Master Equation

— Partitioned configuration space

We partition the entiere 3N-dimensional configuration space (N is the number of atoms) as

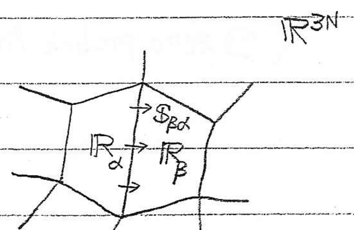
$$\mathbb{R}^{3N} = \bigcup_{\alpha} \mathbb{R}_\alpha \; ; \quad \mathbb{R}_\alpha \cap \mathbb{R}_\beta = \phi , \tag{1}$$

where a 3N-dimensional configuration $\mathbb{q} \in \mathbb{R}_\alpha$ converges to the α-th local minimum.

Let's define the probability to find the system in $\mathbb{R}_\alpha$ at time t as

$$\mathbb{P}_\alpha(t) = \iint_{\mathbb{R}_\alpha} \frac{d\mathbb{q}\, d\mathbb{P}}{h^{3N}} f(\mathbb{q}, \mathbb{P}, t) \tag{2}$$

where $\mathbb{q} = (q_1, \ldots, q_{3N})$, $\mathbb{P} = (P_1, \ldots, P_{3N})$, and $f(\mathbb{q}, \mathbb{P}, t)$ is the phase space distribution.



— Time derivative.

$$\frac{d\mathbb{P}_\alpha}{dt} = \iint_{\mathbb{R}_\alpha} \frac{d\mathbb{q}\, d\mathbb{P}}{h^{3N}} \frac{\partial}{\partial t} f(\mathbb{q}, \mathbb{P}, t) \tag{3}$$

$$= \iint_{\mathbb{R}_\alpha} \frac{d\mathbb{q}\, d\mathbb{P}}{h^{3N}} \left[-L f(\mathbb{q}, \mathbb{P}, t) \right] \tag{4}$$

$$= \iint_{\mathbb{R}_\alpha} \frac{d\mathbb{q}\, d\mathbb{P}}{h^{3N}} \left[-\left(\frac{\partial H}{\partial \mathbb{P}} \cdot \frac{\partial}{\partial \mathbb{q}} - \frac{\partial H}{\partial \mathbb{q}} \cdot \frac{\partial}{\partial \mathbb{P}} \right) f(\mathbb{q}, \mathbb{P}, t) \right] \tag{5}$$

where L is the Liouville operator and $H(\mathbb{q}, \mathbb{P})$ is the Hamiltonian.

Consider a Hamiltonian

$$H(\mathbb{q},\mathbb{P}) = \sum_{i=1}^{3N} \frac{P_i^2}{2m_i} + V(\mathbb{q}) \tag{6}$$

where m_i is the mass associated with the i-th degree of freedom.
Substituting Eq.(6) in (5),

$$\frac{dP_\alpha}{dt} = -\iint_{\mathbb{R}_\alpha} \frac{d\mathbb{q}\,d\mathbb{P}}{h^{3N}} \sum_{i=1}^{3N} \frac{P_i}{m_i}\frac{\partial}{\partial q_i} f(\mathbb{q},\mathbb{P},t) + \underbrace{\iint_{\mathbb{R}_\alpha} \frac{d\mathbb{q}\,d\mathbb{P}}{h^{3N}} \sum_{i=1}^{3N} \frac{\partial V}{\partial q_i}\frac{\partial}{\partial P_i} f(\mathbb{q},\mathbb{P},t)}_{\mathcal{Q}} \tag{7}$$

The second term in Eq.(7) is

$$\mathcal{Q} = \sum_{i=1}^{3N} \int_{\mathbb{R}_\alpha} \frac{d\mathbb{q}}{h^{3N}} \frac{\partial V}{\partial q_i} \int dP_1 \cdots dP_{i-1}\, dP_{i+1} \cdots dP_{3N} \underbrace{\int_{-\infty}^{\infty} dP_i \frac{\partial}{\partial P_i} f(\mathbb{q},\mathbb{P},t)}_{\left[f(\mathbb{q},\mathbb{P},t)\right]_{P_i=-\infty}^{P_i=+\infty} = 0}$$

