = -\frac{1}{\pi} P \int_{-\infty}^{+\infty} \frac{\alpha_{\text{r}}(y)}{y - \omega} dy$$

Note:

→ these constitute Kramers-Kronig Relations ⇔ sometimes called dispersion relations.

→ only properties used in proof are:

- linearity of response

- $\alpha(\omega)$ regular in UHP ⇔ CAUSALITY

→ K-K. Reln. ⇔ link, constrain structure of alpha.
 ⇔ constrain structure of the response.

→ How are k_1 - k_2 Relations modified by $\chi(\omega)$ having a pole at $\omega=0$.

→ How can we exploit the structure of $\chi_{IM}(\omega)$ to simplify the relation for $\chi_{real}(\omega)$.

This brings us to:

3.) the Fluctuation-Dissipation Theorem

Recall definition of spectral density:

$$\left\{ \begin{aligned} \langle X_\omega X_{\omega'} \rangle &= 2\pi (X^2)_\omega \delta(\omega + \omega') \\ \phi(t) = \langle X(0) X(t) \rangle &= \int_{-\infty}^{+\infty} (X^2)_\omega e^{-i\omega t} \frac{d\omega}{2\pi} \end{aligned} \right.$$

For X interpreted as an operator \hat{X} ?

$$2\pi (X^2)_\omega \delta(\omega + \omega') = \frac{1}{2} \langle \hat{X}_\omega \hat{X}_\omega + \hat{X}_\omega \hat{X}_\omega \rangle \quad (\text{symmetrize order})$$

Now, the body which \hat{X} 'acts on' / 'measures' is assumed to be in n^{th} stationary state, so

$$\frac{1}{2} (\hat{X}_\omega \hat{X}_{\omega'} + \hat{X}_{\omega'} \hat{X}_\omega)_{nn} = \frac{1}{2} \sum_m \left[(X_\omega)_{nm} (X_{\omega'})_{mn} + (X_{\omega'})_{nm} (X_\omega)_{mn} \right]$$

\uparrow
 diagonal matrix
 element \rightarrow
 expectation

Must calculate time dependence of $\hat{X}(t)$ via matrix elements \Rightarrow need time-dependent wave functions.
 matrix element (time independent)

so

$$(X_\omega)_{nm} = \int_{-\infty}^{+\infty} dt X_{nm} e^{i(\omega_{nm} + \omega)t} = 2\pi X_{nm} \delta(\omega_{nm} + \omega)$$

$$\omega_{nm} = (E_n - E_m) / \hbar$$

so

$$\frac{1}{2} (\hat{X}_\omega \hat{X}_{\omega'} + \hat{X}_{\omega'} \hat{X}_\omega) = 2\pi^2 \sum_m |X_{nm}|^2 \left[\delta(\omega_{nm} + \omega) \delta(\omega_{nm} + \omega') + \delta(\omega_{nm} + \omega') \delta(\omega_{nm} + \omega) \right]$$

$(X_{nm} = X_{mn}^*)$

$$= 2\pi^2 \sum_m |X_{nm}|^2 \left[\delta(\omega_{nm} + \omega) \delta(\omega + \omega') + \delta(\omega_{nm} + \omega) \delta(\omega + \omega') \right]$$

and since

$$2\pi (X^2)_\omega \delta(\omega + \omega') = \frac{1}{2} \langle \hat{X}_\omega \hat{X}_{\omega'} + \hat{X}_{\omega'} \hat{X}_\omega \rangle$$

have finally,

$$(X^2)_\omega = \pi \sum_m |X_{nm}|^2 \left[d(\omega + \omega_{nm}) + d(\omega + \omega_{mn}) \right]$$

→

Now, body is subject to periodic perturbation:

$$+V = - \hat{X} f = -\frac{1}{2} (f_0 e^{-i\omega t} + f_0^* e^{i\omega t}) \hat{X}$$

An perturbation is time-dependent, body makes transitions, and probability-per-time of the

transition $n \rightarrow m$ is given by Fermi Golden Rule, i.e.

