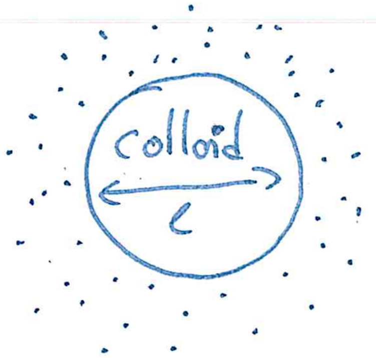
Chapter II: the Langevin Equation

Idea: show that a single, mesoscopic particle inserted in an equilibrated fluid relaxes to equilibrium, i.e. $P(q) \propto e^{-\beta E(q)}$ and characterize its dynamics.



liquid molecules $\sim 10^{-10}$m (3.4 Å for water)
colloid $l \sim 10^{-6}$, area $\sim 10^{-12}\,m^2$
area of water molecules $\sim 10^{-20}\,m^2$ } 10^8 water molecules in contact with colloid
$\Rightarrow$ lots of random collisions

I/ Introduction

Colloid: $M, \cancel{x}, p$; Fluid particles $m_i = 1$, q_i, p_i

Hamiltonian $$H = \frac{p^2}{2M} + V(x) + \underbrace{\sum_i V_{FC}(x-q_i)}_{\equiv H_{FC}\text{; interactions between fluid and colloid}} + \underbrace{\sum_i \frac{p_i^2}{2} + \sum_{i,j} V_{FF}(q_i-q_j)}_{H_{FF}\text{ interactions between fluid particles}}$$

Equations of motions: $\dot{x} = \frac{p}{M}$; $\dot{p} = -V'(x) - \sum_i V'_{FC}(x-q_i)$ (*)

fluid particles $\dot{q}_i = p_i$; $\dot{p}_i = V'_{FC}(x-q_i) - \sum_{j\neq i} V'_{FF}(q_i-q_j)$

Problem: ① impossible to solve ; ② too much information

Idea: eliminate q_i, p_i to get a self consistent equation for x & p.

Intuitively: Imagine that the colloid is at rest at time t, i.e. $p=0$.
Then, by symmetry there is no net force on average.
$\Rightarrow \langle \sum_i V'_{FC}(x-q_i) \rangle = 0$ where $\langle \ldots \rangle$ is an average over realisations. | repeated samples

Imagine that, suddenly, there is some motion $X(t+dt) \neq X(t)$

i.e. $X(t+dt) = X(t) + \Delta$; $\Delta \simeq \frac{P(t)\,dt}{M} \neq 0$ then

$$\sum_i V_{FC}'(X(t+dt) - q_i) \simeq \sum_i V_{FC}'(X(t) - q_i) + \Delta\, V_{FC}''(x(t) - q_i)$$

$$\langle \text{———} \rangle \simeq \underbrace{\langle \text{———} \rangle}_{\simeq 0} + \Delta \langle V_{FC}''(x(t) - q_i) \rangle$$

$\Rightarrow$ < force felt by colloid> $\propto \Delta = \frac{P(t)\,dt}{M} \propto P(t) \Rightarrow$ friction!

The motion of the colloid breaks the isotropy of space and generate a non-zero net force from the fluid.

<u>Idea</u> $\dot{p} = -V'(x) - \gamma p +$ fluctuations ; let's derive it!

<u>Problem</u>: this is far too difficult $\Rightarrow$ make two approximations

1. V_{FC} generic $\Rightarrow$ too complicated $\Rightarrow$ use harmonic oscillators
2. $M \gg 1$; motion of colloid is slow and we assume that the fluid dynamics make it equilibrate so that, at $t=0$,

$$P(q_1, \dots, q_N; p_1, \dots, p_N) \propto e^{-\beta\left[H_{FP}(X, \{q_i, p_i\}) + H_{FF}(\{q_i, p_i\})\right]}$$

II An exactly solvable case: the Ford, Kac and Mazur model

(Also known as Caldeira-Leggett for its quantum version)

<u>Ref</u>: J. Math. Phys. 6, 504 (1965)

$$H = \sum_j \left(\frac{p_j^2}{2} + \frac{\omega_j^2}{2}(q_j - X)^2 \right) + \frac{P^2}{2M} + V(X)$$

A) A self-consistent dynamics for X & P

<u>Equations of motion</u>: $\dot{q}_i = p_i$ ① ; $\dot{p}_i = -\omega_j^2 (q_j - X)$ ②

$$M\dot{X} = P \quad ③ \quad ; \quad \dot{P} = -V'(X) - \sum_j \omega_j^2 (X - q_j) \quad ④$$

Note $A_j \equiv X - q_j$

Todo: assume $X(t)$ given; solve formally ① + ② as functions of $X(t)$; inject back in ③ + ④ to get self-consistent equations.