(∵ zero probability for infinite momentum)

$= 0$

$$\therefore \frac{dP_\alpha}{dt} = -\iint_{\mathbb{R}_\alpha} \frac{d\mathbb{q}\,d\mathbb{P}}{h^{3N}} \sum_{i=1}^{3N} \frac{\partial}{\partial q_i}\left(\frac{P_i}{m_i} f(\mathbb{q},\mathbb{P},t)\right) \quad \left(\because \frac{\partial}{\partial q_i} \text{ \& } P_i \text{ commute}\right)$$

Gauß theorem

$$= -\int_{\partial \mathbb{R}_\alpha} \sum_{i=1}^{3N} dS_i \int \frac{d\mathbb{P}}{h^{3N}} \frac{P_i}{m_i} f(\mathbb{q},\mathbb{P},t) \tag{8}$$

Here, $d\mathbb{S}$ is the surface element pointing outward normal to the surface $\partial\mathbb{R}_\alpha$, and thus Eq.(8) is the negative of the outward flux through the surface $\partial\mathbb{R}_\alpha$.

Let's partition $\partial\mathbb{R}_\alpha$ into

$$\partial\mathbb{R}_\alpha = \bigcup_\beta \underleftarrow{\mathbb{S}_{\beta\alpha}} \tag{9}$$

where $\mathbb{S}_{\beta\alpha}$ is the surface splitting $\mathbb{R}_\alpha$ and $\mathbb{R}_\beta$, with normal pointing from α to β. We also distinguish the outgoing $\left(\sum_i dS_i \frac{P_i}{m_i} > 0\right)$ and incoming $\left(\sum_i dS_i \frac{P_i}{m_i} < 0\right)$ fluxes.

$1 = \underset{\text{Obama}}{\Theta(x)} + \underset{\text{Hilary}}{\Theta(-x)}$

Then

$$\frac{dP_\alpha}{dt} = -\sum_\beta \int_{\mathbb{S}_{\beta\alpha}} \sum_{i=1}^{3N} dS_i \int \frac{d\mathbb{P}}{h^{3N}} \frac{P_i}{m_i} \Theta\left(\sum_i dS_i \frac{P_i}{m_i}\right) f(\mathbb{q},\mathbb{P},t)$$

$$- \sum_\beta \int_{\mathbb{S}_{\beta\alpha}} \sum_{i=1}^{3N} dS_i \int \frac{d\mathbb{P}}{h^{3N}} \frac{P_i}{m_i} \Theta\left(-\sum_i dS_i \frac{P_i}{m_i}\right) f(\mathbb{q},\mathbb{P},t) \tag{10}$$

Redefining the surface $\mathbb{S}_{\beta\alpha} \to \mathbb{S}_{\alpha\beta}$ (or flipping the surface normal $d\mathbb{S} \to -d\mathbb{S}$) in the second term,

$$\frac{dP_\alpha}{dt} = -\sum_\beta \int_{\underleftarrow{\mathbb{S}_{\beta\alpha}}} \sum_{i=1}^{3N} dS_i \int \frac{d\mathbb{P}}{h^{3N}} \frac{P_i}{m_i} \Theta\left(\sum_i dS_i \frac{P_i}{m_i}\right) f(\mathbb{q},\mathbb{P},t)$$

$$+ \sum_\beta \int_{\underleftarrow{\mathbb{S}_{\alpha\beta}}} \sum_{i=1}^{3N} dS_i \int \frac{d\mathbb{P}}{h^{3N}} \frac{P_i}{m_i} \Theta\left(\sum_i dS_i \frac{P_i}{m_i}\right) f(\mathbb{q},\mathbb{P},t) \tag{11}$$

In the above $\Theta(x) = 1$ $(x > 0)$ and 0 $(x < 0)$ is the step function.