$$W_{m,n} = \frac{\pi |f_0|^2}{2\hbar^2} |X_{m,n}|^2 \left\{ d(\omega + \omega_{m,n}) + d(\omega + \omega_{nm}) \right\}$$

transition probability

→ Total energy absorption of body is:

$$dE/dt = Q = \sum_m W_{m,n} (\hbar \omega_{m,n})$$

∴

$$Q = \frac{\pi}{2\hbar} |f_0|^2 \sum_m |X_{nm}|^2 \left\{ \delta(\omega + \omega_{mn}) + \delta(\omega - \omega_{nm}) \right\} \omega_{mn}$$

$$Q = \frac{\pi}{2\hbar} |f_0|^2 \omega \sum_m |X_{nm}|^2 \left\{ \delta(\omega + \omega_{nm}) - \delta(\omega - \omega_{mn}) \right\}$$

using δ prop.

$$\text{but } Q = \frac{1}{2} \omega \alpha_{IM}(\omega) |f_0|^2$$

$$\text{so } \alpha_{IM}(\omega) = \frac{\pi}{\hbar} \sum_m |X_{nm}|^2 \left\{ \delta(\omega + \omega_{nm}) - \delta(\omega - \omega_{mn}) \right\}$$

Note: $\alpha_{IM}(\omega) \Leftrightarrow$ dissipation clearly closely related to

$$\langle X^2 \rangle_\omega = \pi \sum_m |X_{nm}|^2 \left\{ \delta(\omega + \omega_{nm}) + \delta(\omega - \omega_{mn}) \right\}$$

which is the fluctuation level, so

are "almost there" on F-D.T. ↓

- Key Points:
- Fermi Golden Rule
 - $Q = \sum_m \hbar \omega_{mn} W_{mn}$

To complete F-D. Thm, need relate dissipation $\alpha_{IM}(\omega)$ and fluctuation $(X^2)_\omega$ to temperature of body ----

to do this, average over distribution function:

$$\text{d.e.} \quad (X^2)_\omega = \pi \sum_{n,m} \int_0^1 \exp[-(En)/T] \rho_n |X_{nm}|^2 \left\{ d(\omega + \omega_{nm}) + d(\omega + \omega_{mn}) \right\}$$

noting interchangeability of indexes, have (flip in 2nd term):

$$\begin{aligned} (X^2)_\omega &= \pi \sum_{m,n} (\rho_n + \rho_m) |X_{nm}|^2 d(\omega + \omega_{nm}) \\ &= \pi \sum_{m,n} \rho_n (1 + e^{-\hbar \omega_{nm}/T}) |X_{nm}|^2 d(\omega + \omega_{nm}) \\ &= \pi (1 + e^{-\hbar \omega/T}) \sum_{m,n} \rho_n |X_{nm}|^2 d(\omega + \omega_{nm}) \end{aligned}$$

$$\therefore \left(X^2 \right)_\omega = \pi (1 + e^{-\hbar \omega/T}) \sum_{m,n} \rho_n |X_{nm}|^2 d(\omega + \omega_{nm})$$

and can similarly show for $\alpha_{IM}(\omega)$:

$$\alpha_{\text{IM}}(\omega) \cong \frac{\pi}{\hbar} (1 - e^{-\hbar\omega/T}) \sum_{m,n} \rho_n |X_{n,m}|^2 \delta(\omega + \omega_{n,m})$$

and had

$$\langle X^2 \rangle_{\omega} \cong \pi (1 + e^{-\hbar\omega/T}) \sum_{m,n} \rho_n |X_{n,m}|^2 \delta(\omega + \omega_{n,m})$$

$$\langle X^2 \rangle_{\omega} = \hbar \alpha_{\text{IM}}(\omega) \coth \frac{\hbar\omega}{2T}$$

$$= 2\hbar \alpha_{\text{IM}}(\omega) \left\{ \frac{1}{2} + \frac{1}{e^{\hbar\omega/T} - 1} \right\}$$

and, integrating over ω :

$$\langle X^2 \rangle = 2 \int_0^{\infty} \frac{d\omega}{2\pi} \langle X^2 \rangle_{\omega} = \frac{\hbar}{\omega} \int_0^{\infty} \alpha_{\text{IM}}(\omega) \coth \frac{\hbar\omega}{2T}$$

this proves F-D. Thm!

