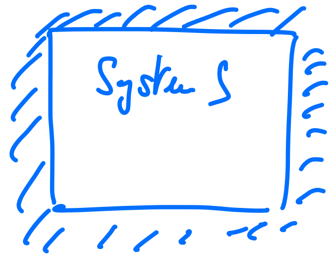
Chapter I: The Langevin equation

1) Brief recap of equilibrium stat mech

Microcanonical ensemble



Isolated system

Configurations $\{q\}$ & Hamiltonian $H(q)$

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

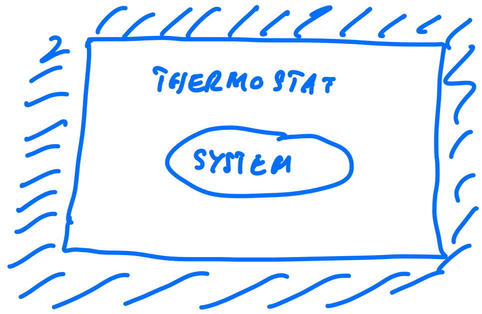
Energy H_0 then
$$p(q) = 0 \quad \text{if } H(q) \neq H_0$$
$$= \frac{1}{\Omega(H_0)} \quad \text{otherwise}$$

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

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

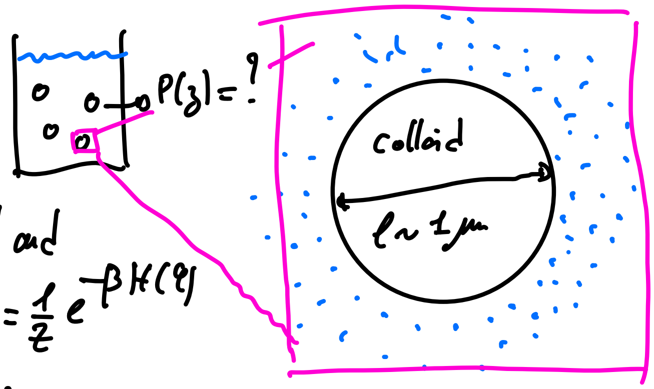
and $Z = \sum_q e^{-\beta H(q)}$ a normalization constant called the partition function

Limitations: $\rightarrow$ rather abstract setting
$\rightarrow$ 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 $P(q) = \frac{1}{Z} e^{-\beta H(q)}$



liquid molecules $\sim 10^{-10}\,m \Rightarrow$ area $\sim 10^{-20}\,m^2$
colloid $\sim 10^{-6}\,m \Rightarrow$ area $\sim 10^{-12}\,m^2$ $\Big\}$ $\mathcal{O}(10^8)$ 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

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

$$\langle f_{FC} \rangle = -p(t) \frac{dt}{M} \left\langle \sum_i V_{FC}''(x(t)-q_i) \right\rangle$$

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 $\quad \dot{p} = -V'(x) - \gamma p$ + 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, and we will thus make some approximations

1. V_{FC} generic $\Rightarrow$ too complicated $\Rightarrow$ use harmonic oscillators instead
2. Since $n \gg 1$, 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 $\quad \dot{q}_i = p_i \quad (1) \qquad \dot{p}_i = -\omega_i^2(q_i - x) \quad (2)$

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

$\Rightarrow$ 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 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 & righ hand side, we see that we need

$f(0) = 0$

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

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

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

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

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

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

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

<u>Now, we can close our system of equations</u>

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

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

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 <u>fluctuating</u> part of the force, that depends on the positions & momenta of the fluid at $t=0$.