Lecture 1 b – Langevin Eqn. and Brownian Motion, cont'd.

Recall:

- introduced Langevin Eqn.

$$m \frac{\partial v}{\partial t} = -\gamma v + \underbrace{\tilde{f}}_{\text{random force}}$$

N.B. Random $\tilde{f}(t)$ cannot be obtained from L or H indep. time.

- F.D.T. : $\boxed{\gamma T = \frac{|\tilde{f}_0|^2}{2} \tau_{ac}}$ (Damping) T ~ (Forcing spec.)

- Diffusion (Brownian Motion : $\boxed{\langle x^2 \rangle = 2DT}$

$$D = \frac{|\tilde{f}_0|^2 \tau_{ac}}{2\gamma^2}$$

$$\boxed{D = T/\gamma}$$

Kubo Formula. → $\boxed{D = \int_0^\infty dt \, \langle v(0) v(t) \rangle}$

Further items on Langevin Equation:

→ Velocity correlation function

→ Chemical Reactions application

→ Dynamical Model of "heat bath" (!?!)

↔ Markovian Langevin Eqn. / Non-Markovian ? {what is it?}

i) Velocity Correlation for Brownian Particle:

Now,

$$\langle v(t)\, v(t')\rangle = \frac{1}{\tilde{T}}\int_0^{t} ds\, \langle v(t+s)\, v(t'+s)\rangle$$

and $v(t) = \int_0^{\infty} e^{-\gamma t/m}\, \frac{\tilde{f}(t-u)}{m}\, du$

Plug:

so then correlation function, $\frac{1}{\tilde{T}}\int_0^{\tilde{T}}$

hist:

$$\langle v(t)\, v(t')\rangle = \int_0^{\infty} du_1 \int_0^{\infty} du_2\, e^{-\frac{\gamma}{m}(u_1+u_2)}\, \frac{1}{\tilde{T}} * \frac{1}{m^2} * \int_0^{\tilde{T}} ds \left[\tilde{f}(t-u_1+s)\, \tilde{f}(t-u_2+s)\right]$$

avg.

so

$$\langle \tilde{v}(t)\tilde{v}(t')\rangle = \int_0^\infty du_1 \int_0^\infty du_2 \; \exp\left[-\frac{\gamma}{m}(u_1+u_2)\right] *$$

$$\frac{1}{T}\int_0^{\tilde{T}} ds \, \frac{|f_0|^2 \tilde{\tau}_{ac}}{m^2} \, \delta(t-u_1-t'-u_2)$$

$\Rightarrow$

$$\langle \tilde{v}(t)\tilde{v}(t')\rangle = \frac{1}{2\gamma/m} e^{-\gamma|t-t'|/m} \frac{|f_0|^2 \tilde{\tau}_{ac}}{m^2}$$

$$= \frac{e^{-\gamma|t-t'|/m}}{2\gamma} \frac{|f_0|^2 \tilde{\tau}_{ac}}{m}$$

$\Rightarrow$

$$|f_0|^2 \tilde{\tau}_{ac} = 2\gamma T \qquad \text{(using FDT)}$$

$$\langle \tilde{v}(t)\tilde{v}(t')\rangle = e^{-\gamma|t-t'|/m} \frac{\cancel{2\gamma} T}{\cancel{2\gamma} m}$$

$$\boxed{\langle \tilde{v}(t)\tilde{v}(t')\rangle = \frac{T}{m} e^{-\frac{\gamma}{m}|t-t'|}}$$ ← could have guessed.

So have:

$$\boxed{\langle \tilde{v}(t)\, \tilde{v}(t') \rangle = \frac{T}{m} e^{-\frac{\gamma}{m}|t-t'|}}$$

→ note abs. in time difference.

→ $t = t'$ $\langle \tilde{v}^2 \rangle = T/m$ ✓

(ii)
→ Chemical Reactions / Fluctuations

Two species, A, B: → # of each population

$$\frac{dA}{dt} = -k_1 A + k_2 B$$

typical of Lotka-Volterra

$$\frac{dB}{dt} = -k_2 B + k_1 A$$

Now,

→ observe fluctuations in total number! → why notable?

→ What can one deduce about drive for fluctuations? ⟷ forcing. → If steady fluctuations, ∃ forcing. → structure?