Transition state theory (TST) approximation

In the TST approximation, we assume that within each $\mathbb{R}_\alpha$ the phase-space distribution is locally in thermal equilibrium weighted to reproduce the current probability, i.e.,

$$f(\mathbf{q},\mathbb{P},t) = \frac{P_\alpha(t)}{P_\alpha(eq)} f_{eq}(\mathbf{q},\mathbb{P}) \qquad (\mathbf{q}\in\mathbb{R}_\alpha) \tag{12}$$

where

$$f_{eq}(\mathbf{q},\mathbb{P}) = \frac{1}{Q} e^{-\beta H(\mathbf{q},\mathbb{P})} \tag{13}$$

$$Q = \iint \frac{d\mathbf{q}\,d\mathbb{P}}{h^{3N}} e^{-\beta H(\mathbf{q},\mathbb{P})} \tag{14a}$$

which region to pick.

$$= \sum_\alpha \iint_{\mathbb{R}_\alpha} \frac{d\mathbf{q}\,d\mathbb{P}}{h^{3N}} e^{-\beta H(\mathbf{q},\mathbb{P})} = \sum_\alpha Q_\alpha \tag{14b}$$

$$P_\alpha(eq) = \frac{Q_\alpha}{Q} = \frac{1}{Q}\iint_{\mathbb{R}_\alpha} \frac{d\mathbf{q}\,d\mathbb{P}}{h^{3N}} e^{-\beta H(\mathbf{q},\mathbb{P})} \tag{15}$$

and $\beta = 1/k_B T$ is the inverse temperature.

Substituting the TST approximation (12) in Eq. (11),

$$\frac{dP_\alpha}{dt} = -\sum_\beta \int_{S_{\beta\alpha}} \sum_{i=1}^{3N} dS_i \int \frac{d\mathbb{P}}{h^{3N}} \frac{P_i}{m_i}\,\Theta\!\left(\sum_i dS_i \frac{P_i}{m}\right) f_{eq}(\mathbf{q},\mathbb{P}) \frac{P_\alpha(t)}{P_\alpha(eq)} \quad \left(\text{☺ only } \mathbb{R}_\alpha \text{ contribute to this integral}\right)$$

$$+ \sum_\beta \int_{S_{\alpha\beta}} \sum_{i=1}^{3N} dS_i \int \frac{d\mathbb{P}}{h^{3N}} \frac{P_i}{m_i}\,\Theta\!\left(\sum_i dS_i \frac{P_i}{m}\right) f_{eq}(\mathbf{q},\mathbb{P}) \frac{P_\beta(t)}{P_\beta(eq)} \quad \left(\text{☺ only } \mathbb{R}_\beta \text{ contributes to this integral}\right) \tag{16}$$

$$\therefore \frac{dP_\alpha}{dt} = -\sum_\beta W_{\beta\alpha}\, P_\alpha(t) + \sum_\beta W_{\alpha\beta}\, P_\beta(t) \tag{17}$$

where

$$\underset{\leftarrow}{W_{\alpha\beta}} = \int_{\underset{\leftarrow}{\mathbb{S}_{\alpha\beta}}} \sum_{i=1}^{3N} dS_i \int \frac{d\mathbb{P}}{h^{3N}} \frac{p_i}{m_i}\, \theta\left(\sum_i dS_i \frac{p_i}{m_i}\right) f_{eq}(\mathbb{q},\mathbb{P}) \Big/ P_\beta(eq) \tag{18a}$$

$$= \int_{\mathbb{S}_{\alpha\beta}} \sum_{i=1}^{3N} dS_i \int \frac{d\mathbb{P}}{h^{3N}} \frac{p_i}{m_i}\, \theta\left(\sum_i dS_i \frac{p_i}{m_i}\right) e^{-\beta H(\mathbb{q},\mathbb{P})} \Big/ \iint_{\mathbb{R}_{\cancel{\alpha}\,\beta}} \frac{d\mathbb{q}\, d\mathbb{P}}{h^{3N}} e^{-\beta H(\mathbb{q},\mathbb{P})} \tag{18b}$$