Approach to Equilibrium: Master Equation

Microscopics of time evolution:

$$i\hbar \frac{d}{dt} \Psi^k(\vec{r},t) = \hat{H}\, \Psi^k(\vec{r},t)$$

Let Ψ^k be wavefunction k of N identical systems

$\Rightarrow$ Ensemble of N identical systems

$\Rightarrow$ want statistical average for thermodynamics

Let $\varphi_n(\vec{r})$ be energy eigenstate of $\hat{H}$:

$$\Psi^k = \sum_n a_n^k(t)\, \varphi_n(\vec{r})$$

where

$$a_n^k(t) = \int d^3r\; \varphi_n^*(\vec{r})\, \Psi^k(\vec{r},t)$$

$\equiv$ prob amplitude to find Ψ^k in state φ_n at time t

Require

$$\sum_n |a_n^k(t)|^2 = 1 \quad \text{for all } k.$$

$\Rightarrow |a_n^k(t)|^2 \equiv$ prob to find k^{th} system in state n at time t.

Ensemble Averages for observable Θ:

$$\langle \Theta \rangle = \frac{1}{N} \sum_{k=1}^{N} \int d^3r \, [\Psi^k]^* \, \hat{\Theta} \, \Psi^k$$

operator for observable Θ

$$= \frac{1}{N} \sum_{k=1}^{N} \sum_n \sum_m \left[a_n^k(t)\right]^* a_m^k(t) \cdot \int d^3r \, \varphi_n^*(\vec{r}) \, \hat{\Theta} \, \varphi_m(\vec{r})$$

$$= \sum_n \sum_m \rho_{nm} \, \Theta_{nm}$$

where

$$\Theta_{nm} = \int d^3r \, \varphi_n^* \, \varphi_m$$

and

$$\boxed{\rho_{nm}(t) = \frac{1}{N} \sum_{k=1}^{N} \left[a_n^k(t)\right]^* a_m^k(t) = \text{"density matrix"}}$$

In Dirac notation, useful to define operator $\hat{\rho}$. Then with

$$\Theta_{nm} = \langle n | \hat{\Theta} | m \rangle$$

$$\langle O \rangle = \sum_m \sum_n \overset{\frac{1}{N}}{\sum_k} \langle m | \psi^k \rangle \langle \psi^k | n \rangle \cdot O_{nm}$$

where

$$\rho_{nm} = \frac{1}{N} \sum_k \langle m | \psi^k \rangle \langle \psi^k | n \rangle$$

$$= \langle m | m \rangle \, \rho_{mn} \, \langle n | n \rangle$$

Call "statistical operator"

$$\hat{\rho} = \sum_m \sum_n |m\rangle \rho_{mn} \langle n|$$

In energy eigenstate basis, one can show

$$\rho_{mn} = \rho_n \, \delta_{nm} \qquad \text{(diagonal)}$$

$$\boxed{\Rightarrow \quad \hat{\rho} = \sum_n |n\rangle \rho_n \langle n|}$$

Shorthand notation for averages:

$$\langle O \rangle = \mathrm{Tr}\,(\hat{\rho}\,\hat{O})$$

$$\equiv \sum_n \langle n | \hat{\rho}\,\hat{O} | n \rangle$$

$$= \sum_n \rho_n \, O_{nn}$$

Equilibrium Ensembles:

- Stationary: $\frac{d}{dt}\rho_n = 0$

- Microcanonical: $\frac{1}{N}\sum_k |a_n^k|^2 = 1$
- Canonical: $\frac{1}{N}\sum_k |a_n^k|^2 = \frac{e^{-\beta\epsilon_n}}{\sum_n e^{-\beta\epsilon_n}} = \frac{e^{-\beta\epsilon_n}}{Z}$

- Grand Canonical:

$$\frac{1}{N}\sum_k |a_n^k|^2 = \frac{e^{-\beta(\epsilon_n - \mu n)}}{\sum_{n,n} e^{-\beta(\epsilon_n - \mu n)}}$$

$$= \frac{1}{Z_G} e^{-\beta(\epsilon_n - \mu n)}$$

Non-equilibrium:

At time t,

$$\hat{\rho}(t) = \sum_n |n\rangle \rho_n(t) \langle n|$$

At time $t+\tau$,

$$\hat{\rho}(t+\tau) = \sum_n \hat{U}(\tau)|n\rangle \rho_n(t) \langle n| \hat{U}^\dagger(\tau)$$

time evolution operator

Now use

$$\hat{1} = \sum_m |m\rangle\langle m| \quad \& \quad \hat{1} = \sum_\ell |\ell\rangle\langle \ell|$$

to write

$$\hat{\rho}(t+\tau) = \sum_n \sum_m \sum_\ell \rho_n(t) |m\rangle\langle m| \hat{U}(\tau) |n\rangle \cdot \langle n| \hat{U}^+(\tau) |\ell\rangle\langle \ell|$$

$$= \sum_n \sum_m \sum_\ell \rho_n(t) \, |m\rangle \, U_{mn} U^+_{n\ell} \, \langle \ell|$$

where $U_{mn} = \langle m| \hat{U}(\tau) |n\rangle$.

Key Point: In thermodynamic average, only non-cancelling terms have $\ell = m$. Thus

$$\langle \rho(t+\tau) \rangle = \sum_n \sum_m \rho_n(t) \, U_{mn} U^*_{nm}$$

$$= \mathrm{Tr}(\hat{\rho})$$

Define $W_{mn} = |U_{mn}|^2$. Then

$$\hat{\rho}(t+\tau) = \sum_n \sum_m \rho_n(t) \, |m\rangle \, W_{mn} \, \langle m|$$

From original definition, also

can write:

$$\hat{\rho}(t+\tau) = \sum_m |m\rangle \rho_m(t+\tau) \langle m|$$

Then make identification

$$\rho_m(t+\tau) = \sum_n \rho_n(t) W_{mn}$$

$\equiv$ no. in to state m
due to transitions
from states $n \neq m$

Look at time reversal for number leaving n:

$$\rho_n(t-\tau) = \sum_m \rho_n(t) W_{mn}$$

$\equiv$ no. in state n
due to transitions
to states $n \neq m$

The nett change in state m is thus

$$\rho_m(t+\tau) - \rho_m(t-\tau) = \sum_n \rho_n(t) W_{mn} - \sum_n \rho_m(t) W_{nm}$$

$$= \sum_n \left[\rho_n(t) W_{mn} - \rho_m(t) W_{nm} \right]$$

Expand for small τ:

$$2\tau \frac{d}{dt} \rho_m(t) = \sum_n \left(\rho_n(t) W_{mn} - \rho_m(t) W_{nm} \right)$$

Define transition rate $w_{\alpha\beta} = \frac{1}{2\tau} W_{\alpha\beta}$:

$$\boxed{\frac{d}{dt} \rho_m = \sum_n \left(w_{mn} \rho_n - w_{nm} \rho_m \right)}$$

This is the "Master Equation".

At equilibrium, require detailed balance:

$$w_{mn} \rho_n = w_{nm} \rho_m$$

<u>For the canonical ensemble</u>,

$$w_{mn} \frac{e^{-\beta\epsilon_n}}{Z} = w_{nm} \frac{e^{-\beta\epsilon_m}}{Z}$$

$$\Rightarrow \quad \frac{w_{mn}}{w_{nm}} = e^{-\beta(\epsilon_m - \epsilon_n)}$$

Define $\quad \lambda = w_{mn} e^{-\beta\epsilon_n} = w_{nm} e^{-\beta\epsilon_m}$