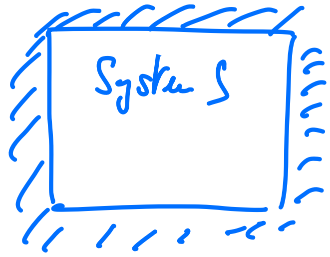
Chapter I: The Langevin equation

1) Brief recap of equilibrium stat mech

Microcanonical ensemble



Isolated system

Configurations $\{\mathcal{C}\}$ & Hamiltonian $H(\mathcal{C})$

Boltzmann hypothesis: If the dynamics is sufficiently chaotic, then, after a long time, all configurations with the same energy are equally likely

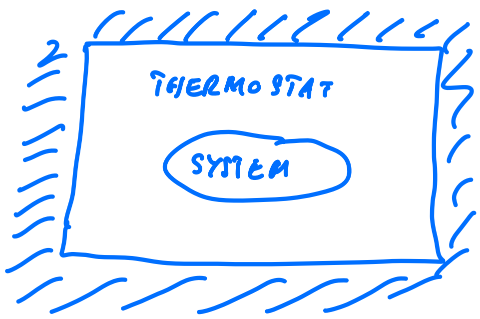
Energy H_0 then $p(\mathcal{C}) = 0$ if $H(\mathcal{C}) \neq H_0$

$= \frac{1}{\Omega(H_0)}$ otherwise

Here $\Omega(H_0)$ is a normalization constant $\propto$ area of the energy surface of energy H_0

Microcanonical entropy $S = k_B \ln \Omega(H_0)$

Microcanonical temperature $\frac{1}{T} = \frac{\partial S(H_0)}{\partial H_0}$



Canonical ensemble

System & Thermostat can exchange energy, but they are isolated from the rest of the world.

System + Thermostat are in the microcanonical ensemble $\Rightarrow$ **Boltzmann weight** for the system

$$P(\mathcal{C}) = \frac{1}{Z} e^{-\beta H(\mathcal{C})} \; ; \; \beta = \frac{1}{k_B T_{th}}$$ with T_{th} the microcanonical temperature of the thermostat

and $Z = \sum_{\mathcal{C}} e^{-\beta H(\mathcal{C})}$ a normalization constant called the **partition function**

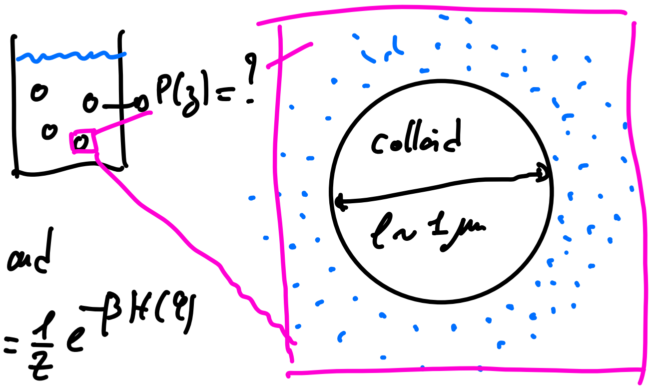
Limitations: → rather abstract setting

→ says nothing on the dynamics of the system

Goal: Do better.

2/ The Langevin equation

Idea: We want to start from a full model for the bath & the colloid & derive a closed effective dynamics for the colloid and show that, at long time, it converges to $P(q) = \frac{1}{Z} e^{-\beta H(q)}$



$$\left.\begin{array}{l}\text{liquid molecules} \sim 10^{-10}\,m \Rightarrow \text{area} \sim 10^{-20}\,m^2 \\ \text{colloid} \sim 10^{-6}\,m \Rightarrow \text{area} \sim 10^{-12}\,m^2\end{array}\right\} \mathcal{O}(10^8) \text{ liquid molecules in contact with the colloid}$$

$\Rightarrow$ Lots of random collisions $\Rightarrow$ want to build a statistical treatment of these collisions.

Framework: For simplicity, we work in $d=1$ space dimension.

Colloid: mass M, position X, momentum P.

Fluid molecules: mass $m = 1 \ll M$, positions $\{q_i\}$, momenta $\{p_i\}$.