Note: Fixed pts + flctns.

$$\frac{dA}{dt} = \frac{dB}{dt} = 0 \qquad \text{Fixed pts.}$$

$$\left.\begin{aligned} k_1 A &= k_2 B \\ k_2 B &= k_1 A \end{aligned}\right\} A_{eq} = (k_2/k_1) B_{eq}$$

→ define A_{eq}, B_{eq}

and:

$$\frac{d}{dt}(A+B) = 0 \qquad \boxed{\text{Total \# conserved}}$$

So if fluctuations: C

$$\left.\begin{aligned} A &= A_{eq} + C \\ B &= B_{eq} - C \end{aligned}\right\} \text{→ to conserve number}$$

$\therefore$

$$\frac{d(\cancel{B_{eq}}+c)}{dt} = -k_1(\cancel{A_{eq}}+c) + k_2(\cancel{B_{eq}}-c)$$

$$= -(k_1+k_2)\,c$$

$$\frac{dc}{dt} = -(k_1+k_2)\,c$$

Fluctn will decay.

$\Rightarrow$ absent anything else, c should decay!.

But: stationary fluctuations in c present!?

$\therefore$ there must be noise $\rightarrow$ what is it?

$$\frac{d\tilde{c}}{dt} = -(k_1+k_2)\,\tilde{c} + \tilde{F}$$

Langevin Eqn

noise necessary to maintain fluctuations

what

$\downarrow$

how calculate?

obvious analogy:

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

so

mean sq fluctuation level

$$(k_1+k_2)\langle\tilde{c}^2\rangle = \langle\tilde{F}\tilde{c}\rangle$$

$$\partial_t\tilde{c} + (k_1+k_2)\tilde{c} = \tilde{F}$$

if

$$\langle\tilde{F}(t)\tilde{F}(t')\rangle = \delta(t-t')|\tilde{F}|^2$$

delta correlated

$\Rightarrow$ FDT:

$$\boxed{|\tilde{F}|^2 = 2(k_1+k_2)\langle\tilde{c}^2\rangle_{eq}}$$

rate const info of damping

equilibrium fluctuation level.

So

$$\boxed{\langle\tilde{F}(t_1)\tilde{F}(t_2)\rangle = 2(k_1+k_2)\langle\tilde{c}^2\rangle_{eq}\,\delta(t_1-t_2)}$$

specifies noise to maintain $\langle\tilde{c}^2\rangle_{eq}$.

(iii) A Dynamical Model of a Heat Bath, and How Interact with?
(Zwanzig '73)

What does Heat Bath Mean?

How dynamically describe arbitrary motion in a heat bath?

System: q, p

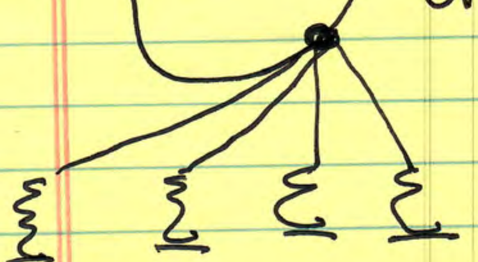
$$H_s = \frac{p^2}{2m} + U(x) \quad \text{— system.}$$

Bath: collection of h.o.'s coupled to motion

$$H_B = \sum_j \left(\frac{p_j^2}{2} + \frac{1}{2}\omega_j^2 \left(q_j - \frac{\gamma_j}{\omega_j^2} x \right)^2 \right)$$

collection of oscillators

coupling to system



Write EOMs:

$$\frac{dx}{dt} = p$$

$$\frac{dp}{dt} = -U'(x) + \sum_j \gamma_j \left(q_j - \frac{\gamma_j}{\omega_j^2} x \right)$$

and

elim in terms p [illegible]

$$\frac{dq_j}{dt} = p_j$$

$$\frac{d}{dt} p_j = -\omega_j^2 q_j + \gamma_j x.$$

Ultimately :- Seek Langevin Eqn.
(generalized)

- express q_j in terms p, x
i.e. bath coords irrelevant.