~~Homogeneous solution:~~

① + ②: $\ddot{q}_j = -\omega_j^2 q_j + \omega_j^2 X$

Homogeneous solution: $q_j^H = A\cos\omega_j t + B\sin\omega_j t$

General solution: $q_j(t) = q_j^H(t) + q_j^P(t)$ with $q_j^P(t)$ a particular solution of ① + ②

$\Rightarrow$ look for $Y(t)$ s.t. $\mathcal{L}Y(t) = \omega_j^2 x(t)$ with $\mathcal{L} = \frac{d^2}{dt^2} + \omega_j^2$

let f be such that $\mathcal{L}f(t) = 0$ and look for $Y(t) = \int_0^t dt' \, f(t-t')x(t')$

then $Y'(t) = f(0)x(t) + \int_0^t dt' f'(t-t')\, x(t')dt'$

$$Y''(t) = f(0)x'(t) + f'(0)x(t) + \int_0^t dt' f''(t-t')\, x(t')dt'$$

$$\mathcal{L}Y = f(0)x'(t) + f'(0)x(t) + \int_0^t dt' \underbrace{\left[f''(t-t') + \omega_j^2 f(t-t')\right]}_{=\mathcal{L}f = 0} x(t')dt'$$

Need $f(0) = 0$ and $f'(0) = \omega_j^2 \Rightarrow f(t) = \omega_j \sin\omega_j t$

$$Y(t) = \int_0^t \omega_j \sin\omega_j(t-t')x(t')dt'$$

Initial conditions: $q_j(t=0) \equiv q_j(0)$; $p_j(t=0) \equiv p_j(0)$

ok because $m_j = 1$ so that $p_j(0) = \dot{q}_j(0)$

$$\Rightarrow \boxed{q_j(t) = q_j(0)\cos\omega_j t + \frac{p_j(0)}{\omega_j}\sin\omega_j t + \omega_j \int_0^t \sin\omega_j(t-t')x(t')dt'}$$

Solely depends on the constants $q_j(0), p_j(0), \omega_j$; the variable t and the trajectory $x(t)$.

Going back to ③ + ④ $\rightarrow$ simplify $A_j = x - q_j$

$$A_j = \underbrace{X(t) - \int_0^t x(t')\omega_j \sin\omega_j(t-t')dt'}_{} - q_j(0)\cos\omega_j t - \frac{p_j(0)}{\omega_j}\sin\omega_j t$$

$$= X(t) - \left[X(t')\cos\omega_j(t-t')\right]_0^t + \int_0^t \frac{p(t')}{M}\cos\omega_j(t-t')dt' - [\dots]$$

$$A_j = X(0)\cos\omega_j(t) + \int_0^t \frac{p(t')}{M}\cos\omega_j(t-t')dt' - q_j(0)\cos\omega_j t - \frac{p_j(0)}{\omega_j}\sin\omega_j t$$

All in all:

$$\dot{p} = -V'(x) - \int_0^t \frac{p(t')}{M} \sum_j \omega_j^2 \cos\omega_j(t-t')\,dt' + \sum_j \left\{ \omega_j p_j(0) \sin\omega t + \omega_j^2 (q_j(0) - x(0)) \cos\omega_j t \right\}$$

or $$\dot{p} = -V'(x) - \int_0^t \frac{p(t')}{M} K(t-t')\,dt' + \xi(t) \qquad (**)$$

where $K(u) = \sum_j \omega_j^2 \cos(\omega_j u)$

$\xi(u) = \sum_j \left\{ \omega_j p_j(0) \sin(\omega_j t) + \omega_j^2 (q_j(0) - x_j) \cos\omega_j t \right\}$

B) Fluctuations ξ and dissipation K

In principle, $(**)$ is a deterministic equation. In practice, $q_j(0)$ and $p_j(0)$ are impossible to know precisely and they fluctuate widely $\Rightarrow$ use their statistics.

Fluid equilibrated at $t=0 \Rightarrow P(q(0), -, q(N), p(0), -, p(N)) \propto e^{-\beta\left[\sum_j \frac{p_j(0)^2}{2} + \frac{\omega_j^2}{2}(q_j(0) - x\ldots\right.}$

i.e. $P(\{q_i(0), p_i(0)\}) = \prod_i e^{-\beta \frac{p_i(0)^2}{2} - \beta (q_i(0) - x)^2} \equiv \prod_i P_i(q_i(0), p_i(0))$ ok because $m_j = 1$.