Hamiltonian:
$$H = \frac{P^2}{2M} + \underbrace{V(X)}_{\text{e.g. gravity}} + \underbrace{\sum_i V_{FC}(X - q_i)}_{\equiv H_{FC} \text{ models the fluid-colloid interactions}} + \underbrace{\sum_i \frac{p_i^2}{2} + \sum_{i<j} V^{FF}(q_i - q_j)}_{\text{Hamiltonian of the fluid in the absence of the colloid}}$$

Equations of motion:
$$M\dot{X} = P \; ; \; \dot{P} = -\frac{\partial H}{\partial X} = -V'(X) \underbrace{- \sum_i V_{FC}'(X - q_i)}_{f_{FC}}$$

$$\dot{q}_i = p_i \; ; \; \dot{p}_i = V_{FC}'(X - q_i) - \sum_{j \neq i} V_{FF}'(q_i - q_j)$$

Goal: characterize f_{FC} starting from the eq. of motions

Problem:
1. Impossible to solve the eq. of motion in general
2. This level of description contains too much information $\Rightarrow$ need to eliminate $\{q_i, p_i\}$

Idea: Eliminate $\{q_i, p_i\}$ to get a self consistent dynamics for X & P.

Let's try to guess the result

* If the colloid was at rest for $t' \leq t$, $p=0$.
By symmetry, there cannot be a non-zero average force on the colloid

$$-\langle f_{FC}(t)\rangle = \langle \sum_i V'_{FC}(x(t)-q_i)\rangle = 0$$; where $\langle \dots \rangle$ represents an average over repeated experiments on samples.

* Suppose now that at time t, the colloid starts moving so that $x(t+dt)-x(t) \simeq \frac{p(t)}{M}dt \neq 0$

then $$\langle \sum_i V'_{FC}(x(t+dt)-q_i)\rangle = \langle \sum_i V'_{FC}\left(x(t)-q_i + dt\frac{p(t)}{M}\right)\rangle$$

$$\simeq \langle \sum_i V'_{FC}(x(t)-q_i) + dt\frac{p(t)}{M}V''_{FC}(x(t)-q_i)\rangle$$

$$\simeq \underbrace{\langle \sum_i V'_{FC}(x(t)-q_i)\rangle}_{=0} + dt\underbrace{\frac{p(t)}{M}}_{p(t)=\langle p(t)\rangle \text{ is the same in all experiment.}}\langle \sum_i V''_{FC}(x(t)-q_i)\rangle$$

$$\langle f_{FC}(t+dt)\rangle = -p(t)\frac{dt}{M}\langle \sum_i V''_{FC}(x(t)-q_i)\rangle$$

The average force exerted by the fluid is $\propto p(t) \Rightarrow$ friction force / damping!
Total force should be the average force + fluctuations around it

Expected result $\dot{p} = -V'(x) - \gamma p$ + fluctuations $\Rightarrow$ let's show that this is the right intuition & derive this more rigorously.

Problem This result is very difficult to establish for a general case, and we will thus make some approximations

① V_{FC} generic $\Rightarrow$ too complicated $\Rightarrow$ use harmonic oscillators instead

② Since $M \gg 1$, the motion of the colloid is much slower than that of the fluid $\Rightarrow$ adiabatic approximation. We consider that, at an arbitrary time $t=0$, the fluid is equilibrated:

$$P(\{q_i,p_i\}, t=0) = \frac{1}{Z}\exp\left[-\beta H_{FC}(x(0),\{q_i,p_i\}) - \beta H_{FF}(\{q_i,p_i\})\right]$$

$\Rightarrow$ We are going to show that equilibrium is contagious, i.e. that a bath in the canonical ensemble endows an immersed colloid with a dynamics that drives it to equilibrium.

2.1) An exactly solvable case

Inspired by R. Zwanzig, "Nonequilibrium statistical mechanics", that is itself inspired by a series of articles:

- Feynman, Vernon, Annals of Physics 24: 118-173 (1963)
- Ford, Kac, Mazur, J. Math. Phys. 6, 504 (1965)
- Caldeira, Leggett, Phys. Rev. Lett. 46: 211-214 (1981)

Consider: $H = \frac{p^2}{2M} + V(x) + \sum_i \left[\frac{p_i^2}{2} + \frac{\omega_i^2}{2}(q_i - x)^2\right]$

2.1.1) Self consistent dynamics for x & p

Equations of motion

$$\dot{q}_i = p_i \quad (1) \qquad \dot{p}_i = -\omega_i^2(q_i - x) \quad (2)$$

$$M\dot{x} = p \quad (3) \qquad \dot{p} = -V'(x) - \sum_i \omega_i^2(x - q_i) \quad (4)$$