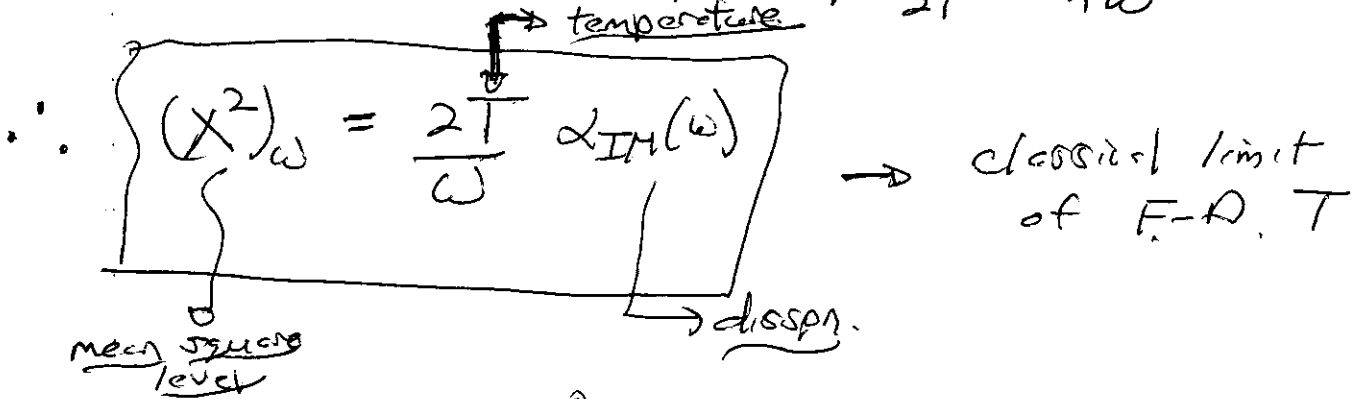
Now, can observe:

- in general $(X^2)_\omega = \hbar \operatorname{Im} \alpha(\omega) \coth \frac{\hbar \omega}{2T}$

in classical limit: $\hbar \omega \ll T$

$$\coth \frac{\hbar \omega}{2T} \approx \frac{1}{\frac{\hbar \omega}{2T}} \approx \frac{2T}{\hbar \omega}$$

→ temperature



and: $\langle X^2 \rangle = \frac{2T}{\pi} \int_0^\infty \frac{\alpha_{IM}(\omega)}{\omega} d\omega$

but K-K. ReIm \Rightarrow $\operatorname{Re} \alpha(\omega) = \frac{2}{\pi} \int_0^\infty \frac{y \alpha_{IM}(y)}{(y^2 - \omega^2)^2} dy$
 (from α_{IM} odd)

$\therefore \frac{2T}{\pi} \int_0^\infty \frac{\alpha_{IM}(\omega)}{\omega} d\omega = T \alpha_{\operatorname{Re}}(\omega) \Big|_0 = T \alpha_{\operatorname{Re}}(0)$

So $\langle x^2 \rangle = T \alpha(\omega)_{\text{Real}} \rightarrow \text{useful form}$

- can re-formulate theory to determine random force rather than mean square level

i.e. $(x^2)_{\omega} = |\alpha(\omega)|^2 (f^2)_{\omega}$

So $(f^2)_{\omega} = \frac{\hbar \alpha_{\text{IM}}(\omega)}{|\alpha(\omega)|^2} \coth \frac{\hbar \omega}{2T}$

\rightarrow Key Elements in Fluctuation-Dissipation Theorem

- stationarity
- causality
- T.F.D. P.T. \rightarrow Fermi Golden Rule

and

- linearity of response.