$\Rightarrow$ independent Gaussian variables.

α The fluctuations ξ

$\xi(t)$ is a linear combination of the Gaussian variables $q_i(0), p_i(0)$; it is thus a Gaussian variable.

Proof: let us show that if $\xi = \mu a + \nu b$ with $p(a) = \frac{1}{\sqrt{2\pi\sigma_a}} e^{-\frac{a^2}{2\sigma_a}}$ and $p(b) = \frac{1}{\sqrt{2\pi\sigma_b}} e^{-\frac{b^2}{2\sigma_b}}$ then ξ is Gaussianly distributed.

① $P(\xi_0) = \int P(\xi)\,\delta(\xi - \xi_0)\,d\xi$ (definition of dirac function)

$= \langle \delta(\xi - \xi_0) \rangle_\xi$ (definition of average)

② $\delta(x) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} e^{ixk}\, \hat{\delta}(k)\,dk$ (Fourier transform)

$\hat{\delta}(k) = \int_{-\infty}^{+\infty} e^{-ixk}\, \delta(x)\,dx = 1 \Rightarrow \delta(x) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} e^{ixk}\,dk$

① + ② $\Rightarrow P(\xi_0) = \langle \delta(\xi - \xi_0) \rangle_\xi = \left\langle \frac{1}{2\pi} \int_{-\infty}^{+\infty} d\lambda \, e^{i\lambda(\xi - \xi_0)} \right\rangle$

$$P(\xi_0) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} da \int_{-\infty}^{+\infty} db \int_{-\infty}^{+\infty} d\lambda \, e^{-i\lambda\xi_0} e^{i\lambda(\mu a + \partial b)} \frac{1}{\sqrt{2\pi\sigma_a}} e^{-\frac{1}{2}\frac{a^2}{\sigma_a}} e^{-\frac{1}{2}\frac{b^2}{\sigma_b}} \frac{1}{\sqrt{2\pi\sigma_b}} \quad (***)$$

③ Gaussian integral: $\int_{-\infty}^{+\infty} dx \, e^{-\frac{1}{2}ax^2 + bx} = \sqrt{\frac{2\pi}{a}} \, e^{\frac{b^2}{2a}}$

$$(***) + ③ \Rightarrow P(\xi_0) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} \frac{d\lambda}{\sqrt{2\pi\sigma_a}} e^{-i\lambda\xi_0} \sqrt{2\pi\sigma_a} \, e^{-\frac{\lambda^2\mu^2\sigma_a}{2}} \frac{\sqrt{2\pi\sigma_b} \, e^{-\frac{\lambda^2\partial^2\sigma_b}{2}}}{\sqrt{2\pi\sigma_b}}$$

$$P(\xi_0) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} d\lambda \, e^{-i\lambda\xi_0} e^{-\frac{1}{2}\lambda^2(\mu^2\sigma_a + \partial^2\sigma_b)} = \frac{1}{\sqrt{2\pi(\mu^2\sigma_a + \partial^2\sigma_b)}} e^{-\frac{\xi_0^2}{2(\mu^2\sigma_a + \partial^2\sigma_b)}}$$

$\Rightarrow \xi$ is a random variable distributed following a Gaussian law of zero mean and variance $\mu^2\sigma_a + \partial^2\sigma_b$.

__exercise__: redo with non-zero mean random variables.

__Comment__: if y is a Gaussian random variable of law $p(y) = \frac{1}{\sqrt{2\pi\sigma_y}} e^{-\frac{1}{2}\frac{(y-y_0)^2}{\sigma_y}}$ then $p(y)$ is entirely characterized by $\langle y \rangle = y_0$ and $\langle y^2 \rangle_c = \sigma_y$.

Going back to $\xi(t) \Rightarrow$ sum of Gaussian variables and hence Gaussian
$\Rightarrow$ entirely characterized by two first cumulants. True for all t
$\Rightarrow$ need to compute $\langle \xi(t) \rangle$ and $\langle \xi(t)\, \xi(t') \rangle$

$* \langle \xi(t) \rangle = \sum_j \omega_j \sin(\omega_j t) \langle p_j(0) \rangle + \omega_j^2 \cos \omega_j t \, \langle q_j(0) - x_j(0) \rangle = 0$

$$\langle \xi(t)\,\xi(t')\rangle = \left\langle \left[\sum_j \omega_j p_j(0)\sin(\omega_j t) + \omega_j^2 (q_j(0)-x_j)\cos(\omega_j t)\right]\left[\sum_i \omega_i p_i(0)\sin(\omega_i t') + \omega_i^2 (q_i(0)-x_i)\cos(\omega_i t')\right]\right\rangle$$

$\rightarrow$ terms involving $\langle p_i(0)^2\rangle$; $\langle (q_j-x)^2\rangle$ and cross terms $\langle p_i p_{j\neq i}\rangle$ or $\langle (q_i-x)(q_{j\neq i}-x)\rangle$

Since $p_i, (q_j-x)$ are independent variables of zero mean, the cross term vanish.