$\Rightarrow$ Solve (1) & (2) in terms of their source $x(t)$ & inject the result into Eq (4)

(1) & (2) $\Rightarrow \ddot{q}_i = -\omega_i^2 q_i + \omega_i^2 x$

homogeneous solution: $q_i^H(t) = A_i \cos(\omega_i t) + B_i \sin(\omega_i t)$

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

Look for a particular solution of the form $q_i^P(t) = \int_0^t ds\, f(t-s)\, x(s)$ where f is a Green's function to be determined.

$$\dot{q}_i^P(t) = f(0)\, x(t) + \int_0^t ds\, f'(t-s)\, x(s)$$

$$\ddot{q}_i^P(t) = f(0)\, x'(t) + f'(0)\, x(t) + \int_0^t ds\, f''(t-s)\, x(s)$$

we need $\ddot{q}_i^P(t) + \omega_i^2 q_i = \omega_i^2 x$

$$\Leftrightarrow f(0)\, x'(t) + f'(0)\, x(t) + \int_0^t ds\, \left[f''(t-s) + \omega_i^2 f(t-s)\right] x(s) = \omega_i^2\, x(t)$$

Comparing left hand side & right hand side, we see that we need

$$f(0) = 0$$

$$f'(0) = \omega_i^2$$

$$f''(u) + \omega_i^2 f(u) = 0 \Rightarrow f(u) = \tilde{A}\cos(\omega_i u) + \tilde{B}\sin(\omega_i u) \text{ with } \tilde{A} = 0 \text{ \& } \tilde{B} = \omega_i$$

$\Rightarrow q_i^p(t) = \int_0^t ds\, \omega_i \sin[\omega_i(t-s)]\, x(s)$

Since $q_i^p(0) = \dot{q}_i^p(0) = 0 \Rightarrow q_i(0) = q_i^H(0) = A_i$ & $\dot{q}_i(0) = \dot{q}_i^H(0) = B_i \omega_i = p_i(0)$

All in all, $\boxed{q_i(t) = q_i(0)\cos[\omega_i t] + \frac{p_i(0)}{\omega_i}\sin[\omega_i t] + \omega_i \int_0^t ds\, \sin[\omega_i(t-s)]\, x(s)}$

This yields $q_i(t)$ in terms of $q_i(0), p_i(0), \omega_i$ & the colloid's trajectory $x(s)$, $s \leq t$.

We now want to go back to the equations (3) & (4) for the colloid

Let's work on $x - q_i$ to see that $p(t)$ is indeed present in the force exerted by the fluid

$$x(t) - q_i(t) = x(t) - \int_0^t ds\, \omega_i \sin[\omega_i(t-s)]\, x(s) - q_i(0)\cos[\omega_i t] - \frac{p_i(0)}{\omega_i}\sin[\omega_i t]$$

$$= x(t) - \Big[\cos[\omega_i(t-s)]\, x(s)\Big]_0^t + \int_0^t ds\, \cos[\omega_i(t-s)]\, \frac{p(s)}{M} - q_i(0)\cos[\omega_i t] - \frac{p_i(0)}{\omega_i}\sin[\omega_i t]$$

$$= \int_0^t ds\, \cos[\omega_i(t-s)]\, \frac{p(s)}{M} + [x(0) - q_i(0)]\cos[\omega_i t] - \frac{p_i(0)}{\omega_i}\sin[\omega_i t]$$

Now, we can close our system of equations

$$\dot{p} = -V'(x) - \int_0^t ds\, \frac{p(s)}{M} \sum_i \omega_i^2 \cos[\omega_i(t-s)] + \sum_i \omega_i p_i(0)\sin[\omega_i t] + \omega_i^2 [q_i(0) - x(0)]\cos[\omega_i t]$$

$$\Leftrightarrow \quad \boxed{\dot{p} = -V'(x) - \int_0^t ds\, \dot{x}(s)\, K(t-s) + \xi(t)} \qquad (*)$$

where $*$ $K(u)$ is a "friction kernel" that tells us how a displacement at time $s < t$ leads to a non-zero force on the colloid at time $t > s$.

$K(u) = \sum_{i=1}^{N} \omega_i^2 \cos[\omega_i u]$ is entirely determined by the constants $\omega_i \Rightarrow$ fixed once the system is defined

$*$ $\xi(t) = \sum_i \{\omega_i p_i(0)\sin(\omega_i t) + \omega_i^2 [q_i(0) - x(0)]\cos(\omega_i t)\}$ will represent the fluctuating part of the force, that depends on the positions & momenta of the fluid at $t = 0$.