→ An Example of an "Inappropriate" Random Process

- i.e. Consider a multiplicative process \Leftrightarrow
typical of intermittency

x_j , for $j = 1, \dots, N$

s/t $x_j = \begin{cases} 0 \\ 2 \end{cases}$; with $p = 1/2$ each

$X = \prod_{j=1}^N x_j = \begin{cases} 2^N & \text{on one realization (all heads)} \\ 0 & \text{on all others} \end{cases}$

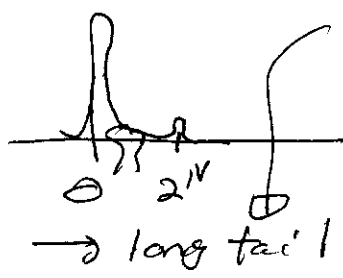
(and obviously 2^N realizations.)

Now, compute $\langle X \rangle = \sum_{\text{real.}} x / 2^N$

$$= 0 + 0 + \dots + 2^N / 2^N = 1$$

$$\langle X^2 \rangle = \sum_{\text{real.}} x^2 / 2^N = (2^N)^2 + 0 + \dots / 2^N$$

$$= 2^N$$

Message: \rightarrow Pdf(X) = 

high moments weight more!
yet
 $\langle X \rangle = 1$
 $\langle X^2 \rangle = 2^N$!!

→ $\langle X^p \rangle$ increases drastically with p

i.e. $\gamma_p = \log_2 \langle X^p \rangle / N = p-1$

↔ high moments weight tail more!

⇒ clearly a case not covered by Central Limit Theorem.

N.B.: Why Are Gaussian Statistics "Ubiquitous"?

A: → For additive processes with convergent well behaved variances,

Central Limit Theorem ⇒ Pdf of sum for $N \rightarrow \infty$ is Gaussian, even if Pdfs of x_i ($X = \sum_{i=1}^N x_i$) are non-Gaussian!

→ Ex. Consider $X = \sum_{i=1}^N x_i$

where Pdf ($\ln x_i$) well defined

i.e. $\int (\ln x_i)^2 \text{Pdf}(\ln x_i) < \infty$.
What can be said about Pdf X ?

b.) A closer look at Diffusion and Random Walks

- Simple Theory of Diffusion I

Consider Langevin Equation:

$$\frac{d\underline{v}}{dt} = -\gamma \underline{v} + \tilde{a}(t)$$

\downarrow drag \downarrow random thermal force.

further, $\langle \tilde{a}(t) \tilde{a}(t') \rangle$ "delta correlated", i.e.

$$\langle \tilde{a}(t) \tilde{a}(t') \rangle = \frac{\gamma^2}{\Delta \omega} \delta(t-t')$$

(corresponds to short τ_{ec} limit)

Now,

$$\underline{v} = e^{-\gamma t} \int_0^t dt' e^{\gamma t'} \tilde{a}(t')$$

directly proceeding \Rightarrow

$$\langle \underline{v}(t_1) \underline{v}(t_2) \rangle = \int_0^{t_1} dt'_1 \int_0^{t_2} dt'_2 e^{-\gamma(t_1+t_2)} e^{\gamma(t'_1+t'_2)} \langle \tilde{a}(t'_1) \tilde{a}(t'_2) \rangle$$

took $t_2 > t_1$, (and need symmetrize), so:

then

$$\begin{aligned} t_+ &= (t_1 + t_2)/2 & t_1 &= t_+ - t_- \\ t_- &= (t_2 - t_1)/2 & t_2 &= t_+ + t_- \end{aligned} \quad \left. \vphantom{\begin{aligned} t_+ \\ t_- \end{aligned}} \right\} \begin{array}{l} \text{standard} \\ \text{change-of-} \\ \text{-variables} \end{array}$$