Using the distributions of p_i and q_i, one gets

$$\langle p_i p_j\rangle = \delta_{ij}\, kT \text{ and } \langle (q_i-x)(q_j-x)\rangle = \delta_{ij}\frac{kT}{\omega_j^2} \text{ and } \langle p_i\,(q_j-x)\rangle = 0$$

$$\Rightarrow \langle \xi(t)\,\xi(t')\rangle = \sum_j \omega_j^2\, kT \sin(\omega_j t)\sin(\omega_j t') + \omega_j^4 \frac{kT}{\omega_j^2}\cos(\omega_j t)\cos(\omega_j t')$$

$$= \sum_j \omega_j^2\, kT\cos[\omega_j(t-t')] = kT\, K(t-t')$$

<u>Comment</u>: $K(t-t')$ characterizes the friction from the medium, i.e. the mean force stemming from a speed $p(t')$ at a later time t. $\xi(t)$ characterizes the fluctuations around this mean behaviour.

$\boxed{\langle \xi(t)\,\xi(t')\rangle = kT\,K(t-t')}$ is a fluctuation-dissipation relation typical of equilibrium dynamics (cf. D. Marenduzzo's lectures)

<u>Comment</u>: $\dot{p}(t)$ depends on $p(t')$ for $t'<t$. The system has a memory, stored in the surrounding fluid. Its dynamics at time t does <u>not</u> solely depends on its position in phase space $(x(t), p(t))$. This is the definition of a non-Markovian dynamics. Here, this results from projecting away some degrees of freedom since the initial dynamics for $x, p, q_1, \dots, q_N, p_1, \dots, p_N$ <u>was</u> Markovian.

(B) The damping term $K(t-t')$

All the oscillators may have different frequencies $\Rightarrow g(\omega)$ the density of operators having a frequency ω (or rather in $[\omega, \omega+d\omega]$)

$$K(t-t') = \sum_j \omega_j^2 \cos[\omega_j(t-t')] \simeq \int_0^\infty d\omega\, g(\omega) \cos[\omega(t-t')]$$

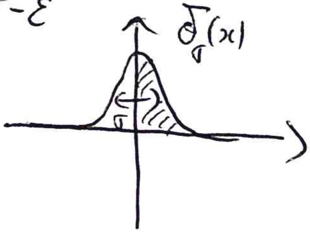
$g(\omega)$ determines $K(t)$.

Let us choose $g(\omega) = \frac{2\gamma}{\pi\omega^2}$; then $K(t) = \frac{2\gamma}{\pi}\int_0^\infty \cos\omega t\, d\omega = \frac{2\gamma}{\pi}\int_{-\infty}^{+\infty} \frac{e^{i\omega t}}{2} d\omega = 2\gamma\,\delta(t)$

The damping term then reads $\int_0^t \frac{p(t')}{M} 2\gamma\,\delta(t-t')$

Comment: $\int_{-\varepsilon}^{\varepsilon} f(t)\delta(t)dt = f(0)$ but $\int_0^{\varepsilon} f(t)\delta(t)dt = ?$

Idea



$\delta(x) = \lim_{\sigma\to 0} \delta_\sigma(x)$ use only one side $\int_0^{\varepsilon} f(t)\delta(t)dt = \frac{f(0)}{2}$

Thus $\int_0^t \frac{p(t)}{m} 2\gamma\,\delta(t-t')\,dt' = \frac{\gamma}{m} p(t)$ and the dynamics reduces to

$$\begin{cases} \dot{q} = p \\ \dot{p} = -V'(x) - \frac{\gamma}{m} p + \xi(t) \end{cases}$$

with $\xi(t)$ a Gaussian white noise such that

$$\langle \xi(t) \rangle = 0 \quad \langle \xi(t)\xi(t') \rangle = 2\gamma k T\,\delta(t-t')$$

This is the celebrated Langevin equation. (1908)

Comment: $K(t)$ is a property of the fluid. Some have memory (visco-elastic media); others don't (Newtonian fluids).