2.1.2) Fluctuation and friction

The fluctuations

If we assume that, at $t=0$, the fluid is equilibrated, then we can characterize the fluctuations of $\xi(t)$.

For concision, we write $q_i(0) \equiv q_i^0$ & $p_i(0) \equiv p_i^0$, and assume

$$P(\{q_i^0, p_i^0\}) = \frac{1}{Z} \exp\left\{-\beta \sum_i \left[\frac{(p_i^0)^2}{2} + \frac{\omega_i^2}{2}(q_i^0 - x(0))^2\right]\right\} = \prod_i P_p(p_i^0) \times P_q(q_i^0)$$

$\Rightarrow$ p_i^0 & $q_i^0 - x(0)$ are independent Gaussian random variables (RV).

* $\xi(t)$ is thus a linear combination of Gaussian RV $\Rightarrow$ it is also a Gaussian RV.

The characteristic function of a Gaussian is a Gaussian

Let z be a GRV; $p(z) = \frac{1}{\sqrt{2\pi\sigma^2}} \exp\left[-\frac{(z-\bar{z})^2}{2\sigma^2}\right]$

$$\langle e^{i\lambda z}\rangle = \frac{1}{\sqrt{2\pi\sigma^2}} \int_{-\infty}^{+\infty} dz\, e^{i\lambda z - \frac{(z-\bar{z})^2}{2\sigma^2}} = \frac{1}{\sqrt{2\pi\sigma^2}} \sqrt{2\pi\sigma^2}\, e^{i\lambda\bar{z}} e^{-\frac{\lambda^2}{2}\sigma^2}$$

$$= e^{i\lambda\bar{z} - \frac{\lambda^2}{2}\sigma^2}$$

Conversely, if $\langle e^{i\lambda z}\rangle = e^{i\lambda\bar{z} - \frac{\lambda^2}{2}\sigma^2}$, the inversion theorem tells us that z is a GRV.

A linear combination of GRVs is a GRV

Let $p(g_i) = \frac{1}{\sqrt{2\pi\sigma_i^2}} e^{-\frac{1}{2}\frac{(g_i - g_i^0)^2}{\sigma_i^2}}$ and $x = \sum_i \alpha_i g_i$

$$\langle e^{i\lambda x}\rangle = \langle e^{i\lambda\sum_i \alpha_i q_i}\rangle = \prod_i \langle e^{i\alpha_i\lambda q_i}\rangle$$

$$= \prod_i e^{i\alpha_i\lambda q_i^0 - \frac{\alpha_i^2\lambda^2}{2}\sigma_i^2} = e^{i\lambda\underbrace{\sum_i \alpha_i q_i^0}_{\bar{x}} - \frac{\lambda^2}{2}\underbrace{\sum_i \alpha_i^2\sigma_i^2}_{\bar{\sigma}^2}}$$

$$\Rightarrow p(x) = \frac{1}{\sqrt{2\pi\bar{\sigma}^2}}\, e^{-\frac{(x-\bar{x})^2}{2\bar{\sigma}^2}}$$

Comment: a Gaussian distribution like $p(x)$ is entirely characterized by its two first cumulants $\langle x\rangle$ and $\langle x^2\rangle_c = \langle x^2\rangle - \langle x\rangle^2$.

For each value of t, $\xi(t)$ is a GRV but $\xi(t)$ and $\xi(t')$ are not independent.

$\Rightarrow$ characterized by $\langle \xi(t)\rangle$ and $\langle \xi(t)\,\xi(t')\rangle_c$.

Using that $P(q_i^0) \propto e^{-\beta\frac{\omega_i^2}{2}(x-q_i^0)^2}$ & $P(p_i^0) \propto e^{-\beta\frac{p_i^{0\,2}}{2}}$, we can now proceed

$$\langle \xi(t)\rangle = \sum_j \omega_j \sin(\omega_j t)\underbrace{\langle p_j^0\rangle}_{=0} + \omega_j^2\cos(\omega_j t)\underbrace{\langle q_j^0 - x\rangle}_{=0} = 0$$

$$\langle \xi(t)\xi(t')\rangle_c = \langle \xi(t)\xi(t')\rangle$$

$$= \Big\langle \sum_j \left[\omega_j \sin(\omega_j t)\,p_j^0 + \omega_j^2\cos(\omega_j t)\,(q_j^0 - x)\right]\sum_k\left[\omega_k\sin(\omega_k t')\,p_k^0 + \omega_k^2\cos(\omega_k t')(q_k^0 - x)\right]\Big\rangle$$

