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 Accel.)

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

Furthur 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,

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

and

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

Plug:

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

hist:

$$\langle v(t)\, v(t')\rangle = \int_0^\infty du_1 \int_0^\infty du_2 \, e^{-\frac{\gamma}{m}(u_1+u_2)} \, \frac{1}{T} * \frac{1}{m^2} *$$

$$\int_0^{\tilde{T}} ds \left[\tilde{f}(t-u_1+s)\, \tilde{f}(t-u_2+s)\right]$$

avg.

so

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

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

$\Rightarrow$

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

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

$\Rightarrow$

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

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

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

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.

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

(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, $\tilde{c}$ $\uparrow$

→ 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

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

$\therefore$

$$\frac{d(\cancel{B}c_{eq}+c)}{dt} = -k_1(\cancel{A}c_{eq}+c) + k_2(\cancel{B}c_{eq}-c)$$

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

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

{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

obvious analogy:

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

how calculate?

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

⇒ FDT:

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

equilibrium fluctuation level.

rate const sets as company

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

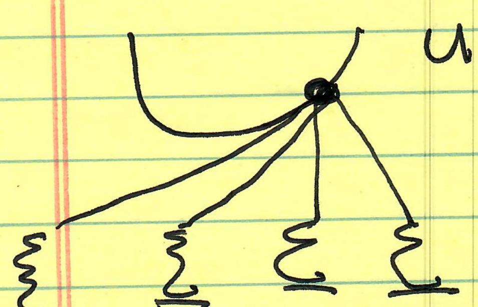
$$H_S = \frac{p^2}{2m} + U(x) \qquad \text{— system.}$$

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 !!

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

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

Ultimately: – Seek Langevin Eqn.

(generalized)

– express q_j in terms

p, x

i.e. bath coords irrelevant.

If x known: formally,

i.c.'s

$$q_j(t) = q_j(0)\cos\omega_j t + p_j(0)\frac{\sin\omega_j t}{\omega_j} + \gamma_j\int_0^t ds\, x(s)\,\frac{\sin\omega_j(t-s)}{\omega_j}$$

Seeking "Langevin Eqn.", I.B.P. ⇒

(RHS dp/dt)

i.c.

$$q_j(t) - \frac{\gamma_j}{\omega_j^2}x(t) = \left(q_j(0) - \frac{\gamma_j}{\omega_j^2}x(0)\right)\cos(\omega_j t)$$

i.c.

$$+ p_j(0)\frac{\sin\omega_j t}{\omega_j} - \gamma_j\int_0^t ds\,\frac{p(s)}{M}\,\frac{\cos\omega_j(t-s)}{\omega_j^2}$$

↓

RHS of p eqn

So plugging into dp/dt eqn.:

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

(Sort of) Langevin Eqn!

Interaction kernel!

Non-Markovian

effective damping / drag

Here:

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

→ kernel set by bath properties.

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

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

$K(s)$ → memory function

i.e. contrast:

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

no memory - local in time

simple ⇒ "Markovian"

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 $\to$ 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)

- $\gamma(\omega) \sim$ const [high freq. wiggles $\Rightarrow$ kicks]

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

no history

and

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

$\downarrow$

$\boxed{\text{Markovian dynamics} \rightarrow \text{bath at high frequ only}}$ $\frac{\gamma^2}{m} p(t)$

Markovian Langevin eqn. structure.

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

} 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!