III The large damping limit (a.k.a. the over-damped limit)

Naively, large damping means large dissipation $\Rightarrow$ loss of energy
$\Rightarrow$ no motion

The life of a Brownian particle is very different.

$$\dot{x} = v \,;\; m\dot{v} = -\gamma v - V'(x) + \xi(t) \text{ with } \langle \xi(t)\,\xi(t')\rangle = 2\gamma k T\,\delta(t-t')$$

or equivalently $m\dot{v} = -\gamma v - V'(x) + \sqrt{2\gamma k T}\,\eta(t)$ with $\langle \eta(t)\eta(t')\rangle = \delta(t-t')$

⚠ Normalisation with sloppily appear in or in front of the noise in the following.

Large friction: slow system $\Rightarrow$ evolution over a very long time-scale

tentative scaling $\underset{\text{large}}{t} = \underset{\text{large}}{\gamma}\ \tau$ $\hookrightarrow \mathcal{O}(1)$?

$$m\frac{d^2x}{dt^2} = \frac{m}{\gamma^2}\frac{d^2x}{d\tau^2} = -\frac{\gamma}{\gamma}\frac{dx}{d\tau} - V'(x) + \sqrt{2\gamma k T}\,\underbrace{\eta(\gamma\tau)}_{=?} \qquad (*)$$

Notice that $\langle \eta(t')\eta(t)\rangle = \delta(t-t') = \delta(\gamma\tau - \gamma\tau') = \frac{1}{\gamma}\delta(\tau-\tau')$

Introduce GRW $\tilde{\eta}(\tau)$ such that $\langle\tilde{\eta}\rangle = 0$ $\langle \tilde{\eta}(\tau)\tilde{\eta}(\tau')\rangle = \delta(\tau-\tau')$

then $\eta(t) = \frac{1}{\sqrt{\gamma}}\tilde{\eta}(\tau)$

$$(*) \Rightarrow \underbrace{\frac{m}{\gamma^2}\frac{d^2x}{d\tau^2}}_{\xrightarrow[\gamma\to\infty]{} 0} = -\frac{dx}{d\tau} - V'(x) + \sqrt{2kT}\,\tilde{\eta} \Rightarrow \frac{dx}{d\tau} = -V'(x) + \sqrt{2kT}\,\tilde{\eta} \quad (**)$$

Thanks to fluctuation-dissipation theorem, $-\gamma v$ and $\sqrt{2\gamma k T}\,\eta$ follow the same scaling as $\gamma \to \infty \Rightarrow$ motion survives

<u>Comment</u>: (**) is nice and simple but $[\gamma] = \frac{M}{T}$

$\tau = \frac{\epsilon}{\gamma}$ is a time counted in $s^2\, kg^{-1}$:-)

Real physicists (i.e. experimentalists) often use proper units $\dot{x} = -\frac{1}{\gamma} V'(x) + \sqrt{\frac{2kT}{\gamma}}\,\eta(t)$

<u>Mobility</u>: If one applies a constant force F to the colloid

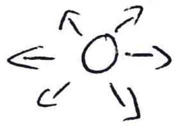
$$\dot{x} = v = \frac{F}{\gamma} + \sqrt{\frac{2kT}{\gamma}}\,\eta \Rightarrow \langle v \rangle = \frac{F}{\gamma} \equiv \mu F$$

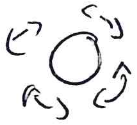
$\mu = \frac{1}{\gamma}$ is called the mobility of the particle; it measures the <u>response</u> of the colloid to an external force.

<u>Comment</u> $\mu = \frac{d\langle v \rangle}{dF}$ looks like a non-equilibrium property (constant drive, no steady-state, etc.) but it is related to $\langle \xi(t)\, \xi(t') \rangle$ which can be measured <u>in the absence of F</u> $\Rightarrow$ equilibrium property.

<u>Comment</u>: μ can be computed using hydrodynamics (Stokes equation)

Sphere $\gamma = 6\pi R \eta$ where η is the dynamic viscosity of the solvent.



Rotational diffusion  $\dot{\theta} = \sqrt{\gamma_R kT}\,\xi$; $\gamma_R = 8\pi R^3 \eta$

<u>Summary</u>: Large object connected to many <u>equilibrated</u> ones

$\downarrow$ statistical treatment

Dynamical equation which | is stochastic
| depends on a <u>small</u> number of parameters $(kT, \gamma, \ldots)$

The Langevin equation is the $PV=NRT$ of non-equilibrium stat Mech