$\Rightarrow$ Three types of terms $\langle p_j^0\; p_k^0\rangle = kT\,\delta_{jk}$

$$\langle (q_j^0 - x)\,(q_k^0 - x)\rangle = \frac{kT}{\omega_j^2}\,\delta_{jk}$$

$$\langle p_\alpha^0\,(q_\beta^0 - x)\rangle = \langle p_\alpha^0\rangle\langle q_\beta^0 - x\rangle = 0$$

$$\langle \xi(t)\xi(t')\rangle = \sum_j \omega_j^2\, kT\sin(\omega_j t)\sin(\omega_j t') + \omega_j^2\, kT\cos(\omega_j t)\cos(\omega_j t')$$

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

$$\boxed{\langle \xi(t)\,\xi(t')\rangle = kT\, K(t-t')}$$

This relation is called the Fluctuation Dissipation Theorem. It shows how, for the dynamics induced by an equilibrated bath, friction and fluctuation are related to each other by the temperature of the fluid.

Non-Markovian dynamics: $p(t)$ depends on $p(s)$ at earlier times $s \leq t$.
The system has a memory, stored in the degrees of freedom of the fluid. Dynamics like (*) which are not entirely determined at time t by the values of the degrees of freedom considered at time t are called non-Markovian.
On the contrary, (1-4) was Markovian for the full set of d.o.f $\{x, p, \{q_i, p_i\}\}$.
Eliminating $\{q_i, p_i\}$ is nice, but it comes at a price $\Rightarrow$ the memory kernel $K(u)$.

The damping

Let us denote by $g(\omega)\,d\omega$ the number of oscillators with $\omega_i \in [\omega, \omega + d\omega]$.

$$K(u) = \sum_j \omega_j^2 \cos(\omega_j u) \simeq \int_0^\infty g(\omega)\, \omega^2 \cos(\omega u)\, d\omega$$

$g(\omega)$ is a property of our "fluid", which determines its memory kernel $K(u)$.

Let us choose $g(\omega)=\frac{2\gamma}{\pi\omega^2}$

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

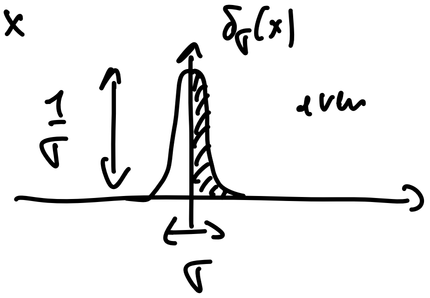
Since $\hat{\delta}(\omega)=\int_{-\infty}^{+\infty}\delta(t)e^{-i\omega t}\,dt = 1$; then $\delta(t)=\frac{1}{2\pi}\int_{-\infty}^{+\infty} d\omega\, e^{i\omega t}\hat{\delta}(\omega)$

$$= \frac{1}{2\pi}\int_{-\infty}^{+\infty} d\omega\, e^{i\omega t}$$

$$\Rightarrow \boxed{K(t)=2\gamma\,\delta(t)}$$

Damping $\quad -\int_0^t \frac{p(s)}{M}\,2\gamma\,\delta(t-s) = ?$

$\int_{-x}^{x} ds\, f(s)\,\delta(s) = f(0)$ $\qquad$ Then $\int_0^x ds\, f(s)\,\delta(s) = ?$



$\delta(x)=\lim_{\sigma\to 0}\delta_\sigma(x)$

$$\int_0^x ds\, f(s)\,\delta(s) = \frac{1}{2}\int_{-x}^{x} ds\, f(s)\,\delta(s) = \frac{f(0)}{2}$$

$$\Rightarrow -\int_0^t \frac{p(s)}{M}\,2\gamma\,\delta(t-s) = -\frac{\gamma}{M}\,p(t)$$

The full dynamics then read

$$\boxed{\dot{q} = p \quad ; \quad \dot{p} = -\frac{\gamma}{M}p - V'(x) + \xi(t)} \qquad (***)$$

where $\xi(t)$ is then a Gaussian white noise:

$$\boxed{\begin{array}{l} \langle \xi(t)\rangle = 0 \\ \langle \xi(t)\,\xi(t')\rangle = 2\gamma k T\,\delta(t-t') \end{array}}$$