Chapter 15: Irreversible processes and fluctuations

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Outline

1. **Transition probabilities and master equation**

2. **Brownian motion**

3. **To be continued...**
   - Correlation functions and the friction constant
   - Fluctuation dissipation theorem

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1. Transition probabilities and master equation
2. Brownian motion
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Isolated system

Consider an *isolated system* A. Hamiltonian:

$$\mathscr{H} = \mathscr{H}_0 + \mathscr{H}_i, \tag{1.1}$$

where

$\mathscr{H}$ —— Hamiltonian of the system;

$\mathscr{H}_i$ —— describing inner interactions of A;

$\mathscr{H}_0$ —— non-interaction part of $\mathscr{H}$.

Isolated system

Let A be in the quantum state of r and E_r the corresponding total energy.

1. If $\mathscr{H}_i = 0$, then A remains at state r.
2. If $\mathscr{H}_i > 0$, then A is able to transition to another state s. Let W_{rs} be the transition probability per unit time from state r to state s of system A.

- For any state r, s, $W_{rs} = W_{sr}$ (by quantum mechanics);
- If $E_s \neq E_r$, then $W_{rs} = 0$.

Isolated system

Let $P_r(t)$ denote the probability that system A is found in state r at time t. Then

$$\begin{aligned} \frac{dP_r}{dt} &= \sum_s P_s W_{sr} - \sum_s P_r W_{rs} \qquad (1.2) \\ &= \sum_s (P_s - P_r) W_{rs}. \end{aligned}$$

- (1.2) is called "master equation".
- If A is in equilibrium, $P_s = P_r$, then the probability P_r does not change with time.
- This equation describes the reversible behavior of a system.

System in contact with a heat reservoir

Consider $A^{(0)} = A + A'$, combining system A and a reservoir A'. Hamiltonian

$$\mathscr{H}^{(0)} = \mathscr{H} + \mathscr{H}' + \mathscr{H}_i, \tag{1.3}$$

where

$$\begin{aligned} \mathscr{H}^{(0)}, \mathscr{H}, \mathscr{H}' \quad &-- \quad \text{respectively, Hamiltonians of } A^{(0)}, A, A', \\ \mathscr{H}_i \quad &-- \quad \text{describing the interaction between } A \text{ and } A'. \end{aligned}$$

Remark

If $\mathscr{H}_i = 0$, then the total system consists of two isolated systems, discussed just now.

System in contact with a heat reservoir

Definition

Let r be the quantum state of A, E_r the energy level and P_r the probability of finding A in state r. Similar definitions r', $E'_{r'}$, $P'_{r'}$ are defined for A'. Besides, W_{rs} and W_{sr} are defined as before. Similarly define $W^{(0)}(rr' \to ss')$ for the combining system.

1. If $E_r + E'_{r'} \neq E_s + E'_{s'}$, then $W^{(0)}(rr' \to ss') = 0$.
2. $W^{(0)}(rr' \to ss') = W^{(0)}(ss' \to rr')$.
3. Note that A' is always in equilibrium so that

$$P'_{r'} = \frac{e^{-\beta E'_{r'}}}{\sum_{r'} e^{-\beta E'_{r'}}} =: Ce^{-\beta E'_{r'}}. \tag{1.4}$$

System in contact with a heat reservoir

4. If $E_r + E'_{r'} = E_s + E'_{s'}$, then the ratio of W_{rs} and W_{sr} is

$$\frac{W_{sr}}{W_{rs}} = \frac{e^{-\beta E_r}}{e^{-\beta E_s}}. \tag{1.5}$$

5. From (1.5), if $E_s > E_r$, then $W_{sr} > W_{rs}$;
6. Master equation

$$\begin{aligned} \frac{dP_r}{dt} &= \sum_s (P_s W_{sr} - P_r W_{rs}) \\ &= \sum_s (P_s e^{\beta E_s} - P_r e^{\beta E_r}) e^{-\beta E_r} W_{rs}. \end{aligned}$$

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Brownian motion

Definition (Brownian motion)

A small macroscopic particle immersed in a liquid exhibits a random type of motion. This phenomenon is called "Brownian motion".

Pay attention to the coordinate x, then

$$m\frac{dv}{dt} = \mathscr{F}(t) + F(t). \tag{2.1}$$

Langevin equation

Equation (Langevin)

$$m\frac{dv}{dt} = \mathscr{F}(t) - \alpha v(t) + \widetilde{F}(t) \qquad (2.2)$$

m	$--$	mass of particle
v	$--$	velocity of particle
$\mathscr{F}$	$--$	external force (gravity, electrcic force, etc.)
$\widetilde{F}$	$--$	a noise force by stochastic processes
α	$--$	a positive constant, called “friction constant”

Markov process

- Consider the Brownian motion again.
- Let $P(v,t)$ be the probability that the particle's velocity at time t lies between v and $v+dv$.
- Assume this probability depends on the original velocity v_0. The probability should be re-expressed like $P(v,t|v_0)$. This kind of motion is called "Markov process".

Master equation

Equation (Master equation under Markov process)

$$\frac{\partial P}{\partial t}\tau = -P(v,t|v_0) + \int_{\mathbb{R}} P(v_1,t|v_0)P(v,\tau|v_1)dv_1. \tag{2.3}$$

Just note

$$\begin{aligned} P(v,t+\tau|v_0) &= P(v,t|v_0) - \int_{v_1} P(v,t|v_0)P(v_1,\tau|v)dv_1 \\ &\quad + \int_{v_1} P(v_1,t|v_0)P(v,\tau|v_1)dv_1 \end{aligned}$$

and

$$\int_{v_1} P(v_1,\tau|v)dv_1 = 1. \tag{2.4}$$

Fokker-Planck equation

Fokker-Planck $\Rightarrow$

$$\begin{aligned}\frac{\partial P}{\partial t}\tau &= -P(v,t|v_0)\\ &\quad + \sum_{n=0}^{\infty}\frac{(-1)^n}{n!}\frac{\partial^n}{\partial v^n}\left[P(v,t|v_0)\int_{\mathbb{R}}\xi^n P(v+\xi,\tau|v)d\xi\right].\end{aligned}$$

Equation (Fokker-Planck equation)

$$\frac{\partial P}{\partial t} = -\frac{\partial}{\partial v}(M_1 P) + \frac{1}{2}\frac{\partial^2}{\partial v^2}(M_2 P). \tag{2.5}$$

Fokker-Planck equation

Equation (Solution for F-P equation)

$$P(v,t|v_0) = \left[\frac{m}{2\pi k_B T(1-e^{-2\gamma t})}\right]^{1/2} \exp\left[\frac{-m(v-v_0 e^{-\gamma t})^2}{2k_B T(1-e^{-2\gamma t})}\right].$$

1. For $t \to \infty$, $P(v,t|v_0) \to$ a Maxwell distribution. Particles should come to equilibrium at temperature T, irrespective of their past history.
2. At any time t, $P(v,t|v_0)$ obeys Gaussian distribution with a mean value $v_0 e^{-\gamma t}$.

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To be continued...

Thank you for your attention!

To be continued...

Fluctuation dissipation theroem

Consider an isolated system A described macroscopically by n parameters $\{y_i\}_{i=1}^{n}$.

Definition (Correlation function relating y_i and y_j)

$$K_{ij}(s) := \langle \frac{dy_i}{dt}(t) \frac{dy_j}{dt}(t+s) \rangle. \tag{3.1}$$

Theorem (Fluctuation dissipation theorem)

$$\alpha_{ij} = \frac{1}{k} \int_{-\infty}^{0} K_{ij}(s) ds. \tag{3.2}$$