18

$$\begin{aligned} \langle \underline{V}(t_1) \underline{V}(t_2) \rangle &= \int_0^{t_+} \int_0^{t_-} dt'_+ dt'_- 4 e^{-2\gamma t'_+} e^{2\gamma t'_-} * \\ &\quad \langle \tilde{q}(t'_+ - t'_-) \tilde{q}(t'_+ + t'_-) \rangle \\ &= \int_0^{t_+} \int_0^{t_-} dt'_+ dt'_- 4 e^{-2\gamma t'_+} e^{2\gamma t'_-} \frac{q_0^2}{\Delta\omega} \delta(t'_-) \end{aligned}$$

$$\begin{aligned} \Rightarrow \\ \langle \underline{V}(t_1) \underline{V}(t_2) \rangle &= 4 \int_0^{t_+} dt'_+ e^{-2\gamma t'_+} e^{2\gamma t'_+} \frac{q_0^2}{\Delta\omega} \\ &= \frac{2}{\gamma} (1 - e^{-2\gamma t_+}) \left(\frac{q_0^2}{\Delta\omega} \right) \end{aligned}$$

$$(\beta t_+ \gg 1) \Rightarrow$$

$$\langle \tilde{V}(t_1) \tilde{V}(t_2) \rangle = \langle \tilde{V}(0) \tilde{V}(t_+) \rangle \approx \left(\frac{2}{\gamma} \right) \frac{q_0^2}{\Delta\omega}$$

$\gamma \gg \gamma^{-1}$

So, again have F-D. T. type result:

$$\langle V^2 \rangle = \frac{\tilde{q}_0^2}{\Delta\omega\gamma} = \tilde{q}_0^2 \tau_{ec} \tau_{damping}$$

↪ diffusion coefficient in velocity

$$= \frac{D_v}{\gamma} = D_v \tau_{damp}$$

$$D_v = \frac{\tilde{q}_0^2}{\Delta\omega}$$

$$= \tilde{q}_0^2 \tau_{ec}$$

$$D_v = \tilde{q}_0^2 / \Delta\omega = \tilde{q}_0^2 \tau_{ec}$$

Now, for position of particle:

$$\underline{r} - \underline{r}_0 = \int_0^t \underline{v}(t') dt'$$

↪ excursion, in position.

$$\underline{r} - \underline{r}_0 = \int_0^t dt' \left\{ \underline{v}_0 e^{-\gamma t'} + e^{-\gamma t'} \int_0^{t'} d\varepsilon e^{\gamma\varepsilon} \underline{a}(\varepsilon) \right\}$$

and crank \Rightarrow

$$\underline{r} - \underline{r}_0 = \frac{\underline{v}_0}{\gamma} (1 - e^{-\gamma t}) + \int_0^t dt' e^{-\gamma t'} \int_0^{t'} d\varepsilon e^{\gamma\varepsilon} \underline{a}(\varepsilon)$$

$$\begin{cases} \underline{r} - \underline{r}_0 - \frac{V_0}{\gamma} (1 - e^{-\gamma t}) = \int_0^t \Psi(\varepsilon) \underline{\tilde{q}}(\varepsilon) d\varepsilon \\ \Psi(\varepsilon) = \frac{\pm 1}{\gamma} (1 - e^{\gamma(\varepsilon - t)}) \end{cases}$$

Now, can choose/define:

$$\begin{aligned} - \underline{V}_0 &= 0 \\ - \underline{r} - \underline{r}_0 &= d\underline{r} \end{aligned}$$

$$\Rightarrow \langle d\underline{r}(t_1) d\underline{r}(t_2) \rangle = \left\langle \int_0^{t_1} \Psi(\varepsilon) \underline{q}(\varepsilon) d\varepsilon \int_0^{t_2} \Psi(\varepsilon') \underline{q}(\varepsilon') d\varepsilon' \right\rangle$$

Taking $\langle d\underline{r} \cdot d\underline{r} \rangle$ for simplicity \Rightarrow

$$\langle d\underline{r}(t) \cdot d\underline{r}(t) \rangle \rightarrow \langle d\underline{r}^2(t) \rangle$$

as before \Rightarrow

$$\langle d\underline{r}(t)^2 \rangle = \int_0^{\tilde{\tau}} \Psi(\varepsilon)^2 d\varepsilon \langle \tilde{q}^2 \rangle T_{eL}$$

where:

$$\int_0^{\tilde{\tau}} \Psi(\varepsilon)^2 d\varepsilon = \frac{\pm 1}{2\gamma^3} (2\gamma\tilde{\tau} - 3 + 4e^{-\gamma\tilde{\tau}} - e^{-2\gamma\tilde{\tau}})$$

so finally, have:

$$\lim_{T \rightarrow \infty} \int_0^T \langle \dot{r}(t) \rangle^2 dt = \frac{T}{\gamma^2}$$

and so

$$\lim_{T \rightarrow \infty} \langle dr^2(T) \rangle = \frac{\tilde{v}_0^2 T c_0}{\gamma^2} T$$

and recall:

$$\frac{\gamma T}{m_p} = \tilde{v}_0^2 T c_0$$

(Brownian motion in 1D)
both at Temp T

so finally:

$$\langle dr^2(T) \rangle = \frac{T}{m_p \gamma} T = D_x T$$

Gives diffusion
in position...

Mean square
excursion grows secularly

Note:

- for particle starting from origin, mean-square particle position radius grows secularly, i.e.

$$\langle dr^2 \rangle \sim D_x T$$

$$D_x = (T/m_p \gamma) = v_{TH}^2 / \gamma = D_v / \gamma^2$$

- γ sets "mean-free-time" for random walk on \underline{r}

$$\text{i.e. } d\underline{r} = \int d\underline{v} \underline{\tau}$$

↑
velocity is kicked in Brownian Motion

$$\langle d\underline{r}^2 \rangle \sim \tau_{\text{eff}}^2 \langle d\underline{v}^2 \rangle$$

$$\sim \tau_{\text{eff}}^2 d\underline{v}^2 = (d\underline{v}/\gamma)^2 \tau = D_x \tau$$

n.b. heuristic only
→ can be confusing

- can work directly with position in long time limit, i.e.

Langevin Equation:

$$\frac{d\underline{v}}{dt} = -\gamma \underline{v} + \tilde{\mathbf{q}}$$

with friction, $\underline{v} \rightarrow \underline{v}_{\text{terminal}}$ as $t \rightarrow \infty$, so $(t \rightarrow \infty)$

$$\underline{v} = \tilde{\mathbf{q}}/\gamma$$

$$\Rightarrow \frac{d\underline{x}}{dt} = \frac{\tilde{\mathbf{q}}}{\gamma} \quad \text{so as before:}$$

relates diffusion to
↓
random force.

$$\therefore \langle d\underline{x}^2 \rangle = D_x \tau$$

$$D_x = \frac{q_0^2 \tau_{c0}}{\gamma^2}$$

Exercise: "Hamiltonian" Brownian Motion

Consider a particle in a (randomly) fluctuating electric field, i.e.:

(1D)

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

Show $D_v = \frac{q^2}{m^2} \frac{\tilde{E}_0^2}{\Delta\omega}$, where: $\langle v^2(t) \rangle = D_v T$

and $\langle dx(t) dx(t) \rangle = D_v T^3 / 3$

Explain physically why $\langle dx^2 \rangle$ grows as T and contrast with dissipative Brownian Motion.

→ Simple Theory of Diffusion II

→ Diffusion and Brownian Motion have a history!

Robert Brown 1828 - discovered Brownian motion
"vitalist" interpretation

(*)
L. Bachelier, 1900 - first solution of diffusion equation

A. Einstein, 1905-1906 - physics of diffusion, Brownian motion, etc.

M. Smoluchowski, 1906 - simplified physics

N. Wiener, 1930-1960 - mathematical foundations.
(Wiener (Path) Integral)

(*)
N.B.: L. Bachelier, "Theorie de la speculation"¹⁾
Ann. Sci. Ecole Norm. Sup. 17 1908
(something practical...)

