Course 6. Irreversible process & fluctuations

(1) master equation : transition between states

(2) Langevin equation : frictional force leading ~~a~~ a system into its equilibrium.
(dissipation)

- fluctuation - dissipation theorem
- Onsager relations
- Correlator

(3) Wiener - Khintchine relations
Nyquist theorem

Note: ⊙ Course 6-(3) is skipped.
It is very easy. So, read the Lecture note and enjoy it.

⊙ Fokker - Planck equation is skipped as well.

8-1. Master eq.

⊙ General form :

$$\boxed{\frac{dP_r(t)}{dt} = \sum_s (P_s W_{sr} - P_r W_{rs})}$$

⊙ Case 1

Isolated system A

$\mathcal{H}_A = \mathcal{H} + \underbrace{\mathcal{H}_i}_{\text{perturbation}}$ (Hamiltonian)

perturbation $\mathcal{H}_i \ll \mathcal{H}$

$\{|r\rangle\}$ ~ eigenstate of $\mathcal{H}$ (NOT that of $\mathcal{H}_A$)

(unperturbed state)

$P_r(t)$: the probability that A is found to be in state r at time t.

W_{sr} : transition rate (transition probability per unit time)

from $|s\rangle$ to $|r\rangle$

$(W_{sr} \equiv W_{s\to r})$

- Some properties of W_{sr} :

① isolated system ⇒ energy conservation

if $E_s \neq E_r$, $W_{rs} = 0$

② $W_{sr} = W_{rs}$

※ $W_{rs} = \delta(E_s - E_r)\frac{2\pi}{\hbar}|\langle r|H_i|s\rangle|^2 \underbrace{\rho(E_r)}$ ← densities of states

(see Fermi golden rule)

Remark.

① Master eq. does not remain invariant under time reversal symmetry. $(t \to -t)$

→ it describes irreversible behavior.

check : Initial $t=t_0$: $P_1 = 1$. $P_2 = 0$ $(E_1 = E_2)$ → at $t=\infty$, $P_1 = P_2$ from master eq.

Now, apply time reversal operation : One can not find $P_1 = 1$ at $t = t_0$

$(\because -\frac{dP_r}{dt} = -P_r W_{rs} + P_s W_{sr}$; at Equilibrium, $-\frac{dP_r}{dt} = 0)$

And one can find $P_1 = P_2$.

② We lose all information of phase

$P_r = |a_r(t)|^2$. $a_r(t) = |a_r(t)| e^{i\phi_r(t)}$.

- in equilibrium :

$P_r = P_s$ (isolated system, equal a priori postulate)

$$\Rightarrow \frac{dP_r}{dt} = \sum_s (P_s W_{sr} - P_r W_{rs}) = \sum_s P_s (W_{sr} - W_{rs}) = 0$$

detailed balance : $P_r W_{rs} = P_s W_{sr}$ for r, s with $E_r = E_s$
(lose = gain)

$$\boxed{P_r W_{rs} = P_s W_{sr}} \Longrightarrow \frac{dP_r}{dt} = 0 \text{ for all } r$$

◎ Case 2. $A \oplus$ heat reservoir A'

$$\mathcal{H}_{tot} = \mathcal{H}_A + \mathcal{H}_{A'} + \underbrace{\mathcal{H}_{int}}_{\text{weak interaction between } A \text{ and } A'}$$

$\mathcal{H}_{int} \ll \mathcal{H}_A, \mathcal{H}_{A'}$

$$\begin{cases} \{|r\rangle\} \sim \text{eigenstate of } \mathcal{H}_A \\ \{|r'\rangle\} \sim \quad \text{"} \quad \mathcal{H}_{A'} \end{cases}$$

P_r : probability that A is in $|r\rangle$

$P_{r'}$ " A' " $|r'\rangle$

$P^{tot}_{rr'} = P_r P_{r'}$ " $A \oplus A'$ in $|r\rangle|r'\rangle$

$W^{tot}(ss' \to rr')$: transition rate from $|s\rangle|s'\rangle$ to $|r\rangle|r'\rangle$

- Properties of W^{tot}

$$\begin{cases} W^{tot}(rr' \to ss') = 0 & \text{if } E_r + E'_{r'} \neq E_s + E'_{s'} \\ W^{tot}(rr' \to ss') = W^{tot}(ss' \to rr') \end{cases}$$

$\because$ $A \oplus A'$ ~ isolated total system

- detailed balancing in equilibrium

$$P_r P'_{r'} \, W^{tot}(rr' \to ss') = P_s P'_{s'} \, W^{tot}(ss' \to rr')$$

(Here, $E_r + E'_{r'} = E_s + E'_{s'}$)

Since $W^{tot}(rr' \to ss') = W^{tot}(ss' \to rr')$,

$$\frac{P_r}{P_s} = \frac{P'_{s'}}{P'_{r'}} = e^{-\beta(E_r - E_s)}$$

- $P_r \propto e^{-\beta E_r}$ (canonical distribution)

  in equilibrium

- Nonequilibrium situation

  assumption : A' is large enough $\to$ A' always remains in equilibrium, irrespective of what A does.