If x known: formally,

$$q_j(t) = \underbrace{q_j(0)}_{\text{i.c.'s}} \cos \omega_j t + p_j(0) \frac{\sin \omega_j t}{\omega_j} + \gamma_j \int_0^t ds \; x(s) \frac{\sin \omega_j (t-s)}{\omega_j}$$

Seeking "Langevin Eqn.", I.B.P. $\Rightarrow$

(Rhs dp/dt)

$$q_j(t) - \frac{\gamma_j}{\omega_j^2} x(t) = \Big(\underbrace{q_j(0) - \frac{\gamma_j}{\omega_j^2} x(0)}_{\text{i.c}}\Big) \cos(\omega_j t) + \underbrace{p_j(0)}_{\text{i.c}} \frac{\sin \omega_j t}{\omega_j} - \gamma_j \int_0^t ds \frac{p(s)}{M} \frac{\cos \omega_j (t-s)}{\omega_j^2}$$

$\downarrow$

RHS of p eqn

So plugging into dp/dt eqn.:

$$\boxed{\frac{dp(t)}{dt} = -U'(x(t)) - \int_0^t ds \; K(s) \frac{p(t-s)}{M} + \overbrace{F_p(t)}^{\text{"noise"}}}$$

(Sort of) Langevin Eqn! Interaction kernel!

Non-Markovian

Here: effective damping / drag

$$\boxed{K(s) = \sum_j \frac{\gamma_j^2}{\omega_j^2} \cos(\omega_j t)}$$

→ { kernel set by bath properties.

Noise $F_p(t)$ from i.c.'s:

$$\boxed{F_p(t) = \sum_j \gamma_j\, p_j(0) \frac{\sin \omega_j t}{\omega_j} + \sum_j \gamma_j \left(q_j(0) - \frac{\gamma_j}{\omega_j^2} x(0) \right) \cos(\omega_j t)}$$

$K(s)$ → <u>memory</u> <u>function</u>

i.e. contrast:

B. M. $\quad \frac{dv}{dt} = -\frac{\gamma}{m} v + \tilde{f}/m$

<u>no</u> memory – local in time

<u>simple</u> ⇒ "<u>Markovian</u>"

Here:

$$\frac{dp}{dt} = -U'(x(t)) - \int_0^t ds\, K(s)\, \frac{p(t-s)}{m} + F_p(t)$$

Memory

general $\Rightarrow$ "Drag" depends on time history $\Rightarrow$ Non Markovian "

Now, in this model, can adjust Memory function .... via bath h.O. distribution

$$K(t) = \sum_j \frac{\gamma_j^2}{\omega_j^2} \cos(\omega_j t)$$

then if:

- continuous spectrum .

- $\sum_j \to \int d\omega\, g(\omega)$

density states

- $\gamma \to \gamma(\omega)$

coupling dependence.

so

$$K(t) = \sum_j \frac{\gamma_j^2}{\omega_j^2} \cos\omega_j t$$

$$\rightarrow \int_0^\infty d\omega\, g(\omega)\, \frac{\gamma(\omega)^2}{\omega^2} \cos\omega t$$

Now if:

- $g(\omega) \sim \omega^2$ (wts high ω)
- $\gamma(\omega) \sim \text{const}$ [high freq. wiggles → "kicks"]

$K(t) = \gamma^2 \delta(t)$ → localized kernel

no history

and

$$\frac{dp}{dt} = -U'(X(t)) - \int_0^t \gamma^2 \delta(s)\, \frac{p(t-s)}{m} + F_p(t)$$

$$\downarrow$$

$$\gamma^2 \frac{p(t)}{m}$$

Markovian dynamics
→ bath at high frequency only

Markovian Langevin eqn. structure.

$\therefore$ - density of states
- $\gamma(\omega)$

$\Bigg\}$ determine memory kernel.

What about noise?

$$F_p(t) = \sum_j \gamma_j\, p_j(0) \frac{\sin \omega_j t}{\omega}$$
$$+ \sum_j \gamma_j \left(q_j(0) - \frac{\gamma_j}{\omega_j^2} x(0) \right) (\cos \omega_j t)$$

$p_j(0)$, $q_j(0)$ distributed according:

$$f_{eq} \cong \exp[-H_B / T]$$

so

$$\left\langle \left(q_j(0) - \frac{\gamma_j}{\omega_j^2} x(0) \right)^2 \right\rangle = \frac{T}{\omega_j^2} \quad \text{etc.}$$

$$\langle p_j(0)^2 \rangle = T$$

can deduce $\langle F_p^2 \rangle$.

FDT:

Memory kernel $\Rightarrow$ damping

$$\boxed{\langle F_p(t) F_p(t') \rangle = T\, K(t-t')}$$

(recall $\langle \tilde{f}(t) \tilde{f}(t') \rangle = \gamma T\, \delta(t-t')$).

Next: Fokker-Planck Theory !