A simple way to derive the diffusion equation is to postulate:

- evolution of P (i.e. $P(x, t)$ is probability density)
 is \rightarrow unbiased (no asymmetry)
 \rightarrow uniform/homogeneous.

for kick in x of size Δ in time τ :

$P \rightarrow n$

$$n(t+\tau, x) = \int_{-\infty}^{+\infty} d\Delta n(t, x-\Delta) T(\tau, \Delta)$$

$\left\{ \begin{array}{l} \text{density at} \\ t+\tau, x \end{array} \right.$
 $\left\{ \begin{array}{l} \text{density at } t \\ \text{one } \Delta \text{ away} \end{array} \right.$
 $\left\{ \begin{array}{l} \text{transition probability} \\ \text{i.e. probability of kick} \\ \Delta \text{ in } \tau \end{array} \right.$

For n smooth:

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

as $\int_{-\infty}^{+\infty} d\Delta T(\tau, \Delta) = 1$ (normalization)

$\int_{-\infty}^{+\infty} d\Delta \Delta T(\tau, \Delta) = 0$ (no bias)

and $\int_{-\infty}^{\infty} d\Delta \Delta^2 T(\tau, \Delta) = \langle \Delta^2 \rangle < \infty$

have:

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

$$\boxed{\frac{\partial n}{\partial t} = \frac{\langle \Delta^2 \rangle}{2\tau} \frac{\partial^2 n}{\partial x^2}} \rightarrow \text{Diffusion Equation}$$

$$D = \frac{\langle \Delta^2 \rangle}{2\tau} \rightarrow \text{diffusion coefficient.}$$

Now, diffusion's equation has well known solution:

$$n(t=0, x) = \delta(x-x_0) \rightarrow \text{particles concentrated at a point}$$

then:

$$n(x, t) = \frac{1}{(2\pi Dt)^{1/2}} \exp\left\{-\frac{(x-x_0)^2}{2Dt}\right\}$$

and in 2D: ($r_0 = \text{cylindrical } r$) $\underline{x_0} = \text{origin}$

$$n(\underline{x}, t) = \left(\frac{1}{2\pi t}\right) \exp\left[-r_0^2/2Dt\right]$$

and in 3D:

$$N(x, t) = \frac{1}{(2\pi t)^{3/2}} \exp(-r^2/2Dt)$$

Aside: Generic Behavior of Diffusion Process varies drastically with dimensionality!

i.e. [In a diffusion process, rms deviation grows $\sim t^{1/2}$, but direction fluctuates (drastically). Does the particle return to the origin in 1D, 2D, 3D, and if so, how often?]

Now, [Probability of Return] = $\int_{t_1}^{\infty} dt P(0, t)$

\uparrow
 PR

\downarrow
 { probability to find particle at origin for finite t

so $PR = \int_{t_1}^{\infty} dt \begin{pmatrix} 1/t^{1/2} \\ 4/t \\ 1/t^{3/2} \end{pmatrix}$

$\sim \begin{pmatrix} \text{Algebraically divergent} \\ \text{Logarithmically divergent} \\ \sim 1/t_1^{1/2} \end{pmatrix}$

So
1D \rightarrow particle sure to return to start
in 1D

2D \rightarrow particle will return to start, but less
likely to do so than in 1D

3D $\rightarrow \lim_{t \rightarrow \infty} PR \rightarrow 0$

so particle won't return to origin,
time asymptotically \downarrow .

→ Brownian Motion and Diffusion : Some Not-so-Simple Aspects

Path of a Brownian Particle Diffusing : Wiener Path (after N. Wiener)

$W_t(\omega)$ → random coordinate of Brownian particle
time realization (i.e. force pdf) → for given ω , W_t is deterministic

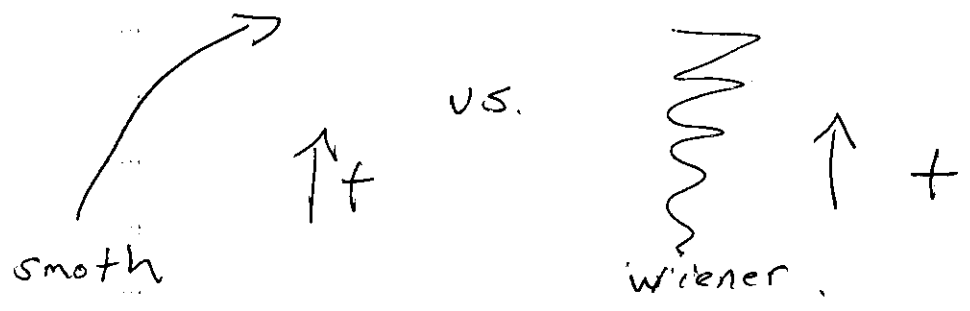
To define $W_t(\omega)$:

$W_0(\omega) = 0$

$W_t(\omega)$ such that: $\langle W_{t+\tau}(\omega) - W_t(\omega) \rangle = 0$

$\langle (W_{t+\tau}(\omega) - W_t(\omega))^2 \rangle = \tau$

∴ path is highly irregular, as for smooth path, $Var \sim \tau^2$, not τ ⇒ lots of cancellation



Properties:

→ continuous

→ not differentiable anywhere

i.e. heuristically: $\frac{dW}{dt} = \frac{\Delta W}{\Delta t}$, in sense of a
 limit i.e. $\frac{df}{dx} = \lim_{\Delta x \rightarrow 0} \left\{ \frac{f(x+\Delta x) - f(x)}{\Delta x} \right\}$

Now $\Delta W \sim (\Delta t)^{1/2}$ ($\langle W^2 \rangle \sim \Delta t$)

so $\frac{\Delta W}{\Delta t} \sim (\Delta t)^{-1/2} \rightarrow \infty$

i.e. Wiener path is said to have derivative of $O(1/2)$.

More precisely:


Probability $|W_{t+\Delta t} - W_t| > C\Delta t$ is given by

$$p \sim 2 \int_{C\Delta t}^{\infty} \frac{dw}{(2\pi\Delta t)^{1/2}} \exp\left(-\frac{w^2}{2\Delta t}\right)$$

now $P \sim 2 \int_{-\infty}^{\infty} \frac{dx}{\sqrt{\pi}} e^{-x^2} \rightarrow 1$ as $\frac{x \rightarrow 0}{\Delta t \rightarrow 0} !$

so $P \{ |W_{t+\Delta t} - W_t| > c \Delta t \} = \underline{\underline{1}}$

so derivative diverges.

Implication: Non-differentiability \Rightarrow Wiener Path is "infinitely crinkly" 

\rightarrow Above suggests that basic notions of calculus must be re-thought for Wiener paths

i.e. usually, $f(x(t)) \Rightarrow \frac{df}{dt} = \frac{df}{dx} \frac{dx}{dt}$

so $df = f' \dot{x} dt$

but in diffusion $dx^2 \sim dt !$

so if $X(t)$ has $\begin{cases} \text{regular} \rightarrow \text{drift} \\ \text{diffusive} \end{cases}$ piece

i.e. $X(t) = X_0(t) + \int dx(t)$
 \uparrow Wiener

then
$$\frac{df}{dt} = f' \dot{x} + \frac{1}{2} f'' \langle dx^2 \rangle$$

$$= f' \dot{x} + \frac{D}{2} f''$$

so
$$df = \left(f' \dot{x} + \frac{D}{2} f'' \right) dt$$

\downarrow note factor is common.
 stochastic correction
 to derivative in Itô calculus.

→ Wiener Process has no memory (cf simple derivation)
 i.e.

seek time correlation $\langle w_t w_s \rangle$

but
$$w_t w_s = \frac{1}{2} [w_t^2 + w_s^2 - (w_t - w_s)^2]$$

and $\langle w_t^2 \rangle = t$

$\langle w_s^2 \rangle = s$

$\langle (w_t - w_s)^2 \rangle = |t - s|$
 (stationarity)

so

$$\begin{aligned}\langle w_t w_s \rangle &= \frac{1}{2} [t + s - |t - s|] \\ &= \min(t, s)\end{aligned}$$

so only correlation is common, earlier time.

$$\langle w_t w_s \rangle = \min(t, s) \leftrightarrow \text{no memory}$$

[Absence of memory is origin/basis/reason for non-differentiability \leftrightarrow Brownian particle has no inertia, ...]

Next: Kinetic Equations, ...