  $\Rightarrow \quad P_{r'} = C e^{-\beta E'_{r'}}$ $\quad \hookrightarrow$ irreversible process

$$W_{rs} = \sum_{r's'} P_{r'} \, W^{tot}(rr' \to ss')$$

$$= C \sum_{r's'} e^{-\beta E_{r'}} \, W^{tot}(rr' \to ss')$$

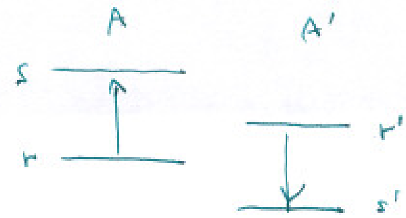
$$W_{sr} = C \sum_{r's'} e^{-\beta E'_{s'}} \, W^{tot}(\cancel{ss'} \to \cancel{rr'})$$

$$= C \sum_{r's'} e^{-\beta E_{r'}} \, e^{-\beta(E_r - E_s)} \, W^{tot}(rr' \to ss')$$

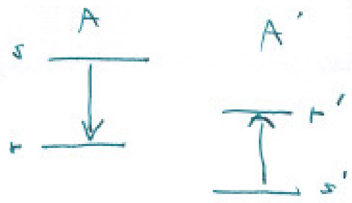
$$= e^{-\beta(E_r - E_s)} \, W_{rs}$$

$W_{sr} \neq W_{rs}$. $\qquad \dfrac{W_{sr}}{W_{rs}} = \dfrac{e^{-\beta E_r}}{e^{-\beta E_s}}$

W_{rs} :



W_{sr}



$W_{rs} < W_{sr}$

($\because$ A' is more likely to be in $|s'\rangle$.)

$$\boxed{\frac{W_{sr}}{W_{rs}} = \frac{e^{-\beta E_r}}{e^{-\beta E_s}}}$$

In equilibrium, $\dfrac{e^{-\beta E_r}}{e^{-\beta E_s}} = \dfrac{P_r}{P_s}$

$\Rightarrow$ $P_r W_{rs} = P_s W_{sr}$ ~ detailed balancing

※ Note something about density matrix $\hat{\rho}$

$$\hat{\rho} = \sum_{n,m} |n\rangle \rho_{nm} \langle m| = \frac{1}{Z} e^{-\beta(H-\mu)}$$

$$Z = \mathrm{Tr}\, e^{-\beta(H-\mu)}$$

※ $W_{rs} = \frac{2\pi}{\hbar} \sum_{r's'} |\langle rr' | H_{int} | ss' \rangle|^2 P_{r'} \, \delta(E_r + E_{r'} - E_s - E_{s'})$

⊙ Example : Magnetic resonance.

A substance with N noninteracting nuclei of (spin ½, magnetic moment μ

under magnetic field B (stationary)

(and alternating external magnetic field of angular frequency ω.

a given spin moment

• ...... reservoir (lattice, other spins) temperature β'

weak interaction

W_{+-} : spin flip rate from up to down spin

W_{-+} down up

$$\frac{W_{-+}}{W_{+-}} = \frac{e^{-\beta\epsilon_+}}{e^{-\beta\epsilon_-}} = e^{-\beta(\epsilon_+ - \epsilon_-)} \qquad \epsilon_\pm = \mp \mu B$$

$$\simeq 1 + 2\beta\mu B \qquad (\beta\mu B \ll 1 \text{ case})$$

Effect of alternating field

$\hbar\omega \simeq \epsilon_- - \epsilon_+ = 2\mu B$ $\Rightarrow$ it induces transitions between up and down spin direction.

(W'_{+-} : transition rate due to the alternating field
(W'_{-+}

$$W'_{+-} = W'_{-+} \simeq W' = w'\, \delta(\hbar\omega - 2\mu B)$$

(remember the case of isolated system)

$$\Rightarrow \quad \frac{dn_+}{dt} = n_-(W_{-+} + w') - n_+(W_{+-} + W')$$

$$\frac{dn_-}{dt} = n_+(W_{+-} + w') - n_-(W_{-+} + W')$$

$$n \equiv n_+ - n_-$$

$$\Rightarrow \quad \frac{dn}{dt} = -2(W + W')n + 2\beta\mu BWN$$

(use $W_{-+} \equiv W(1 + 2\beta\mu B)$, $W_{+-} \equiv W$)

$n_- = \frac{1}{2}N - n \simeq \frac{1}{2}N$.

$n \ll N$ at sufficiently ~~low~~ high temperature

We will focus on it.

Let's see the solution :

① $W' = 0$ case

$$\frac{dn}{dt} = -2W(n - n_0) . \qquad n_0 \equiv N\beta\mu B$$

equilibrium excess number of spins

$$\to n(t) = n_0 + (n(0) - n_0)e^{-2Wt}$$

relaxation to n_0

relaxation time : $(2W)^{-1}$

(in equilibrium,

$$n_\pm = N\frac{e^{\pm\beta\mu B}}{e^{\beta\mu B} + e^{-\beta\mu B}}$$

$n_+ - n_- \simeq \beta\mu BN = n_0$)

$t \to \infty \Rightarrow n \to n_0$, the equilibrium value

② $W = 0$ case

$$\frac{dn}{dt} = -2W'n \quad \to \quad n(t) = n(0)e^{-2W't}$$

$t \to \infty \Rightarrow n \to 0$. $n_+ = n_-$

$\because$ each spin can be treated as an isolated system.

$(\because W = 0)$

$n_+ > n_- \to$ absorption of energy from the alternating field $(\hbar\omega)$

$\Rightarrow$ $n_+ = n_-$ at $t \to \infty$.